

Effect of Inhibitor Component on Inhibitor Efficiency - Inhibitor Types and Intensifier -

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ABSTRACT

Imidazoline, which is known as one of the active ingredients of corrosion inhibitors, is used in a lot of oil and gas facilities in order to mitigate corrosion problems. However, it is easily hydrolyzed to amide, which leads to the change of inhibitor efficiency. Therefore, the inhibitor efficiency of imidazoline-type and amide-type inhibitors was evaluated by several tests such as electrochemical measurements,

weight loss test and quartz crystal microbalance measurement. Furthermore, the effect of one intensifier for corrosion inhibitor was also evaluated by the same tests.

As a result, the large difference of inhibitor efficiency between the imidazoline-type and amide-type inhibitor was not observed by the electrochemical measurements. On the other hand, the weight loss test under turbulent flow indicated that imidazoline-type inhibitor performed higher inhibitor efficiency than that of the amide-type. This intensifier improved the inhibitor efficiency of both types.

Key words: Corrosion inhibitors, Imidazoline, Amide, Carbon dioxide, Carbon steel, Electrochemical measurement, Weight loss test, Quartz crystal microbalance

INTRODUCTION

A lot of oil and gas facilities face corrosion problems because the production fluid contains some corrosive components represented by CO₂. Generally, corrosion inhibitors are used in order to mitigate corrosion problems of tubing and pipeline. Imidazoline is known as one of the active ingredients of corrosion inhibitors and widely used in the oil and gas industries. However, imidazoline-type inhibitor is easily hydrolyzed to amide if water mixes into it. This hydrolysis reaction could progress in the stock tanks exposed to the weather. Once imidazoline changes into amide, not only its physical characters such as solubility to solvent but also its inhibitor efficiency changes^{1, 2}. Consequently, the inhibitor efficiency as expected might not be obtained, and corrosion problems would occur. Therefore, it is necessary to evaluate the inhibitor efficiency of amide-type inhibitor that imidazoline-type inhibitor transforms to under operating condition.

For improving the inhibitor efficiency, an intensifier is added to corrosion inhibitor. The intensifier may assist the adsorption of inhibitors and/or have corrosion inhibition itself. Hence, it is important to select the effective intensifier for corrosion inhibitor, which can lead to preventing corrosion problems. In this study, one intensifier that contains sulfur was chosen and added into both imidazoline-type and amide-type inhibitors. The efficiency of four inhibitor formulations (imidazoline, amide, imidazoline with intensifier and amide with intensifier) and the intensifier itself was evaluated by electrochemical measurements, weight loss test, quartz crystal microbalance (QCM) measurement and time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurement. Through these evaluation tests, each inhibitor efficiency was ranked, and the inhibitor mechanism was considered.

EXPERIMENTAL PROCEDURE

Tested materials

Carbon steel that is used for gas transport piping was used in this study. The size of specimens for each test is described in Table 1. All specimens are cut from the actual pipes. Material grade and chemical composition of carbon steel is shown in Table 2. Especially for weight loss test, specimens with welding line in the middle were used because the actual piping was jointed by weldment and suffered preferential corrosion at welding lines. three weld metals were used for welding, and their grade and chemical composition are described in Table 3. Prior to each experiment, specimens were wet ground with #600 SiC sandpaper and thoroughly degreased ultrasonically in acetone or ethanol.

Table 1
The size of specimens for each test

Test	Size
Corrosion potential measurement	$2^T \times 10^W \times 10^L$ mm
Potentiodynamic polarization measurement	
TOF-SIMS measurement	
Linear polarization resistance (LPR) measurement	ϕ 6 x 20^L mm
Weight loss test	$2^T \times 10^W \times 50^L$ mm

Table 2
Material grade and chemical compositions of carbon steel in wt% (balance Fe)

Grade	C	Mn	P	S
ASTM ^a A135 ³ Gr. A	≤ 0.25	≤ 0.95	≤ 0.035	≤ 0.035

Table 3
Grade and representative chemical compositions of three used weld metals in wt% (balance Fe)

Material	Grade	C	Mo	Cr
Weld metal 1	AWS ^b A5. 18 ⁴ ER70-S-G	0.09	-	-
Weld metal 2	AWS A5. 28 ⁵ ER80-S-G	0.06	0.5	-
Weld metal 3	AWS A5. 28 ⁵ ER80-S-G	0.03	1.0	2.25

