

Corrosion Inhibition of Carbon Steel in Carbonate Acidizing at Elevated Temperature

Limin Xu
Beijing Research Center, Aramco Asia
No.4 Wangjing East Road
Beijing, 100102
China

Tao Chen
EXPEC Advanced Research Center
Saudi Aramco
Dhahran, 31311
Saudi Arabia

Ming Han
EXPEC Advanced Research Center
Saudi Aramco
Dhahran, 31311
Saudi Arabia

Mohammed Bataweel
EXPEC Advanced Research Center
Saudi Aramco
Dhahran, 31311
Saudi Arabia

ABSTRACT

This paper presents an investigation on the performance of corrosion inhibitors in reducing corrosion loss of N80 steel coupons at high temperature in 15 wt.% and 28 wt.% HCl solutions. This work studied the effect of temperature and acid concentration on corrosion inhibitor performance and provided an efficient corrosion inhibitor for application at elevated temperature of 120°C. Five corrosion inhibitors including Mannich base derivatives and pyridine quaternary ammonium salt were selected. The corrosion rates of N80 steel in concentrated HCl solution with and without corrosion inhibitor were evaluated by gravimetric method and the surface of steels after corrosion tests were characterized by microscopy. The results showed that the corrosion rate of N80 steel in 15 wt.% HCl at 120°C was much higher than that at 90°C. As a result, higher concentration of corrosion inhibitor was needed to reduce the corrosion to an acceptable value of 0.05 lb/ft². The corrosion rate could be reduced to 0.0035 lb/ft² in 15 wt.% HCl at 120°C. Increasing the HCl concentration to 28 wt.% at 120°C, the corrosion inhibitor concentration required was several times as much as the dosage for 15 wt.% HCl.

Key words: corrosion, inhibitor, hydrochloric acid, high temperature

INTRODUCTION

A suitable acid package in matrix acidizing application is very important to the stimulation employed to improve the productivity of carbonate reservoirs. Typically, concentrated acids between 5 and 28 wt% are used and the most used mineral acid for carbonate acidizing treatment is hydrochloric acid (HCl)^{1,2}. A significant challenge of acidizing treatment is corrosion loss of metal tubulars due to the high reactivity

of acid and metal, especially at high temperatures. Corrosion inhibitors are needed to reduce the corrosion loss of steel surface of facilities exposed in acidic environment. Most research focuses on corrosion inhibition of steel materials in HCl solution at temperate lower than 100°C². A few studies reported the corrosion control at higher temperature^{3,4}. In the absence of corrosion inhibitors, the general corrosion rate can increase exponentially with increasing temperature^{5,6}. It is still an industrial challenge to have a corrosion inhibitor to efficiently inhibit corrosion on carbon steel in highly concentrated HCl at elevated temperature above 100°C.

Many kinds of organic chemicals containing heteroatoms with N, O, P, S such as imidazoline^{7,8}, indolizine derivative⁹, quinoline derivative¹⁰, quaternary ammonium salts¹¹, pyridine and its derivatives or salts¹² and Mannich bases have been developed to retard the metal corrosion. Mannich bases are made by condensation of amines with an aldehyde and a ketone¹³. All organic inhibitors work by adsorbing on the metal surface^[4]. The inhibitors containing N, O, P, and S could chelate with Fe and form a film on the metal surface which can retard the metal-dissolution process (anodic reaction) as well as the hydrogen-evolution (cathodic reaction).

This work selected several Mannich base corrosion inhibitors and one pyridine quaternary ammonium salt for testing. The inhibition performance of corrosion inhibitors in 15 wt.% and 28 wt.% HCl at 120°C was evaluated by gravimetric method. Tests were also conducted at 90°C to study the temperature effect on the corrosion rate. Morphology of the surface of N80 steel coupons after corrosion were studied by microscopy. The pitting corrosion was evaluated by both visual observation and microscope. The optimal corrosion inhibitor and dosage were selected based on the weight loss and steel coupon surface morphology results.

