

A Further Look at The Impacts of Corrosion Inhibitor on Scale Prevention

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ABSTRACT

In the previous work (paper C2021-16736), we presented the results on calcium carbonate deposition and inhibition in the presence of 50 ppm of corrosion inhibitors. Further studies were performed to investigate the influence of three corrosion inhibitors at high concentrations on calcium carbonate formation and the performance of scale inhibitors, to simulate the conditions where high corrosion inhibitor dosages are applied or during the early flow back stage after batch treatment.

The active ingredients are, respectively, quaternary ammonium, phosphate ester and fatty acid; imidazoline acetate and ethoxylated fatty amine; and quaternary ammonium compounds, in the three corrosion inhibitors. Scale inhibitors are based on polyacrylate, ATMP phosphonate, and DETPMP phosphonate. Tests were conducted at 85 °C using the dynamic tube blocking method and test brine was characterized with high TDS (~ 65,000 mg/L) and high calcium (~ 4,000 mg/L). Change in scale deposition rate was used to assess the corrosion inhibitor impact. Contrary to the reported findings with barium sulfate scale, results from this study showed that even with 500 ppm corrosion inhibitors, no noticeable decreases in scale inhibitor performance were observed. Instead, the corrosion inhibitor based on imidazoline acetate and ethoxylated fatty amine prevented calcium carbonate scale

deposition entirely without scale inhibitor. Additional tests also showed that this corrosion inhibitor had a significant impact on the morphology of calcium carbonate scale precipitates.

Key words: Oilfield scale, scale control, calcium carbonate, CaCO_3 scale, scale inhibitor, corrosion inhibitor, phosphonate

INTRODUCTION

Scale and corrosion inhibitors are commonly used in many oil and gas production systems to prevent inorganic deposition and to protect asset integrity. Scale inhibitor products are based on organic compounds with phosphate or carboxylic functional groups such as amino phosphonates, phosphate esters, phosphino polymers, polycarboxylate and polysulfonates,¹ as shown in Figure 1. These anionic groups have strong affinity to alkaline earth cations and can adsorb on the active growth sites of scale crystal (Figure 2), resulting in stopping or delaying the scale formation process.^{1,2}

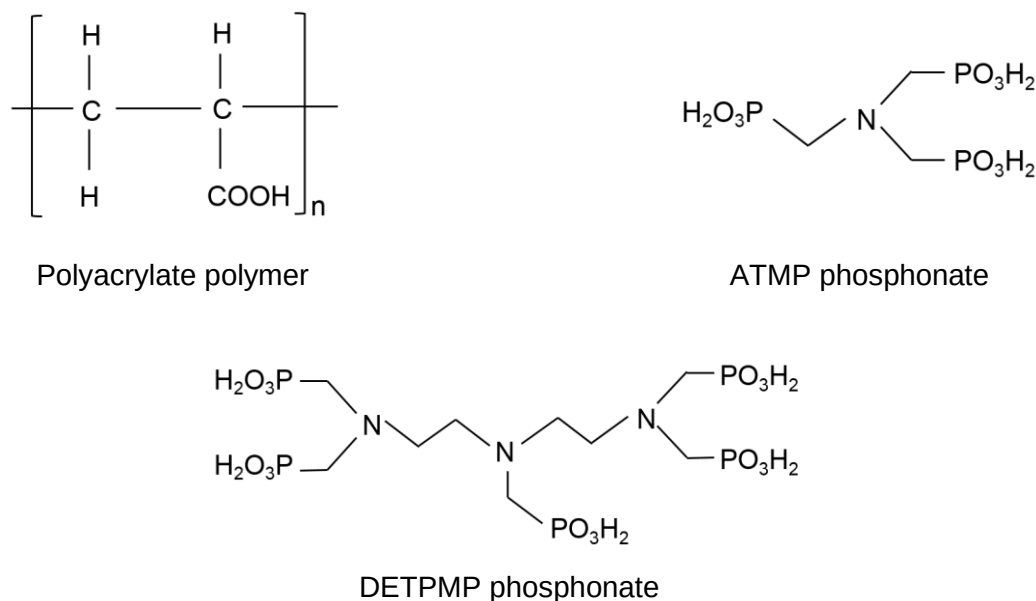


Figure 1: Molecular structure of scale inhibitors.

