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Effect of Inhibitors on Weld Corrosion under Sweet Conditions Using Flow Channel

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***Abstract*—**The aim of this paper is to compare the effectiveness and electrochemical behavior of typical oilfield corrosion inhibitors with previous oilfield corrosion inhibitors under the same electrochemical techniques to control preferential weld corrosion of X65 pipeline steel in artificial seawater saturated with carbon dioxide at a pressure of one bar. A secondary aim is to investigate the conditions under which current reversal takes place. A flow channel apparatus was used in the laboratory to simulate the actual condition that occurs in marine pipelines. Different samples from the parent metal, the weld metal and the heat affected zone in the pipeline steel were galvanically coupled. The galvanic currents flowing between the weld regions were recorded using zero-resistance ammeters and tested under static and flowing conditions in both inhibited and uninhibited media. The results show that a current reversal took place when 30ppm of both green oilfield inhibitors were present, resulting in accelerated weld corrosion.

***Keywords*—**Carbon dioxide, carbon steel, current reversal, inhibitor, weld corrosion.

I. Introduction

CARBON dioxide (CO_2) corrosion of carbon steel pipelines and equipment in the oil and gas industry has received much attention in recent years because of an increased tendency to inject CO_2 into oil wells in order to reduce the viscosity of oil and increase production [1], [2]. It is very well known that CO_2 corrosion causes failure of pipelines and structural components in petroleum production processes, resulting in significant economic and manpower losses by catastrophic accidents and the pollution of water resources and the environment [3], [4].

Despite the fact that carbon steel has low resistance to CO_2 environments, it is widely used in the petroleum industry mainly due to economic reasons [5]. Galvanic corrosion attack on welds in steel components and subsequent failure of the structures has been quite common in seawater pipelines. It is well known that galvanic corrosion can occur between the different regions of a weld due to differences in composition and microstructure [6].

Attempts to control preferential weld corrosion have previously involved making minor additions of noble metals (Ni, Cr, Mo and Cu) in order to make the weld metal cathodic with respect to the adjacent parent metal and the heat affected zone. Nevertheless, these additions must be made with caution since over-alloying can result in enhanced HAZ corrosion [7].

Using inhibitors is one of the most important applications that have been used widely in corrosion protection of carbon steel in CO_2 environments. However, in some cases, the use of inhibitors to control internal pipeline corrosion has the effect of reversing the galvanic currents between the weld regions, such that the weld metal becomes anodic and accelerated rates of galvanic corrosion take place. An example of severe preferential weld corrosion (PWC) in a pipeline containing hydrocarbons and brine saturated with CO_2 is shown in Fig. 1 [8].

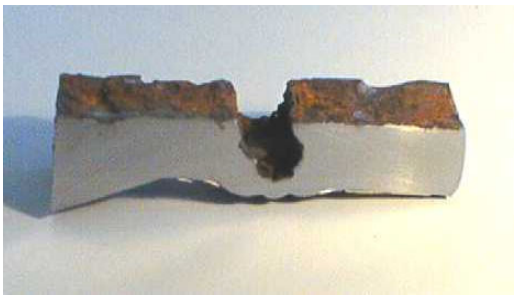


Fig. 1 Severe preferential weld corrosion in carbon steel pipeline carrying inhibited oil and gas [8]

Weld corrosion has been investigated by a range of experimental techniques, such as a flow channel [9], a recirculating flow loop [10] and rotating cylinder electrodes [11]. There are only limited, documented studies concerning the corrosion of welded steel exposed to marine environment in general and in the oil and gas environment in particular.

II. Experimental Work

A. Welded Pipeline Steel

All tests were carried out on samples machined from welded X65 steel pipe with a chemical composition of 0.08% C, 1.6% Mn, and 0.3% Si. The steel had been thermomechanically control-rolled with a fine-grained ferritic microstructure and a hardness of 200-210 Hv. The double-vee weld was produced by the submerged arc process, with a relatively high heat input (5-10 J/mm) and a hardness of 223-230 Hv. A sample was cut from the weld, polished and etched to identify the positions of the parent metal (PM), heat affected zones (HAZ) and weld metal (WM), as shown in Fig.

