

Development of a F22 Compatible Scale Inhibitor

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ABSTRACT

F22, a low alloy steel, has become widely used in oil field production systems. However, current scale inhibitor technologies on the market often cause severe corrosion on F22, particularly at high temperature conditions. Therefore, F22 compatible scale inhibitors are in demand in the oil and gas industry. A F22 compatible scale inhibitor is required to be only mildly corrosive on F22, with a general corrosion rate of ≤ 4 mpy and no pitting corrosion, while maintaining high scale inhibition efficiency with a low minimum inhibitor concentration (MIC). A wide range of scale inhibitor products were evaluated for F22 corrosion rates in inhibitor compatibility testing and scale inhibition in dynamic tube-blocking (DTB) testing. The test temperature was as high as 240 °F (116 °C), and the test brine had positive saturation indices for calcium carbonate (CaCO_3) and iron carbonate (FeCO_3) scales. Based on the performance of both F22 compatibility and scale inhibition, the best blend was selected for further evaluation, i.e., subsea certification. Finally, the developed product has met all the requirements of a F22 compatible scale inhibitor, and has gone through a successful field trial, and it is ready for larger scale applications.

Key words: Scale inhibitor, F22 low alloy steel, high temperature, ferrous iron

INTRODUCTION

F22 is a low alloy steel that typically contains 12% Carbon, 2.25% Chromium, and 1.0% Molybdenum¹. This steel has been widely used in oil production systems, especially in well head design and construction. As a low alloy steel, F22 can be corroded by oilfield chemicals under certain circumstances. For example, it was observed in the Gulf of Mexico that typical scale inhibitor chemistries caused severe corrosion on F22.

Scale inhibitors are referring to the class of chemicals that can prevent or retard scale formation. Typical scales in the oil field include carbonate scales (e.g., calcium carbonate, iron carbonate), sulfate scales (e.g., barium sulfate, calcium sulfate), sulfide scales (e.g., iron sulfide, lead sulfide), and halite². Scales

often form due to temperature and pressure changes during oil and gas production from reservoir to surface, or due to co-mingling of incompatible fluid³. Chemical scale inhibition is an economical and commonly used method for scale control. There are several different types of scale inhibitors, including phosphonate, phosphate ester, sulfonate polymer, polyacrylic acid, polymaleic acid, and more². Different types of scale inhibitors show different corrosion risk on F22⁴. For the same type of scale inhibitor chemistry, scale inhibitor product with low pH is typically more corrosive than scale inhibitor product with neutral pH⁴.

Given the predominate usage of F22 in the oilfield, the goal of the current research is to develop a F22 compatible scale inhibitor which is not only just mildly corrosive to F22 but also highly efficient on scale inhibition. As field brine often contains ferrous iron (Fe^{2+}) and Fe^{2+} can poison many scale inhibitors, the developed inhibitor is also required to be Fe^{2+} tolerant with the potential to inhibit iron carbonate scale. Furthermore, to improve the applicability of the developed inhibitor, it should be qualified for subsea application. This paper illustrates the development of such a F22 compatible scale inhibitor.

EXPERIMENTAL PROCEDURE

F22 compatibility test

F22 compatibility test was conducted to evaluate the corrosion of F22 caused by scale inhibitor chemistries. F22 coupons were used. The following procedure was used. Each coupon was polished to P320 grit and rinsed sequentially with xylene, IPA, and acetone and then dried with a paper towel to ensure no surface liquids remained. After drying, each coupon was weighed to four decimal places and its dimensions were measured. Each coupon was added to individual 60 mL test tubes containing 50 mL of the test chemical. The test tubes were placed in a pressure bomb with a nitrogen atmosphere at 1000 psi in a temperature-controlled oven. The duration of the testing is 30 days at 240 °F / 116 °C.

The weight loss of each metal coupon was measured after the test to determine the general corrosion rate. Chemicals were visually assessed for color, striation, clarity, phase separation, haziness, flocculation, and precipitate before and after the test. Coupons were examined under a microscope to determine the number of pits and the average and maximum pit depth.

The guidelines for interpretation of the results exist with respect as to whether the material under evaluation is suitable for use with the product as follows:

- Corrosion rate ≤ 4 mpy (mils per year) with no pitting corrosion.
- No visual evidence of precipitates, flocculation, suspended solids, and phase separation in test chemical.

Dynamic tube-blocking (DTB) testing

Dynamic tube-blocking (DTB) testing was conducted to evaluate the scale inhibition performance of scale inhibitors. DTB tests were run using Baker Hughes' automated tube-blocking apparatus. The test brine was split into two non-scaling brine components. One component contained twice the final concentration of all anions other than chloride, which is called the anion brine; the other component contained twice the final concentration of all cations other than sodium, which is called the cation brine. The two components split sodium chloride at a certain ratio so that the density of both brines is about the same. When the two components mixed in a 1:1 ratio, it reconstituted the test brine. Table 1 displays the test brine composition of the current research. As the test brine contains 23 ppm Fe^{2+} , the test brine needed to be kept in anaerobic conditions during the whole test. Anion and cation brines were purged with CO_2 and N_2 overnight to remove dissolved oxygen and adjust to the designed pH. The pH was continuously monitored and CO_2 and N_2 were alternately purged with continuous flow of one or the other.

