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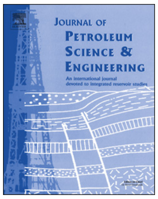

Adsorption and precipitation of scale inhibitors on shale formations

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ABSTRACT

Scale inhibitor is one of the most important ingredients in hydraulic fracturing fluids for shale gas production. However, the adsorption and precipitation behaviors of scale inhibitors on shale formations have never been reported. The objective of this study is to develop mechanistic understanding of interactions between common scale inhibitors and shale formations so that we can predict the fate and transport of scale inhibitors in shale formations. The adsorption and precipitation of DTPMP and PPCA on Eagle Ford and Marcellus shales were studied in batch reactors at oil field temperature of 70 °C. The adsorption kinetics shows a fast adsorption process of inhibitors on shales, and inhibitor concentrations reach equilibrium between 4 and 8 h. In batch adsorption isotherm experiments, initial concentrations of scale inhibitors in aqueous phase varied from 5 ppm to 44,000 ppm. At low DTPMP concentration ranges, surface adsorption occurs on both Eagle Ford and Marcellus. Above certain concentrations, DTPMP and calcium forms precipitate on Eagle Ford, which increases the attachment, and slightly acidic pH and high calcium concentrations enhance the precipitation. The adsorption of PPCA on Eagle Ford was more significant at slightly acidic conditions, and PPCA adsorption onto Marcellus did not exhibit a notable difference between different pH conditions. Due to the strong chelating effect of DTPMP and PPCA, iron was extracted from Marcellus under high inhibitor concentrations.

1. Introduction

Unconventional gas production from shale reservoirs has grown rapidly in recent years as a result of technological advances in horizontal drilling and hydraulic fracturing. During hydraulic fracturing, pressurized liquid made of water, proppant, and chemicals is pumped into shale formation to create fracture, increase permeability, and release the gas. A wide variety of chemicals are added in fracturing fluids for multiple purposes and scale inhibitor is one of the most important ingredients. Scale inhibitor is used to prevent mineral scale formation during fracturing, shut-in and flowback stages. It is reported that the average concentration of scale inhibitor in fracturing fluid is 0.023% (Tollefson, 2013).

Scale inhibitors have been used successfully to control scale formation in conventional oil and gas production (Ramsey and Cenegy, 1985). The most widely used technique to deliver scale inhibitors to the oil and gas production system is a squeeze treatment, during which scale inhibitors are pumped into the formation and retained in the reservoir (Kelland, 2006; Tomson et al., 2006; Yan et al., 2014a). When production resumes, scale inhibitors flow back into produced water, giving protection against scale formation. The reactions between scale inhibitors and formation minerals determine the inhibitor retention and release after inhibitor squeeze treatment. Previous studies on interactions between scale inhibitors and formation have mostly focused on reactions of scale inhibitor in carbonate formation and the mechanism of inhibitor retention in carbonate. These studies show that the primary retention mechanism for scale inhibitors in carbonate formation is precipitation of scale inhibitors with calcium (Baraka-Lokmane and Sorbie, 2010; Kan et al., 2004; Kan et al., 2005). Some studies focused on inhibitor adsorption on sandstone formation, and adsorption is considered the controlling mechanism in sandstone formation (Ibrahim et al., 2012a; Ibrahim et al., 2012b; Kahrwad et al., 2009; Kan et al., 1991; Sorbie, 2010; Veloso et al., 2014; Yan et al., 2014b). Missing in previous studies have been the interactions between scale inhibitors and shale formations. Shales are mixtures of fine grained quartz and clay minerals and can contain other minerals including carbonate minerals, sulfide minerals, and oxide minerals (Chermak and Schreiber, 2014). The reaction between scale inhibitors and shale formations can be totally different from carbonate, sandstone and clay due to the complex nature of shale formations. The adsorption behaviors of scale inhibitors on shale formations have never been reported,

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and whether scale inhibitors precipitate with divalent cations from shale formations also remain largely unknown. It is of great importance to understand the interaction between common scale inhibitors and shale formations to predict the fate and transport of scale inhibitors in shale formations. The primary objective of this study is to develop mechanistic understanding of interactions between common scale inhibitors and shale formations. Two common types of scale inhibitors, i.e. a phosphonate inhibitor and a polymeric inhibitor, were examined in this study. Eagle Ford and Marcellus shale were selected as model shale formations, and the interaction between common scale inhibitors and Eagle Ford and Marcellus shale formations were investigated by batch experiments.

2. Materials and methods

2.1. Materials

Commercial-grade scale inhibitor diethylenetriamine penta (methylene phosphonic acid) DTPMP (Dequest 2060s) was obtained from Solutia. The active concentration of DTPMP in Dequest 2060 s product is 50% by weight. Phosphino-polycarboxylic acid (PPCA) is the active component (50% by weight) of a commercial scale inhibitor Bellasol S29, which was from BWA water additive. These inhibitors were neutralized to pH 7 prior to experiments.

