

# Inhibition Effect of Some Inhibitors on Super 13Cr Steel Corrosion in Completion Fluid

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## To cite this article:

Li Lingjie, Yang Yaohui, Zhou Bing, Zhang Yanjun, Lin Zhu, Tong Hui. Inhibition Effect of Some Inhibitors on Super 13Cr Steel Corrosion in Completion Fluid. *American Journal of Chemical Engineering*. Vol. 5, No. 4, 2017, pp. 74-80. doi: 10.11648/j.ajche.20170504.14

Received: May 27, 2017; Accepted: June 30, 2017; Published: July 19, 2017

**Abstract:** The inhibition effect of some inhibitors on super 13Cr stainless steel corrosion in CaCl<sub>2</sub> completion fluids with 1.0MPa CO<sub>2</sub> was investigated. The results indicated that the super 13Cr stainless steel was susceptible to uniform and stress corrosion cracking (SCC) without inhibitors. After addition urotropine, the uniform corrosion was inhibited, and the SCC sensitivity of super 13Cr steel decreased. Electrochemical noise results indicated that the noise resistance increased obviously after addition urotropine.

**Keywords:** Stress Corrosion Cracking, Inhibitors, Completion Fluid, Electrochemical Noise

## 1. Introduction

Stress corrosion cracking (SCC) of stainless steels is produced by the simultaneous action or synergy of a mechanical tension and a corrosive medium, which is an electrochemical reaction between material and its environment [1-6], SCC is governed by the parameters such as stress, pH, temperature and CaCl<sub>2</sub> concentration etc [7-11]. Some kind of mechanisms for SCC has been reported [12-14], but at present, the mechanism of SCC has not been explained satisfied. Relatively poor measuring techniques are one of the main reasons for this lack of knowledge about SCC processes.

Adding inhibitor is an effective way to control SCC [15-17]. The synergistic effect of CHN with MoO<sub>3</sub>, can reduce the prestressed steel wire SWRH77B in 3.5%NaCl+ saturated solution stress corrosion sensitivity, prevent stress corrosion cracking effectively [18]. N. Cansever examined the inhibition effect of “chloride + molybdate” ions on the SCC of AISI 304 SS [19]. Isao Sekine investigated Corrosion inhibition of mild steel (JIS SS 41, UNS K02600) and stainless steel (type 304, UNS S30400) in hot K<sub>2</sub>CO<sub>3</sub> solution [20].

In this paper, the inhibition effect on SCC and general

corrosion of super 13Cr steel in CaCl<sub>2</sub> completion fluid of some kind of inhibitors was investigated.

## 2. Experimental

### 2.1. Materials and Solutions

The test specimens were cut from super 13Cr stainless steel tube. The chemical component and mechanical property were shown in Table1, where  $E_{mod}$  is the module for elasticity,  $YS$  is the stress corresponding to 0.6% strain,  $t$  is the thickness of specimen,  $H$  is the distance between outer support and  $A$  is the distance between outer and inner support. The four-point-bend test specimens were prepared according to ISO7539-2: 1989(E) [21] and based on the ASTM-30 with dimension 80×12×2 mm. The distance between outer support ( $H$ ) and the distance between outer and inner support ( $A$ ) are 60 mm and 15 mm, respectively. The deflection between inner supports ( $y$ ) was controlled at 2.5 mm, thus the stress of super 13Cr steel corresponding to 2.5 mm of deflection is calculated to be 1158 MPa based on the following equation, which  $t$  is the specimen thickness.

$$\sigma = \frac{12Ety}{3H^2 - 4A^2} \quad (1)$$

**Table 1.** Chemical component and mechanical performance of super 13Cr stainless steel.

Chemical element (wt%)									
C	Si	Mn	Cr	Ni	Mo	P	S	V	Ti
0.01	0.23	0.42	12.0	5.4	1.9	0.014	0.001	0.06	0.09
Mechanical property									
YSMPa		TS, MPa		EL, %		$E_{mod}$ GPa			
825		857		26		191			

For electrochemical measurements under applied tensile stress condition, one end of the specimen was connected with an aviatic lead by welding and sealed with hydroxybenzene titanium lacquer, only leaving the tensile side between outer supports ( $3.6 \text{ cm}^2$ ) exposed to test solutions.

