

Formulation of Novel Combination Production Chemicals for Deepwater Oil and Gas Fields

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ABSTRACT

Deepwater oil and gas fields are generally classified as developments located in water depths greater than 500 m.¹ Applying production chemicals in deepwater fields presents multiple challenges because the operating temperature of deepwater oil fields is often greater compared to that of shallow or onshore developments. Furthermore, the extended reach of deepwater chemical umbilicals results in longer residence times for the chemicals within them and lengthy exposure to the high-pressure (HP), low-temperature environment. Long-term stability of chemicals under these conditions is an essential requirement in maintaining the integrity of the injection system and product efficacy. The HP in the umbilical can increase the viscosity of a product to such an extent that it cannot be injected. In extreme circumstances, production chemicals can become totally unstable in the umbilical, causing a blockage that results in costly remediation workovers.

To reduce the costs associated with constructing deepwater fields, the number of chemical umbilicals installed is often minimized, which necessitates the use of combination production chemicals. The most common multipurpose products used in deepwater fields are combined scale and corrosion inhibitors. This work details the approach taken to develop two deepwater multifunctional products that have functionality not generally found in a single product. The first product is a bifunctional corrosion inhibitor/demulsifier, and the second is a corrosion inhibitor blended with a non-triazine hydrogen sulfide (H₂S) scavenger.

Key words: deepwater, corrosion inhibitor, H₂S scavenger, combination products

INTRODUCTION

Hydrocarbon production currently occurs in a variety of onshore and offshore locations. Most offshore production in shallow water (< 500 m) has reached maturity, with most of the more accessible reserves having already been exploited. As a result, exploration and production in offshore environments has been extended to deeper water (> 500 m), which usually incurs more expense and overall project risk for operators and service providers. Production from deepwater oil fields is expected to grow by 40%, to 10 million bpd (10% of total global output), by 2025.² Figure 1 shows the regions where deepwater oil production is expected to grow. Large development projects are already underway in deepwater Atlantic areas of the UK and Norway, the Gulf of Mexico, Campos pre-salt basin in Brazil, West Africa, and Australia.



Figure 1: Deepwater oil production map.

Most deepwater fields have tough operating conditions, whether it is the need to work in rough seas, long distances from land, or more complex geological features compared to those of shallow-water fields. Deepwater rigs, subsea production templates, subsea production lines, and umbilical systems all add significant costs to developing deepwater fields. As a result, exploiting these fields using a minimum number of wells and sophisticated subsea equipment is key to maximizing the economic viability of these projects. During the drilling phase, the trend has been to design long-reach, horizontal, and multilateral wells to maximize contact with the hydrocarbon and gas pay zones, often with multiple tiebacks to a single producing platform or floating production, storage, and offloading (FPSO) vessel. The deployment of production chemicals in these fields is important to ensure effective flow assurance and asset integrity. Applying these chemicals downhole or at the subsea wellheads usually requires the use of chemical injection lines inside umbilicals, which also provide power, hydraulic fluids, and well monitoring technology. Traditional production chemical applications for the control of scale, corrosion, H₂S, hydrates, paraffin, asphaltenes, and emulsions are usually performed using mono-functional chemicals. The injection of multiple chemicals in a topside production process requires the provision of separate chemical injection skids and tanks, which are relatively inexpensive when compared to the overall production systems. However, performing multiple chemical injections by means of umbilicals can result in significant increases in cost because the injection lines must be sized for each application and, in some cases, cover distances of many kilometers from the onshore base or production asset.³ The general trend with subsea field development has been to increase the lengths of tiebacks as part of cost control, with some more than 100 km in length.⁴ Any method that reduces the umbilical length or quantity can therefore have a significant cost benefit to the overall subsea field development cost. The use of multifunctional production chemicals can reduce the need for separate umbilicals for each chemistry type.

Production chemicals injected by means of umbilicals in deepwater fields remain exposed to the subsea temperatures and high umbilical pressures for extended periods.⁵ To maintain the integrity of the injection

system and the effectiveness of the chemicals, it is essential that deepwater chemicals can withstand the harsh environments found in the umbilicals and at the injection location (e.g., downhole or deepwater flowline). Therefore, extensive testing is carried out to confirm that exposing the production chemical to the umbilical and production temperatures and pressures will not have a detrimental effect on product performance or its stability. Every production chemical injected in deep water is required to have low viscosity (typically $< 0.1 \text{ Pa}\cdot\text{s}$) at HP and at seabed temperatures (0 to 10°C). Products must also demonstrate long-term stability under umbilical and injection location conditions. Deepwater umbilicals are HP, low-temperature environments, therefore hydrates can form within them should there be an ingress of gas from the production streams. Consequently, deepwater production chemicals are formulated to minimize the risk of hydrate formation in the chemical injection umbilicals. This is achieved by using water-free formulations or by adding enough monoethylene glycol (MEG) or methanol to the product to suppress hydrate formation should gas ingress occur.

