The Effect of Fe_3O_4 on the Performance of an Imidazoline-Type Corrosion Inhibitor at 150°C

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Introduction

Research of high temperature corrosion inhibition of mild steel is important due to the increasing number of high temperature wells coming into the oil and gas production [1]. Operating such wells presents challenging economic, materials selection, design and corrosion problems; in particular, high temperature (T>150°C) corrosion of mild steel and more importantly, its mitigation. Most research focused on high temperature corrosion inhibition has only investigated the efficiency of the inhibitor without further clarifying the reasons of a lower corrosion rate; for example, whether the mitigation is due to the adsorption of the inhibitor or formation of corrosion products. However, in earlier research activities related to investigating inhibition properties of an imidazoline-type inhibitor by this author [2], it was found that performance of an imidazoline-type inhibitor at 150°C was governed by the formation of corrosion product instead of by the adsorption of the inhibitor itself. It is understood that the formation of corrosion product (more specifically, Fe_3O_4) at elevated temperatures has a significant influence on high temperature corrosion [3]. However, its influence on mitigating mechanisms related to the use of corrosion inhibitors has heretofore not been studied.

In this research study, an innovative autoclave system was designed, commissioned and used to control timing of inhibitor injection at high temperature to elucidate the corrosion behavior of mild steel in a CO_2-saturated environment at 150°C using an imidazoline-type inhibitor. Corrosion rates were measured using linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). Specimens retrieved after the experiments were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Hypothesis

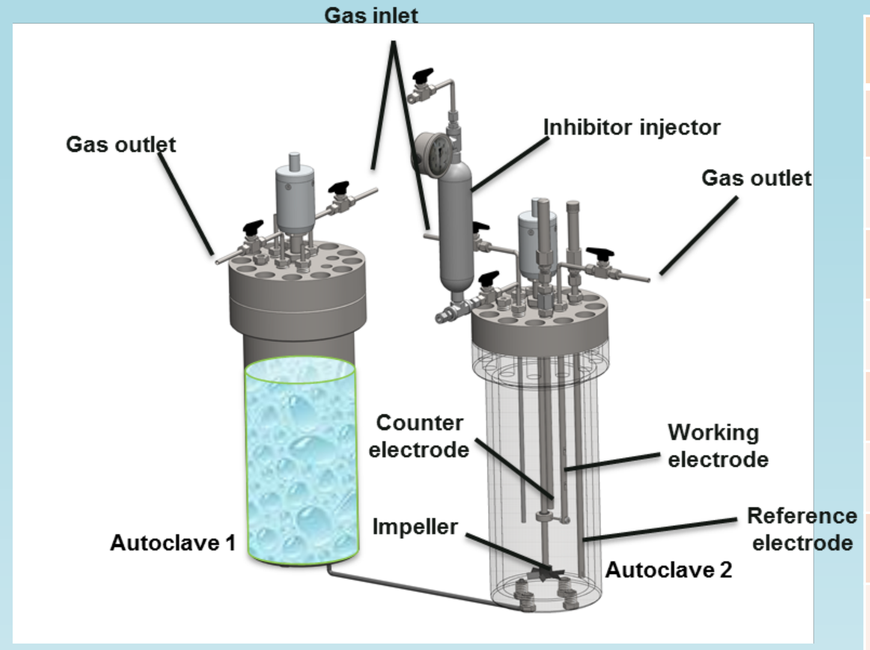
At 150°C, the formation of Fe_3O_4 is kinetically favored. The protectiveness of Fe_3O_4 is dominant and controls the corrosion rate.

Objectives

- Investigate the effect of pre-corrosion on the performance of the imidazoline-type inhibitor at 150°C.
- Identify the relationship between corrosion product formation and the adsorption of corrosion inhibitor at 150°C.

