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Calcium Carbonate Scale Deposition and Inhibition: Effects of Corrosion Inhibitors

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ABSTRACT

Scale and corrosion inhibitors are often applied simultaneously in order to prevent inorganic deposition and protect system integrity of oilfield facilities. The compatibility between these chemicals is a major concern during chemical selection. Corrosion inhibitor compounds may form complex with scale inhibitor molecules and interfere with the interactions of scale inhibitor and scaling crystal, and consequently, affect the scale inhibitor performance. Understanding their interplay is of importance for the development of cost effective treatment programs.

In this work, the impacts of corrosion inhibitors on calcium carbonate deposition and inhibition were investigated. Experiments were carried out using the dynamic tube blocking method at 85°C and 350 psi. Three scale inhibitors tested were, respectively, based on tri-phosphonate, penta-phosphonate, and polyacrylate; whilst three corrosion inhibitors were blend products of different active ingredients. Results attained in this study suggested that at 50 ppm of corrosion inhibitor concentration, its impact on the scale inhibitor performance was minimal. Test data also showed that, in the absence of scale inhibitor, the influence of corrosion inhibitors on the kinetics of calcium carbonate scale deposition was insignificant under the test conditions.

Key words: Oilfield scale, scale control, calcium carbonate, CaCO₃ scale, scale inhibitor, corrosion inhibitor

INTRODUCTION

Scale and corrosion are two major flow assurance concerns in many oil and gas production systems, largely due to the high contents of dissolved solids and acidic gases (CO_2 and H_2S) in the associated waters. Changes in physical conditions or chemical composition disrupt chemical equilibrium and water could become supersaturated with respect to certain inorganic compounds, which leads to the commencement of scale precipitation. Scale deposits restrict fluid flow, decrease productivity, and cause premature failure of equipment. Corrosion reaction is a naturally occurring phenomenon when water is in contact with metals. Given sufficient time, such reaction can degrade any materials, causing dangerous and expensive damages to the oilfield facilities.

Use of inhibition chemicals has been the time-proven method to prevent scale and control corrosion damages in oilfield operations. Often the scale and corrosion inhibitors are used simultaneously. Dual-functional combo products containing both inhibitors have also been developed and applied.^{1,2} Corrosion inhibitors adhere to metal surface and create a continuous layer between the metal and water, thus reducing the attack by corrosive elements. Similarly, scale inhibitors prevent scaling process by adsorbing on the surface of scale precipitates. Both types of 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. In addition, the active ingredients in scale inhibitors are negative charged compounds, while corrosion inhibitor chemicals are usually positively charged. Formation of complexes between these inhibitors possibly changes the effectiveness of scale inhibitors.

Although the importance of the potential interference aforementioned, very few studies have been reported on this subject. Graham et al. examined the influences of two corrosion inhibitors on the performance of two scale inhibitors under North Sea field conditions.³ They found that one corrosion inhibitor (CI#1) had a significant impact on the performance of the scale inhibitor based on polyvinyl sulphonate (PVS), with barium sulfate scale inhibition efficiencies decreased from >70% without corrosion inhibitor to <5% with 500 ppm corrosion inhibitor at 50 ppm scale inhibitor concentration. Another corrosion inhibitor had only a marginal impact on the scale inhibitor performance against sulfate scale and no reduction in carbonate scale control under one test condition; but it resulted in significant reduction in the performance of scale inhibitors in a very severe sulfate scaling brine. Significant increase in scale inhibitor concentration was required in order to maintain scale control.