Certain multifunctional chemicals have been used in deepwater fields for many years, with the most common examples being combined scale/corrosion inhibitors; the use of other combination products has been uncommon.⁶ However, this paper demonstrates that it is possible to develop new combinations of deepwater production chemicals (i.e., a combined corrosion/ H_2S scavenger and a combined corrosion inhibitor/demulsifier). To confirm that the new products were suitable for injection in deepwater umbilicals, in addition to performance tests, several physical-property tests were carried out in accordance with American Petroleum Institute (API)⁽¹⁾ TR 17TR6.⁷ The results of the performance and physical tests confirmed that both products are suitable for use in deepwater oil and gas fields.

EXPERIMENTAL PROCEDURE

Combination Corrosion Inhibitor/ H_2S Scavenger Testing

The combination corrosion inhibitor/ H_2S scavenger was developed for application in a deepwater oil field located offshore West Africa. The first phase of the product development consisted of blending common H_2S scavenger chemistries (3,3'-methylenebis(5-methyloxazolidine) (MBO), (ethylenedioxy)dimethanol (EDDM), and monoethanolamine triazine) with corrosion inhibitor actives, and their performance was screened in corrosion kettle tests and H_2S removal tests. During the early stages of product development, it became apparent that triazine was not a viable option for the formulation. Triazines as manufactured contain high concentrations of water (as much as 50%). Therefore, to develop a triazine-based product suitable for deepwater application, it would need to contain a high proportion of MEG (for hydrate prevention), which would result in a dilute product that would require a high treatment rate. Consequently, development concentrated on products based on EDDM and MBO (which do not contain water) blended with corrosion inhibitor components. H_2S removal screening testing showed that products based on MBO had faster reaction kinetics and a greater H_2S capacity than those based on EDDM. Although many products were developed and their efficacy screened, the testing and results of the most effective chemical developed for this application (Product A) are described in this paper. Product A is a blend of MBO, film-forming corrosion inhibitor actives, and a synergist formulated in glycols.

Corrosion Kettle Test Method

The corrosion protection provided by the combined corrosion inhibitor/ H_2S scavenger (Product A) was initially assessed using the partition kettle test. A summary of the kettle test conditions is provided in Table 1. Synthetic field brine was added to the kettle test vessel and heated to 68°C while bubbling with ultrapure carbon dioxide (CO_2). After two hours, a linear polarization resistance (LPR) probe and deaerated odorless kerosene was added to the test vessel and LPR measurements commenced with recordings taken every 10 minutes. The LPR scanning rate was 0.33 mV/s , and the scan was performed from -10 to $+10 \text{ mV}$ versus the open circuit potential. The corrosion rate was calculated using the Stern-

¹ American Petroleum Institute (API), 1220 L St. N.W., Washington, DC, 20005-4070, USA

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Geary equation with Tafel constants (β_a and β_b) of 113 mV.⁸ The carbon steel electrodes were corroded for three hours before the addition of Product A, and the test was then left to run for an additional 21 hours to enable the corrosion rate to equilibrate. Upon completion of the test, the percent corrosion protection was calculated using the baseline and final inhibited corrosion rates (Equation [1]). An acceptable inhibited corrosion rate for this test is less than 0.1 mm/y (4 mpy).

$$\% \text{ corrosion protection} = (CR_u - CR_i)/CR_u \times 100 \quad (1)$$

Where: CR_u = uninhibited (blank) corrosion rate and CR_i = inhibited corrosion rate.

Table 1
Summary of Kettle Test Conditions

Parameter	Value
Brine phase	Synthetic brine
Oil phase	Field crude
Water cut	70%
Inhibitor	Product A
Inhibitor doses	50 and 100 ppm
Temperature	68 °C
Electrode material	Carbon steel (UNS G10180) ⁽²⁾
Gas sparge	100% CO ₂ throughout
Pre-corrosion	3 hours
Test duration	24 hours

Brine Composition	
Ion	Brine (mg/L)
Chloride (Cl ⁻)	12,300
Bromide (Br ⁻)	70
Sulfate (SO ₄ ²⁻)	640
Bicarbonate (HCO ₃ ⁻)	1,037
Acetate (CH ₃ COO ⁻)	1,121
Sodium (Na ⁺)	7,810
Magnesium (Mg ²⁺)	240
Potassium (K ⁺)	115
Calcium (Ca ²⁺)	180

