The Inhibition of Imidazoline Type Inhibitor against Pitting Corrosion in Oil Gas Pipes

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***Abstract*—**The pitting inhibition of an imidazoline against pitting corrosion in N80 oil pipe was investigated using simulated occluded cell (OC), chemical analysis and potentiodynamic polarization. The results showed that the pH and inhibition efficiency (η % value) in the OC increased, Cl- and S2- concentrations in the OC decreased with the increase in inhibitor concentration, and η % value reached the maximum above 95 % at 0.3 ~ 0.4 wt % inhibitor addition in the bulk solution at 55 ℃.The pH and η % value decreased and Cl- and S2- concentrations increased slightly with rise in temperature at 0.4 wt % inhibitor addition.

***Keywords*—** Pitting corrosion; N80 steel; Polarization; EIS .

I. Introduction

N80 steel is the most commonly used construction material for pipelines in the oil and gas industry. However, they are very susceptible to corrosion in environment containing H_2S and NaCl [1]. Corrosion of pipes caused by H_2S and Cl^- is a significant problem in the oil and gas production and transportation systems in China as the continuous oil and gas exploration leads to higher and higher concentrations of H_2S and NaCl in oil and gas in recent decades, which causes costly economic losses due to frequent replacement of oil pipelines to ensure production safety [2]. Imidazoline-based inhibitors have been widely used for protecting carbon steels in acidic environment. The inhibiting efficiency and the mechanism of imidazoline-based inhibitors for carbon steels has been investigated. And the midazoline inhibitors shows a good inhibiting effect on metals in H_2S and Cl^- coexisting medium [3]. However, so much effort has been taken on the globally corrosion inhibition and adsorption behavior of imidazoline-based inhibitors on carbon steels, none of these investigations have involved the inhibiting effect as well as efficiency of imidazoline-based inhibitors against pitting corrosion in H_2S and Cl^- coexisting medium.

Therefore, the aim of this work is to explore the inhibiting effect and efficiency of a synthesized imidazoline derivative against pitting corrosion in N80 oil pipe in H_2S and NaCl coexisting medium, which can provide the theoretical basis for pitting corrosion and protection for pipelines in oil and gas production. For experimental condition the pitting corrosion was s imulated using simulated occluded cell (OC) method [4], subsequently, the pH value, Cl^- and S^{2-} concentration as well as electrochemical behaviour of the simulated occluded solution were measured by chemical analysis, potentiodynamic polarization and EIS tequniques, also the corrosion morphology of metals inside the simulated cavity was observed by SEM.

II. Experimental Methods

A. Simulated Occluded Cell (OC) Corrosion

The pitting corrosion in this work was simulated using a simulated occluded cell (OC) with constant current [5], 1 mA/cm^2, under flowing condition as shown in Fig.1. The OC made of a durable glass tube (Fig.1 (7)) with effective volume around 5 ml was fixed in the middle of the glass tank (Fig.1 (2)). A glass tube at the bottom of the OC with inner diameter 1.5 mm and length 15 mm was filled with filter paper scraps, where the difficult diffusion of the corrosion medium through the microporous of filter paper occurs and lead to an occluded state. The prepared corrosion medium with volume 500 ml and 2 ml was filled into the glass tank and OC respectively, and the heights of the bulk and occluded solution were kept the same in all experiments. The occluded specimen (Fig.1 (5)) was plugged into the occluded solution with a rubber stoppers at the top of the durable glass tube, which was connected with the anode while the bulk specimen (Fig.1 (4)) was connected with the cathode of a HDV-7C potentiostat for the purpose of keeping the specimen activity in the OC according to publication. The current density of the occluded specimen was controlled at 1 $mA \cdot cm^2$ to simulate the internal and external galvanic current and the occluded specimen works as anode, which is equivalent to the metals inside the cavity when pitting corrosion happens. All of the devices used in the simulated OC were made from materials that would not affect the pH value of the solution. It is noticed that during inhibitor addition, the inhibitor should be added into the glass tank, i.e., bulk solution (Fig.1 (2)), and keep the occluded solution uninhibited at the start.