The completion fluid was prepared by adding 39 wt%  $\text{CaCl}_2$  brine, and deaerated by bubbling  $\text{N}_2$  gas for 12h and bubbling  $\text{CO}_2$  for 6h. Then 0.2% acetic acid was added which was used as a blank solution. The inhibitor-containing solutions were prepared by adding inhibitors in the blank solution.

## 2.2. Polarization Curves Measurements

For the polarization curves measurements, the four-point-bend test specimen was placed in a conventional three-electrode electrolyte cell system and used as a working electrode. A platinum electrode and an Ag/AgCl electrode were used as the reference electrodes, respectively. Polarization curves were obtained by sweeping the electrode potential from -250 mV to +250 mV versus the open circuit potential (OCP) at a scan rate of  $0.3 \text{ mV s}^{-1}$  after the working electrode reached a steady-state in the test solution. The test solutions were the completion fluids with and without inhibitors. After the test solutions and specimens placed in autoclave,  $\text{CO}_2$  was purged into the autoclave and partial pressure of  $\text{CO}_2$  was maintained at 1.0MPa, the temperature was controlled at  $125^\circ\text{C}$ .

## 2.3. Electrochemical Noise Measurements

For electrochemical noise (EN) measurements, a four-point-bend test specimen and an unloaded super 13Cr steel specimen with the dimension of  $80 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$  were used as working electrodes. Also an Ag/AgCl electrode was used as the reference electrode. EN was measured in a freely corroding system (without an externally applied current or voltage). A home-made zero resistance ammeter (ZRA, current sensitivity  $> 10 \text{ pA}$ , voltage sensitivity  $> 10 \text{ } \mu\text{V}$ ) measurement system with a sampling rate of 10 Hz was used to record the current and potential noise simultaneously, that is, the galvanic current flowing between two working electrodes and the potential difference between the coupled working electrodes and the reference electrode. The test solutions also were the completion fluids with and without inhibitors. And the EN was measured in autoclave at  $125^\circ\text{C}$  with 1.0MPa  $\text{CO}_2$ .

## 2.4. Surface Observation

After 14 days of immersion in solutions with and without inhibitors, the four-point-bend test specimens surface morphologies were observed using Phillips Quanta 200 SEM. The experiments were carried out three times, and were highly reproducible.

# 3. Results and Discussion

## 3.1. Inhibition Effect on Super 13Cr Steel of Some Inhibitors

The test solutions were the completion fluids with 1% inhibitors. The solution was purged into the autoclave and partial pressure of  $\text{CO}_2$  was maintained at 1.0MPa, the temperature was controlled at  $125^\circ\text{C}$ . The following nine different inhibitors were tested, including urotropine, tungstate, thiourea, imidazoline, molybdate, iodide, chromate, dodecylamine and propargyl alcohol (PA). Figure 1 showed the polarization curves of super 13Cr steel in the completion fluids with and without 1% (Wt) inhibitor.

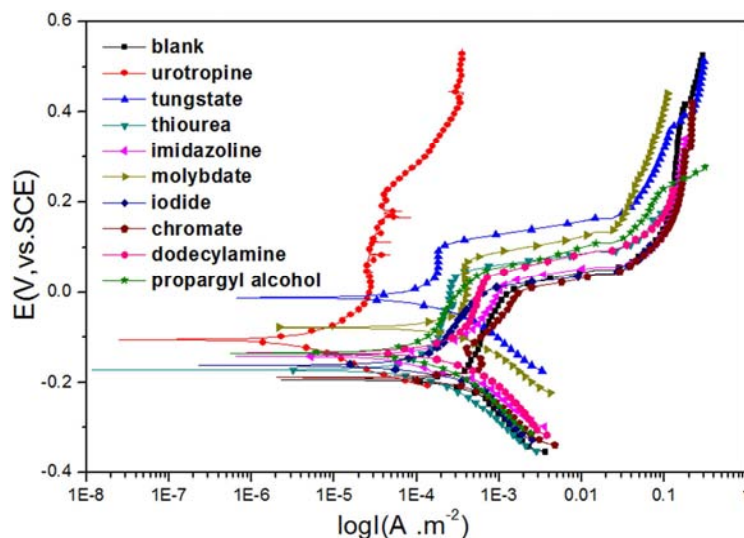
**Figure 1.** Polarization curves of super 13Cr steel in the completion fluids with and without 1% (Wt) inhibitor.

