Impact of Iron Minerals in Promoting Wettability Alterations in Reservoir Formations

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ABSTRACT: Asphaltene adsorption and deposition onto rock surfaces are predominantly the cause of wettability and permeability alterations which result in well productivity losses. These alterations can be induced by rock–fluid interactions which are affected by well operations such as acidizing, stimulation, gas injections, and so forth. Iron minerals are found abundantly in sandstone reservoir formations and pose a problem by precipitation and adsorption of polar crude components. This is due to rock–fluid interactions, which are dependent on reservoir pH; thus, this research work studied the surface charge development of pyrite, magnetite, and hematite. To ascertain conditions that will result in iron mineral precipitation and adsorption of asphaltene on iron mineral surfaces, zeta potential measurement was carried out. This is to determine the charge and colloidal stability of the iron mineral samples across wide pH values. Experimental results show that the charge development of iron minerals is controlled by mineral dissolution, the formation of complexes, adsorption of ions on the mineral surface, and the collapse of the double layer. The findings provide insights into the implications of iron mineral contacting crude oil in reservoir formations and how they contribute to wettability alterations due to different well operations.

1. INTRODUCTION

Wettability alteration in reservoir rocks is often attributed to the coating of the rock surface by polar molecules like asphaltenes and resins.1 Wettability alteration has been looked at by many researchers2–7 from a fluid–fluid interaction point of view; however, this work is an attempt to provide insights into solid–fluid interaction contribution to asphaltene depositional problem. asphaltene is the most polar and heaviest fraction of crude oil and is often defined as a solubility class that is insoluble in alkanes and soluble in aromatic fluids.8 Due to the complexity of the asphaltene molecule and lack of definite knowledge about its behavior in different fluid environments and its interactions with different rock mineralogy, a robust solution to its adsorption on reservoir rocks is still an area of investigation. asphaltene is said to be negatively charged,9 which goes to say that its adsorption on rock surfaces can only be possible at sites that are positively charged. Iron minerals (hematite, pyrite, magnetite, and ankerite) are one of such minerals that provide a site for asphaltene molecules due to precipitation of ferric and ferrous ions. The adsorption of ions to rock surfaces is a fundamental phenomenon that influences several subsurface processes including transport of colloidal particles, mineral dissolution and kinetics, and migration of cations and anions in the porous media.9 Thus, understanding the prevailing process that controls ion exchange in reservoir conditions becomes critical as iron mineral interactions are controlled by their stability, dissolution rates, specific surface area as well as their mineral structure and behavior in different environments. Well operations such as low salinity water flooding (pH = 6–7), treatment after drilling operation (pH < 4), alkaline flooding (pH > 10), acidizing (pH < 2–3), and so forth induce pH change in the reservoir and turn to alter the rock surface, thus initiating rock–fluid interactions that otherwise were not possible. This, then, promotes mineral particle precipitation, change in surface chemistry, and asphaltene adsorption onto the surface. Colloidal particles in aqueous solutions such as the hydroxides, oxides, sulfides, and oxyhydroxides develop charges on their surfaces as a result of mineral dissolution, adsorption of counterions, and formation of complexes which are responsible for maintaining the chemical equilibrium in the reservoir. Zeta potential values of colloidal suspension depict not just the sign of the charge on the particle surface but also the colloidal stability of the particle in suspension.10 Thus, if all particles have large negative or positive values of zeta potential, they will repel each other and their dispersion is considered.
stable. Alothi et al.11 pointed out that zeta potential values of particles within ±30 mV are considered unstable and could reverse their charges upon interaction with other fluids. Positive charges arise due to protonation of a neutral surface hydroxyl group where a corrosion product such as magnetite (M=OH) is formed.

The charge development of the iron minerals is dependent on the nature (pH) of the environment and different well operations such as acidizing, fracturing, low salinity water flooding, and CO₂ injection, inducing different pH environments in the reservoir. Thus, it is imperative to explore the wide range of surface charge possibilities of the iron minerals to ascertain the conditions that would promote the adsorption of asphaltene molecules and induce wettability alterations. Although the surface charge of fully oxidized iron minerals has been reported in the literature,12−19 to the best of our knowledge, no one has explored its potential to provide an adsorption site for asphaltene molecules. With the conditions promoting asphaltene adsorption identified, proper design of remedial action can be implemented to mitigate production loss due to wettability alterations especially around the wellbore.