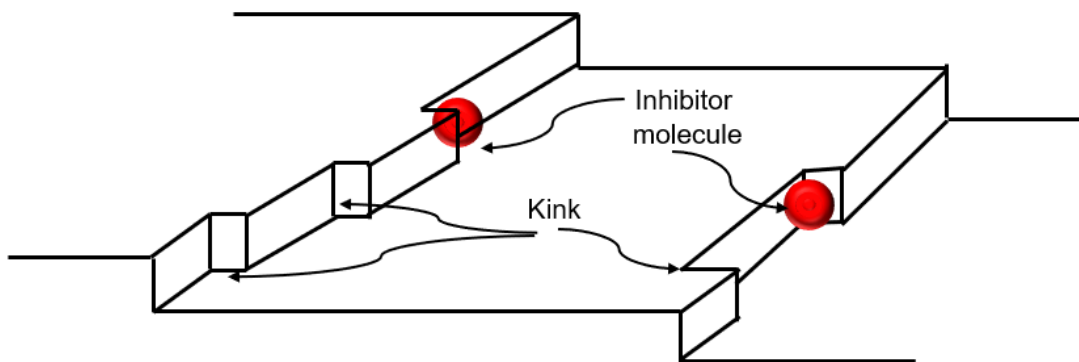


Figure 2: Surface structure of growing scale crystal.

Corrosion inhibitors used in oilfields are, in general, cationic surfactant compounds with an amphiphilic molecular structure and are often referred to as film forming as they form very thin protective films by adsorbing at steel surfaces. They consist of a polar head group and a nonpolar hydrocarbon tail. Polar heads often contain unsaturated bonds or atoms, such as N, O, S, etc.^{2,3} The polar head groups provide bonding between inhibitor molecules and the steel surface, either by chemisorption or by physisorption,^{4,5} forming a thin-layer protective film (Figure 3). The hydrophobic tails provide a diffusion barrier for corrosive species because of steric repulsion of the hydrophobic tails. Some common corrosion inhibitor molecules are shown in Figure 4.

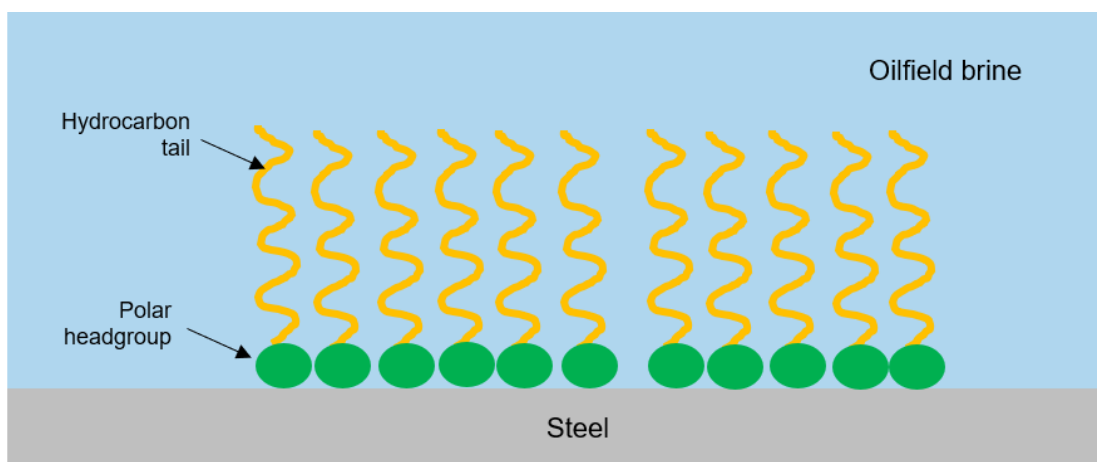


Figure 3: Film forming corrosion inhibitor.