Table 2. Fitting results of the polarization curves.

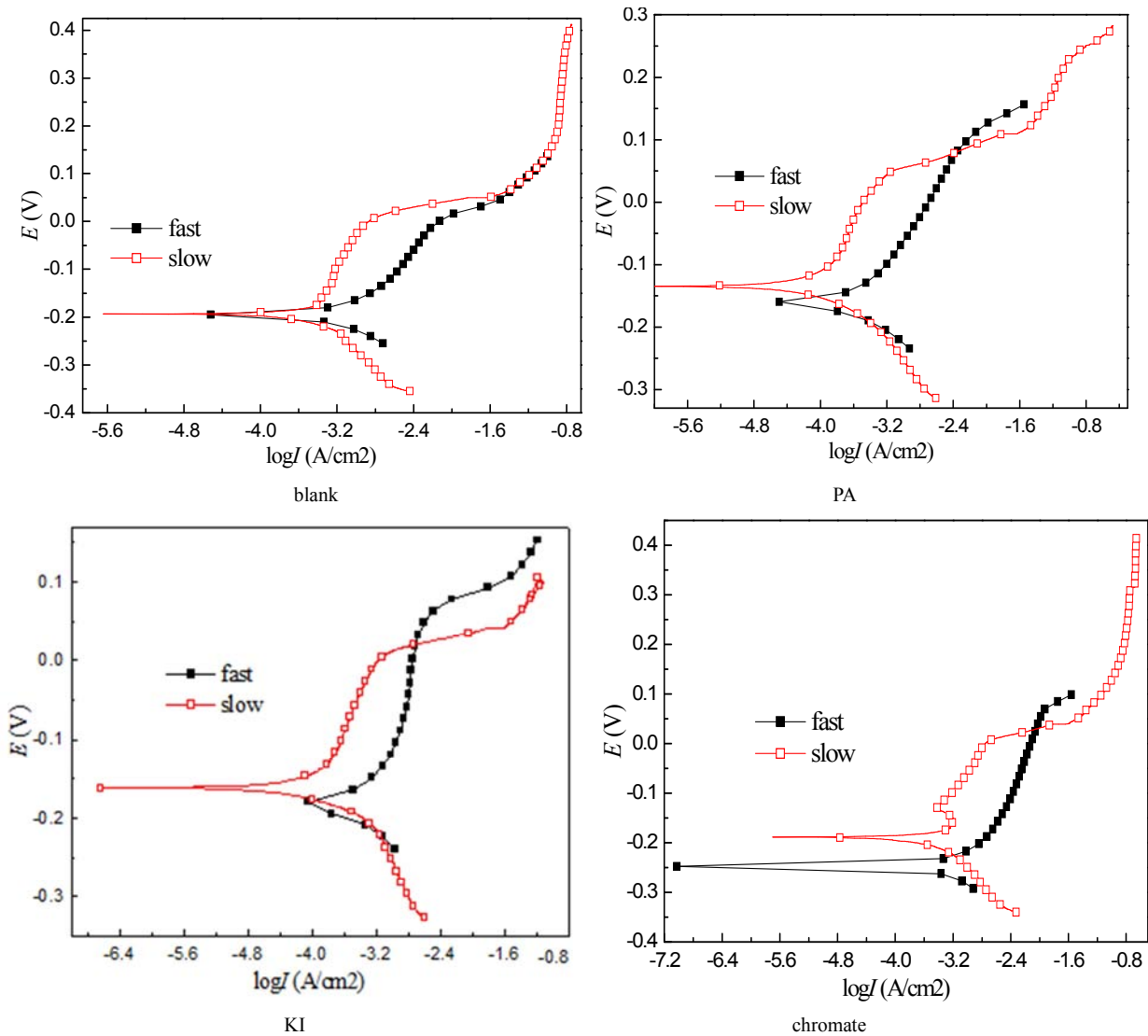
Inhibitors	$I_{corr}(\mu A/cm^2)$	$E_{corr}(mV)$	$\eta$
blank	422.0	-194	—
PA	81.6	-135	80.66%
KI	89.2	-162	78.86%
$CrO_4^{2-}$	454.6	-189	—
Imidazoline	105.3	-141	75.05%
Dodecylamine	147.5	-134	65.05%
Thiourea	90.7	-171	78.51%
Urotropine	5.5	-105	98.70%
$MoO_4^{2-}$	221.3	-78	47.56%
$WO_4^{2-}$	102.8	-12	75.64%

