

High Temperature Stable Corrosion Inhibitor Development for Deepwater Applications

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ABSTRACT

As offshore deepwater oil production is reaching new high levels, producers and service companies are challenged with harsher conditions of temperature ($> 177^{\circ}\text{C}/350^{\circ}\text{F}$), shear ($> 25\text{Pa}$) and high-pressure systems ($> 1000\text{psi}$). Therefore, the demand for new technologies and production chemistries under these extreme conditions are on the rise. This paper discusses the development of high temperature stable, water soluble corrosion inhibitors for slightly sour deepwater systems. These corrosion inhibitors exhibit thermal stabilities at high temperatures for lengthy periods of time and are extremely effective for general and localized corrosion. This paper describes various laboratory corrosion testing techniques used to simulate field conditions and the results obtained from these testing are presented.

The chemical injection via umbilical plays a vital role in deepwater and ultra deepwater chemical applications. Therefore, the chemical cleanliness is extremely important in these harsher environments for umbilical applications. Exceptional measures are taken to ensure the corrosion inhibitor performance are not compromised due to these harsher conditions. Furthermore, the rigorous qualification process of qualifying chemicals for deepwater application are discussed^{1,2,3}.

Key words: High temperature corrosion inhibitors, water soluble corrosion inhibitors, corrosion inhibitor for deepwater applications, sour systems, deepwater chemical qualification, umbilical application

INTRODUCTION

With increasing world energy demands and total supply getting lowered, petroleum industry has been forced to drill deeper into much more hostile subsea environments. This created a large number of high-temperature and high-pressure oil and gas wells around the globe. Hence the demand for high temperature stable and umbilical deliverable corrosion inhibitors increased. The demand is even higher for high-temperature effective, environmentally acceptable corrosion inhibitors^{4,5,6}.

Examples reported for high-temperature effective corrosion inhibitors are few in the literature. However, most of the publications are on oil soluble, filming corrosion inhibitors. Lindsay et al., studied amine, polyamines and amino alcohols as corrosion inhibitors at very high temperatures. These amines are added to neutralize the carbonic acid formed from residual CO₂ and to provide a basic environment to prevent acid corrosion. However, at higher temperatures (above 177°C/350°F) most water-soluble corrosion inhibitors would decompose. The effectiveness of most chemicals reduces to less than 50% indicating possible polymerization or decomposition, which can be attributed to particulate formation or gunking inside the tubing and flowlines. Therefore, it is important to use high-temperature effective and stable products for these conditions.

It is very challenging to develop chemicals that are thermally stable and effective for high-temperature and pressure for deepwater applications. As part of this study, several water-soluble and oil soluble products have been developed that are thermally stable above 200°C (390°F) and maintains a high corrosion inhibition effectiveness. One product was found to be stable at 200°C for 2 months under inert and high-pressure conditions. This paper discusses the detailed procedures and methods conducted to evaluate and qualify these products for extremely harsh deepwater and ultra deepwater chemical applications.

EXPERIMENTAL

More than hundred new corrosion inhibitors were formulated and tested during this study. These chemicals were blended with solvents to yield 35% to 40% activity for equal comparison convenience. Products that were unstable, and phase separated were rejected. The remaining products were screened and evaluated to qualify for subsea high temperature applications by following ASTM⁽¹⁾ G170, ASTM G184, ASTM G185, ASTM G208, API 17 TR5 and API 17 TR6 for qualifying subsea production chemicals. After undergoing a suite of testing three products were selected. Two of them were oil soluble and one water soluble. The water-soluble product was selected and denoted as product B in this study. This high temperature/high pressure stable corrosion inhibitor chemical (Product B) for subsea applications was formulated in our laboratory using ethylene glycol, ethylene glycol monobutyl ether and water as solvents.