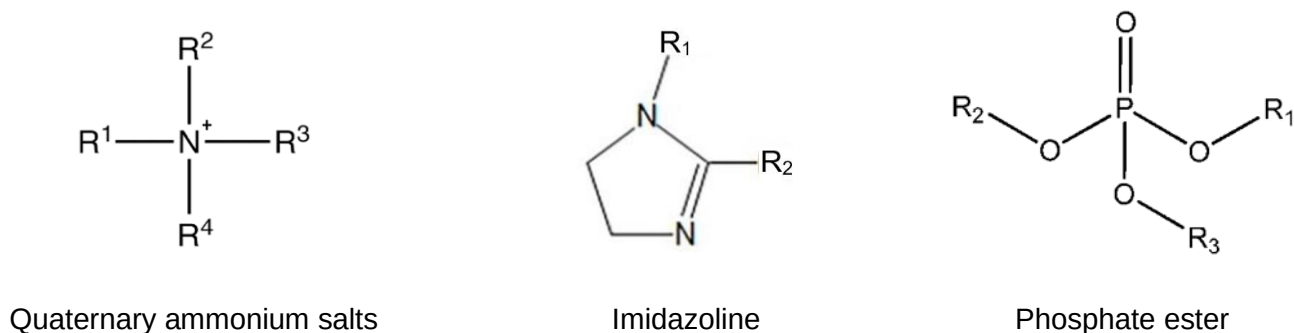


Figure 4: Examples of common corrosion inhibitor molecules.

Both corrosion and scale inhibitors are based on surface active organic compounds and they gravitate towards the exciting surfaces. Thus, corrosion inhibitors adsorbed on steel surfaces could affect the scale formation process, and the adsorption on scale particles could alter the interaction of scale inhibitor molecules with scale particles. Also, the positively charged corrosion inhibitor compounds can form ion pairs with the negative charged scale inhibitors are compounds.

These interactions have potentials to affect either scale inhibition efficacy, corrosion inhibition efficacy, or even both inhibitors performance. In paper C2021-16736,⁶ we presented the results on calcium carbonate deposition and inhibition in the presence of 50 ppm of corrosion inhibitors. In this study, further laboratory studies were performed to assess the impacts of corrosion inhibitors at elevated

concentration (500 ppm) on calcium carbonate (CaCO_3) inhibition, to simulate the conditions where high corrosion inhibitor dosages are applied or during the early flow back stage after batch treatment.

EXPERIMENTAL

The test conditions were the same as described before.^{6,7} The brine composition is listed in Table 1, which is characterized by high calcium ions and total dissolved salts. Synthetic brines were prepared with the reagents grade chemicals and used throughout the laboratory tests. Brine was divided into cation and anion solutions and a mixture of equal volumes of these two solutions resulted the desired test brine composition as listed in Table 1. The anion brine contained sodium sulfate and sodium chloride salt, and cation brine contained sodium chloride and calcium, magnesium, strontium and potassium ions. The prepared brines were then filtered through 0.45 μm filter paper and degassed under vacuum for at least two hours before use. Bicarbonate salt (NaHCO_3) was added to the anion brine after degassing treatment, in order to minimizing the change of pH value due to the loss of carbon dioxide (CO_2).

Table 1: Geochemical composition of test brine

Ion	mg/L
Sodium	18420
Potassium	703
Calcium	3942
Magnesium	1286
Bicarbonate	500
Sulfate	485
Chloride	39120

The scale and corrosion inhibitors used in this study were commercial products. The three scale inhibitors (SI-1, SI-2 and SI-3) were based on, respectively, acrylate polymer, ATMP [amino tri(methylene phosphonic acid)] and DETPMP [diethylenetriamine penta (methylene phosphonic acid)]. They represent the most commonly used CaCO_3 inhibitor chemistries.^{8,9} The active ingredients of corrosion inhibitors (CI-1, CI-2 and CI-3), based on material Safety Data Sheet (MSDS), are listed in Table 2.