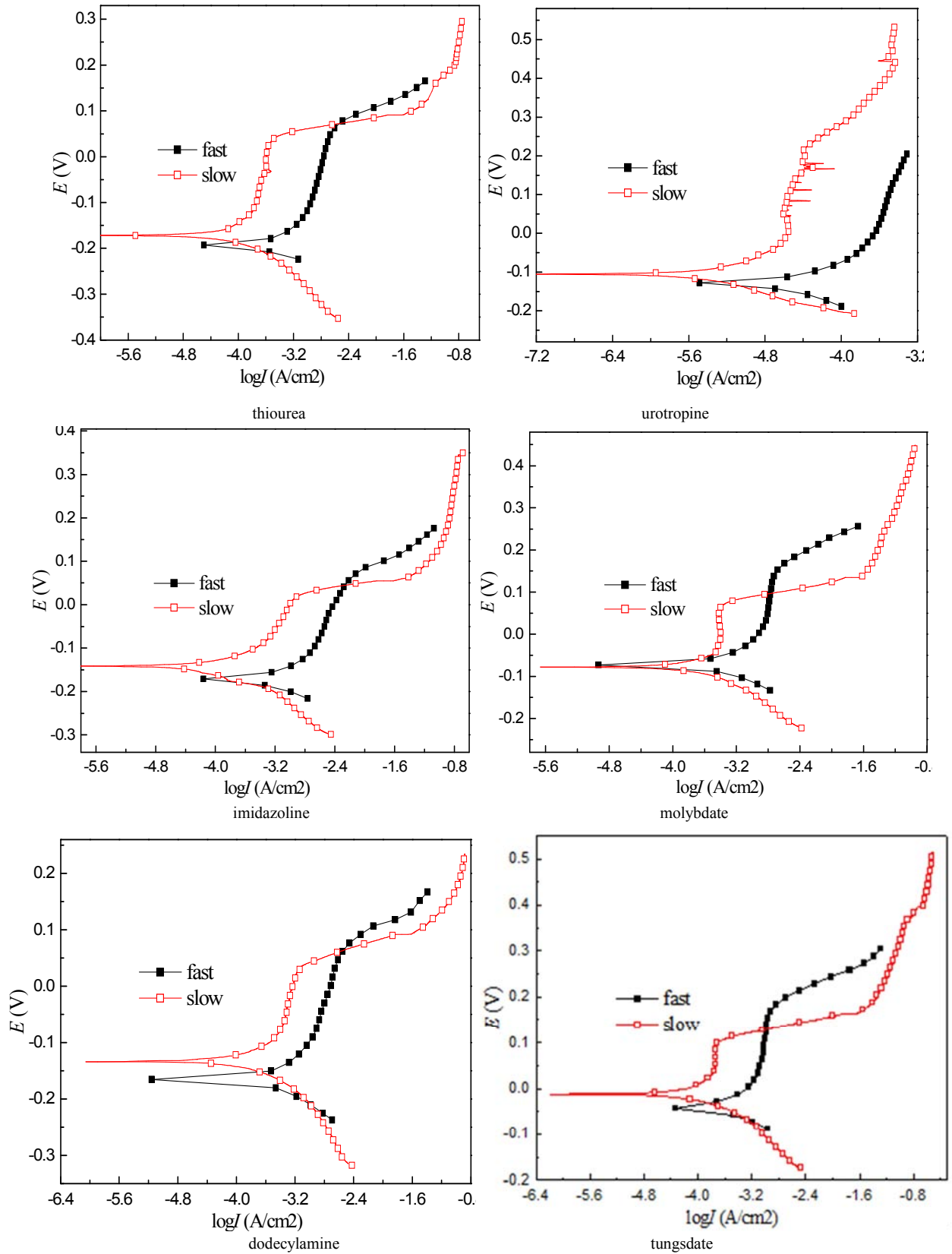
The fitting results of Figure 1 were shown as Table 2. Which  $I_{corr}$  is corrosion current,  $E_{corr}$  is corrosion potential, and  $\eta$  is Corrosion inhibition efficiency

