

The Development of Environmentally Acceptable Corrosion Inhibitors for Sour Applications

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ABSTRACT

Production chemical regulations in the North Sea oil and gas sector restrict the use of environmentally harmful substances and require chemical providers to replace such products with environmentally acceptable alternatives. Environmentally acceptable corrosion inhibitors that are used in oil and gas production are non-toxic, biodegradable, and have a low impact on the marine environment. Such inhibitors are designed to protect mild steel from the effects of corrosion in systems containing acid gas, organic acids, and the influence of temperature. In this work, two oilfields in the North Sea required the development of environmentally acceptable corrosion inhibitors, to replace environmentally harmful products. The new products were required to offer similar or improved efficacy to the incumbent inhibitors in a sour environment and to be cost-effective. Laboratory tests were performed to represent field conditions and ranged in temperature, H₂S, and CO₂ concentration as well as water cut and shear stress. Products were found to be effective to the corrosion rate limit of <4 mpy and with no pitting.

Key words: Chemical treatment, Corrosion inhibitors, Hydrogen sulfide

INTRODUCTION

The decomposition process of ancient marine species in the seabed for millions of years coupled with the presence of specific geological conditions such as high pressures and temperatures led to the formation of what is known today as fossil fuels. For this reason, they can be found either on the earth's surface where ancient seas were located or beneath the seabed. Considering that the ocean covers three-quarters of the Earth's surface the offshore oil and natural gas exploration entail an enormous economic and strategic benefit.¹

Since the first offshore well produced oil in shallow waters near Summerland, California in 1897² drilling activity has moved to deeper areas driven by a remarkable improvement in technology. Nowadays the offshore production is high with the North Sea, the Gulf of Mexico, the Atlantic Ocean off Brazil and West Africa, the Arabian Gulf, and the seas off of South East Asia being the most productive areas. In the United States alone, the offshore federal production in 2020 reached approximately 641 million barrels of oil and 882 billion cubic feet of gas, almost all of which was produced in the Gulf of Mexico. In addition, the Bureau of Ocean Energy Management (BOEM) attached to the U.S. Department of Interior estimated the untapped fossil fuel reserves in the outer continental shelf at 68.79 billion barrels of oil and 229.03 trillion cubic feet of gas.³

The increasing development of offshore drilling is also associated with a concern for the environment. It is known that routine oil and gas activities can have detrimental ecological impacts, especially on the marine ecosystem during each of the main phases of exploration, production, and decommissioning.⁴ In this context, serious dangers can arise from the accidental spillage of contaminants such as hydrocarbons and production chemicals. The above emphasizes the importance of maintaining the integrity of the offshore platform through corrosion control above and below the surface,⁵ and the use of environmentally friendly chemicals whenever possible.⁶ In the case of the subsea area, the use of cathodic protection, coatings, and corrosion inhibitors^{7,8} are some of the most efficient measures that can be implemented.

United Kingdom Production Chemical Regulations

In the United Kingdom offshore sector, the use of all production chemicals including corrosion inhibitors is strictly regulated by the Harmonized Mandatory Control System (HMCS) and the Chemical Hazard Assessment and Risk Management (CHARM)⁹. These control systems rank the products based on toxicity, bioaccumulation, and biodegradation which has led to an increasing amount of work in the development of environmentally acceptable corrosion inhibitors. This process requires that any component present in a production chemical used offshore has to be >20% biodegradable and every component used must meet at least two of the following three criteria:

1. Biodegradation >70% in 28 days (OECD 301A, 301E) or >60% in 28 days (OECD 301B, 301C, 301D, 301F or 306)
2. Toxicity >10 mg/L (LC₅₀ or EC₅₀)
3. Bioaccumulation log P_{ow}<3 (if molecular weight <700) or bioconcentration factor (BCF) <100

The log P_{ow} is a partition coefficient that is the ratio of the concentration of a chemical between two phases (octanol and water). A low log P_{ow} value indicates a chemical is predominantly water soluble and is less likely to accumulate in living species. If the molecular weight of a product is >700, then it is assumed to be non-bio accumulative and automatically given a bioaccumulation log P_{ow} of 0.

If a substance does not meet the above requirements, the product will be given a substitution warning. If this is the case, temporary permission will be given for use of the product (whilst more environmentally friendly products are found) or the use of the product offshore will be refused.

From this categorization process, a Hazard Quotient (HQ) is calculated for each finished product. The HQ value indicates the likelihood of what adverse effects might occur if the chemical was discharged into the sea under a realistic worst-case scenario. Products with low HQ values (<1) are the more environmentally acceptable. In the UK, oilfield chemicals are categorized into bands based on their HQ values. Each band is given a color code from gold (most environmentally friendly) to purple (least environmentally friendly); HQ values and color codes are summarized in Table 1. With this consideration in mind herein we report the development and corrosion testing results of novel continuous,

environmentally acceptable corrosion inhibitors to replace non-environmentally friendly corrosion inhibitors currently in use in two oilfields in the North Sea.

Table 1
HMCS Categories (UK Scheme)

Category	HQ Min Value	HQ Max Value
Gold	>0	<1
Silver	≥ 1	<30
White	≥ 30	<100
Blue	≥ 100	<300
Orange	≥ 300	<1000
Purple	≥ 1000	

Field Overview

The target system for which corrosion inhibition is required consists of two shallow water installations producing from two fields located in the Northern part of the North Sea. In 2016-2107, the combined production was 16,465 b/d (2,695 m³/d) oil, 314,350 b/d (51,446 m³/d) water, and 12.06 MMScf/d (341,501 Sm³/d) gas from two reservoirs having 42 completed wells, of which 14 were production wells and 10 were dedicated to seawater injection. Approximately 60% of the production wells were classified as sour service wells. Oil is processed through a production, drilling, and accommodation platform and exported by pipeline to an onshore terminal. Produced water is piped to subsea templates for reinjection with some discharged overboard from the platform process trains. Gas is used for inter-field power generation and to flare.

The corrosion inhibitor is applied at the wellheads via umbilical to protect subsea flowlines and topside production facilities. The estimated consumption of the corrosion inhibitor in 2017 was 260 tonnes. Laboratory testing was performed to develop a new environmentally acceptable corrosion inhibitor to replace the incumbent inhibitor which had an unacceptable environmental profile. A client requirement was to use representative test conditions to drive sulfide film formation in the laboratory to confirm penetration and inhibition under potentially stagnant conditions.

EXPERIMENTAL PROCEDURE

Inhibitor Development

Most environmentally acceptable corrosion inhibitors are derived from plant extract and biomass wastes.⁶ Although they are an alternative option against more traditional corrosion inhibitors, they still possess several limitations that prevent them from being used in industrial applications. Among them is the concern for long term storage and the dependence of the chemical composition with the extraction method having both a negative impact on product performance. The previous facts initiated a research project to develop environmentally acceptable corrosion inhibitors for sour applications that were not obtained from natural and/or biological sources, and that at the same time would be categorized as gold according to the environmental regulations described above. Through this process, we were able to identify three anti-corrosion compounds whose generic chemical description is shown in Table 2. They were combined into two stable corrosion inhibitor formulations G-CI-1 and G-CI-2 using an aqueous glycol ether mixture as a solvent package. The solvent selection was made considering that glycol ethers, in general, are not bio accumulative and they are also practically non-toxic to aquatic organisms based on acute toxicity studies.¹⁰ G-CI-1 and G-CI-2 are Gold with no substitution warning based on the chemical ecotoxicology data provided in Table 3.