Corrosion Inhibitors for Acid Jobs

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Corrosion is all around us—from rusty nails to pitted pots and pans. The oilfield is no exception. Casing and tubing strings corrode continuously and require protection throughout the life of a well, particularly if hydrogen sulfide or carbon dioxide is produced. Special care is required when concentrated hydrochloric (HCl) or hydrofluoric (HF) acid is pumped down a well to clean up wellbore damage, create fissures deep into the formation or simply remove scale from casing and tubing. Without special chemicals that inhibit corrosion, these acids would quickly destroy well tubulars. This article reports advances by chemists at Dowell Schlumberger in Tulsa, Oklahoma, USA concerning how inhibition works. It also describes recently developed inhibitors that improve protection in hot wells.

Corrosion inhibitors are an indispensable part of the fluid mix pumped downhole when a well is acidized. To prevent acid damaging well tubulars, inhibitors must function for at least two hours during a fracturing job and up to 24 hours when acid is being used to clean wellbore damage or scale. They must not fail at high temperature when corrosion intensifies (left). And they must inhibit corrosion effectively for the variety of steel grades used to complete wells. These range from the commonly used API grade J55 (which has a 55,000-pound-per-square-inch [psi] minimum yield strength) to the increasingly popular stainless steels containing chrome. Finding improved inhibitors that satisfy these constraints provides a tough challenge to the research chemist.

Downhole Corrosion: Mechanism and Inhibition

The process of corrosion has been well understood for years.¹ When acid meets steel, the two materials act like a battery. The steel surface provides both the battery’s cathode and anode, while the acid constitutes the electrolyte (below, left). Parts of the steel surface, acting as anodes, lose positive iron ions to the acid and generate free electrons in the steel:

$$\text{Fe} \rightarrow \text{Fe}^{++} + 2e^-$$

Other parts of the steel surface, acting as cathodes, use these electrons to reduce positive hydrogen ions in the acid to form hydrogen gas:

$$2H^+ + 2e^- \rightarrow H_2$$

Together these reactions create small currents that loop between the steel and the acid. As long as current flows, anodic sites steadily lose iron and corrode. But if either the anodic or cathodic reactions are impeded, current stops flowing and corrosion

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1. For an overview of acidizing techniques:

2. For an in-depth study of corrosion chemistry and types of corrosion and inhibitors:
slows. This is precisely what inhibition seeks to achieve (right).

Until the 1960s, the most common inhibitors were arsenic salts, which interfere with corrosion by impeding the cathodic reaction. Since then, these salts have been replaced by organic materials that adhere to steel surfaces and form protective films that prevent both anodic and cathodic reactions.

Today, two or more organic inhibiting compounds are typically mixed with an "aid" or "intensifier" to enhance inhibition at high temperature, a solvent, and various additives to facilitate pumping the mixture downhole. Additives include demulsifiers, wetting agents and iron and silicate stabilizers that reduce shale swelling.

The most important group of organic inhibitors, acetylenic alcohols, was the focus of research at Dowell Schlumberger. To simplify the number of reactions that occur in a typical inhibition system, researchers investigated a system with just three components: steel, hydrochloric acid and an acetylenic alcohol inhibitor, octynol \( \text{[CH}_3\text{-(CH)}_2\text{CH(OH)}-\text{C}==\text{CH}] \). Using a variety of surface analytical techniques, they unraveled the chemical and physical processes by which acetylenic alcohols inhibit corrosion. The techniques also guided them in synthesizing new organic compounds that give improved protection. Their first goal was understanding the chemistry of a polymer thought to form when octynol, acid and steel meet, possibly aiding inhibition.\(^3\)

**Probing Polymer Chemistry**

Their main tool for understanding chemistry was infrared spectroscopy. With this technique, researchers note the frequencies of incident infrared radiation that the sample absorbs and thereby identify molecular groupings in a sample, such as CH, OH, and the carbon-carbon triple bond, C==C.

