This study evaluated geochemistry between the Utica-Point Pleasant shale and reservoir/hydraulic fracturing fluid mixtures under simulated reservoir conditions in a batch reactor system. Analytical techniques were utilized to monitor fluid composition with time along with pre- and post-trial shale microscopy and phase identification analyses. Formation of iron-based precipitate was evident through results from fluid and material analyses. Ferrous iron was the predominant iron form found in the aqueous phase, with oxidation to ferric iron and subsequent precipitate formation. Geochemical modeling further supported ferric iron was the favorable phase for precipitation.

KEYWORDS
crystallization (precipitation), geochemical, hydraulic fracturing, oil shale/tar sands, reaction kinetics

1 | INTRODUCTION

U.S. tight oil has had a tremendous impact on stabilizing global oil prices and increasing energy security. Such light crude is recovered from low permeability rock formations, primarily shale, using unconventional methods such as horizontal drilling with hydraulic fracturing. As of March 2019, the Energy Information Association (EIA) reports approximately 60% total U.S. oil production comes from tight oil. While unconventional wells have shown promise in terms of oil production, economic viability is still uncertain due to rapid production decline leading to shorter well life. Peak performance of an unconventional oil well occurs during the first quarter of production, with up to 74% production decline after 1 year. Solutions explored to counteract production decline include refracturing or other enhanced oil recovery methods. Simulation studies have been developed to evaluate the effects of stimulation techniques on production to determine if profitable recovery is feasible. Although simulation of refracturing and enhanced oil recovery methods have shown promise, these techniques do not fully account for phenomena encountered in unconventional wells.

Various approaches have been utilized to mimic downhole phenomena. An approach by Luo evaluated confinement effects on hydrocarbon bubble point. This study found octane and decane confined in nanoporous media possess two distinct bubble point temperatures, with lower/higher bubble point temperatures differing ±15 K in comparison to respective bulk properties. By understanding various in-situ well phenomena, proper recovery analysis can be performed and modifications to hydraulic fracturing processes can be developed to increase well productivity and lifetime.

Aqueous phase chemical reactions are another key phenomenon occurring in shale reservoirs. Such reactions occur during well completion, when hydraulic fracturing fluid (HFF) mixes with rock and formation water, potentially causing precipitate formation, more commonly referred to as scale. Scales form when dissolved solid concentrations
result in supersaturation, resulting in formation of insoluble solids.\textsuperscript{10} If scale formation occurs in a critical flow path, that is, fracture network or hydrocarbon bearing pores, hydrocarbon flow and production will be hindered negatively impacting well production. The most probable time frame for reservoir scaling is during the shut-in period of the completion process.\textsuperscript{11} During this period, the HFF is in a nearly stagnant flow regime and at peak reactivity. Therefore, prevention of scale formation during initial well completion requires further consideration. Addition of chelating agent or scale inhibitor to the HFF is a common method to prevent scale formation. Prevalent scaling ions found in shale reservoirs include Ba\textsuperscript{2+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Fe\textsuperscript{2+/3+}, P\textsuperscript{3-}, and S\textsuperscript{2-}.\textsuperscript{11-14} Chelating agents bind to metal ions forming soluble complexes preventing formation, while scale inhibitors adsorb onto growth sites or incorporate into scale crystal lattice hindering or preventing further growth.\textsuperscript{15,16} Examples of industrial chelating agents include citric acid, acetic acid and sodium erythorbate; examples of commonly used scale inhibitors include sodium polycarboxylate, phosphonic acid salts and copolymers of acrylamide and sodium acrylate.\textsuperscript{17}

