

New Class of “Green” Corrosion Inhibitors: Development and Application

Use of chemical corrosion inhibitors is common in production and processing operations. Particularly challenging is the development of new chemistries, which maintain good protection of materials under a variety of conditions while being environmentally acceptable. This paper illustrates patented work in the chemistry of Alkylpolyglucosides (APGs) and their synergistic effect with polyaspartates. This inhibitor class demonstrated good general inhibitor performance in several oilfield brines, showed good filming characteristics under conditions of shear, and provided an excellent environmental profile.

Introduction

Chemical inhibitors play an important role in the protection and mitigation strategies for retarding corrosion. Several chemistries have been successful, primarily amines, quaternary salts of amines, and imidazolines, all of which act as filming protection agents either filming on the metal surface or on a variety of scales (e.g., calcium carbonate) deposited on these surfaces. In addition to filming characteristics, corrosion inhibitors must slow the corrosion rate, usually by a combination of increasing the anodic or cathodic polarization behavior, reducing the movement or diffusion of ions to the metal surface, and increasing the electrical resistance of the metal surface.

The mixture of crude oil, condensate, and connate and other waters (brines)

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can result in highly aggressive and corrosive media in contact with carbon steel. To challenge this environment further, these mixtures often are under high-flow-rate conditions, creating several shear-stress conditions.

Traditionally, chemical corrosion inhibitors needed the ability to film, within fluid mixtures, at the surface between liquid and solid (i.e., surfactant like materials) and needed resistance to removal under high-flow-rate conditions. In general, these materials are excellent corrosion inhibitors under a variety of field conditions. However, they do have performance boundaries, such as high temperature, and have properties relating to marine toxicity and biodegradation that make them less acceptable for use in highly regulated offshore environments such as the North Sea and northeast Atlantic.

Producing more-acceptable environmental profiles for inhibitor properties could compromise the desired technical effects (e.g., persistent materials usually are not readily biodegradable). Similarly, several chemistries are nitrogen based and possess inherent toxic properties.

Faced with this challenge, various strategies were studied to reduce environmental effects while maintaining desired surfactant properties and persistency (e.g., amino acid, aspartic acid, and polyaspartates). However, these chemistries require high dosage rates or have insufficient biodegradation to meet the required environmental regulations.

Earlier works showed that agents other than filming surfactants could provide good corrosion protection under high-flow-rate conditions. However, the chemistry did not provide complete answers to biodegradation problems. It was found that, under certain conditions, APGs can provide good filming and protective characteristics and an

excellent environmental profile without losing significant persistency.

Base Chemistry

In examining chemistries for application as corrosion inhibitors without compromising technical efficacy yet having environmental acceptability, the glycosides and polyglycosides seemed to offer promise.

Experiments

Tests were performed for a variety of conditions on three products formulated from the identified chemistry. The conditions were static (bubble test), high-shear, sour, and high-temperature. Tests also were performed to show the synergistic effect between the components, how the formulated inhibitor partitioned in the presence of oil and brine, the compatibility of the products with various oilfield chemicals and materials, and any emulsifying effect caused by the formulated products. The formulated products were referred to as Formulation A, B, and C for the purposes of this paper.

The products were tested with linear-polarization-resistance (LPR) and rotating-cylinder-electrode (RCE) techniques. In all cases, tests were performed on mild steel under CO₂-saturated conditions. All tests were performed in brine only, although investigations into partitioning effects were performed and are detailed in the full-length paper.

The bubble-test method involves evaluating the corrosion of a given metal in simulated brine saturated with CO₂ at a temperature equivalent to that in the field. During the test, CO₂ gas is sparged continuously into the test solution. The rate of corrosion is determined instantaneously with the LPR technique, in which a small direct-current voltage is applied to a pair of identical electrodes and the resultant current is measured. A limitation of the bubble-test method is that it does not provide information on

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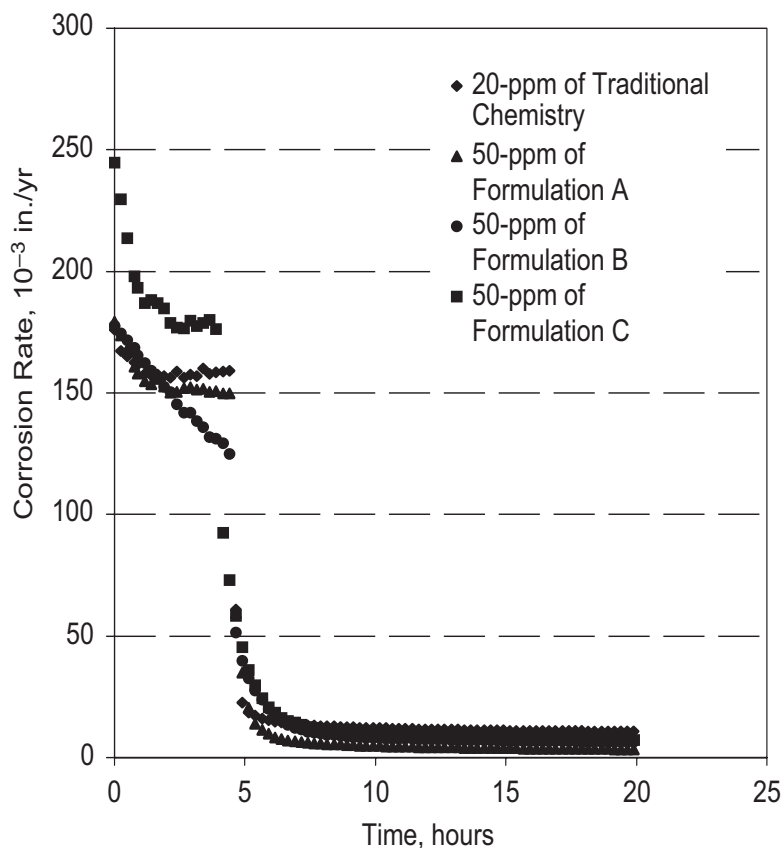


Fig. 1—LPR chart comparing effect of 50 ppm of new “green” corrosion inhibitors with 20 ppm of traditional corrosion inhibitor in CO₂-saturated North Sea Brine D at 149°F.

the effect of shear stress on the performance of a given corrosion inhibitor.