Sandstone reservoirs have more abundant iron minerals compared to the carbonate formation. However, with the sandstone rock containing predominantly quartz, iron minerals, feldspar, and clays as well as iron minerals, which is most controlling of the wetting state is unclear. Thus, sandstone is been reported to be oil wet,20−24 neutral wet,25,26 and water wet,27−29 with the effect of minerals on surface wetness well documented. Though in this work, the effect of iron minerals is studied. Iron oxides have been recently reported to have applicability as Enhanced Oil Recovery (EOR) fluids owing to their magnetic response properties.30 More so, their nanoparticles result in a reduction in interfacial tension which can be attributed to their high hydrophobicity, adsorption, and magnetoresponsive properties which serve as a driving force for their interactions with surfaces.30

Pyrite is the earth’s most abundant mineral and its presence in reservoir rocks is been reported to have both economic and environmental importance.31 Pyrite is also a sulfide mineral that is found in igneous rocks, sedimentary beds, and hydrothermal deposits.32 It has less economic value but its presence in the reservoir rock even as little as 1% may pose a risk to crude oil production. This is due to its precipitation and surface charge which may contribute to the adsorption of polar crude components (asphaltene) onto the rock surface, thus resulting in wettability alteration. Pyrite surface charge has a significant effect from a solid−fluid interaction point of view and is highly dependent on the medium pH,33 which also is controlled by the amount and type of salts present as well as the environmental (anoxic or oxygen-rich) conditions. Weerasooriya and Tobschall34 report the effect of pH on the surface charge of pyrite in pyrite−water interactions and concluded that the surface charge is controlled by the presence of H⁺, OH⁻, and Fe²⁺. More so, pyrite is determined to be negatively charged down to a pH value of 2 under anoxic conditions and in the absence of potential determining ions (PDIs) which are mostly present in reservoir water. Thus, the surface charge of iron sulfide is not only dependent on pH but also on the ion activity in the solution.32

Bebić and Schoonen35 investigate the interactions between low-molecular weight organic compounds and pyrite under anoxic conditions using a combination of batch sorption experiments and electrophoresis measurements. The authors based on their observations suggested the existence of interactions among acetate, ethylamine, purine, carbamide, adenine, and amino acid cysteine, as well as D-ribose, glycine, and alanine despite the negative charge of the pyrite surface. These interactions were said to be dictated by specific surface site interactions rather than electrostatic forces. Pyrite interactions with water and36 organic compounds,35 as well as its surface charge in acidic and basic mediums35 have been reported. However, limited work exists on the surface charge of pyrite over a wide range of pH aimed at elucidating the potential of asphaltene adsorption.

Hematite (Fe₂O₃) is a naturally occurring iron mineral and an important raw material used in steel and iron production, with over 8 million tons of its superfine lost yearly in iron ore washing plants.37 To recover this superfine, the magnetic flotation method is implemented by coating the hematite surface with sodium hexametaphosphate or sodium silicate which makes the surface negatively charged and keeps the hematite in suspension. Similarly, humic acid is used to improve the colloidal stability and thus modifies its surface chemistry and stability.38 Isoelectric points (IEP) and point of zero charge (PZC) of hematite are fundamentally different concepts that have been used wrongly in the literature by some researchers. The PZC is the pH at which the surface charge equals zero, whereas the IEP occurs when the zeta potential becomes zero.39 The values can be similar but in real-life cases can be significantly different; thus, it is important to avoid the wrong use of terms. Natural and synthetic hematite have different zeta potential values, which can be attributed to the presence of silica in the natural mineral samples.18 Several studies16,37−40 have been published on the effect of pH on hematite with no consideration given in the context of petroleum reservoir and asphaltene adsorption.