A limited set of studies have been performed to replicate the geochemistry and conditions in unconventional reservoirs during completion; however, only select studies have characterized precipitate products.\textsuperscript{11,18-24} A study by Dieterich, indicated an in-situ scale formation may occur between Marcellus shale and synthetic HFF and Huntersville Chert exposed to recycled HFF at reservoir conditions. This study found formation of gypsum (CaSO\textsubscript{4}·2H\textsubscript{2}O) on the Marcellus shale, while formation of barite (BaSO\textsubscript{4}), strontianite (SrCO\textsubscript{3}), celestine (SrSO\textsubscript{4}) and apatite (Ca\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}(F,Cl,OH)) on Huntersville Chert.\textsuperscript{21} A study by Jew et al., evaluated interactions between Marcellus, Eagle Ford and Green River shales and HFFs, found the occurrence of iron precipitation as a potential source for production decline in some wells.\textsuperscript{24} These studies provide the basis for current and future research into unconventional reservoir geochemistry with respect to in-situ scale formation during initial completion. However, these studies are tailored to well-developed formations such as the Marcellus, Bakken and Eagle Ford and at this point to the author's knowledge, no studies exist involving the Utica-Point Pleasant (UPP) shale.

The UPP shale formation has been proven productive in eastern Ohio, western Pennsylvania, and northern West Virginia and consists of two separate members deposited during the middle Ordovician period. The upper member, the Utica shale, is composed of black calcareous shale with total organic carbon (TOC) up to 3.5%. This upper member has seen tremendous development in eastern Ohio and is known for producing significant quantities of wet shale gas. The underlying member of the Utica, the Point Pleasant shale, consists of interbedded limestone and shales and is organic-rich with TOC content up to 4–5%.

The Point Pleasant shale is the primary oil target of the UPP due to its higher organic content. Across the play, the Point Pleasant shale ranges in thickness from 25 to 200 ft (7.6–61 m), at depths from 3,800 to over 10,500 ft (1,158–3,200 m) and bottom-hole temperatures ranging from 100 to 210°F (38–99°C). Compared to other well-studied unconventional formations, the Point Pleasant shale generally has a higher carbonate content, higher concentrations of calcium, iron and strontium, and lower concentrations of barium in the produced water.\textsuperscript{13,25-30} Additionally, the reservoir depths, pressures and temperatures will differ in comparison to other formations, such as the Bakken with depths between 8,500 and 11,500 ft. (2,931 and 2,963 m) and initial reservoir pressures and temperatures of 8,000 psi (55.2 MPa) and 240°F (115.6°C), the Eagle Ford with depths between 5,000 and 11,500 ft. (457.2 and 4,267.2 m) and initial reservoir pressures and temperatures at 10,000 psi (68.9 MPa) and 300°F (148.9°C) and the Niobrara with depths between 5,500 and 8,500 ft. (457.2 and 4,267.2 m) with initial reservoir pressures and temperatures of 4,500 psi (31.0 MPa) and 240°F (115.6°C).\textsuperscript{31-33}

On the western side of the UPP play, the depth and thermal maturity of the Point Pleasant shale is such that rich oil deposits are found, forming the UPP Oil Window (OW). A study by Patchen et al., estimates the mean technically recoverable oil volume within the UPP OW to be approximately 2 billion barrels (bbl).\textsuperscript{25} Other liquids-rich unconventional shale plays in the U.S. include the Permian, Bakken, Eagle Ford, and Niobrara. Compared to the UPP, these plays are further-along in development due to early success in well production. While the UPP OW has the potential to be a significant tight oil reservoir, it has yet to be fully developed.

In this study, aqueous phase reactions taking place in hydraulic fracturing/reservoir fluids with UPP shale samples are studied at relevant reservoir conditions using experimental and geochemical modeling methods. Experimental trials were conducted, monitoring solution chemistry in combination with pre- and post-trial shale analyses to assess scaling potential. Geochemical modeling is also reported and compared with experimental results.

2 | MATERIALS AND METHODS

2.1 | UPP shale

Shale core samples were provided by Anadarko and Artex Energy, LLC. Cores from the Brookfield 3H well were located at a depth of 6,670 ft (2,033 m) in Noble County, Ohio. Testing samplers were prepared by wet cutting a core into several chips (1.6 × 1.0 × 0.3 in.) (4.1 × 2.5 × 0.8 cm) containing at least one parallel bedding plane for feature relocation. Remaining core scrap was crushed via a mortar and pestle into powder samples (~150 μm) and used to simulate bulk chemistry.