Table 2: Main active ingredients in corrosion inhibitors

Corrosion Inhibitor	Active Ingredients
CI-A	Quaternary ammonium, phosphate ester, fatty acid
CI-K	Imidazoline acetate, ethoxylated fatty amine
CI-M	Quaternary ammonium compounds

Experiments were performed using a dynamic tube blocking apparatus (Figure 5a) at 85 °C and 350 psi. Cation and anion brines were pumped into the preheating coils separately at 5 ml/min. The preheated brines were comingled in a mixing chamber and then entered into the stainless-steel capillary coil (ID = 1.0 mm, L = 1 m). The installation of the mixing chamber increased the residence time of scaling brine in test rig, which significantly improved the repeatability of test results and also enabled the tests of mild-scaling brines without considerably change the brine composition or test temperature.⁷ Pressure difference (ΔP) across the capillary coil was measured continuously and recorded. Formation of scale deposition was indicated by ΔP increase with time, and the scaling time was defined as the time elapse for ΔP increase to reach 1 psi from the initially stabilized value (Figure 5b).

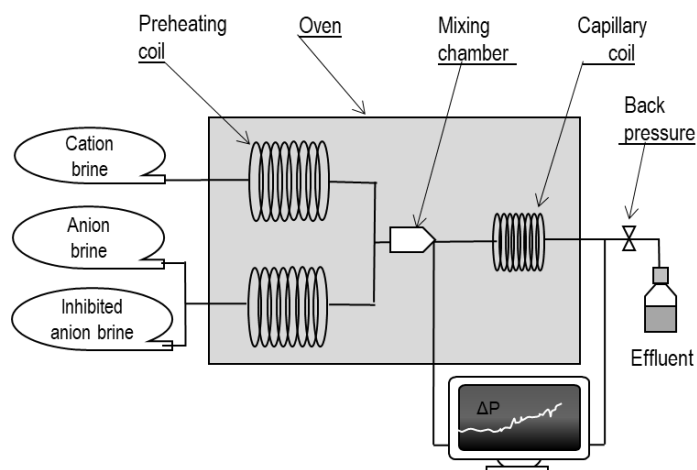


Figure 5a: Schematic drawing of dynamic tube blocking apparatus.

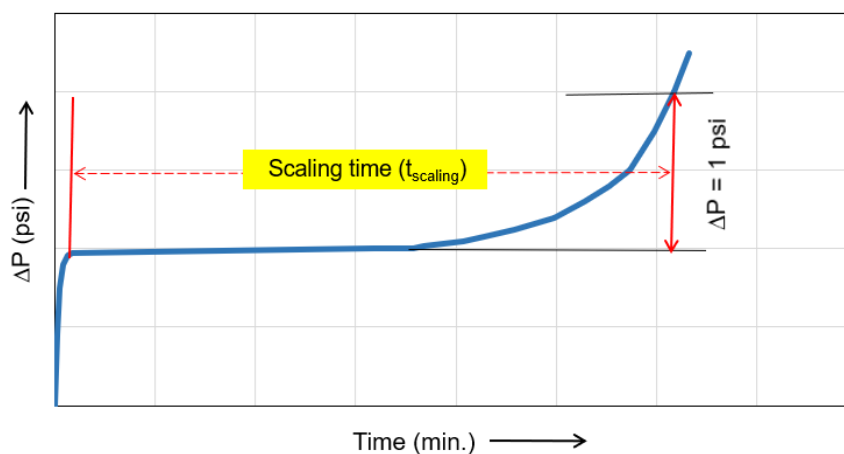


Figure 5b: Schematic drawing of dynamic tube blocking test results.

The impacts of corrosion inhibitor on scale formation and inhibition were determined by the change of scaling time in the absence and the presence of scale inhibitors (2 and 5 ppm) and corrosion inhibitors (500 ppm) (see Table 3). The sequence of experimental runs in each test is illustrated in Figure 6. Blank run was carried out first, followed with run with corrosion inhibitor only, then with scale inhibitor only and with both corrosion and scale inhibitors. The run duration with scale inhibitors was set at ~ 3