Each absorbed frequency coincides with a particular grouping's natural frequency of vibration, which is well-documented. Infrared spectroscopy used to be a time-consuming business. Previously, radiation was split into its different frequencies using a grating or prism and laboriously guided through the sample. Today, a technique called Fourier transform infrared (FTIR) spectroscopy uses the more efficient technique of moving-mirror interferometry to convert broad-band infrared radiation into its individual frequency components (left). The single beam is split, led through the sample, detected, reconstituted into a conventional spectrum, which is converted into its frequency components using a fast Fourier transform algorithm.\(^4\) One spectrum takes less than a second to generate, so hundreds of scans can be easily made to increase spectrum quality.

The FTIR spectrum of pure octynol reveals numerous inverted absorption peaks that correspond to the compound's molecular groupings (next page, middle). Five peaks are caused by the C–H grouping, two by C–O, and one each by OH and C==C. This spectrum is octynol's fingerprint.
The Dowell Schlumberger researchers first checked that without steel, hydrochloric acid did not affect the octynol structure. Using a 15-percent HCl solution, they mixed the two compounds for 24 hours, then stripped off the acid by dissolving the octynol in chloroform. After the chloroform evaporated, they measured the octynol spectrum again and found it unchanged.

Mixed with steel beads, however, the octynol-acid mixture created a greasy protective film over the beads. Removing this film with chloroform and analyzing it with FTIR spectrometry, they found a significantly different spectrum. The C–H peaks were still present, as expected. But new peaks indicated C=C bonds, the presence of a small number of unsaturated carbons (meaning they possess free electrons) and the probability of terminal double bonds. (Terminal means one end of the bond sits on the outside of the structure.) Octynol’s triple bond was not present.

To verify that extraction using chloroform had not affected the film’s structure, an FTIR spectrum was made by bouncing the infrared beam off a steel mirror that had been exposed to the octynol-acid mixture (bottom). This spectrum, of poorer quality due to the thickness of the film, produced the same peaks as the previous experiment as well as evidence of unreacted octynol.

Armed with clues about the film’s chemical structure, the researchers next used size-exclusion chromatography to investigate the size of the molecules in the film. In this technique, a sample is injected in a column containing porous material. Large molecules in the sample move rapidly through the porous medium whereas small molecules follow longer, more tortuous paths. As the sample’s molecular components emerge from the column, they are detected by an ultraviolet (UV) spectrophotometer. This device shines UV light through molecules and measures the amount of light absorbed. The researchers used a wavelength of 254 nanometers because it is absorbed by the triple carbon bonds found in octynol. It is also the wavelength absorbed by another bond they suspected was in the film, conjugated double bonds (alternating chains of single and double carbon bonds).

The size-exclusion chromatogram of the film extracted from the beads shows two compounds (above). The sharp absorption peak recorded later was interpreted as unreacted octynol. The broad peak occurring earlier was interpreted as a polymer of variable length, but larger than octynol, and having conjugated double bonds.

Combining the structural information provided by the FTIR spectra with clues about the molecular size of the film given by the


Chemical chain reaction that forms the polymer film. The proposed chemical structure of the polymer is based on infrared spectra and size-exclusion chromatography.

Inhibition Mechanism

With the film's structure and development understood, the researchers next investigated how the octynol and polymer worked together to inhibit corrosion. Their main tool was an alternating current impedance spectroscopy (ACIS), a device for measuring the AC impedance between the steel surface and the acid-octynol mixture at many different frequencies. They interpreted the results in terms of an equivalent circuit comprising a resistance representing the electrolyte, $R_e$, in series with a parallel combination of a resistor, $R_i$, the resistance to charge transfer across the steel-electrolyte interface, and a capacitor, $C_d$, the capacitance of the interface double-layer (below, left).

Because corrosion is caused by ion flow across the interface, the transfer resistance, $R_i$, directly yields the degree of protection—the greater $R_i$, the more corrosion is inhibited. The capacitance, $C_d$, is interpreted to yield the amount of surface area covered by the inhibitor and polymer film.