2.2 | X-ray diffraction mineralogy

Portions of the UPP shale core samples were pulverized into powder. The powder was used to determine mineral composition via X-ray diffraction (XRD; Rigaku Ultima IV). XRD patterns were captured at 2θ between 10° and 70° with a scan rate of 1°/min. Approximate weight percentages were calculated using the relative intensity ratio (RIR) method with the XRD pattern.
2.3 Synthetic fracturing fluids

The simulated HFF used in this study contained chemicals and concentrations similar to the formula used in the initial Brookfield 3H well completion, the HFF composition is shown in Table 1. For experimentation, two synthetic HFF compositions were tested. To simplify aqueous system chemistry, scale inhibitor was omitted from HFF solutions to create a favorable precipitation environment. Iron control was included in the Trial 1 HFF solution, with its omission in Trial 2 and 3 HFF solutions. Industrial chemicals used include CC-1, SC-2 and FR-1 obtained from Halliburton and Ecopol-FEAC and Ecopol 2000PTW from Economy Polymers.

2.4 Produced water

Produced water was collected from the Brookfield 3H well in February 2018, approximately 6 years after onset of production. Water collected at this stage of production was deemed to be similar in composition to the well’s formation water. To protect against oxidation, the water was continuously purged with nitrogen during collection and storage. Water composition was analytically quantified using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Ion Chromatography (IC) and pH measurements. Chloride concentrations were calculated using the Geochemist’s Workbench Spreadsheet module using dissolved ion results from ICP to determine chloride ion concentration to achieve solution charge neutrality. The pH of the water was found to be 5.64 and the Brookfield 3H produced water ion composition is shown in Table 2.

2.5 Analytical methods

Pre- and post-trial analyses of shale samples were completed using scanning electron microscopy with an energy dispersive x-ray spectroscopy attachment (SEM/EDS; JEOL JSM-6390LV/QUANTAX 400 with XFlash 6) and Laser Induced Breakdown Spectroscopy (LIBS, Applied Spectra J200). SEM samples were captured using a voltage of 15 kV. LIBS samples were ablated at 20% energy (~3.6 mJ) and analysis was completed at Applied Spectra’s facility in Fremont, CA. Relocation analysis via SEM-EDS and LIBS was performed by preselecting regions and features of interest in the bedding plane and relocating these features post-trial allowing physical and chemical transformations to be analyzed.

The test fluid was characterized for changes in dissolved ions concentrations (shown in Table 2) via ICP-OES and Fe$^{2+}$ was determined via ultraviolet-visible spectroscopy (UV-Vis; Hach DR6000) using the 1,10-phenanthroline method. Fe$^{3+}$ concentration was determined via difference between total iron, determined via ICP-OES, and Fe$^{2+}$ concentrations.

2.6 Experimental procedure

Experimental trials were completed in a 1.2 L nonstirred autoclave reaction chamber lined with Teflon, shown in Figure 1. The setup

| Chemical | Brookfield 3H (wt.%) | Trial 1 (wt.%) | Trial 2 and trial 3 (wt.%) | Purpose |
|----------|---------------------|---------------|---------------------------|---------|
| Deionized water | 99.24 | 99.26 | 99.27 | Carrier fluid |
| 7.5% hydrochloric acid | 0.424 | 0.424 | 0.424 | Acid |
| 1 wt.% propargyl alcohol | 0.002 | 0.002 | 0.002 | Acid inhibitor |
| 5 wt.% 2,2-dibromo-3-nitrilopropionamide (DBNPA) | 0.024 | 0.024 | 0.024 | Biocide |
| CC-1 | 0.183 | 0.183 | 0.183 | Cationic clay stabilizer |
| Ecopol-FEAC | 0.003 | 0.003 | 0.0 | Iron control |
| SC-2 | 0.024 | 0.0 | 0.0 | Anionic scale inhibitor |
| FR-1 | 0.076 | 0.076 | 0.076 | Anionic friction reducer |
| Sodium persulfate | 0.001 | 0.001 | 0.001 | Breaker |
| Ecopol-2000PTW | 0.024 | 0.024 | 0.024 | Gellant |