Magnetite is an iron oxide (Fe₃O₄) with high solubility due to the formation of Fe²⁺ complexes with chloride.9 This property along with its surface chemistry has been reported to vary with temperature, however, can retain its surface charge even at high-temperature conditions.41,42 Furthermore, magnetite is a good adsorbent for hazardous species from aqueous solutions (uranium, cesium, etc.) and as such provides an adsorption site even in the case of petroleum reservoirs.43 However, limited reports exist about its role in crude oil polar fraction adsorption which results in wettability alteration. Also, studies are scarce that map well operations to changes in magnetite interfacial and surface chemistry.

So, it is safe to say that the presence of iron minerals in reservoir rocks poses concerns especially when they are crude oil contacting minerals. This is because their surface chemistry (charge) is controlled by the surrounding fluid which affects their colloidal stability and propensity to the precipitate. The surface charge of iron minerals in different pH environments and their interactions with salts are studied here using electrophoresis measurements. This is to provide insights into the nature of their charge and how stable the particles are in a different environment. Thus, the objective of this study is to establish the contributions of iron minerals as potential determining minerals in asphaltene deposition in reservoir rocks. This is based on the premise that asphaltene which is negatively charged will only adsorb on the rock if it is contacted by a positively charged rock mineral. These minerals however possess different charges and may as well experience charge reversal. So, in an attempt to combat wettability

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alteration due to asphaltene adsorption onto the rock surface, it becomes imperative to understand the behavior of rock minerals under different conditions and ascertain their role in aiding polar compound adsorption due to their surface charge interactions.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction. X-ray diffraction (XRD) analysis of the samples was conducted to determine the presence of other crystalline phases. Figures 1–3 present the XRD diffractogram of the pyrite, hematite, and magnetite samples used in this study overlaid with peaks of pure samples for reference, and as vivid, the XRD results show dominant peaks and a small percentage of impurity (quartz). The percentage of quartz in the samples is 22, 28.4, and 1.6%, respectively, for pyrite, hematite, and magnetite. The presence of quartz in the samples depicts that the samples used in this study are natural mineral samples as the synthetic samples do not have quartz content. Furthermore, with the high percentage of the iron mineral samples in our study, it can be said to be a good representative of the minerals as they are found in the reservoir. Thus, our analysis can be translated to depict how these minerals would interact in situ.

2.2. Zeta Potential Measurements. Zeta potential measurements of pyrite, hematite, and magnetite particles suspended in a buffer solution of varying pH (1–13) were conducted as a function of salt type (NaCl, CaCl₂, MgCl₂, NaHCO₃, and Na₂SO₄) and concentrations found in the
reservoir to quantify the effect of salts on the charge modification of the mineral surfaces. Methods of measuring zeta potential can be said to be four (electrophoresis, electroacoustic, electroosmosis, and streaming potential). Each method is useful in a different scenario with consideration to particle size, for example, streaming potential works best with particles too coarse to remain suspended in solution, electrophoresis is useful for particles fine enough to remain suspended in solution for an extended period, whereas for nanosized particles, recent advancement has made electroacoustic popular however requires lots of samples.

Zeta potential measurements of such minerals with high settling characteristics must be conducted with care with attention paid to the concentration optimization procedure. The particle sizes of the mineral powders in this study are 6.6, 1.33, and 13.93 μm, respectively, for pyrite, hematite, and magnetite powder, and with such sizes and using the Zetasizer Nano Z instrument, high noise to signal ratio becomes a problem which poses repeatability concerns. However, with a
sample concentration of 10 mg/100 mL, good measurement with high repeatability and a standard deviation of ±3 mV is achieved.

2.2.1. Pyrite. Zeta potential values of pyrite particle in 0.1 M salt solutions across a pH range of 1−13 are presented in Figure 4. The reference sample is referred to as base with no salt interactions. Vivid from the trend of the base in Figure 4, the zeta potential values across pH 1−11 are less than ±10 and at pH 12 and above, a zeta potential value above ±30 is recorded. Zeta potential values provide insights into the nature of the surface charge and the colloidal stability of the particles owing to electrostatic repulsion between particles of similar charge resulting in their segregation. A large positive or negative value of zeta potential above ±30 mV is considered to indicate good physical colloidal stability. On the other hand, values less than ±30 can result in particle aggregation, flocculation, and precipitation due to the van der Waal forces of attraction which result in physical instability of the colloidal suspension. Thus, pyrite mineral has a high propensity to precipitate at pH values less than 11 and this is without putting into consideration its interaction with salts.