The results indicated that urotropine had the best inhibition effect on uniform corrosion of super 13Cr steel in completion Fluid.

3.2. Fast and Slow Scan Curves for Super 13Cr Steel

The susceptible potential range can be found through fast and slow scan curves. The test solutions were 39wt%  $CaCl_2$  brine, The solution was deaerated by bubbling  $N_2$  gas for 12h and bubbling  $CO_2$  for 6h, then 300ppm acetic acid and 1% inhibitor were added in, the temperature was controlled at  $125^{\circ}C$ , the applied stress on super 13Cr steel was 100%YS. The fast scan rate was 0.3mV/s, and the slow one was 15mV/s. Figure 2 showed the fast and slow scan curves for super 13Cr steel.





**Figure 2.** Fast and slow scan curves for super 13Cr steel.

The parameter  $P_i$ , which expressed the SCC susceptibility, can be calculated through the following equation based on the fast and slow scan curves.

$$P_i = (i_f)^2 / i_s \quad (2)$$

Where,  $i_f$  is the fast scan current density,  $i_s$  is the slow scan current density. The bigger is the  $P_i$  value, the more sensitivity to SCC the metal will be.

Figure 3 showed the  $P_i$  value of super 13Cr steel in 39%  $\text{CaCl}_2$  solution with and without 1% inhibitor. Figure 3 indicated that after the addition of inhibitor, the SCC susceptibility of super 13Cr steel decreased.

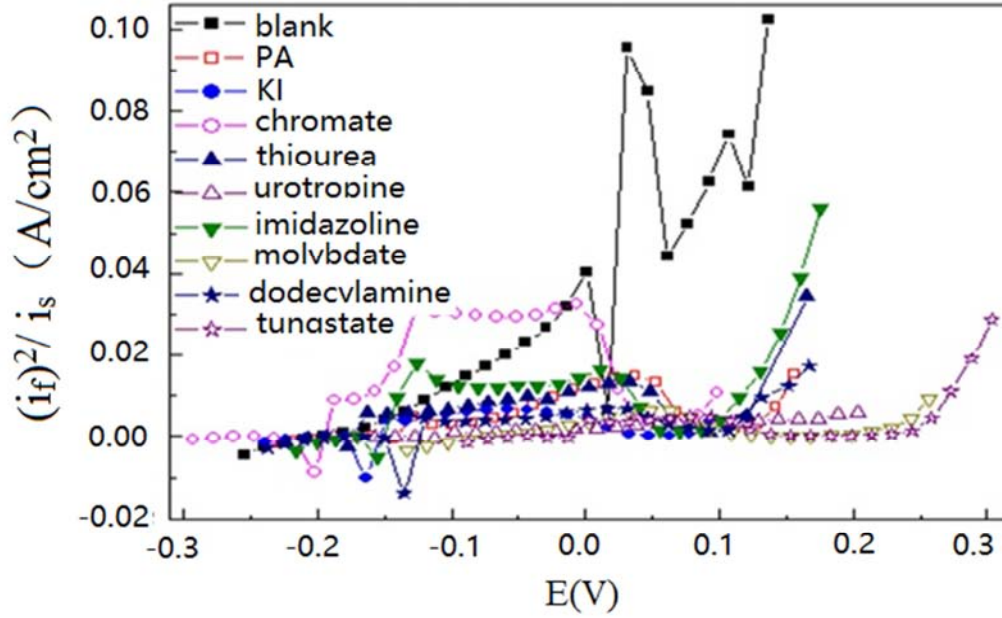


Figure 3.  $P_i$  value of super 13Cr steel in 39%  $\text{CaCl}_2$  solution with and without 1% inhibitor.