| Ion | Concentration (mg/L) |
|-----|----------------------|
| B$^{3+}$ | 1.47 |
| Ba$^{2+}$ | 2.32 |
| Ca$^{2+}$ | 32,820.0 |
| Fe$^{2+/3+}$ | 129.0 |
| K$^{+}$ | 744.0 |
| Li$^{+}$ | 40.3 |
| Mg$^{2+}$ | 3,890.0 |
| Mn$^{2+}$ | 1.48 |
| Na$^{+}$ | 49,700.0 |
| P$^{3-}$ | 1.61 |
| S$^{2-}$ | 290.0 |
| Si$^{4+}$ | 132.0 |
| Sr$^{2+}$ | 2,450.0 |
| CO$_3^{2-}$ | 76.1 |
| SO$_4^{2-}$ | 621.0 |
| Cl$^{-}$ | 150,600.0 |
consists of a stainless steel sampling system with a ball valve (BV 102) and needle valve (NV 101) for controlled sample collection, three heating bands (1,000 W, Watlow) with a temperature controller, a dual piston pump (HPLC) and a pressure relief system attached to a relief tank.

Experimental trials were completed at 57°C (135°F) and 26.9 MPa (3,900 psi) matching downhole conditions of the Brookfield 3H well. The system was leak checked at operating conditions with a mixture of synthetic fracturing fluid and produced water (30/70 ratio by mass) to avoid background reactions between the fluids and reactor material of construction. Experiments were initiated placing a shale chip and 6 g of powder into the equilibrated reactor and removed after duration of the trial.

Liquid samples (30 ml of fluid) were collected at initiation of each trial and on days 0, 1, 3, 6 and 12. Samples were split into two sets for further analysis. 15 ml of sample was filtered through 0.45 μm filter and preserved by adding 50 μl of HNO₃ for ICP-OES analysis. An unfiltered sample was used for a pH measurement and preserved with 50 μl of HNO₃.

3.1 | UPP shale core mineralogy

UPP shale sample composition was evaluated using XRD. Mineralogy for the UPP shale core was determined using the RIR method and is presented in Table 3. Mineralogy was divided into three categories: carbonates, clays and other minerals to compare with other producing unconventional formations. Mineralogy results are in good agreement with characterizations of UPP shale from other locations within the play. Pyrite (FeS₂) was not observed via XRD in this study; however, SEM/EDS analyses of pretrial samples indicate Fe and S are found in the same locations, indicating presence of pyrite. Shown in Figure 2 are EDS signals of iron (red), sulfur (blue) and overlap of iron and sulfur signals, likely pyrite (purple). Mineralogy results from this and other published studies for UPP, Bakken, Eagle Ford and Marcellus shale formations are shown in Figure 3 with data provided in Table S1.

3.2 | Absence of scale inhibitor

To develop an understanding of scaling phenomena between UPP shale and associated HFF, a trial was performed using the fluid composition (Table 1) without addition of scale inhibitor (SC-2, Halliburton). The purpose of this trial was to serve as a baseline for future work, create an environment favorable to precipitation, and identify precipitate form(s).

Soluble elemental species likely to precipitate from the reservoir formation fluid include Ba²⁺, Ca²⁺, Fe²⁺/³⁺, Sr²⁺, P³⁻ and S²⁻; therefore, these ions were monitored during the trials. In the Brookfield 3H well, scaling ions with highest concentrations are calcium and strontium, 32,820 and 2,450 mg/L, respectively. These ions form sulfate-based scales and whether these ions will precipitate will be dependent upon the thermodynamics and sulfate concentration. In the Brookfield 3H well, the sulfate concentration (621 mg/L) is

### TABLE 3
Approximate mineral composition of Brookfield 3H shale core as determined by XRD analysis

| Mineralogy | Mineral | Weight (%) |
|------------|---------|------------|
| Clays      | Chlorite (Mg₆Fe₃Al₃Si₃Al(OH)₂) | 11 |
|            | Muscovite (K₉(Fe₆Al₂O₃)(SiO₂)₉) | 25 |
| Carbonates | Calcite (CaCO₃) | 35 |
|            | Dolomite (CaMg(CO₃)₂) | 4 |
| Other minerals | Quartz (SiO₂) | 25 |
greater than the median value for Marcellus shale flowback water (41 mg/L). This elevated sulfate concentration increases the likelihood calcium and strontium will form sulfate precipitates in UPP wells. Additionally, barium also forms sulfate scales and has the lowest solubility product of the three divalent cation sulfates. In the Brookfield 3H well barium has the lowest concentration of the scaling ions (2.32 mg/L) and orders of magnitude lower than the median flowback concentration for Marcellus shale wells (164 mg/L). Although at lower concentrations, barium still has a high probability to precipitate due to its low solubility product and elevated sulfate content of the reservoir water.