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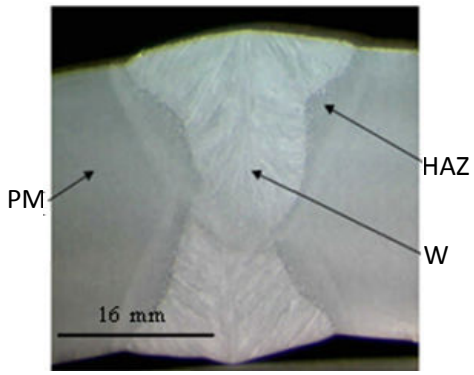


Fig. 2 Sections of the weld (parent metal, heat affected zone and weld metal)

B. Flow Channel Apparatus

The working electrodes were machined from commercial steel pipe grade API X65 and had wires attached to carry the electrochemical signals. The surface preparation was carried out by grinding/polishing with 1200 grit of silicon carbide paper and then degreasing with isopropanol to remove any dust and scratches in order that only the examined corrosion remained in the cell. The three regions were then separated by carefully cutting along the boundaries and were reassembled by mounting in epoxy resin. A Perspex plate was attached to the samples, separated by a 1mm thick rubber gasket, to form a flow channel through which brine saturated with CO_2 was pumped using a peristaltic pump, as shown in Fig. 3.

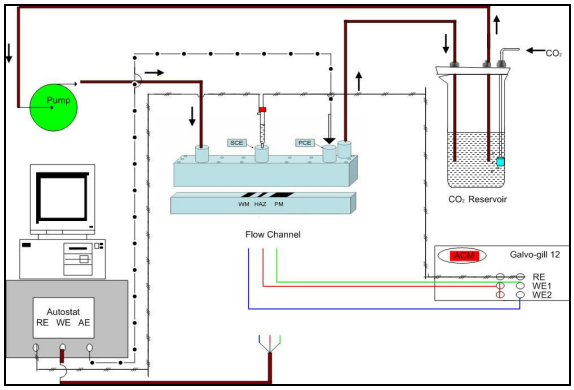


Fig. 3 Flow loop assembly

The areas of the exposed parent metal, heat affected zone and weld metal were in the ratio of 8:1:2 to represent the approximate proportions of each region in the vicinity of a typical pipeline weld.

The wall shear stress for the channel was calculated from (1) [12]:

$$\tau = f \frac{V^2}{8g} \quad (1)$$

where v is the flow velocity and f is the friction factor.

C. Electrochemical Measurements

The galvanic currents between each weld region were recorded every 60 s during the test using a multi-channel zero resistance ammeter (ACM Instruments GalvoGill 12) connected to a data logging PC. The currents from the parent metal to the weld metal and from the HAZ to the weld metal were recorded on two channels and, as the three electrodes were in the short-circuit condition, their individual galvanic currents were established from (2)

$$I_{PM} + I_{HAZ} + I_{WM} = 0 \quad (2)$$

D. Experimental Conditions

The experiments were carried out at ambient temperature (20°C) in a flow channel containing artificial seawater as shown in Table I, saturated with CO_2 with absence and presence of 30 ppm by volume of a 'green' oilfield corrosion inhibitor. The flow channel was equipped with a fixed rubber hose for inlet and outlet of flow, while the glass cell (reservoir) was filled at 0.8L capacity of 3.5% artificial seawater with chemical composition, as shown in Table I, and fitted with a suitable cover lid with 3 inlets to allow for the CO_2 injection as well as the discharge and suction of the electrolyte solution. Moreover, a peristaltic pump was used to maintain a uniform flow circulation and direction of 0.6 ms^{-1}, which corresponded to a shear stress of 2.56 Pa. In one experimental run, galvanic currents were recorded at 60 s intervals throughout the test. Performances of CORRTREAT 05-193 and CORRTREAT CT04-020 [13] inhibitors as shown in Table II, supplied by Clariant Oil Services, UK were tested and compared in order to determine the more efficient inhibitor and whether they would provide enough corrosion protection to be used in real conditions.

TABLE I
CHEMICAL COMPOSITION OF ARTIFICIAL SEAWATER

Element	Cr	Se	Ca	Ph	Si	Mn
Ppm	0.0002	0.0009	114	0.008	2.9	0.0004

Element	Co	P	V	Zn	S	Fe
Ppm	0.0066	0.009	0.0019	0.005	0.0005	0.00039

Note: ppm = parts per million

TABLE II
PRODUCTS COMPARED WITH GENERIC NAME AND BASIC CHEMISTRY

Product	Active Ingredient
Corrosion inhibitor A CT04-020	Ethanediol, thioglycolic acid and phosphoric acid ester
Corrosion inhibitor B 05-193	Neutralizing amines and synergists in a water/glycol based solvent package.