Experimental Details

Experimental set-up

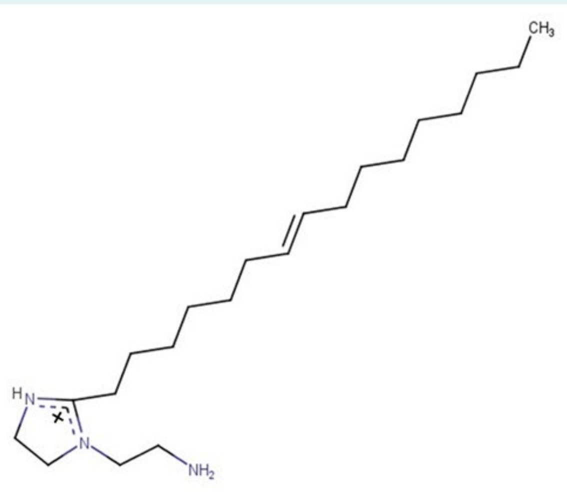


Test matrix

Parameters	Description		
Specimens	API 5L X65		
Test solutions	1 wt.% NaCl		
Test temperature/°C	150		
Inhibitor concentration/ppmv	0	440	880
Impeller speed/rpm	200		
Initial pH at 80°C	4.30		
Test duration/hour	24		
Pre-corrosion/hour	0/0.5		

Inhibitor Information

TOFA/DETA imidazolinium

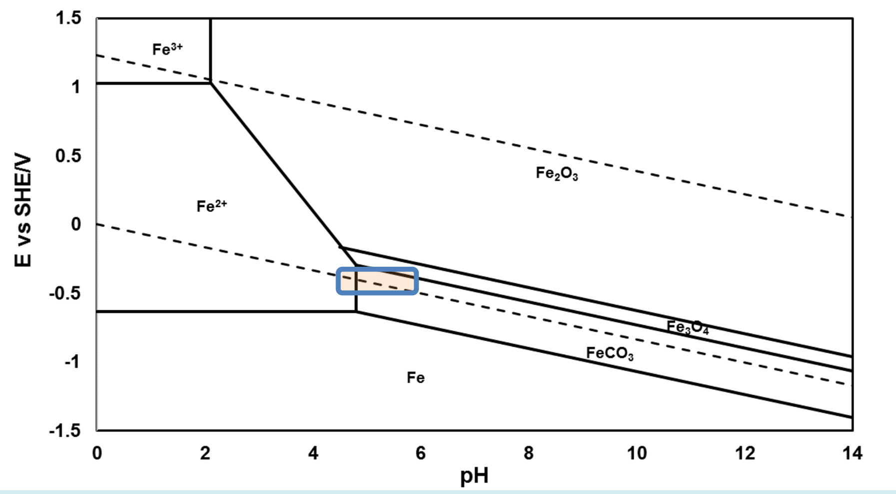


Package information

Ingredients	Percentage/ vol.%
TOFA/DETA imidazolinium	24
Acetic acid	10
2-Butoxyethanol	13
Water	53