Iron is another component which may precipitate based upon produced water concentrations. In the Brookfield 3H well, the iron concentration (129 mg/L) is greater than the median flowback concentration for Marcellus shale wells (29.7 mg/L). Additionally, when iron is in the ferrous state and oxygen is present, there is a high likelihood for oxidation to the ferric state. In conjunction with ferric hydroxide's low solubility product, iron precipitation is favorable in the Brookfield 3H well.

Data for these scaling ions was normalized to solution chemistry at trial initiation (i.e., Day 0) and used to assess formation of insoluble precipitates during the trial. Increase in normalized ion concentration would indicate dissolution of shale species, decrease in normalized concentration would indicate scale precipitation, while no change would indicate the ion was in chemical equilibrium. Normalized ion concentration trends and solution pH for the trial without scale inhibitor are shown in Figures 4 and 5 with data provided in Table S2.

In the absence of scale inhibitor, Ba$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ appear to be in chemical equilibrium. Dissolution of S$^{2-}$ and P$^{3-}$ occurs initially, followed by chemical equilibrium after 6 days. P$^{3-}$ can be conservatively assumed to be orthophosphate (PO$_4^{3-}$). However, with low initial P$^{3-}$ concentration, it is difficult to discern if the source is via dissolution of phosphorus containing minerals or experimental/analytical error. Ba$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$ prefer to form sulfate-based precipitates as shown in Equations (1) through (3).

Solubility of sulfate products from these ions decreases with increasing cation atomic radius, with

![FIGURE 2](image-url)  
UPP shale SEM image with EDS signals for iron and sulfur [Color figure can be viewed at wileyonlinelibrary.com]

![FIGURE 3](image-url)  
Mineralogical comparison of producing unconventional formations [Color figure can be viewed at wileyonlinelibrary.com]
Ca, Sr, P increase in elemental S_2^\text{−}\) formation of these scales. This hypothesis is further supported by the barite possessing a very low solubility; solubility products for each mineral are provided next to their respective mechanism. Due to Ba^{2+}, Ca^{2+}, and Sr^{2+} all failing to form sulfates in this trial, lack of sulfate is likely limiting formation of these scales. This hypothesis is further supported by the increase in elemental S_2 with favored Fe^{2+/3+} precipitation regions. Due to Ba^{2+}, Ca^{2+}, and Sr^{2+} scales are likely unnecessary components in this study was a mixture of citric and acetic acid, which is known to chelate to metal ions, preventing their precipitation under thermodynamically favored conditions.

\begin{align*}
\text{Ba}^{2+}(aq) + \text{SO}_4^{2−}(aq) &\rightarrow \text{BaSO}_4(s); \log(K) = 9.97 \at \text{25}°C \\
\text{Sr}^{2+}(aq) + \text{SO}_4^{2−}(aq) &\rightarrow \text{SrSO}_4(s); \log(K) = 6.63 \at \text{25}°C \\
\text{Ca}^{2+}(aq) + \text{SO}_4^{2−}(aq) &\rightarrow \text{CaSO}_4(s); \log(K) = 4.36 \at \text{25}°C \\
\text{FeS}_2(s) + \text{H}_2\text{O} + \frac{7}{2}\text{O}_2 &\rightarrow \text{Fe}^{2+}(aq) + 2\text{SO}_4^{2−}(aq) \\
&+ 2\text{H}^+(aq); \log(K) = 207.3 \at \text{25}°C
\end{align*}