Pyrite particle interaction with monovalent salt like NaCl (Figure 4B) has a similar effect to the base case in the acidic pH regions as close values are recorded; however, a reduction in the zeta potential values in the alkaline pH region is recorded, which further reduces its stability. Sodium chloride has a high propensity to precipitate at pH values less than 11 and this is without putting into consideration its interaction with salts.

Pyrite particle interaction with divalent salt like CaCl₂ and MgCl₂ (Figure 4C), the stability of pyrite particle in the solution across all pH is further compromised with charge reversals observed which is not surprising as these two ions have been reported to be PDIs and find applications in the low salinity waterflooding process. The pyrite particle charge reversal by the PDIs possesses concerns as it would induce adsorption of polar compounds like asphaltene, resins, surfactants, polymers, and other negatively charged molecules to the reservoir which would invariably result in wettability alteration or reduction in production efficiency. In the case of the 0.1 M anionic salts (Na₂SO₄ and NaHCO₃) solutions (Figure 4D), negative zeta potential is observed which can be attributed to the adsorption of the anions on the mineral surface. From the trends of both anionic salts, the stability of pyrite mineral is increased with the higher negative values recorded. In this case, an increase in acidity of the medium results in a reduction in the zeta potential values; thus, the impact of pyrite interaction with anionic salts is more pronounced in an alkaline pH environment.

Figure 5 shows the zeta potential values of pyrite in 1 M salt solutions and its interactions with five different salts. Compared to the trend of NaCl in Figure 4B, the effect of 1 M NaCl solution (Figure 5B) on the surface charge pyrite is

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c05954)
more drastic as charge reversal is overserved at pH values 4−7 and less negative values in an alkaline pH environment. For 1 M divalent salts (CaCl2 and MgCl2) solutions (Figure 5C), similar behavior is recorded for the MgCl2; however, the CaCl2 exhibits high positive values of zeta potential, thus making its effect more pronounced compared to the MgCl2. Charge development of the pyrite mineral is due to oxidation and, adsorption of ions on the mineral surface however, charge reversal could also be due to the collapse of the double layer owing to an increase in counter ion charge density around the surface. Lower values of zeta potentials are depicted for the 1 M salt solutions of the NaHCO3 and Na2SO4 in Figure 5D as compared to the values in Figure 4D. This can be attributed to compression of the double layer around the particles due to an increase in the ionic strength of the solutions however, all negative surface charge is observed for both cases due to the adsorption of the SO2− and HCO3− ions on the pyrite mineral surface.

High negative zeta potential value is likened to water wetness, whereas low negative zeta potential values and positive zeta potential values are associated with oil wetness.26  Thus, pyrite particle charge development is due to elemental sulfur oxidation which results in a hydrophobic nature of pyrite surfaces in an acidic medium.35 Also, the hydrophilicity of the pyrite surface in an alkaline medium is due to the hydrolysis of ferrous hydroxide and then oxidation of ferrous hydroxide to ferric hydroxide. So invariably, the subtle changes in the surface charge of pyrite are due to local oxygen concentration fluctuation, as depicted in eqs 1 and 2.

\[
\text{Fe}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_2 + 2\text{H}^+ \quad \text{positive (1)}
\]

\[
\text{Fe(OH)}_2 + \text{OH}^- \leftrightarrow \text{Fe(OH)}_3 + e^- \quad \text{negative (2)}
\]