Corrosion Product Prediction

Pourbaix diagram at 150°C

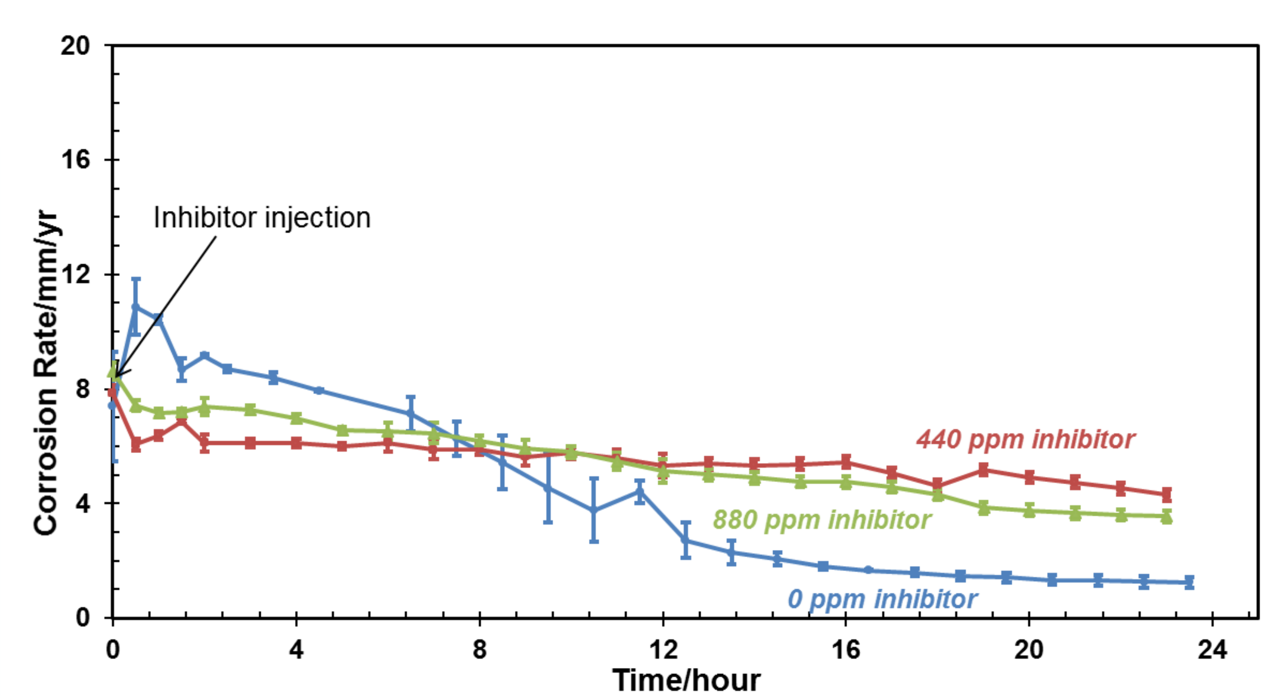


The corrosion product is likely a mixture of $FeCO_3$ and Fe_3O_4 at the tested conditions: 150°C, 2 bar CO_2.

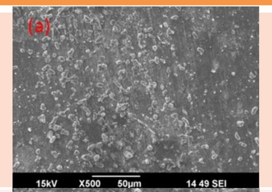
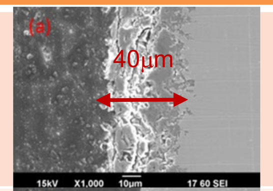
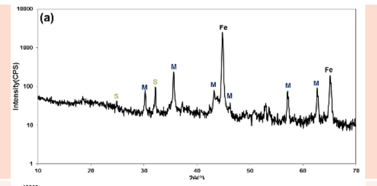
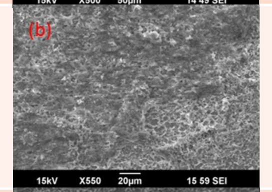
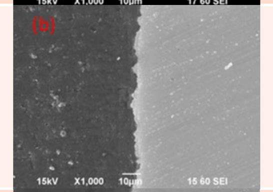
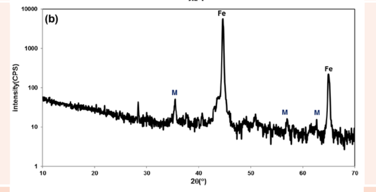
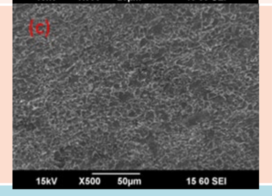
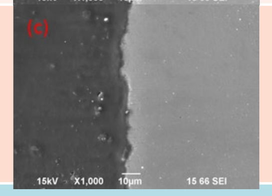
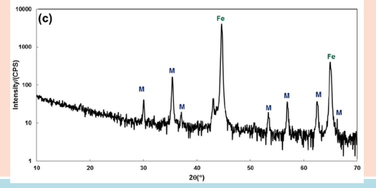
Results and Discussion