Test solution and used chemicals

The test solution for all measurements was 3,000 ppm Cl⁻ + 300 ppm CH₃COOH, which simulates the production water of our field. Table 4 shows tested corrosion inhibitors and intensifier. Amide-type inhibitor was generated by imidazoline-type inhibitor mixed with water. The selected intensifier was one of the sulfur compounds and was added to both types of inhibitors. The dosage of chemicals was 200 ppm to the test solution volume and each formulation was adjusted in such a way that the amount of each active ingredient and intensifier was same for five chemicals.

Table 4
Tested corrosion inhibitors and intensifier

Chemicals	Remarks
Imidazoline-type inhibitor	-
Amide-type inhibitor	Generated by imidazoline-type inhibitor
Intensifier	Organic compound including sulfur
Imidazoline + Intensifier	Mixed imidazoline with intensifier
Amide + Intensifier	Mixed amide with intensifier

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^b American Welding Society, 8669 NW 36 Street, #130, Miami, FL 33166-6672

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Electrochemical measurement

Electrochemical measurements were conducted to investigate how chemicals influence corrosion reactions. Corrosion potential measurement, potentiodynamic polarization measurement and linear polarization resistance measurement were carried out.

Corrosion potential measurement and potentiodynamic polarization measurement

Corrosion potential measurement and potentiodynamic polarization measurement were tested in a standard three-electrode cell, consisting of a carbon steel working electrode whose exposure area is about 1 cm², a Pt counter electrode and a saturated Ag/AgCl reference electrode. These measurements were conducted in 1 L of the test solution at 70 °C under atmospheric pressure. The solution was deaerated with CO₂ for 5,400 s before measurement. After deaeration, the specimen was immersed in the solution, and the corrosion potential was measured for 3,600 s. Chemicals were dosed into the solution 600 s after the start of the measurement in order to observe the change of the potential. Potentiodynamic polarization measurement was carried out from measured corrosion potential -150 mV to the potential where the current density reached 1 mA/cm² with a scan rate of 10 mV/min in accordance with ASTM G5-14⁶.

LPR measurement

LPR measurement was performed to investigate inhibitor performance under high pressure. LPR was measured in an autoclave with three-electrode system that the working and reference electrode were carbon steel and the counter was Platinum, and the solution volume was 1.8 L. Before measurement, the solution was deaerated with CO₂ for 7,200 s, and then the autoclave was pressurized to 0.3 MPa at room temperature by CO₂ and heated to 70 °C with a stirring speed of 350 rpm. The pressure reached about 0.75 MPa at 70 °C. After that, LPR measurement was started, and the chemical was added into the solution after the measured data were almost stable (approximately after a half day). Then 10 mL (about 5,600 ppm) aromatic solvent was added into the solution three times every 3,600 s.

Weight loss test

Weight loss test was carried out in an autoclave with rotating cage in order to evaluate the inhibitor efficiency quantitatively. The solution was 1.6 L, and 200 ppm inhibitor and 4 vol.% aromatic solvent were added into the solution. Before test, the solution was deaerated with CO₂ for 7,200 s, and then the autoclave was pressurized to 0.3 MPa at room temperature with CO₂ and heated to 70 °C. The pressure reached approximately 0.75 MPa at 70 °C. After that, the specimens were immersed for seven days with the rotating speed of 2,000 rpm (corresponding to 8 m/s). The weight of specimens was measured before and after test to calculate the weight loss.

QCM measurement

QCM measurement, useful to understand the adsorption behavior of inhibitors^{7,8}, was conducted to evaluate the adsorption behavior of inhibitors with/without intensifier. Gold-coated quartz crystals were used as the measured cells. As pretreatment, the cells were washed with 1% sodium dodecyl sulfate solution, and organic compounds on Au surface were removed with piranha solution, a mixture of sulfuric acid and hydrogen peroxide. After that, the cells were water-washed sufficiently and dried. 440 µL test solution without deaeration was added into the cells and stirred at a speed of 500 rpm at 25 °C. 10 µL inhibitor-containing solution was dosed into the test solution after the measured data became stable. The test was continued until the data after the dosing inhibitor became stabilized.