Furthermore, Dos Santos et al.,47 using the density function theory plane-wave calculations, affirm the formation of Fe(III)−OH in the pyrite oxidation process and assert the existence of two types of the oxidation process, with the overall reaction represented in eq 3 with the formation of what is popularly called the yellow boy. To break the reactions down into their elementary process, we have three equations to completely describe the reaction of pyrite in the presence of oxygen and water. The first reaction involves the oxidation of pyrite by oxygen, with sulfur being oxidized to sulfate and ferrous ion is released (eq 4). The second reaction (eq 5) involves the conversion of ferrous ion to ferric ion. This reaction is pH-dependent and is said to be the rate-limiting step as it is the slowest of the reactions in acidic mediums and faster in basic mediums. It is mostly accelerated by bacteria.31 The third reaction (eq 6) which may occur is the hydrolysis of iron which results in the splitting of the water molecule and results in the formation of ferric hydroxide. The fourth reaction (eq 7) is a cyclic and self-propagating reaction that involves the oxidation of additional pyrite by ferric ion until pyrite is depleted. It is worthy to note that the oxidation is by iron and not by oxygen.

\[
4\text{FeS}_2 + 15\text{O}_2 + 14\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}^+ + 8\text{H}_2\text{SO}_4 \quad \text{(3)}
\]

\[
\text{pyrite} + \text{oxygen} + \text{water} \rightarrow \text{“yellow boy”} + \text{sulfuric acid}
\]

\[
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad \text{(4)}
\]
pyrite + oxygen + water
→ ferrous iron + sulfate + acidity

\[ 4 \text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (5) \]

ferrous iron + oxygen + acidity → ferric iron + water

\[ 4\text{Fe}^{3+} + 12\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}^{3-} + 12\text{H}^+ \quad (6) \]

ferric iron + water
→ ferric hydroxide (yellowboy) + acidity

\[ \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (7) \]

Generally, it can be said that the pH mediums result in instability of the pyrite mineral and may result in precipitation and adosorption of polar molecules which makes pyrite mineral surface oil wet in high pH. Generally, the low zeta potential exhibited by pyrite mineral makes it an oil wetting material based on its interactions and will induce adsorption of oil wetting materials however, contrary to our observation of oil wetness (low zeta potential values) of the pyrite mineral, Philpott et al. reported adsorption of a water molecule on the pyrite surface using molecular dynamic simulation and made assertion based on analysis of the binding energy between the water molecule and pyrite surface that the pyrite surface should be strongly water wet. However, the effects of salt interactions were not considered by the authors and since the authors did not state the pH of the medium with which their observation was made, these observations were likely made in an alkaline pH environment which is congruent with our findings, as shown in the base trend. So the presence of pyrite in a reservoir rock gives cause for concern if the pyrite is a contacting mineral as it provides an adsorption site for amino acids, alanine, and polar fractions of crude oil; however, each adsorbed species has its fingerprint. Furthermore, the presence of bicarbonate in the reservoir brine results in the formation of iron carbonate and iron oxides which are non-sulphide scales that affect the non-acid solutions used in dissolving iron sulphide scales.

2.2.2. Magnetite. Figure 6 shows the experimentally measured zeta potential values of magnetite particle suspended in 1M salt solution. (A) Base case with no salt interactions, (B) NaCl salt solution effect, (C) CaCl\(_2\) and MgCl\(_2\) salt solution effect, and (D) Na\(_2\)SO\(_4\) and NaHCO\(_3\) salt solution effect.

![Graph A](image1)

![Graph B](image2)

![Graph C](image3)

![Graph D](image4)