Corrosion behavior of X65 mild steel at 150°C with no pre-corrosion

Corrosion rate

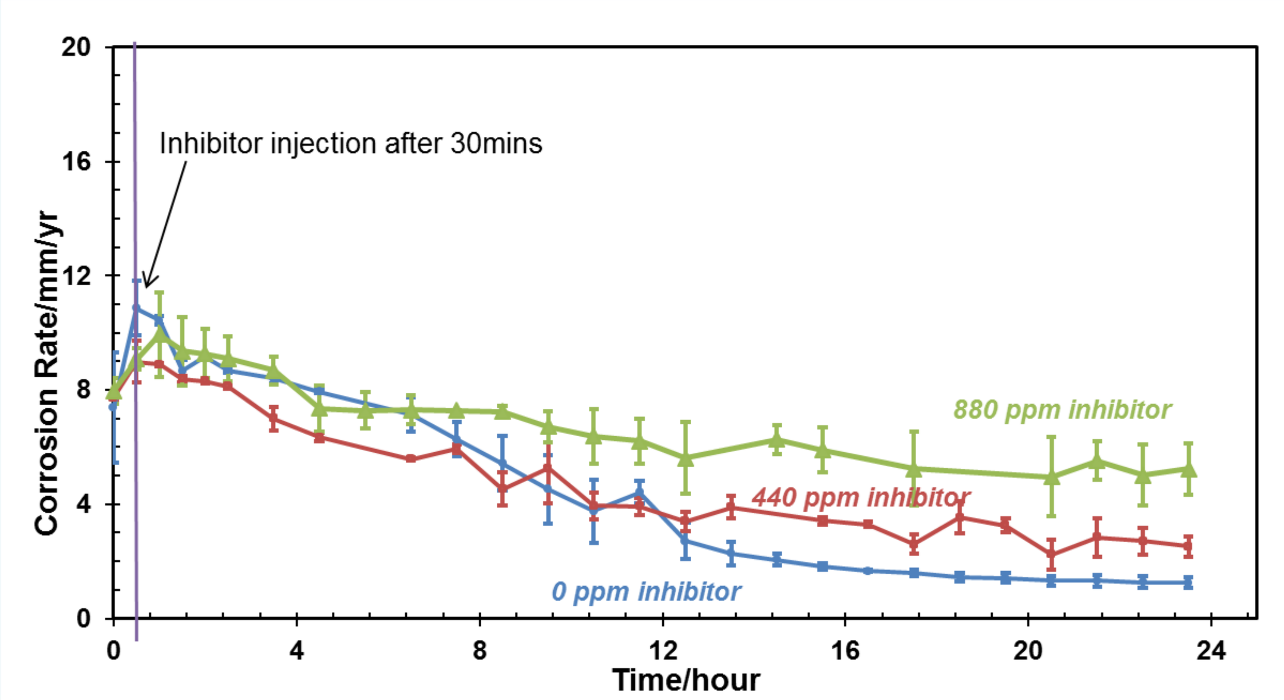


Surfaces analysis

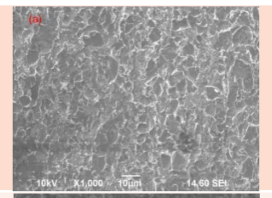
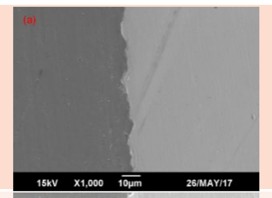
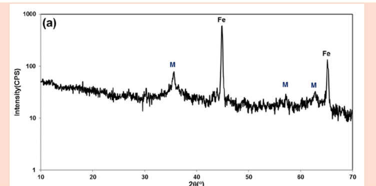
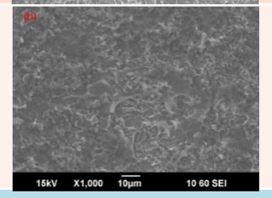
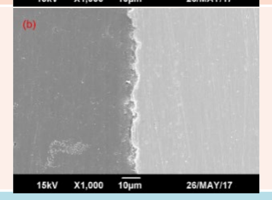
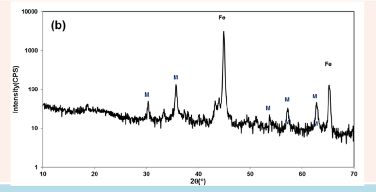
Inhibitor package concentration	Surface morphology	Cross-section images*	XRD pattern
0ppmv			
440ppmv			
880ppmv			

Corrosion behavior of X65 mild steel at 150°C with 30 minutes pre-corrosion

Corrosion rate



Surfaces analysis

Inhibitor package concentration	Surface morphology	Cross-section images*	XRD pattern
440ppmv			
880ppmv			

* From the left to the right in cross-section images: Epoxy→ Corrosion product layers→ Steel matrix.