3.3 | Absence of scale inhibitor and iron control

Additional trials were performed without scale inhibitor or iron control (Ecopol-FEAC), to assess the inhibiting effect of the iron control agent. Normalized ion and pH results in the absence of iron control were consistent with the previous trial, with iron as the only precipitating specie. Figure 7 presents the solution pH with time, showing Fe^{3+} precipitation favored over Fe^{2+}, while normalized iron results are shown in Figure 8 with data provided in Table S3.
concentration was found to be lower in the absence of iron control (Trial 1), as minimal Fe\(^{3+}\) remained in solution at trial’s end. Pre- and post-trial analyses were performed via SEM/EDS relocation. EDS results were used to qualitatively assess precipitation or dissolution at the shale surface (i.e., signal intensity was used to assess shale surface elemental composition changes). Figure 9 presents SEM/EDS images for a pre- and post-trial sample at the same location. EDS results indicate iron to be the only element with noticeable change after the trial. Some noticeable differences can be seen in shale’s surface structure, appearing smoother after exposure to the HFF. This smoothing appearance is likely caused by dissolution of carbonate minerals located at the sample’s surface when in contact with the acidic HFF solution. The pretrial iron signal is likely from iron bearing minerals such as pyrite and chlorite in the shale, while post-trial analyses appears to be from an iron-based precipitate on the shale surface. Identification of iron hydroxide on the shale surface was not possible, as EDS is unable to assess light elements (such as H) and likely presence of multiple iron forms between the shale and precipitate(s). However, SEM/EDS analyses do support solution chemistry results indicating iron precipitation occurred during the trial. Scaling elements such as Ba\(^{2+}\), Ca\(^{2+}\) and Sr\(^{2+}\) did not exhibit any discernible changes in post-trial signal intensity, also corroborating solution chemistry results.

A second trial with HFF without scale inhibitor and iron control was completed to allow for pre- and post-trial LIBS analyses. Normalized ion concentration and solution pH results were consistent with the previous trial, indicating the precipitation of iron-based species. Pre- and post-trial LIBS analyses were completed at a shale bedding plane. Elements studied in the analyses include: Al, Ba, C, Ca, Fe, H, K, Mg, Na, O, Fe, Si, Sr and Ti. To acquire data, a 15x15 grid pattern (2.5 mm × 2.5 mm area) was used for LIBS elemental mapping. At each grid point, ten 30 μm laser pulses with a laser energy output of 20% were applied. The first three shots at each location were used to remove any surface contamination and omitted from analyses. Qualitative analyses were performed using the J200 LIBS instrument’s Clarity software. Similar to qualitative EDS analyses, element signal intensity was used as a means to assess element precipitation/dissolution. Si signal intensity is assumed to remain constant as the element is associated with inert minerals. Pre- and post-trial LIBS analyses for Ca, Fe, Si and Sr are shown in Figure 10.

LIBS results indicate a decreased intensity for all element signals, except Fe and H. This signal decrease is likely caused by formation of an iron-based precipitate surface with sufficient thickness to mask intensities of other elements. Pre- and post-trial iron results clearly indicate an increase in iron content at the shale surface, especially in the upper and right portions of the examined area. Formation of iron precipitate would likely affect results as the layer would not be removed with cleaning shots. Scaling elements such as Ba\(^{2+}\), Ca\(^{2+}\) and Sr\(^{2+}\) did not show increased intensity, indicating lack of precipitate formation, consistent with both solution chemistry and SEM/EDS analyses. Furthermore, Ba\(^{2+}\) was undetected in both the pre- and post-trial samples indicating barite formation is not of concern in this location. Similar studies involving Marcellus shale samples have shown barite to form after treatment with HFF.11,21 Due to the geographical proximity of the Marcellus and UPP shales and the tendency to reuse flowback and/or produced water, introduction of barium laden water into UPP wells may induce barite formation.43