**Figure 7.** Experimentally measured zeta potential values of magnetite particle suspended in 1M salt solution. (A) Base case with no salt interactions, (B) NaCl salt solution effect, (C) CaCl\(_2\) and MgCl\(_2\) salt solution effect, and (D) Na\(_2\)SO\(_4\) and NaHCO\(_3\) salt solution effect.
an increase in zeta potential values with an increase in ionic strength of the salt solutions. This can largely be attributed to the collapse of the double layer around the magnetite particle due to an increase in counter ion charge density. Second, this is also due to the decrease in the repulsion energy between the particles as ionic strength increases resulting in increased colloidal stability. Values of the zeta potential of magnetite at 0.1 M salt solutions show that at all conditions, the stability of magnetite is a concern and provides an adsorption prone surface for asphaltene. The effect of an increase in the ionic strength of salt solutions on the surface charge of magnetite is depicted in Figure 7. A look at the trend for the effect of NaCl salt (Figure 7B) shows a wave-like behavior; however, of pertinent interest is the behavior between pH value of 9−13. The surface charge is positive at pH value of 9 and reverses to negative at pH value of 10; this can be attributed to the presence of Cl$^-$ and OH$^-$ in the solution, thereafter a gradual reduction in the negative value of the zeta potential is recorded with an increase in pH until a pH 13 where charge reversal is observed. This behavior is due to the collapse of the double layer around the magnetite particle in solution. Similar behavior is observed in the Na$_2$SO$_4$ trend in Figure 7D; however, with the increase in the ionic strength of the salt solutions, the behavior is observed to be a repetitive one in the case of Na$_2$SO$_4$. So conclusively, the charge development of magnetite particles can be said to be controlled by ion specie adsorption and charge reversal due to double-layer collapse owing to an increase in counter ion charge density. Furthermore, even though colloidal stability may have improved in higher ionic strength solutions, it still presents an adsorption prone surface which is a concern with consideration to asphaltene. Also, this goes to imply that crude oil in contact with magnetite at all pH will result in asphaltene adsorption.

2.2.3. Hematite. Figure 8 shows the zeta potential values of hematite across pH 1−13 and its interactions with different salt solutions of 0.1 M ionic strength. The values of the base trend (Figure 8A) which represent hematite surface charge without salt interaction, clearly show that the particles are unstable (zeta potential values less than ±30). The positive surface charge in the acidic pH region and its subsequent decreases can be attributed to the presence of the H$^+$ ion which is a PDI in hematite interactions. Also, the effect of an increase in the OH$^-$ as the pH increase in the alkaline region is also observed as an increase in pH results in compression of the double layer and results in almost collapsing at pH of 13. Hematite interactions with all of the salt (NaCl, CaCl$_2$, NaHCO$_3$, Na$_2$SO$_4$, and MgCl$_2$) solutions (Figure 8A−D) show similar trends, however, resulted in a different zeta potential value which is all less than ±30 mV, except for NaHCO$_3$ which attains a close value to +30 mV at pH of 1. Thus, it is safe to say that the PDIs in hematite interactions across all pH are H$^+$ and OH$^−$.

Hematite interactions with NaCl, CaCl$_2$, and MgCl$_2$ (Figure 8A−D) show a positive surface charge around the acid pH values which represent adsorption of cations on the hematite surface. On the other hand, the interaction with NaCl (Figure 8B) around the alkaline pH values shows the combined effect of the presence of Cl$^−$ and the OH$^−$ which form complexes as in the case of magnetite. In the cases of hematite interactions with NaHCO$_3$ salt solution (Figure 8D), the adsorption of H$^+$ and Na$^+$ dominates in the acid pH region thus, the surface has a positive zeta potential however, from pH of 6−13, the increase in OH$^−$ ions with an increase in pH dominates, thus
resulting in the negative charge of the surface. On the other hand, interactions with divalent ions like SO$_4^{2-}$ as compared to HCO$_3^-$ showed significant effect around all pH which resulted in predominantly all negative surface charge. This however is still below $-30$ mV. Also, across all pH, hematite presents an adsorption prone surface and exhibits colloidal instability. Owing to an increase in the ionic strength (Figure 9) of the salt solutions, the stability of the colloidal particle is improved. This observation is attributed to the collapse of the double layer around the particle due to double-layer compression with an increase in charge density. Figure 9B shows that with an increase in the ionic solution of NaCl salt, zeta potential values are increased; however, the same trend is observed as in the solution of 0.1 M ionic strength (Figure 8B). Hematite interactions with 1 M solutions of CaCl$_2$ and MgCl$_2$ (Figure 9C) showed improved colloidal stability at extreme pH values (1, 2, 12, and 13). This is to say that hematite is physically stable at extreme pH conditions, however, presents precipitation, flocculation, and oil wetting surface at all pH ranges. Thus, the mere presence of hematite presents a flow assurance challenges like the other iron minerals.