EXPERIMENTAL PROCEDURE

Materials

Five corrosion inhibitors were used in this work. YD-M1, RX-M2, YT-M1 and YT-M2 are Mannich base derivatives. AN-P1 is a kind of pyridine quaternary ammonium salt. The concentration of the corrosion inhibitors in the tests is presented in mass/volume %.

N80 steel coupons were used and the chemical compositions in wt.% are listed in Table 1.

Table 1.
Chemical compositions in weight percentage of N80 steel

Ingredient	C	Si	Mn	P	S	Al	Cr	Cu
Weight percentage, %	0.35	0.32	1.55	0.02	0.015	0.014	0.15	0.02

15 wt.% and 28 wt.% HCl solutions were prepared by diluting 37 wt.% HCl with distilled water.

Corrosion Test

The corrosion test was conducted using an autoclave with poly tetra fluoroethylene (PTFE) liner. For corrosion tests in 15 wt.% HCl solution, the dosage of inhibitor varied from 0.5% to 2.0%. For tests in 28 wt.% HCl solution, the dosage of inhibitor varied from 2.0% to 5.0%. The size of the N80 steel coupon was 40*13*2mm. The surface area is about 12 cm². The accurate surface area of each coupon was determined by measurement of dimensions before test. The steel was washed using acetone, ethanol and water before test. The autoclave with 210mL HCl solution and N80 steel coupon was placed in an

oil bath of 120°C. It takes one hour for the autoclave to reach 120°C. After another 3 hours, the autoclave was taken out and cooled by water for half-hour. Then the metal coupon was carefully taken out from the acid solution, washed, dried and weighed. The corrosion rate was calculated using the following equation:

$$\text{Corrosion Rate} = \frac{W_i - W_a}{S} \quad (1)$$

where W_i is the initial weight of metal coupon, W_a is the metal weight after corrosion test and S is the surface area of steel coupon.

Microscopy

The morphology of metal coupon surface and the depth of pits on surface were characterized by optical microscope.

RESULTS

Weight loss analysis

The corrosion tests of N80 steel coupon in 15 wt.% HCl solution without corrosion inhibitor at 90°C and 120°C were conducted to study the temperature effect. As shown in Figure 1, only a small part of metal was left after test at 120°C. The calculated uninhibited corrosion rates at 90°C and 120°C were 0.73 and 1.32 lb/ft², respectively. The acid concentration was reduced from 15 wt.% to 12.3 wt.% after the test at 90°C and reduced to 10.2% at 120°C. Since the corrosion rate increases exponentially with HCl concentration^{5,14-16}, both corrosion rates are underestimated especially the value of 120°C due to acid consumption. This is the reason that the corrosion rate at 120°C was less than 2 times of that at 90°C. Barmatov et al.⁴ claimed that all corrosion rates exceeding 0.05 lb/ft² may not be accurate and should be used for rough estimates. ASTM G31¹⁷ standard recommends a minimum acid solution volume of 0.4mL per 1mm² of sample to avoid any appreciable change in its corrosivity during the test. However, this is quite high which is not practical in routine laboratory testing. In this work, roughly 17mL acid solution was used per 1cm² of steel sample.

Corrosion inhibitor AN-P1 was added into 15 wt.% HCl to reduce the weight loss. 0.5% dosage was used and the corrosion rate reduced to an extreme low value of 0.0085 lb/ft² which was much lower than requirement of 0.05 lb/ft².¹⁸ However, the corrosion rate at 120°C was 0.18 lb/ft² which is too high for application. Higher concentration of AN-P1 or a new corrosion inhibitor are required to prevent corrosion at 120°C.