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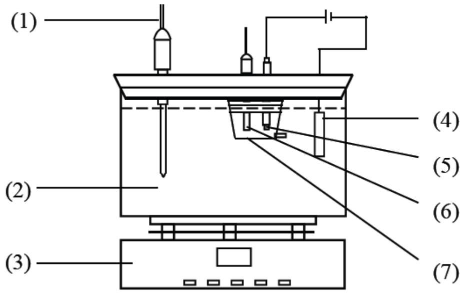

Fig.1 The schematic diagram of simulated occluded cell
(1) thermostat; (2) glass tank; (3) magnetic stirrer with heater; (4) bulk specimen; (5) occluded specimen; (6) reference electrode (SCE); (7) occluded cell(OC).

B. Materials and Corrosion Medium

The material used for the present investigation was special oil pipelines material N80 steel, with a chemical composition of C:0.42 wt.%, Si:0.24 wt.%, Mn:1.55 wt.%, S:0.004 wt.%, P:0.012 wt.%, Cr: 0.051 wt.%, Mo: 0.18 wt.%, V0.005 wt.%, Ni0.034 wt.%, and Fe as the balance, was used as a test material. The occluded specimens(Fig.1 (5)) were cut into coupons of dimension 10 mm × 50 mm × 5 mm, which were embedded in epoxy resin with every exposed working area 1 cm^2, and the bulk specimens (Fig.1 (4)) were cut into coupons of dimension 25 mm × 40 mm × 10 mm. The effective area ratio of the bulk specimen to the occluded specimen was about 100:1. Prior to each experiment, the exposed surface of the occluded electrode (of area 1 cm^2) and the bulk electrode (of area100 cm^2) were polished with a series of silicon carbide papers up to 800 grits, then they were washed with distilled water and degreased in acetone and air dried for standby. The imidazoline quaternary ammonium salt used as inhibitor for this study was prepared in the lab. The standard corrosion medium for corrosion study in oil industry, i.e, 0.5 % CH_3COOH + 5 % NaCl solution saturated with H_2S, was prepared from analar grade chemicals using distilled water, after being deoxygenated by bubbling nitrogen for at least 1 h, the hydrogen sulfide was purged into the solution until it was fully saturated. The initial pH value of the standard corrosion medium was 4.5.

C. Analysis of Corrosion

After 48h simulated OC, the OC was taken out of the glass tank. Subsequently, the pH value, the Cl- and S2- concentrations of the occluded solution were measured at room temperature. The pH values of solutions were determined using pHS-25 pH meter with E-210-C-9 composite electrode. The S2- and Cl- concentrations were analyzed by iodometry [6] and silver nitrate titration method [7] respectively. 4 ml tetraphenyl boron sodium solution (7 g/L) and potassium nitrate solution (7 g/L) with the same volume were added into the occluded solution to clear the imidazoline derivative at the beginning before titration.

III. Results and Discussion

A. Effect of Imidazoline Inhibitor on the Chemistry in the OC (Pit)

Table.1 shows the variations in the pH values and concentrations of the aggressive ions for the occluded solution after 48h simulated OC at 55 ℃ with imposed anodic current density, 1mA/cm^2, in H_2S-saturated 5 % NaCl + 0.5 % CH_3COOH solutions in absence and presence of the imidazoline inhibitor at various concentrations. It can be seen that in the absence of inhibitor there is an reduction in the pH value for the occluded solution from initial 4.5 to 3.6 after simulated OC for 48 h at 55 ℃, this reduction indicates the acidification in the occluded solution. However, in the presence of the imidazoline inhibitor at various concentrations, the pH value for the occluded solutions increases remarkably when compared with that in the uninhibited solution as the extent of the acidification in the occluded solution decreases. With 0.4% addition of imidazoline inhibitor in the bulk solution, there is a small decrease in the pH value of the occluded solution from initial 4.5 to 4.3 after 48 h simulated OC, suggesting that the imidazoline derivative can effectively block the acidification of the occluded solution (the solution in a cavity during pitting corrosion), consequently, the decrease of the pH value for the occluded solution is retarded to be as slow as possible.