III. RESULTS

A. Measurements under Uninhibited Conditions

The galvanic current measurements for both the inhibitors (A and B) are shown in Fig. 4 under uninhibited conditions. The current behavior is observed to be similar, with the parent metal and the HAZ both being anodic (positive currents) with respect to the weld metal at test temperature. Clearly, it was

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favorable for the weld metal to be the cathodic (negative currents) component in the couple as this condition ensured that its corrosion rate was reduced by sacrificial protection of the other weld regions.

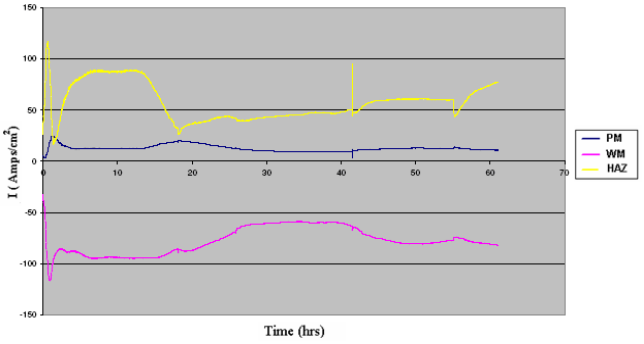


Fig. 4 (a) Galvanic current densities of flow condition (polished) for inhibitor A [13]

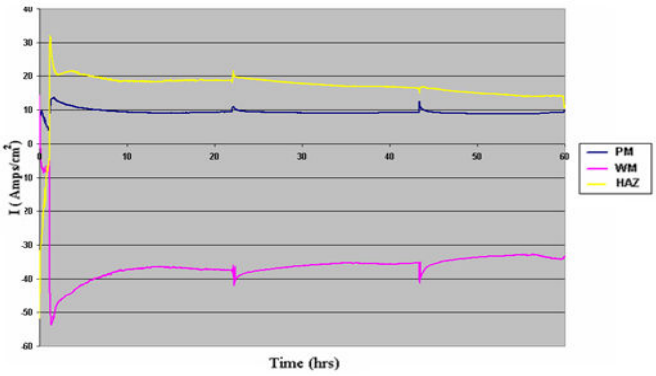


Fig. 4 (b) Galvanic current densities of flow condition (polished) for inhibitor B

B. Measurements under Inhibited Conditions

The presence of 30ppm of both oilfield corrosion inhibitors caused a marked change in the galvanic corrosion behavior, as shown in Fig 5. At the beginning of the exposure, both inhibitors appear to be unstable due to current reversal. However, after exposure for almost 20 hours, galvanic current for both inhibitors can be considered as stable since current reversal behavior disappeared.

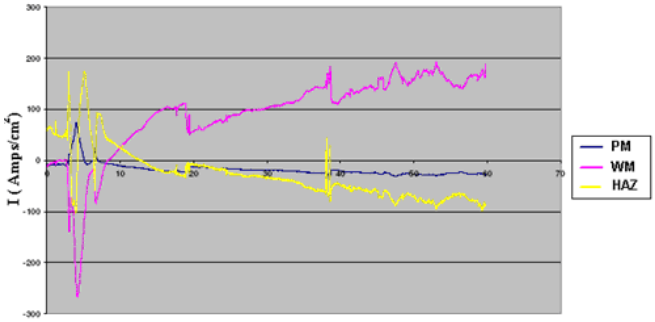


Fig. 5 (a) Galvanic current densities of flow condition using inhibitor (A)