High-Pressure Autoclave Method

The effectiveness of Product A under HP and moderate shear conditions was assessed using a HP autoclave. A mix of 70% synthetic brine and 30% crude was placed in a large glass vessel on a hot plate stirrer. The vessel was heated to 60 °C while continuously bubbling with CO₂ through a dispersion tube. When the vessel reached 60 °C, Product A was dosed into the oil phase (100 ppm). The oil/brine was vigorously mixed for 30 minutes and then allowed to fully separate for an additional 30 minutes. The pre-partitioned brine was transferred to the autoclave, and an additional 1% of hydrocarbon was added to the autoclave. After the fluids were transferred, carbon steel coupons (pre-corroded for three days at 68°C with 100 kPa CO₂) were mounted on coupon holders that were fixed to a rotating shaft and immersed in the test fluid. The autoclave was then assembled and purged with nitrogen for two hours to remove any oxygen that entered the fluids during the fluid transfer process. The vessel was heated to 68°C and pressurized with the required gas mixture. Throughout the duration of the test (28 days), the coupons were rotated to provide a shear stress of 40 Pa on the face of the coupons (Equation [2]). At the end of the test, the coupons were removed, cleaned using an inhibited acid solution (10 g/L N,N'-dibutylthiourea diluted in 1 L of 18.5% hydrochloric acid), reweighed, and the corrosion rate was calculated (Equation [3]). An uninhibited test was conducted to obtain a baseline corrosion rate so that the percent inhibitor protection could be calculated. The pass criteria for this test was a general corrosion rate of less than 0.1 mm/y (4 mpy) and no pits > 10 µm in depth. A typical surface and depth profile of the coupons was scanned using a profilometer to assess localized corrosion. Autoclave tests were run under sweet and sour conditions because when applied in the field, Product A would remove H₂S from the system. Therefore, the corrosion mechanism would change from being predominately H₂S corrosion

² Unified Numbering System for Metals and Alloys (UNS). UNS numbers are listed in Metal & Alloys in the Unified Numbering System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2004).

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to being predominantly CO₂ corrosion after chemical injection. A summary of the autoclave test conditions is provided in Table 2.

Table 2
Summary of Autoclave Test Conditions

Parameter	Value
Temperature	60 °C
Brine	Synthetic (see Table 1)
Oil	Field crude
Oil/water ratio	70%
Inhibitor	Product A
Dose rates	0 and 100 ppm
Partial pressure of CO ₂	1.72 bar (172 kPa)
Nitrogen	6.89 bar (689 kPa)
H ₂ S	0.028 bar (2.8 kPa) (sour tests only)
Coupon metallurgy	Carbon steel (X65)
Duration	28 days
Wall shear stress	40 Pa

$$\text{Coupon shear stress (Pa)} = 0.0791 \text{ Re}^{-0.3} \rho r^2 \omega^{2.3} \quad (2)$$

Where: Re is the Reynolds number ($\text{Re} = \omega r^2 / \nu$), ρ is density, r is radius, ω is the angular velocity, and ν is the kinematic viscosity.

$$\text{Corrosion rate (mm/y)} = 87,563 \times W / (A T D) \quad (3)$$

Where: W is mass loss (g), A is coupon area (cm²), T is time (hours) and D is coupon density (g/cm³).

H₂S Removal Test Method

The H₂S scavenger test setup consisted of a set of mass flow controllers that enabled known amounts of various gases to be delivered by means of a sintered glass tube to a glass vessel filled with a known volume of combined corrosion inhibitor/H₂S scavenger. The gas composition downstream of the vessel was monitored by means of a gas chromatograph (GC) calibrated for sulfur detection. Figure 2 provides an overview of the test apparatus. The glass vessel enabled testing to be conducted at ambient and elevated temperatures. The gas mixtures were bubbled at a constant rate through the chemical until H₂S was detected by the GC in the downstream gas, indicating that H₂S breakthrough had occurred. From the results, the experimental H₂S uptake capacity of the product under the given conditions was calculated.

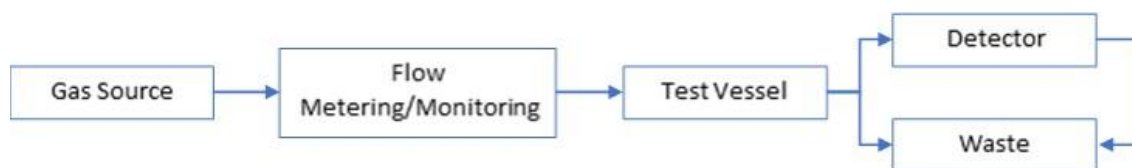


Figure 2: H₂S scavenger test setup diagram.

Combination Corrosion Inhibitor/Demulsifier Testing

As limited chemical injection umbilicals were available, a multifunctional corrosion inhibitor/demulsifier product was needed for a deepwater oil field located offshore Brazil. The demulsifier, which had previously been selected for use in the field, was blended with an oil-soluble, water-dispersible corrosion