Rotating Cylinder Electrode (RCE) Test for Product Screening

RCE tests were used to initially screen all experimental blends using ASTM G185. The tests were conducted with 810ml synthetic brine (see Table 1) and 90ml LVT-200 synthetic oil under continued purging of testing gas at 90°C. The electrode rotation rate was set at 2,000 RPM, which generated a wall shear stress of 7 Pa, the wall shear stress was calculated as shown in equation (1). Gas flow meters were used to ensure the gas mixture (CO₂ and H₂S) flow rates were identical among all testing kettles. The working electrode was made of an AISI⁽²⁾ 1018 carbon steel cylinder with a surface area of 3.16 cm². The corrosion inhibitors were added at 50 ppm based on the brine volume after the baseline corrosion rate was monitored for approximately 1.5 hours. The electrochemical information was recorded during the testing and data was compiled and calculated after the testing. The experimental setup for the RCE tests is shown in Figure 1.

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$$\tau = 0.0791 R_e^{-0.3} \rho r^2 \omega^{2.3} \quad (1)$$

where:

τ = wall shear stress,
 R_e = Reynolds number,
 ρ = density,
 r = radius of the electrode cylinder,
 ω = angular velocity

Table 1: Synthetic Brine Composition

Ionic Species	mg/L
Na^+	23,440
K^+	495
Ca^{2+}	2,080
Mg^{2+}	1,070
Ba^{2+}	175
Sr^{2+}	375
Fe^{2+}	1
Cl^-	42,350
SO_4^{-2}	16
HCO_3^-	12



Figure 1: Experimental Setup for RCE Test

Flow Regime Performance Tests

To ensure the products perform in variety of flow conditions, both low and high shear conditions were emphasized to test the product performances in different flow regimes⁷. The lower shear tests were performed using 1L autoclaves with an 800ml testing fluid capacity at 40 Pa (eq. 1). The higher shear testing was performed on a jet impingement device with an intermittent shear stress of 1,500 Pa (eq. 1).

1L Rotating Cage Autoclave Test (ASTM G184)

The test solution consisted of 720ml of synthetic brine and 80ml of LVT-200 synthetic oil. The brine solution was deaerated with CO₂ for 4 hours before pressurizing into the autoclaves using CO₂. Three weight loss coupons fixed on the rotating cage were used in each autoclave. The coupon shafts rotated at 1,000 RPM that corresponded to a 40 (eq. 1). General corrosion rates were calculated by weight loss measurement. The autoclave setup is shown in Figure 2. Test conditions are summarized below, and brine composition is shown in Table 1.



Figure 2: 1L-Autoclave Setup

Jet Impingement Test (ASTM G208)

A recirculating jet impingement flow loop was used to evaluate the flow effects on an AISI 1018 carbon steel electrode and gauge the corrosion and erosion under a much higher shear (>40 Pa, see eq. 1) than an RCA. Linear polarization resistance (LPR) measurements were used to obtain the instantaneous corrosion rate.

The synthetic brine solution was de-aerated for approximately 16 hours with ultra-pure CO₂ before being drawn into the de-aerated Jet impingement system with a vacuum pump. The entire Jet system was purged of oxygen by pulling a vacuum and then being pressurized to 1.7 Bar (25 psi) with CO₂. The vacuum cycle was repeated three times. The testing pressure was set to 24.8 Bar (360 psi), and the testing temperature was set to 150°C.

Once the test temperature was achieved, the bypass line was closed, the system flow was adjusted to 5.8 m/s which generated a wall shear stress of 1,500 Pa. The baseline corrosion rate was monitored for 1 to 1½ hours before the inhibitor was injected, and then the inhibited corrosion rate was monitored for 17 hours. The Jet impingement setup is shown in Figure 3.



Figure 3: Jet Impingement system for high shear testing

Inhibitor Partitioning

Product B partitioned brines were used to show the degrees to which the inhibitor could transport to the aqueous phase. In general, high water partitioning of the inhibitor is important in a stratified flow regime, therefore, an oil/water ratio of LVT-200/Brine (Table 1) = 30/70 was used. The CI concentrations used for portioning were 500, 250, 125, 62.5, 31.3 and 0ppm. The partitioning of Product B was determined by measuring chemical residuals of the inhibitor in water following equilibration with hydrocarbon.