Two types of shale formations, i.e. Eagle Ford and Marcellus, were purchased from Kocurek Industries INC (Caldwell, TX). Shales were crushed and sieved, and ground minerals with a particle diameter between 0.106 mm and 0.210 mm was collected. It was washed by 1% acidic acid to remove highly reactive fines first and then washed by DI water. Finally minerals were dried at 70 °C.

2.2. Characterization

Shales were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET surface area analyzer. XRD patterns were recorded on a Ragaku D/max Ultra II Powder Diffractometer equipped with a Cu Kα radiation source at 40 kV and 40 mA. SEM images were obtained by FEI Quanta 400 ESEM FEG at 15 keV for mineral morphology measurement. Specific surface areas were measured by Quantachrome Autosorb-3b BET Surface Analyzer.

Common cation elements, such as Ca, Mg, and Fe, were extracted from shales by EPA method 3050B-Acid digestion of sediments, sludges, and soils. Concentrations of cation were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.3. Adsorption/precipitation experiments

Adsorption/precipitation experiments were conducted in batch reactors at 70 °C. 0.4 g of shale was added to 40 mL brine with inhibitors in 50 mL plastic vials (solid to liquid ratio = 0.01 g/mL). The brine was 1 M NaCl equilibrated with 1% CO_2 or 100% CO_2 at 70 °C. Carbon dioxide was continuously purged to reactors during the adsorption process to maintain a constant partial pressure of carbon dioxide. Shale is a mixture of clay and other minerals, such as carbonate. Purging with carbon dioxide dissolved a small amount of carbonate from shale formations first and then solution with dissolved carbonate was at equilibrium with carbon dioxide to prevent further dissolution of carbonate. Varying partial pressure of purging carbon dioxide allows different equilibrium pH conditions in brine.

Prior to adsorption isotherm experiments, adsorption kinetics experiments were conducted to estimate the time to reach equilibrium for two inhibitors in ground shale slurries. Once equilibrium time was determined, adsorption isotherm experiments were carried out for a time period long enough to reach equilibrium.

After reactions, supernatants of the slurries were filtered by 0.45 um filter and analyzed for inhibitor concentrations, common cation concentrations, and alkalinity. Inhibitor concentrations of DTPMP and PPCA were analyzed by the content of phosphorus. Phosphorus and cation concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) or mass spectrometry (ICP-MS). Standard solutions of ICP-OES and ICP-MS, which cover concentration range between 0.1 ppm to 50 ppm, were prepared in 1% HNO_3 or 1% HNO_3 in 1 M NaCl. The samples were diluted by 1% HNO_3 to fit the range calibrated or measured directly without dilution. Alkalinity measurement was performed by titration (Rice et al., 2012). Inhibitor concentration c_s in the solid phase (mg/kg) was calculated by mass balance as follows:

$$c_s = \frac{(c_0 - c_{aq})V}{m} \tag{1}$$

Where c_0 is the initial inhibitor concentration in aqueous phase (mg/L), c_{aq} is the equilibrium concentration of inhibitor in aqueous phase (mg/L), V is solution volume (L) and m is mineral mass (kg).

3. Results and discussion

3.1. Characterization and solution pH

Fig. 1 shows X-ray diffraction patterns of Eagle Ford shale and its automatic phase identification results. Peaks of calcite, quartz and kaolinite were identified in XRD patterns of Eagle Ford. Previous research identified Eagle Ford as a carbonate rich or calcareous hydrocarbon-bearing formation (Slatt and Rodriguez, 2012), and XRD result in this study confirmed the presence of calcite in Eagle Ford formation. Although illite was not identified by XRD, it may be present in Eagle Ford shale as well (Chermak and Schreiber, 2014). Fig. 2 displays XRD patterns of Marcellus shale, and quartz and pyrite were identified in the XRD pattern. Marcellus Shale has been characterized by its black color, and high pyritic content before (Chermak and Schreiber, 2014; Jin et al., 2013), and this study also shows that Marcellus shale may contain significant amount of pyrite. Figs. 3 and 4 shows SEM of Eagle Ford and Marcellus shale respectively, and these images show similar structure as observed in clay minerals. The specific surface areas determined by BET surface area analyzer are 3.0 and 41.6 m^2/g for Eagle Ford and Marcellus, respectively. The concentrations of common cations that can be extracted by acid digestion are shown in Fig. 5. Calcium concentration in Eagle Ford is extremely high at 223 g/kg, which confirms Eagle Ford as a carbonate rich mineral. Iron concentration in Marcellus is relatively high at 4.6 g/kg. If all iron is present in the form of pyrite (FeS_2) in Marcellus, it would give a pyrite content of about 1%.

During the adsorption process, partial pressure of carbon dioxide was controlled for the solution, and this practice could generate different experimental conditions that are of interest. Assume that the solution is at equilibrium with headspace carbon dioxide,

$$CO_2(g) = CO_2(aq) \tag{2}$$

$$K_H = \frac{a(CO_2(aq))}{P(CO_2)\gamma(CO_2)} \tag{3}$$