Table 1
Test brine composition

Ion (mg/L)	Test brine
Na ⁺	45,750
K ⁺	347
Mg ²⁺	554
Ca ²⁺	4,491
Sr ²⁺	700
Ba ²⁺	72
Fe ²⁺	23
Cl ⁻	79,500
SO ₄ ²⁻	34
Alkalinity (HCO ₃ ⁻)	300
pH (no unit)	5.80 or 6.80

The inhibitors were mixed at fixed concentrations in portions of anion brine. The concentrations were at least twice the highest concentrations to be tested. Inhibited anion brine was mixed with uninhibited anion brine in various proportions to yield various lower concentrations of inhibitor in the anion brine. This inhibited anion brine mixture was combined with the cation brine in a 1:1 ratio to give the final inhibitor concentration and create a scaling condition.

The anion and cation brines were heated by passing through separate 3-meter-long heat exchange tubes in an oven. The heated brines entered a mixing tee. The mixture immediately ran through a 1-meter-long capillary tube with an inner diameter of 1.0 mm. The differential pressure across this capillary tube was measured while the scaling brine flowed at a constant rate. An increase in differential pressure would indicate that solids formed in the tube and adhered to the walls. The flow rate of the scaling brine was fixed at 10.0 ml/min.

Figure 1 illustrates a typical DTB apparatus. The equipment is automated and controlled by computer. Once brines are prepared and conditions set by the operator, the equipment will run until a set time elapses or a set differential pressure is reached. Once a test is complete, the tube is cleaned using a chelator and an acid, and then the process is repeated with next test.

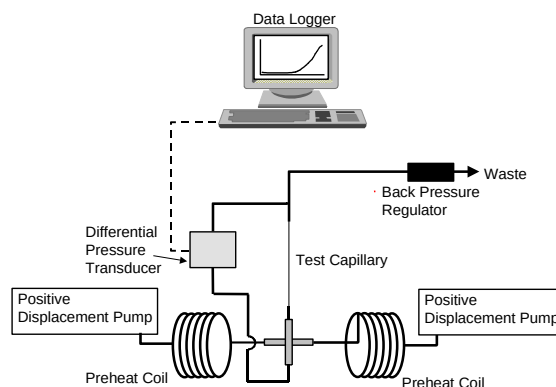


Figure 1: Dynamic tube-blocking rig schematic diagram

Inhibitor-brine compatibility test

Volumes of each scale inhibitor sufficient to make 100 ppm, 1,000 ppm, and 10,000 ppm (1%) solutions were added to the test brine. Samples were prepared in test tubes in volumes of 10 mL that were then

capped and placed inside a pressure bomb. Nitrogen was then added to the bomb with the pressure of 500 psi. The pressure bomb was then placed in a pre-heated oven at designed test temperature. Visual observations of test solution were made initially and at 2 hours after the addition of each scale inhibitor. A blank and a control were also tested along with the samples for comparison purposes. The blank was the test brine with no inhibitor, and the control consisted of half de-ionized water and half cation water with no inhibitor.

Visual observations are reported using the following terms: Clear, Cloudy, Flocculation, Precipitation, and Scale. "Clear" means no cloudiness or haziness and the test bottle should have the same visual appearance as that of the control. "Cloudy" is anything that is not as clear as the control but is not yet visually determinable as a solid and appears evenly dispersed throughout the test bottle. "Flocculation" is anything merely suspended in a liquid and not actually dissolved in a solution and usually appears fluffy and "soft". "Precipitation" means visually observable solid particles are obviously settling to the bottom and/or top of the test bottles. "Scale" means test scale forms at the bottom of the test bottles and the solid amount is usually very small. Scale has different visual look than precipitation in compatibility testing.

Subsea certification test

FATHOM™ XT is the subsea certification test of Baker Hughes. It is designed based on the recommendations from API 17TR6, 'Attributes of Production Chemicals in Subsea Production Systems'. It consists of 16 tests which are designed to test the candidate products for their deliverability, compatibility, reliability, and to minimize the risk of subsea umbilical blockages at low and high temperatures and high pressures. The 16 tests are hydrate susceptibility determination, pour point determination, general viscosity determination, electrochemical pitting susceptibility, low temperature stability, high pressure viscosity determination, low temperature, high pressure umbilical qualification, temperature cycling stability, long-term "shelf" stability, high temperature thermal stability, high temperature, high pressure capillary qualification, vapor pressure determination, chemical-fluid compatibility, metals compatibility for deep water application, plastics & elastomers compatibility for deep water application, and high pressure density determination.

RESULTS

Scale modeling

Scale modeling was conducted for the test brine with software ScaleSoftPitzer 2021 (SSP 2021). Table 2 shows the modeling result. The potential scales include calcite (i.e., calcium carbonate), siderite (i.e., iron carbonate), and barite (i.e., barium sulfate).

Table 2
Scale modelling result of the test brines

Temperature	Pressure (psi)	pH	Calcite		Barite		Siderite	
			SI	mg/L	SI	mg/L	SI	mg/L
240 °F / 116 °C	500	5.80	0.83	135	0.22	22	0.06	4.3
		6.80	1.79	175	0.22	22	1.02	37.5

F22 compatibility results

More than a dozen scale inhibitor candidates were selected to evaluate for F22 compatibility and scale inhibition performance. In this paper, only three scale inhibitors, A, B, and C, were selected as representatives. The three inhibitors have totally different types of active scale inhibitor chemistries. After 30 days compatibility testing at 240 °F (116 °C), the corrosion rate of F22 was calculated based on coupon weight loss and the coupons were examined under white light interferometry to determine pitting corrosion. Note that duplicates of compatibility tests were run for each scale inhibitor.