In a first experiment, the researchers mixed several concentrations of octynol with a 15-percent HCl solution for 20 minutes and allowed the mixtures to react with N80 oilfield carbon steel (80,000-psi minimum yield strength), frequently used in wells of moderate temperature, 95°C to 150°C (203°F to 302°F) (below). Measuring the steel surface's impedance spectra, they deduced the degree of protection and surface area covered by the film and plotted both parameters versus octynol concentration. As expected, protection and coverage increased with concentration. But surprisingly, protection always exceeded coverage.

Corrosion protection and surface coverage versus octynol concentration, for octynol in a 15%-HCl solution at 25°C (77°F). The degree of protection is always greater than surface coverage, a surprising finding that is explained by the inhibitor preferentially adsorbing onto the most chemically active sites on the steel surface.
increased, dropped precipitously \( \text{(left)} \). Degree of protection also began dropping. This seemed to indicate that polymer growth somehow interfered with inhibition.

More insight into inhibition was obtained with Fourier transform ellipsometry, a technique that determines the average thickness of very thin films. The time dependence of film growth on steel was determined using various concentrations of octynol mixed with a 0.02 mole/liter concentration of HCl \( \text{(below)} \). At the lowest octynol concentration of 0.025 millimole/liter, the film appears to develop in two stages (see the two plateaus on the plot). This could indicate a change in orientation of the octynol molecule with time. The molecule is

![Diagram](image)

\[\text{ACIS measurements made using a 21-millimole/liter octynol concentration in a strong 28\% HCl solution at 65^\circ\text{C} [149^\circ\text{F}]. The drop in coverage and protection occurs because the polymer film consumes octynol, leaving none for inhibition.}\]

This difference was also seen in a second experiment in which impedance spectra were measured after a fixed concentration of octynol mixed with 15-percent HCl was allowed to react with a steel surface for different times \( \text{(below)} \). Protection reached a high value after 1 minute and improved only slightly over the next 100 minutes whereas the surface coverage was less than 50 percent after 1 minute and increased slowly thereafter.

To explain why protection is always higher than surface coverage, the Dowell Schlumberger team proposed that octynol adsorbs nonuniformly, acting preferentially on steel components that drive corrosion. Cementite, \( \text{Fe}_2\text{C} \), a brittle iron carbide, is an example. It enhances corrosion by accelerating \( \text{H}_2 \) evolution \( \text{(page 15, bottom)} \). Cementite, however, occupies much less of the steel's surface than less reactive phases such as ferrite, a form of pure iron.\(^7\)

A similar impedance spectra experiment with stronger acid, 28 percent, began similarly but ended differently. At around 40 minutes, surface coverage, having steadily assumed to be initially adsorbed parallel to the surface, the major attachment point being the triple bond and the OH group. At later times, the molecule may assume a more perpendicular attitude.

At higher concentrations, film thickness increases linearly with time. This was interpreted as the development of polymer, confirmed by observing absorption at the frequency of the visible spectrum where conjugated double bonds absorb light. In time, as the film thickened, the absorption maxima shifted toward the red part of the spectrum, indicating an increase in the number of conjugated carbon bonds and therefore polymer growth.

The Fourier transform ellipsometry also confirmed the ACIS data. Assuming a uniform distribution of material on the covered

![Diagram](image)

\[\text{Ellipsometric measurements of film thickness for various concentrations of octynol in a 0.02 mole/liter concentration of HCl on a steel surface. At the lowest octynol concentration, 0.025 millimole/liter, two plateaus are seen, indicating a possible change in the orientation of the octynol molecule as a function of time. At higher concentrations, the thickness of the adsorbed layer increases linearly with time, indicating the development of the polymer film.}\]


portions of the surface, film thickness can be converted to fractional coverage. Coverage can then be compared to degree of inhibition estimated from the electrochemical corrosion rate (see “Ellipsometric Results in Coverage/Protection,” right). As the ACIS measurements indicate, fractional coverage is always less than degree of inhibition, but particularly so at low octynol concentrations.