The RCE method is useful in evaluating the film persistency of a given corrosion inhibitor under high-shear stress that is common in multiphase-flow conditions. The same technique is used to measure the corrosion rates as with the bubble test; however, a three-electrode system is used, and the working electrode is rotated in the brine to create the effect of shear. To subject the inhibitor to challenging conditions, RCE tests used a shear stress of approximately 0.007 psi. This shear rate is equivalent to the production of 150,000 B/D through a 10-in.-internal-diameter pipeline, equivalent to a rotation rate of 5,000 rev/min for a 0.30-in.-radius electrode.

Oilfield Brines Under Nonshear Conditions. Formulation A, a corrosion inhibitor developed from the chemistry, is effective in typical North Sea brines. Significant reductions in corrosion rates were observed at typical worst-case process temperatures. An initial period of

4 hours without inhibitor showed the corrosion rate of each brine on mild steel under the test conditions.

Injecting 50 ppm of Formulation A instigated a rapid reduction in corrosion rate. The corrosion rate then stabilized at 0.004 in./yr. Beginning 16 hours after injection, the low corrosion rates were maintained for the duration of the test.

Oilfield Brines Under High-Shear Conditions. While the brines from the Shearwater and Njord fields had initial corrosion rates less than those under static conditions, the Forties brine had a similarly high corrosion rate under both shear and static conditions. Therefore, the formation of a passive iron carbonate layer on the surface of the electrode was enhanced by the effect of mass transfer experienced under shear conditions for the Shearwater and Njord brines. However, the formation of this passive layer was not enhanced by rotation of the electrode in the Forties brine.

The presence of 50 ppm of Formulation A in Forties brine under the RCE-test conditions reduced the corrosion rate very quickly. Importantly, it also maintained this low corrosion rate for the remainder of the test period.

A similar effect was observed for the Shearwater and Njord brines, although it was not as clearly visible as the effect in Forties brine because of the lower initial corrosion rates.

Inhibitor Performance in Sour Conditions. The pH of the brine was reduced in the presence of 70 ppm of dissolved H₂S, forcing the more-rapid formation of a passive layer on the surface of the electrode. This action explained an initial rapid decrease in corrosion rate before inhibitor injection.

A further reduction was observed after 5 hours when 50 ppm of Formulation A was injected. The chemistry was effective in the presence of dissolved H₂S, reducing the corrosion rate and maintaining it at a low level.

Inhibitor Performance Under High-Temperature Conditions. Again, there was a rapid initial decrease in corrosion rate following injection. The low corrosion rate was maintained for the duration of the test despite the high temperature. At temperatures as high as 167°F, Formulation A was effective, reducing the corrosion rate considerably.

Inhibitor Performance in High-Salinity-Brine Conditions. An initial decrease in corrosion rate before injection was typical of high-salinity brines. The passive layer formed on the surface of the electrode quicker because of the high salt concentration. The initial corrosion rate was lower than that observed in other tests, again because of the high salinity of the brine. The effects of the inhibitor were similar to those observed in previous tests: a rapid knockdown following injection, and a low final corrosion rate.

Synergistic Effects of Inhibitor Components. While the individual components of Formulation A reduced the corrosion rate, there was a marked improvement in performance when the two were combined. The most noticeable effect was the increase in the knockdown rate. The two chemistries complemented each other, and the rate of the film-forming mechanism increased. A 10-ppm

Formulation-A dose resulted in a more rapid reduction in corrosion rate initially than 20 ppm of either the APG or the polyaspartate and a lower final corrosion rate than 20 ppm of polyaspartate.

Comparison With Traditional Oilfield-Corrosion Inhibitor. As part of the development of the new chemistry, products were tested against a benchmark traditional corrosion-inhibitor chemistry. **Fig. 1** shows the comparable performance between 20 ppm of traditional oilfield-corrosion inhibitor and 50-ppm doses of different formulations of the new corrosion-inhibitor chemistry. Both have similar knockdown rates and final corrosion rates. However, the “green” corrosion inhibitors showed slightly improved performance under static conditions. All three formulations provided lower final corrosion rates and greater levels of inhibition than traditional inhibitor.

Generally, the new “green”-inhibitor range does require a higher dose than the traditional inhibitors to achieve the same performance. If results were monitored over a longer test period, the corrosion rate could match that of the traditional inhibitor.

Environmental Profile. This range of new corrosion-inhibitor chemistry had excellent environmental categorization. The formulations do not contain any products that are deemed candidates for substitution.

Conclusions

The polymeric glycoside nature of these materials exhibited surfactancy. Indeed, many are used in domestic cleaning applications (e.g., dishwasher fluids), hence their favorable environmental characteristics. This work demonstrated applicability as a film-forming corrosion inhibitor under oilfield-production conditions. This work also showed synergistic effects with polyaspartates, which are believed to enhance filming characteristics. The work showed a pronounced improvement in performance when these two chemistries were carefully formulated. The active components have excellent ecotoxicological properties that have been translated into formulated products while maintaining good corrosion-inhibition characteristics that, under certain formulation conditions, have been enhanced. JPT