XRD patterns confirmed the presence of both $FeCO_3$ and Fe_3O_4 in the 150°C corrosion product, as indicated by Pourbaix diagram at 150°C. In addition, corrosion rate seemed to be governed by the formation of corrosion product when there was pre-corrosion.

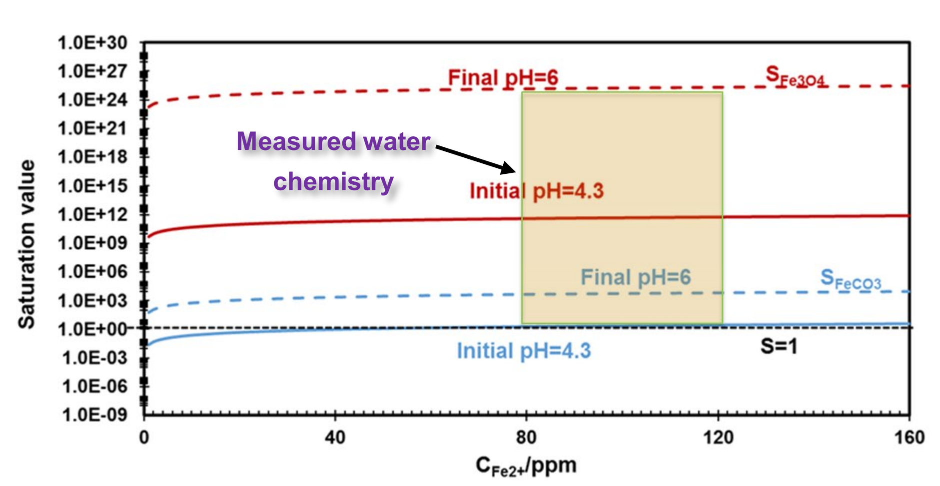
Formation of corrosion product with the presence of inhibitor

Solubility of $FeCO_3$

$$K_{sp,FeCO_3} = e^{-59.3498-0.041377T_K-\frac{2.1963}{T_K}+24.5724log(T_K)+2.518I^{0.5}-0.6571}$$

Solubility of Fe_3O_4

$$K_{sp,Fe_3O_4} = e^{-\Delta G_{Fe_3O_4}/RT_k}$$



The absence of apparent corrosion product layer at a high saturation value suggested that the imidazoline-type inhibitor can also prevent the formation of corrosion product.

Conclusions

- A competitive relationship was observed between the formation of corrosion product and the addition of corrosion inhibitor at 150°C.
- At 150°C, the formation of Fe_3O_4 dominated the corrosion behavior. However, by minimizing the formation of Fe_3O_4, the performance of inhibitor on the steel surface was still detected, although the inhibitor performance was poor.
- Instead of providing corrosion protection, the major effect of the inhibitor is seen to be prevention of protection by corrosion product.

References

[1]. A. Shadravan and M. Amani, "HPHT 101-what petroleum engineers and geoscientists should know about high pressure high temperature wells environment," Energy Sci. Technol., 4.2: 36–60, 2012.

[2]. Y. Ding, B. Brown, D. Young, and M. Singer, "Effectiveness of an imidazoline-type inhibitor against CO2 corrosion of mild steel at elevated temperatures (120°C-150°C)," CORROSION 2018, paper no. 2018-11622.

[3]. S. Gao, B. Brown, D. Young, and M. Singer, Formation of iron oxide and iron sulfide at high temperature and their effects on corrosion. Corrosion Science, 135, 167-176, 2018.

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