### 3. CONCLUSIONS

Iron mineral surface charge development was investigated in this research work using zeta potential measurements. This work is unique in that it provides insights into the different states of iron mineral surface charge across different pH environments which mimic well operations that induce a change in the pH of the reservoir or around the wellbore. Based on the experimental results, the following conclusions are made:

1. The presence of iron minerals in the reservoir rock presents a problem of asphaltene adsorption, mineral scale formation, and is dependent on well operations that would induce the change in surface charge.
2. Calcium and magnesium ions are PDIs in the interactions of pyrite and magnetite, whereas, in the case of hematite, the interaction is controlled by H$^+$ and OH$^-$ ions.
3. Of the iron minerals, magnetite poses to be the most critical if present as a contacting mineral in the formation and would pose serious concerns.
4. Surface charge development of iron minerals is dominated by adsorption of ion species (cations and anions) on the mineral surface as well as the collapse of the double layer due to counterion charge density increase around the particles.
5. The zeta potential of sandstone rocks with iron minerals having contacting mineral is highly dependent on the surface charge development of the iron minerals as they may precipitate and result in adsorption prone surfaces.

### 4. MATERIALS AND METHODS

**4.1. Materials.** Pyrite, hematite, and magnetite samples were crushed to a fine powder with an average particle size of 6.6, 1.33, and 13.93 μm, respectively, measured using a laser diffraction particle size analyzer by HELOS by Sympatech GmbH. The particle sizes were not reduced to nanoscale because crushing and grinding of the minerals induce changes in the surface structure and destroy the crystallographic orientations. $53–55$ Five different ACS reagent grade salts [sodium chloride (NaCl); calcium chloride (CaCl$_2$); magne-
sium chloride (MgCl₂); sodium bicarbonate (NaHCO₃); and sodium sulfate (Na₂SO₄) were used to prepare the salt solutions of 0.1 and 1 M solutions. The pH control was achieved using a buffer solution prepared using 0.1 M nitric acid and sodium hydroxide (ACS reagent grade).

4.2. Sample Preparation. Powdered samples were washed with deionized water (HPLC grade from Sigma-Aldrich), with the suspension agitated using an orbital shaker for a period of 24 h after which insoluble particles were filtered and dried overnight at 80 °C in a vacuum oven. Aqueous salt solutions (100 mM) were freshly prepared on the day of the experiment, with lower concentrations of 0.1 and 1 mM prepared by dilution of the stock solution. Ingress of CO₂ from the atmosphere was minimized by ensuring that all containers and bottles are sealed throughout sample preparations and measurements.

Samples of 10 mg were conditioned in a 30 mL buffer solution of varying pH (1−13) for 24 h before measurements are taken with the same time frame adopted for the study of the effect of salt concentrations on the surface charge. Samples for zeta potential measurement for the effect of salt solutions on the surface charge were prepared by adding 1 mL of the conditioned sample in a buffer solution to 1 mL of salt solutions (0.1 and 1 mM). The sample mixture was sonicated and allowed to attain equilibrium before measurements were conducted.

4.3. X-ray Diffraction. X-ray powder diffractometry of the samples was conducted using the Rigaku Ultima IV which is a state-of-the-art multipurpose XRD system (Cu-source).

4.4. Zeta Potential Measurements. Zeta potential measurements of samples in electrolytic solution was conducted using a Malvern Zetasizer Nano Z instrument. Laser doppler electrophoresis was used to measure the zeta potential of the colloidal suspensions, and with the application of a voltage across the cell, the mobility of particles undergoing electrophoresis is determined and used to calculate the particle zeta potential using the Henry equation.

\[
U_e = \frac{2E\zeta f(kR)}{3\eta} \tag{8}
\]

where \(U_e\) is electrophoretic mobility, \(E\) is dielectric constant, \(\zeta\) is zeta potential, \(f(kR)\) is Henry’s function (Smoluchowski approx. of 1.5 was used), and \(\eta\) is viscosity. Sample zeta potential was measured at 25 °C and ambient pressure, with each measurement, repeated four times, and the means value with the standard deviation recorded. All measurements are conducted using disposable capillary cells, with the cell and instrument calibrated before measurements.

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Notes

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