

Effect of Additives to Corrosion inhibitor for Duplex Stainless Steel in Acidizing

Hiroataka Mizukami
INPEX CORPORATION
9-23-30 Kitakarasuyama
Setagaya-ku, Tokyo, 157-0061
Japan

Ayano Yasui
INPEX CORPORATION
9-23-30 Kitakarasuyama
Setagaya-ku, Tokyo, 157-0061
Japan

Susumu Hirano
INPEX CORPORATION
9-23-30 Kitakarasuyama
Setagaya-ku, Tokyo, 157-0061
Japan

Toshiyuki Sunaba
INPEX CORPORATION
9-23-30 Kitakarasuyama
Setagaya-ku, Tokyo, 157-0061
Japan

Tsuyoshi Ooba
Kao Corporation
1334 Minato
Wakayama, Wakayama Prefecture, 640-8580
Japan

Mitsuru Uno
Kao Corporation
1334 Minato
Wakayama, Wakayama Prefecture, 640-8580
Japan

ABSTRACT

Duplex stainless steel (DSS) tubing is known to suffer the selective corrosion in acidizing operation. This study considers the effect of additives to corrosion inhibitor (CI) for DSS. Several additives were selected from copper and iodine. Some laboratory tests were conducted with the general CI for acidizing, which is the mixture of cinnamaldehyde and so on.

As a result of immersion corrosion test in 7 wt% HCl solution at 60 °C, the corrosion rate of 22Cr DSS decreased with CI or CI + additives compared to blank. However, the reduction rate of corrosion varied by additives. CuI and CuCl had better protection effect than the others and inhibited selective corrosion of 22Cr DSS (cross-section observation). The protection effect of CuI was confirmed in higher HCl concentration (15 and 28 wt% HCl). Some electrochemical measurements showed that adding CuI made the corrosion resistance of DSS higher as well.

Key words: Acidizing, Corrosion inhibitor, Duplex stainless steel, CuI

INTRODUCTION

In the oil and gas industry, an acidizing operation is generally conducted to improve wells' productivities, whose purposes are dissolving scales and other particles plugging the completion and fracturing. Using acidic fluid such as HCl, HCOOH and HF mostly has corrosive to steel products (tubing, casing and other completion equipment) and then the lifetime of wells will reduce. Therefore, corrosion inhibitor (CI) is used during the acidizing operation to mitigate corrosion problem.

22Cr duplex stainless steel (DSS) with two phases, austenitic and ferritic phase, has an excellent corrosion resistance. This material is used for a severely corrosive environment such as high pressure, high temperature, high salinity and high CO₂ content. However, 22Cr DSS is known to suffer the selective corrosion in acidizing conditions even using CI, because of the slight difference of corrosion resistance between austenitic and ferritic phases. Thus, the acidizing operation for 22Cr DSS tubing has to be careful.

Copper and other copper compounds are known for additives to enhance the inhibitor efficiency in acidizing conditions and some patents¹⁻⁴ and papers⁵ were published. However, they do not clear the selective corrosion of 22Cr DSS and the mechanism of corrosion inhibition.

As mentioned above, immersion corrosion tests and electrochemical measurements are conducted in acidizing conditions with several copper compounds to confirm whether selective corrosion of 22Cr DSS is inhibited or not and clarify the mechanism of corrosion inhibition.

EXPERIMENTAL PROCEDURE

Tested material

The chemical composition of 22Cr DSS used in this study is shown in Table 1. It was cut into 2^T x 10^W x 50^L mm and 2^T x 10^W x 10^L mm for immersion corrosion test and electrochemical measurement, respectively. Prior to each experiment, test specimens were wet ground with #600 SiC sandpaper, thoroughly degreased ultrasonically in acetone or ethanol.

Table 1
Chemical composition of 22Cr DSS in wt% (balance Fe)

C	Si	Mn	P	S	Cr	Ni	Mo	N
0.22	0.39	1.19	0.22	0.00	22.61	5.17	3.21	0.17

Used corrosion inhibitor

Table 2 shows the chemical composition of the CI used in this study. The inhibitor consists of cinnamaldehyde, long-chain alkyl imidazoline and methanol. Cinnamaldehyde and imidazoline are the main elements which perform as the film-form type inhibitor, and methanol is a solvent. The similar mixture is used as the inhibitor for acidizing.