Emulsion Tendency Test

50 mL each of synthetic brine and LVT-200 oil were filled into 100 ml prescription bottles. Tests were conducted by manually mixing with 50 hard shakes by hand. Inhibitor was dosed at 400 ppm and 4,000 ppm. The parameters measured were separation time, interface standing, and water quality.

Foaming Tendency Test

Foam tendency was evaluated by utilizing a Waring Blender. 200 mL brine was dosed with 400 ppm and 4,000 ppm of the corrosion inhibitors and added to the blender. The solution was then mixed for 30 seconds on the high RPM to induce foaming. The foamed test solution was then immediately transferred to a 1,000 mL graduated cylinder. The initial foam height was recorded, and the time of “half-life” and the foam final height were also recorded.

Fluid Compatibility Test

Corrosion inhibitors must be compatible with produced fluids to ensure that they will work in conforming environments. For solubility and compatibility comparisons, Products were dosed at 400 and 4,000 ppm in fully saturated CaCl_2 and CaBr_2 brines and monitored for 5 days for any precipitates or solubility issues.

Chemical Thermal Stability Tests

Chemical thermal stability evaluation is a common test for all oil production chemicals. However, it is much more stringent for ones used in subsea applications. While the dynamic stability testing is designed to stress the chemical fully, products were also subjected to static temperature testing over a specified period (7 days in this study).

Low Temperature Stability

An 80ml of corrosion inhibitor was placed in a sealed test jar at 4°C (39°F) and cooled at 4°C (39°F) for 7 days. After 7 days of cooling, a visual inspection for phase separation, particle size and Fourier transform Infrared Spectroscopy (FTIR) correlation was measured at >95% in all temperatures after the 7-day cooling.

High Temperature Stability

An 80ml of corrosion inhibitor was placed in a sealed test jar at 60°C (140°F) and a pressurized cylinder at 121°C (250°F) and heated in an oven for 7 days. After 7 days of thermal aging, a visual inspection for phase separation, particle size and Fourier Transform Infrared Spectroscopy (FTIR) correlation was measured at >95% in all temperatures after the 7-day thermal aging.

Extra High Temperature Stability Test

Corrosion inhibitors passed Standard Chemical Thermal Stability Tests for DepFlux qualification were heated at 200°C for 48 hours and any solid precipitates, haziness or phase separations noted. FTIR was run before and after thermal aging. This thermal aging at 200°C was attempted for high temperature stable (>200°C) corrosion inhibitors for deepwater applications.

SAE Filtration Test

SAE filtration must be performed on all products for deepwater applications to ensure no clogs occur to umbilical tubing and chemical injection lines. Specification filter pot for this filtration process must be SAE 8 Class or better. A single-particle optical sensing (SPOS) or an optical

particle counting (OPC) is used to measure particle sizes. The liquid suspension under examination flows through an illuminated region, and the passage of a particle through several channels is collected and detected by the illumination/detection sensor.

High Pressure Viscosity Test

To ensure that the selected inhibitors could be pumped through the umbilical section, the viscosity of the corrosion inhibitors was measured at varied pressures at low temperature (4°C / 39°F).

A High-Pressure Viscometer is used to calculate the viscosity of the chemical in a range of temperature and pressure. For this measurement, approximately 10 mL of fluid was added to an unpressurized HP piston cell and cooled to 39°F (4°C). When the sample reached 39°F (4°C), the viscosity was calculated from the travel time of a magnetically driven piston at 0 psi. When the reading stabilized, the system pressure was increased to 10,000 psi via a screw piston. The chemical is conditioned for a period of seven days and should maintain a stable viscosity measurement at this initial screening condition for at least seven days.

Dynamic Stability Loop Test

Our inhouse deepwater flow loop (Figure 4) provides a dynamic method to assess the suitability of production chemicals for umbilical use based on their stability over a range of flow rates and shut-in periods through differential pressure measurements.



Figure 4: Subsea Chemical Flow Loop Equipment