3.4 | Geochemical modeling

Geochemical modeling was performed to compare with experimental observations using the GSS Module in the GWB v.11 software.
FIGURE 9  Pre- and post-trial SEM/EDS results for UPP shale samples exposed to HFF w/o scale inhibitor or iron control. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 10  Pre- and post-trial UPP shale bedding plane LIBS analyses for Fe, Ca, Sr, Si, C, H and O after exposure to HFF without scaling inhibitor or iron control. [Color figure can be viewed at wileyonlinelibrary.com]
Saturation indices of common scale formations were determined for the following cations: Ba\(^{2+}\), Ca\(^{2+}\), Fe\(^{2+}\), Fe\(^{3+}\) and Sr\(^{2+}\). These indices were calculated using solution ion concentrations, pH and temperature for the investigated solution chemistries. Saturation indices were determined for each day and plotted as log(Q/K) with time. Saturation indices versus time for barite, ferrous hydroxide and ferric hydroxide are shown in Figure 11 through Figure 13, respectively with data provided in Tables S4 and S5. Saturation indices for minerals consisting of Ba\(^{2+}\), Ca\(^{2+}\), Fe\(^{2+}\) and Sr\(^{2+}\) indicated all were undersaturated (i.e., precipitation should not occur), while saturation indices for Fe\(^{3+}\) were negative after 3 days, becoming positive for the duration of the trial. Precipitation onset for each mineral varies due to kinetics, meaning there is no set saturation value to definitively determine when precipitation occurs. Instead, the saturation indices are a tool to create an informed decision based on thermodynamics and needs to be paired with experimental observations to make an educated assessment with regards to precipitation.

The saturation index for barite (Figure 11) indicates scale precipitation is negative for the duration of both trials. Normalized Ba\(^{2+}\) concentration results from the experimental trials indicate trace barium dissolution from the shale occurred within the first days, but then remained constant through the remainder of the trials. Further, post-trial analyses (EDS and LIBS) did not indicate an increase in barium signal intensity at the shale surface. This combination of solution chemistry results and post-trial analyses indicates barite precipitation is not favored.

Saturation indices for ferrous and ferric hydroxides indicate very dissimilar tendencies toward precipitation. Specifically, ferrous hydroxide's saturation index (Figure 12) indicates the solution is highly undersaturated throughout the trial and precipitation is not thermodynamically favored. However, ferric hydroxide’s saturation index (Figure 13) is initially negative becoming positive by day three, indicating the solution has become supersaturated and precipitation is thermodynamically favored. The thermodynamic results clearly indicate iron scale formation is thermodynamically favored via an Fe\(^{3+}\) route, which paired with ICP-OES and UV–Vis results indicates Fe\(^{2+}\) is oxidized to Fe\(^{3+}\), Equation (5), providing a path for hydrolysis to occur, Equation (6), resulting in the formation of iron hydroxide scale. Furthermore, post-trial EDS and LIBS analyses clearly indicate iron scale formation occurred during the trials. In addition, chelating agent effect is also shown in the saturation indices. When citric and acetic acid is present, some Fe\(^{3+}\) remains in solution, causing the higher saturation indices observed in Figure 13.

4 | CONCLUSIONS

This research provides a preliminary assessment of UPP well geochemistry during initial completion activities. Experimental trials along with pre- and post-trial material analyses indicate iron scaling is a concern in UPP shale wells. During experimentation, Fe\(^{2+}\) was found to oxidize to Fe\(^{3+}\), which then hydrolyzed forming a precipitated scale. Under in-situ conditions Ba\(^{2+}\), Ca\(^{2+}\) and Sr\(^{2+}\) appear to remain in solution indicating scaling inhibitors targeting these ions may have little utility within this formation. Post-trial LIBS and EDS analyses agree that an iron-based precipitate(s) formed on the surface of the shale samples and are the cause for aqueous iron decline observed in ICP-OES and UV–Vis results. Further, geochemical modeling corroborates experimental results indicating Fe\(^{2+}\) oxidation and subsequent Fe\(^{3+}\) precipitation as the likely path to iron scale formation.
The presented research provides an effective experimental methodology to mimic downhole geochemistry phenomena within UPP wells. A limitation of this study is the omission of proppant which is present within the fracked shale/fluid mixture. Proppant which is predominantly composed of silica should be inert and would only react in this study if hydrofluoric acid was used in the fracturing fluid. Future work will evaluate the effect of iron control on the kinetics of iron oxidation to identify a cost-effective solution to prevent or slow iron scale formation within UPP wells.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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