In a subsequent study, Graham and McMahon investigated the impacts of both commercial and generic corrosion inhibitors (500 ppm) on the performance of scale inhibitors based on penta-phosphonate (DETPMP) and phosphinopolycarboxylate (PPCA), in addition to PVS and VS-Co.⁴ Static bottle test results showed that the generic products impacted the scale inhibitors performance less than the commercial products, with the quaternary ammonium salt showed slightly less impact than imidazoline. It was also noted that the impacts changed with temperature and scale inhibitor type. For example, one commercial corrosion inhibitor showed no significant impact on PVS's performance at 20°C, but a significant reduction in performance was recorded at 90°C; the performance of DETPMP was the least affected than other scale inhibitors by the presence of corrosion inhibitors. They also studied the scale surface adhesion on the Hastelloy C276 metal coupons under laminar flow conditions. They found that the commercial corrosion inhibitors prevented ~75% of the barium sulfate adhesion to the metal coupon without scale inhibitor, although they had no inhibition effects on bulk precipitation.

Wylde et al. further investigated the influence of corrosion inhibitors on sulfate scale adhesion and observed that corrosion inhibitors could improve the performance of scale inhibitors.⁵ Studies were conducted at 25°C with three scale inhibitors: DETPMP at 100 ppm, 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) at 300 ppm, and VS-Co at 25 ppm, whilst corrosion inhibitor concentration was

varied between 10 ppm and 100 ppm. Test results indicated that the corrosion inhibitors dramatically affected the mechanism of scale inhibition. The performance of DETPMP was enhanced by corrosion inhibitors. For VS-Co and PBTC, corrosion inhibitors suppressed the initial scaling rates; at later stage, the rate of scale deposition was increased to a level similar to that without corrosion inhibitor in the VS-Co inhibited brine and even greater in the PBTC inhibited brine.

This study will focus on the impact of corrosion inhibitors on calcium carbonate (CaCO_3) deposition and inhibition. CaCO_3 is the most common type of scale in oilfield surface facilities. Many studies have been conducted on its formation process and the factors affecting the inhibitor performance,⁶⁻¹³ but the potential impacts of corrosion inhibitor, which is often applied simultaneously, have not been investigated.

EXPERIMENTAL

Table 1 lists the geochemical composition of test brine. It was based on the produced water from a dolomitized carbonate reservoir where seawater is used for pressure support. Scale inhibitor treatment was applied in field to control CaCO_3 deposition. Synthetic cation and anion brines were separately prepared with the reagents grade chemicals. Anion brine contained sulfate ions and cation brine had calcium, magnesium and potassium ions. Sodium chloride salt was divided equally into the two brines. 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 pH change due to the loss of carbon dioxide (CO_2). A mixture of equal volumes of cation and anion brines resulted in the desired test brine composition as listed in Table 1.

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-A, SI-B and SI-C) were based on, respectively, acrylate polymer, ATMP [amino tri(methylene phosphonic acid)] and DETPMP [diethylenetriamine penta (methylene phosphonic acid)]. Their chemical structures are shown in Figure 1. The formulations for the corrosion inhibitors (CI-1, CI-2 and CI-3) were proprietary and the concentrations of active ingredients were unknown.

Experiments were performed using a dynamic tube blocking (DTB) apparatus, as illustrated in Figure 2. The test temperature and pressure were 85°C and 350 psi. Cation and anion brines were pumped into the preheating coils separately at 5 ml/min. Then the preheated brines were mixed and entered into a stainless steel capillary coil (ID = 1.0 mm, L = 1 m). Pressure difference (ΔP) across the capillary coil was

measured continuously and recorded every 10 seconds. Formation of scale deposition was indicated by ΔP increase with time, and the scaling time was defined as the time elapse for the ΔP increase of reach 1 psi from the initially stabilized value.