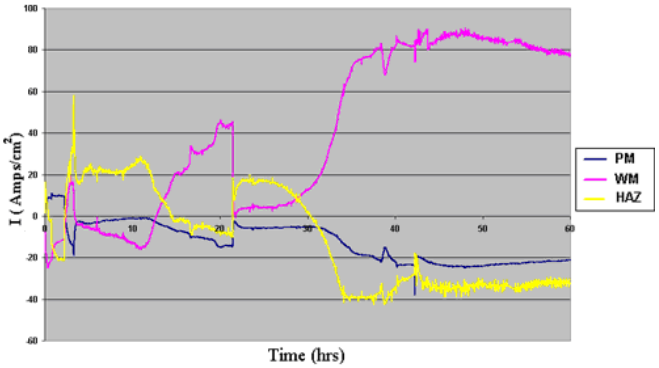


Fig. 5 (b) Galvanic current densities of flow condition using inhibitor (B)

In terms of galvanic currents, inhibitor B seems to be more efficient as it enables reduction of galvanic corrosion given that the values are quite small compared to the values obtained for inhibitor A. Besides, with inhibitor A, the peaks representing reversals reached high values (more than 100 $\mu A/cm^2$ which is equivalent to more than 1 mm/y). This is not the case observed with inhibitor B.

The galvanic current for inhibitor A was particularly high on the weld metal than for inhibitor B, suggesting that the inhibitor A film was more adversely affected by flow causing preferential removal of the inhibitor film from the WM compared to inhibitor B.

After 20 hours of exposure, both the inhibitors had similar behavior, with the WM becoming anodic and both PM and HAZ becoming cathodic. Galvanic currents gradually rose for inhibitor A toward anodic side for the WM, while for inhibitor B, the WM remained anodic but the currents were fairly constant over the test period.

It would appear that, in this case, film removal was most pronounced on the WM for both inhibitors but was more severe with inhibitor A compared to inhibitor B. Clearly, for such current reversal to take place, further damage to the inhibitor film must have occurred. This situation is undesirable and would be expected to result in localized weld corrosion of the type that has sometimes been reported to occur in service.

C. Measurements for Open Circuit Potential

The OCP values with a potential shift to positive values in the absence of inhibitors for the galvanic couples tested (parent metal and weld metal) are shown in Fig. 6. This variation of open circuit potential with time reveals the corrosivity of the galvanic couples tested. Initially the OCP for both parent metal and weld metal were recorded as -655mV and -500mV respectively, but after a certain time, both potentials move fast toward negative values around −720mV and reached a reasonably steady value as a result of the breakdown of the film inhibitor. It was noticed that both galvanic coupled potentials fluctuate continuously and many positive and negative peaks in high ranges are observed due to localized corrosion of both parent metal and weld metal.

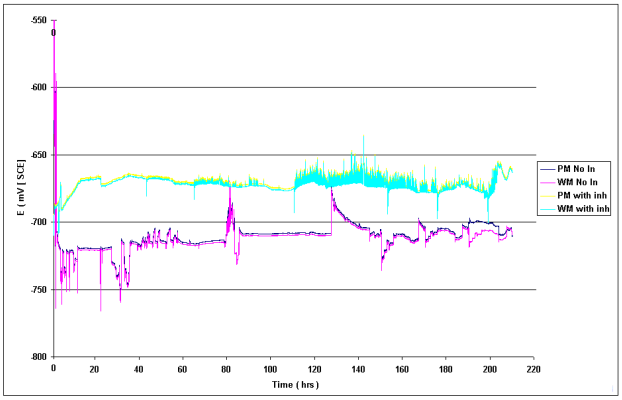


Fig. 6 Variation of the open-circuit potential as a function of time under uninhibited and inhibited conditions (Inhibitor B)

In contrast, with the presence of the inhibitor, the steady state potentials for the galvanic couples tested were shifted towards the noble direction and the potentials remained noiseless for the first 110 hrs, and then an increase was observed with reasonably steady fluctuating peaks in a small range as a result of the breakdown of the film inhibitor.

IV. Conclusions

1. In uninhibited conditions, the weld metal was cathodic to the parent metal and HAZ. This is the ideal solution as corrosion is distributed over the large area of the parent metal.
2. The addition of two oilfield corrosion inhibitors caused a current reversal under flowing conditions. The inhibitor film was removed preferentially from the weld metal, so that it became strongly anodic and lead to a condition that would result in severe localized weld corrosion.
3. Inhibitor CORRTREAT 10-569 seems more efficient based on the galvanic current results since it displays stable behavior through the exposure time.
4. It appears that preferential weld corrosion is caused by unstable conditions in which the inhibitor film is selectively disrupted on the weld metal but remains effective on other weld regions.

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