TABLE I: Effect Of Imidazoline Inhibitor At Various Concentrations On The Chemistry In The Occluded Solutions At 55℃

Temperature(□)	OC	C(*wt %*)	PH	Cl^- (*mol/L*)	S^{2-} (*mol/L*)
	Before simulated OC	0	4.5	0.847	0.114
		0	3.6	1.600±0.002	0.136±0.003
		0.1	3.9	1.176±0.001	0.128±0.005
55	After simulated OC	0.2	4.1	1.058±0.003	0.122±0.002
		0.3	4.2	0.964±0.002	0.119±0.001
		0.4	4.3	0.917±0.004	0.117±0.002

From Table.1, the results reveale that the pH value of the occluded solution decreases and the Cl^- and S^{2-} concentrations increase remarkably in the absence of inhibitor in the bulk solution, which can be attributed to the corrosion of metals as anode inside the OC (pit), when the dissolution of metal ions in the OC (pit) into the occluded solution occurred, the occluded solution become electropositive due to the enrichment of metal ions in the OC. In order to maintain the occluded solution itself in electric neutrality, the Cl^- and S^{2-} in the bulk solution migrate into the OC and metal ions in the OC migrate out into the bulk solution, that's the reason for the presence of the multiples of Cl^- and S^{2-} enrichment. Consequently, on the one hand, the enrichment of Cl^- can aggravate the possibility for hydrolysis reaction of $FeCl_2$ according to the following equation:

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + HCl \quad (1)$$

From Eq. (1), it is suggested that the occluded solution become more acidic due to the occurrence of hydrolysis reaction of $FeCl_2$, resulting in the decrease in the pH values, which in return accelerates the dissolution of metals inside the OC (pit). On the other hand, the presence of S^{2-} in the occluded solution can remarkably reduce the active potential for Fe dissolution in the OC, which also in return accelerates the dissolution of metals inside the OC (pit) [8]. In these cases, the "Autocatalytic Nature" in the OC (within pit) is formed.

It also can be seen from Table.1 that the concentrations of Cl^- and S^{2-} are enriched to 1.600±0.002 and 0.136±0.003 mol/L respectively in the absence of inhibitor in the bulk solution after 48 h simulated OC, and that is a 1.89 and 1.19 times enrichment by comparison with that 0.847 and 0.114 mol/L of the initial solution before simulated OC. However, in the presence of inhibitor, Cl^- and S^{2-} concentrations in the OC decrease remarkably, especially, with 0.4 % imidazoline addition in the bulk solution, the Cl^- and S^{2-} concentrations reduce nearly 1.74 and 1.16 times respectively when compared to that in the absence of inhibitor. This indicates that imidazoline inhibitor can effectively prevent the corrosion of the occluded metal leading to the decrease of Fe^{2+} concentration in the OC, as a result, the driving force for Cl^- and S^{2-} diffusion was decreased. With the decrease in Cl^- concentration in the OC, the hydrolysis reaction of $FeCl_2$ (within OC) is blocked, leading to the retard of the pH reducing.

Table.2 shows the variations in the pH value and concentrations of the aggressive ions for the occluded solution after 48 h simulated OC with imposed current density, 1 mA/cm^2, in H_2S-saturated 5 % NaCl + 0.5 % CH_3COOH solutions in absence and presence of the imidazoline inhibitor at 25, 40, 55 and 70 ℃. It can be seen that with the increase in temperature from 25 ℃ to 70 ℃, the pH value of the occluded solution decreases from 4.1 to 3.3, the Cl^- and S^{2-} concentrations increase from 1.341±0.004 and 0.120±0.002 mol/L to 1.670±0.002 and 0.140±0.003 mol/L respectively in the absence of inhibitor in the bulk solution after 48h simulated OC, suggesting that the pH value become smaller and the Cl^- and S^{2-} concentrations become higher with the increase in temperature from 25 ℃ to 70 ℃ in the absence of inhibitor in the bulk solution. However, with 0.4 % imidazoline addition in the bulk solution, the reduction in the pH value and the increase in the Cl^- and S^{2-} concentrations are slowly. The pH value remains above 4.2, and the Cl^- and S^{2-} concentrations remain as low as 0.941±0.001 and 0.119±0.004 mol/L respectively, suggesting that the imidazoline inhibitor can effectively block the acidification and the enrichment of the aggressive ions in the occluded solution at 25, 40, 55 and 70 ℃. Generally, with the increase in temperature, the dissolution of the anodic metals, i.e, the corrosion rate within the pit during pitting corrosion increases, meanwhile, the solution viscosity decreases [9] resulting in the increase in the passing rate of the imidazoline molecules into the OC, which can benefit the process of the imidzoline molecules passing from the bulk solution into the occluded solution, but because the desorption of the imidazoline molecules adsorbed on the steel surface in the OC tend to be promoted by the increase of the temperature [10,11], the variation of the pH value as well as the Cl^- and S^{2-} concentrations are not remarkable.