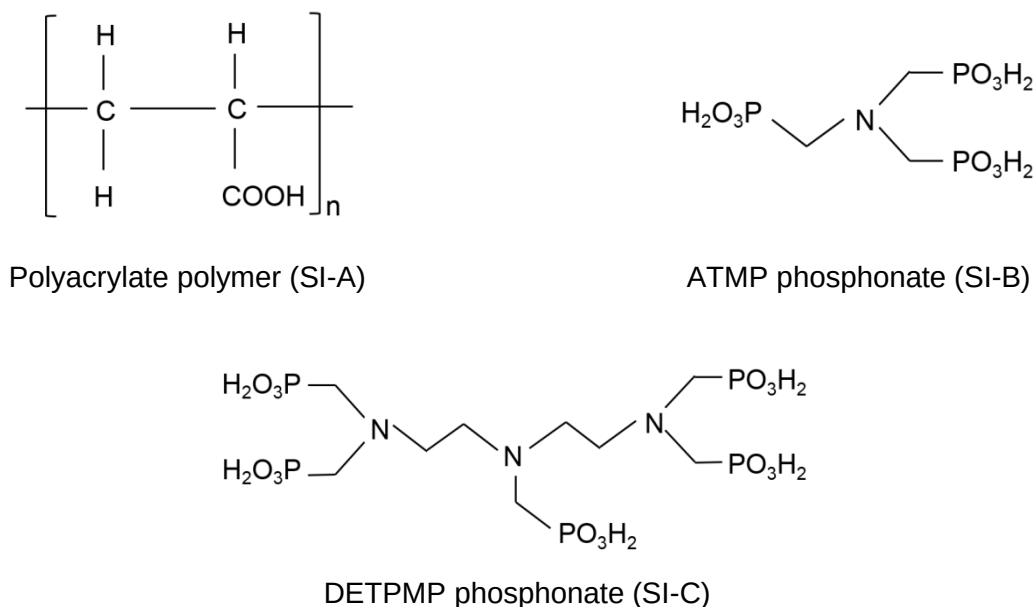


Figure 1: Molecular structure of scale inhibitors.

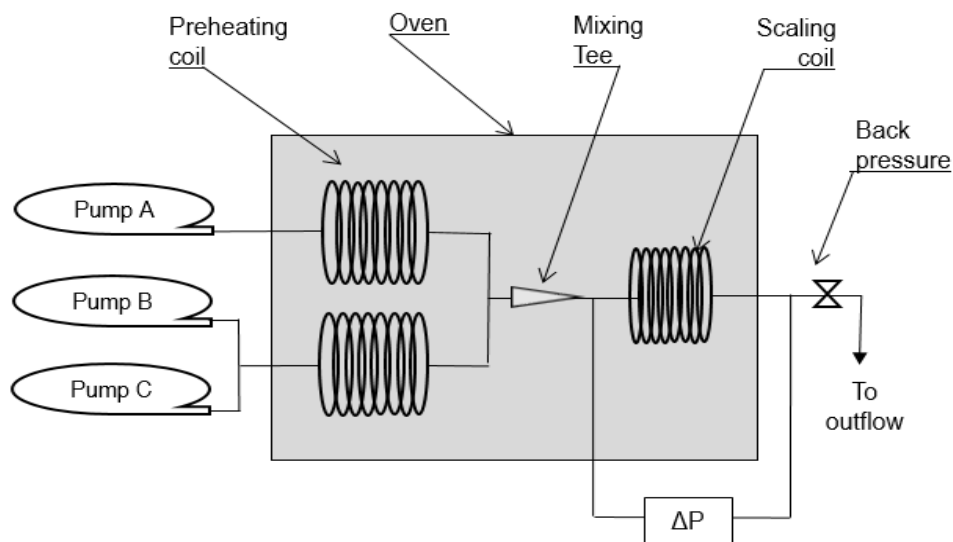


Figure 2: Schematic drawing of dynamic tube blocking apparatus.

The impacts of corrosion inhibitor on scale formation and inhibition were determined by the change of scaling time of uninhibited and inhibited brines in the absence and the presence of corrosion inhibitors. Corrosion inhibitor concentration was set at 50 ppm, representing the treatment dosage applied in oilfield surface facilities. Tests were first conducted at 10 ppm of scale inhibitors. Further detailed tests were performed at 5 and 2 ppm of scale inhibitors and the sequence of experimental runs in each test is