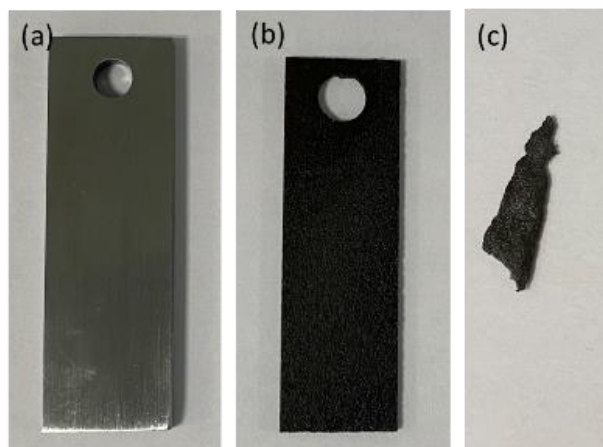


Figure 1: N80 coupons before test (a) and after corrosion tests in 15 wt.% HCl (b) at 90°C and 120°C (c).

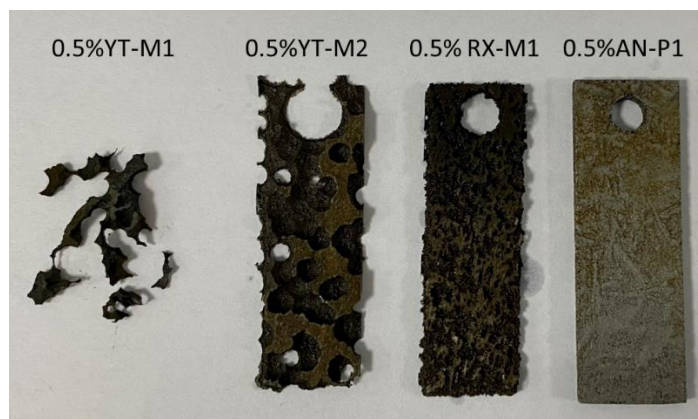
© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

Table 2.**Corrosion rates of N80 steel in 15 wt.% HCl with and without AN-P1 at 90°C and 120°C.**

Temperature (°C)	Corrosion inhibitor	Corrosion rate (lb/ft ²)
90	None	0.73
	0.5%	0.0085
120	None	1.32
	0.5%	0.18

The corrosion rates of N80 steel using other 4 corrosion inhibitors RX-M1, YT-M1, YT-M2 and YD-M1 with 0.5% dosage were also measured at 120°C. Figure 2 and Table 3 show the steel shape and the corrosion rates after tests. No steel was left after test using YD-M1 with a high corrosion rate of 1.40 lb/ft² which is even higher than the rate without corrosion inhibitor. YT-M1 slightly reduced the corrosion loss to 1.17 lb/ft² with several small pieces left. RX-M1 and YT-M2 reduced the corrosion rate to 0.55 and 0.79lb/ft², respectively. All these 5 corrosion inhibitors couldn't efficiently reduce the corrosion loss to 0.05 lb/ft² at this dosage.

**Figure 2: N80 coupons after corrosion tests in 15 wt.% HCl with 0.5% corrosion inhibitors at 120°C.****Table 3.****Corrosion rates of N80 steel in 15 wt.% HCl with 0.5% corrosion inhibitors at 120°C.**

Corrosion inhibitor	Corrosion rate (lb/ft ²)
RX-M1	0.55
YT-M1	1.17
YT-M2	0.79
AN-P1	0.18
YD-M1	1.40

Higher concentrations of corrosion inhibitors were used to look into the concentration effect on corrosion inhibition. RX-M1, YT-M2 and AN-P1 were selected due to their lower corrosion rate at 0.5% than YT-M1 and YD-M1. Figure 3 shows that the surface of metal coupons became smoother with increasing of concentration of AN-P1. This is consistent with the corrosion rates listed in Table 4. The corrosion rate was reduced from 0.087 to 0.073 and 0.039 lb/ft² by increasing the concentration of AN-P1 from 1.0% to 1.5% and 2.0% respectively. The corrosion rate was reduced from 0.55 to 0.028 lb/ft² by increasing RX-