TABLE II: EFFECT OF TEMPERATURE ON THE CHEMISTRY IN THE OCCLUDED SOLUTIONS IN ABSENCE AND PRESENCE OF 0.4 % IMIDAZOLINE INHIBITOR IN THE BULK SOLUTION

i(*mA/cm*^{2})	C(*wt* %)	T(℃)	pH	Cl^- (*mol/L*)	S^{2-} (*mol/L*)
1	0	25	4.1	1.341±0.004	0.120±0.002
		40	3.9	1.482±0.001	0.130±0.002
		55	3.6	1.600±0.005	0.136±0.005
		70	3.3	1.670±0.003	0.140±0.004
	0.4	25	4.5	0.870±0.004	0.115±0.003
		40	4.4	0.905±0.003	0.116±0.005
		55	4.3	0.917±0.001	0.117±0.002
		70	4.2	0.941±0.001	0.119±0.004

B. Potentiodynamic Polarization Analysis

Fig.2 shows the polarization curves for N80 steel in the OC (pit) in H_2S-saturated 5 %NaCl + 0.5 % CH_3COOH solutions in absence and presence of the imidazoline inhibitor at various concentrations after 48 h simulated OC at 55 ℃. It is observed that in the presence of inhibitor in the bulk solution, the curves are shifted to more positive potential as well as lower current region, and the shifts are found dependent on concentration of the inhibitor. Electrochemical corrosion kinetics parameters such as corrosion potential (E_{corr}) and corrosion current density(I_{corr}) obtained by extrapolation of Tafel lines in Fig.2, as well as inhibitor efficiency, η %, are listed in Table.3.Theoretically, the inhibition efficiency is defined *as:*

$$\eta\% = \left(I^0_{corr} - I_{corr}\right) / I^0_{corr} \times 100\% \qquad (2)$$

where I^0_{corr} and I_{corr} are corrosion current densities in solutions without and with inhibitor, respectively, determined by extrapolation of Tafel lines to the corrosion potential.

TABLE III: POTENTIODYNAMIC POLARIZATION PARAMETERS FOR N80 STEEL IN THE OC(PIT) IN H2S-SATURATED 5 % NACL + 0.5 % CH3COOH SOLUTIONS IN ABSENCE AND PRESENCE OF IMIDAZOLINE INHIBITOR AFTER 48 H SIMULATED (OCC) AT 25 ~ 70 ℃

T(℃)	C (*wt* %)	Polarization method		
		E_{corr}(*mv*)	I_{corr} (*μA/cm*^{2})	η/%
25	0	-635.93	182.31	--
	0.4	-584.30	3.01	98.34
40	0	-685.04	304.92	--
	0.4	-595.92	7.36	97.59
55	0	-739.25	374.42	--
	0.1	-646.11	39.11	89.55
	0.2	-639.40	26.44	92.93
	0.3	-627.80	17.68	95.27
	0.4	-608.04	16.42	95.61
70	0	- 786..62	1014.40	--
	0.4	-619.23	79.25	92.19

From Table.3, these results revealed that the corrosion current densities (I_{corr}) of the curves in the OC (pit) in the presence of imidazoline inhibitor in the bulk solution at 55 ℃ are far smaller than that in the OC (pit) in the absence of imidazoline inhibitor. The I_{corr} in the OC decreases remarkably with the increasing inhibitor concentrations, leading to the increase of inhibition efficiency. η % value of the imidazoline in the OC is 95.27 % when 0.3 % inhibitor was added into the bulk solution, and the η % value reaches 95.61 % when continuously increase the concentration of the inhibitor in the bulk solution to 0.4 %, suggesting that the imidazoline inhibitor can effectively decrease the corrosivity of the occluded solution or even retard the OC (pitting corrosion) when 0.3 % ~ 0.4 % imidazoline inhibitor is added in H_2S-saturated 5 % NaCl + 0.5 % CH_3COOH solutions.