Conclusion from Experiments
From the considerable number of chemical and surface analytical measurements, the researchers pieced together how octynol inhibits HCl corrosion on steel. During the first minute, octynol molecules adsorb on the more active surface sites of the steel, such as cementite, and begin inhibiting corrosion. The polymer then begins to form. This shuts off more corrosion by physically blocking access of acid to the metal. Beneath the film, however, corrosion continues because the polymer lacks a sufficient electron density to remain chemically adsorbed to the steel surface. This corrosion uncovers active sites to which remaining octynol adsorbs, followed by more polymer generation. Eventually, polymer growth consumes so much octynol that none remains to protect the steel. Polymer coverage then falls, as seen on the last ACIS experiment, and corrosion picks up.

Search for Better Inhibitors
To the researchers, the weak link in octynol technology seems to be the polymer’s inability to adhere to the steel. They therefore began searching for organic compounds that would produce polymers with better sticking power, or in chemical terms, polymers with more free electrons to bond to the steel surface. They chose the α-alkenylphenone family because of multiple unsaturation within the molecule (a benzene ring, a carbon–carbon double bond and a ketone double bond). Five phenones were synthesized and tested as inhibitors under a variety of conditions (next page, top). Mixed with conventional additives such as surfactant and intensifier, they performed similarly to octynol at low temperatures and dramatically better at higher temperatures (see “Octynol vs. Phenones,” below, left). FTIR studies showed that these diverse chemicals appear to form a polymer called polyphenylvinylketone (PPVK). This polymer is rich enough in free electrons to remain adsorbed to the steel surface and inhibit corrosion as it is consumed (next page, bottom).

Two new Dowell Schlumberger acid inhibitors, A-260 for wells at 95°C to 150°C [203°F to 302°F], and A-270 for wells above 150°C [302°F] are based on the alkenylphenone technology and will significantly improve inhibition during acid jobs. A-260 is a mixture of polyvinylketones (PVKs), formulated with appropriate organic solvents and surfactants to achieve solubility and dispersibility. A-270 is a mixture of a PVK and a quaternary ammonium salt (in which nitrogen bonds to four carbons). It inhibits more effectively than either component alone (see “A-270 Synergism,” below) and easily outperforms most other inhibitors.

The interaction of A-270 and steel is less known than that of octynol and steel, but research into its surface chemistry may lead to inhibitors that provide even better protection to well tubulars.

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<tr>
<th>Octynol vs. Phenones¹</th>
<th>Corrosion Rate (lb/ft²)</th>
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<tbody>
<tr>
<td>Octynol</td>
<td>0.940</td>
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<tr>
<td>BAA</td>
<td>0.019</td>
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<tr>
<td>BDP</td>
<td>0.018</td>
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<tr>
<td>BDO</td>
<td>0.019</td>
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<tr>
<td>PVK</td>
<td>0.014</td>
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1. 8.8% inhibitor mixed with 0.2% additives and a 15%-HCl solution for 6 hours at 121°C (250°F).


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<table>
<thead>
<tr>
<th>A-270 Synergism¹</th>
<th>Corrosion Rate (lb/ft²)</th>
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<tbody>
<tr>
<td>None</td>
<td>2.0</td>
</tr>
<tr>
<td>PVK</td>
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<tr>
<td>Quat</td>
<td>0.4</td>
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<tr>
<td>PVK + Quat</td>
<td>0.05</td>
</tr>
</tbody>
</table>

1. Inhibitors mixed with a 28%-HCl solution and tested on N80 steel (30,000 psi minimum yield strength) for 6 hours at 121°C (250°F).
Five phenones tested in the search for polymers with sticking power.

Chain of chemical reactions forming the polymer polyphenylvinylketone (PPVK).

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