Table 2
Chemical composition of corrosion inhibitor used in this study

Chemicals	Volume (%)
Cinnamaldehyde	25
Long-chain alkyl imidazoline	20
Methanol	55

Immersion corrosion tests

(1) Evaluation for the effect of various additives

To investigate what component inhibits corrosion, various additives from Cu and/or iodine compound were studied. The acidizing condition operated in Japanese onshore field was simulated as the test condition. 7 wt% HCl solution is used as acid media and the bottom hole temperature is about 60 °C in that field. The test matrix is shown in Table 3. The dosage of both was 0.2% and the solution volume to specimen area ratio was 16 mL/cm²

Table 3
Test matrix for corrosion inhibitor and additives

Test No.	CI	Additive
1		
2	✓	
3		CuI
4	✓	CuI
5	✓	KI
6	✓	KI + CuCl
7	✓	Cu
8	✓	CuCl ₂
9	✓	CuSO ₄

The solution was heated to 60 °C and then CI and/or additives were added into the HCl solution. After stirring, test specimens were immersed in HCl solution for 24 hours. Test specimens were weighed before and after immersion, and the weight loss was used to calculate the corrosion rate.

Tested specimens were cut into appropriate size and buried in resin to observe cross-section with a laser microscopy (OLYMPUS LEXT OLS-4000^a). X-ray diffraction (XRD; SHIMADZU EDX-8100^b) technique was also operated to confirm that the selective corrosion was occurred or not.

(2) Evaluation for the efficiency of corrosion protection in higher concentration HCl solution

The threshold of HCl concentration was studied to demonstrate the corrosion protection of CuI. 15 and 28wt% HCl solutions were used to simulate the field operation. The test conditions and procedure were the same as the initial test. Table 4 shows a combination of HCl concentration, inhibitor and CuI.

Table 4
Test matrix for HCl concentration, corrosion inhibitor and CuI

Test No.	HCl concentration (wt%)	CI	CuI
10	15		
11	15		✓
12	15	✓	✓
13	28		
14	28		✓
15	28	✓	✓

^a Trade name

^b Trade name

Electrochemical measurements

To investigate how CuI works in corrosion reaction, electrochemical measurements were carried out in a standard three-electrode cell, consisting of a 22Cr DSS working electrode whose exposure area is about 1 cm², a Pt counter electrode and a saturated Ag/AgCl reference electrode. All measurements were conducted with a potentiostat (Biologic SP-150°).

(1) Corrosion potential measurement

Corrosion potential was measured in 500 mL of 0.1 M HCl solution at room temperature. Immediately after polishing, the specimen was immersed in a solution and the corrosion potential was measured for 3,600 s. CuI was added after 600 s to evaluate its effect.

(2) Electrochemical impedance spectroscopy (EIS)

EIS was measured in 500 mL of 0.1 M HCl solution with/without CuI at room temperature. The specimen was immersed after polishing in the solution, and then the measurement was started instantly. CuI was added in the solution after the first measurement and stirred for 1 min. After that, the second measurement was conducted, and then conducted every 10 min up to 90 min. All EIS is carried out in the frequency range from 100 kHz to 100 mHz with the modulation amplitude of 10 mV.

RESULTS AND DISCUSSION

Immersion corrosion tests

(1) Evaluation for the effect of various additives

Result of the immersion corrosion test in 7 wt% HCl solution with various additives is shown in Figure 1. The corrosion rate decreased by adding Cl and/or additives and the decrease depended on additives. Table 5 shows the corrosion rate and decrease of corrosion rate compared with blank. The corrosion protection performance was not good in the case of adding Cl only, Cl + KI and Cl + Cu. This means that adding only Cl is insufficient for 22Cr DSS under HCl acidizing condition. And also, it seems that KI (K⁺ and I⁻) and metal Cu have less corrosion protection ability under this condition. In contrast, Cu compounds, including Cu¹⁺ and Cu²⁺, give 22Cr DSS excellent corrosion protection. The decreases of corrosion rate with these additives were over 98%. It is implied that Cu ion probably influences the corrosion protection performance.

^c Trade name