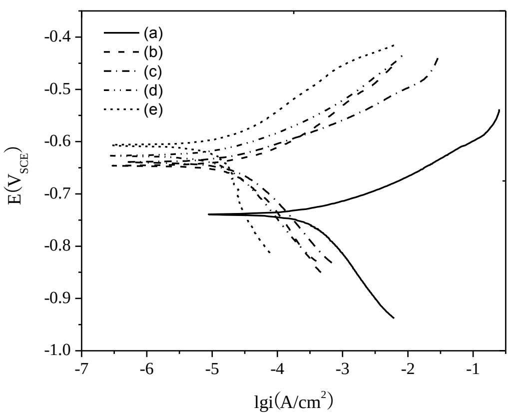

Fig.2: Polarization curves for N80 steel in the OC in H_2S-saturated 5 % NaCl + 0.5 % CH_3COOH solutions in absence and presence of imidazoline inhibitor at various concentrations after 48h simulated OCC at 55℃: (a) 0%; (b) 0.1%; (c) 0.2%; (d) 0.3%; (e) 0.4%

IV. Conclusions

(1) The imidazoline inhibitor exhibites good inhibition against pitting corrosion in N80 steel in H_2S-saturated 5 % Na Cl + 0.5 % CH_3COOH solutions, which can effectively increase the pH values of the occluded solutions and retard the migration of Cl^- and S^{2-} into the occluded solution at 55 ℃, thus, remarkably decrease the multiples of Cl^- and S^{2-} enrichment. Also, the pH value increases, Cl^- and S^{2-} concentrations in the OC decrease and η % value in the OC increases with the increase in inhibitor concentrations in the bulk solution, and η % value reachs the maximum above 95 %.

(2) With the increase in temperature from 25 ℃ to 70 ℃, the pH value of the occluded solution decreases from 4.1 to 3.3, Cl^- and S^{2-} concentrations increase from 1.341±0.004 and 0.120±0.002 mol/L to 1.670±0.003 and 0.140±0.004 mol/L respectively in the absence of inhibitor in the bulk solution after 48 h simulated OC corrosion. The imidazoline also exhibited good pitting inhibition for N80 steel in H_2S-saturated 5 % NaCl + 0.5 % CH_3COOH solutions at 25 ~ 70 ℃, η % value in the OC (pit) can still remain above 92 % at 70 ℃.

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References

[1] L. Y. Xiao and W. H. Qiao. "Development of Imidazoline Corrosion Inhibitor for Corrosive Media", *Corrosion Science and Protection Technology*, vol. 21, pp. 397-400, August 2009.

[2] ASM Handbook: Corrosion ASM Internacional, 2007 Vol. 13, Chapter 10, The Materials Information Society.

[3] P. C. Okafor, X. Liu and Y. G. Zheng. "Corrosion inhibition of mild steel by ethylamino imidazoline derivative in CO_2-saturated solution", *Corrosion Science*, vol. 51, pp. 761-768, April 2009. http://dx.doi.org/10.1016/j.corsci.2009.01.017

[4] C. C. Xu, X. P. Fu, and Y. P. Liu. "Migration of Bariou Inorganic Anions and Their Effects on Occluded Corrosion Cell", *Corrosion Science and Protection Technology*, vol. 12, pp. 130-137, May 2000.

[5] W. Z. Ouyang, C. C. Xu and L. J. Yue. "On chemical states within occluded cell of rusted cast iron in chloride solution", *Journal of Beijing University of Chemical Technology*, vol. 31, pp. 51-59, September 2004.

[6] GB/T223.68-1997, Water Quality-Determination of Sulfieds-Idometric Method.

[7] GB/T 15453-95, Industrial Circulation Cooling Water-Determination of Chloride-Silver Nitrate Titration Method.

[8] F. P. Wang, W. L. Kang, and H. M. Jing. *Electrochemical Corrosion Principle and Its Aplication.* Beijing, China.:Chemical Industry Press.

[9] X. Liu and Y. G. Zhen. "Inhibition Behavior of Two Imidazoline-Based Inhibitors with Different Hydrophilic Groups in Single Liquid Phase and Liquid/Particle Two-Phase Flow", *Acta Physico-Chimica Sinica*, vol. 25, pp. 713-718, April 2009.

[10] B. Wang, M. Du and J. Zhang. "Inhibition Performance of an Imidazoline Derivative as a Gas-Liquid Two-Phase Inhibitor for Q235 Steel against CO_2 Corrosion", *Acta Physico-Chimica Sinica*, vol. 27, pp. 120-126, January 2011.

[11] Q. He, S. T. Zhang and W. H. Li, et al. "Adsorption Behaviour of New Triazole Derivative as Inhibitor on Mild Steel in Acid Medium", *Corrosion and Protection*, vol. 29, pp. 243-246, May 2008