### 3.3. Electrochemical Noise Results on SCC of Super 13Cr Steel with and Without Inhibitor

The test solution was 39wt%  $\text{CaCl}_2$  brine, the solution was deaerated by bubbling  $\text{N}_2$  gas for 12h and bubbling  $\text{CO}_2$  for 6h, then 0.2% acetic acid and 1% inhibitor were added in. Finally, the solution was pumped in autoclave.  $\text{CO}_2$  was purged into the autoclave and partial pressure of  $\text{CO}_2$  was maintained at 1.0MPa, the temperature was controlled at 125°C, the applied stress on super 13Cr steel was 100%YS. Urotropine was selected as the inhibitor. Figure 4 showed the electrochemical noise of super 13Cr steel in the completion with and without 1% (Wt) inhibitor.

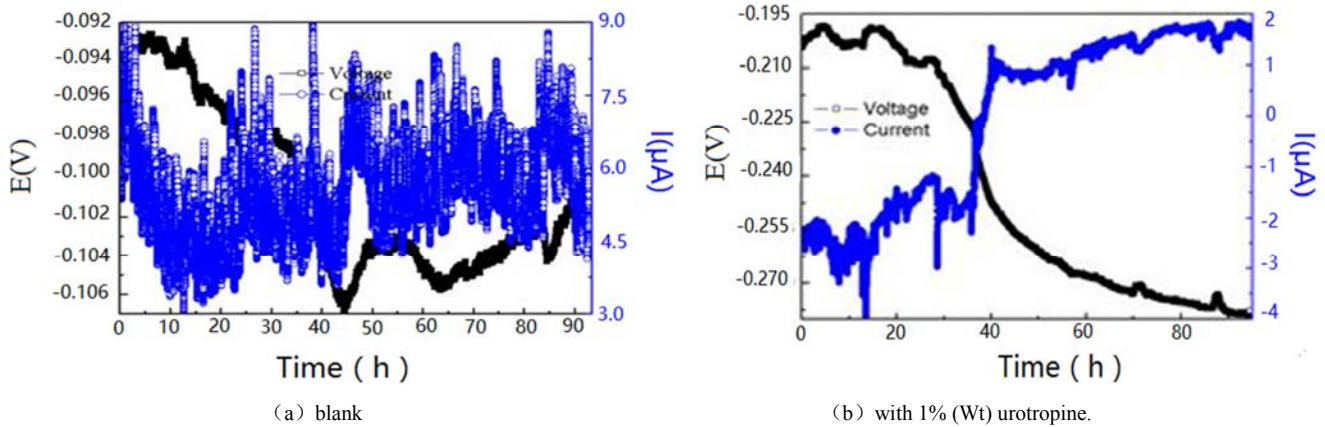


Figure 4. Electrochemical noise of super 13Cr steel in the completion with and without 1% (Wt) inhibitor a) blank; b) with 1% (Wt) urotropine.

Figure 4 indicated that the electrochemical noise was restrained after the addition of urotropine. The noise resistance ( $R_n$ ) was calculated based on the following equation: Where  $S_v$  and  $S_i$  are the voltage and current standard deviation respectively.

$$R_n = \frac{S_v}{S_i} \quad (3)$$

The  $S_v$  and  $S_i$  were the voltage and current standard deviation respectively. The  $R_n$  of super 13Cr steel in blank solution was 1808Ω and the  $R_n$  of super 13Cr steel in



solution with 1% (Wt) urotropine was  $18633\Omega$ , the  $R_p$  increased obviously after the addition of urotropine, which indicated that the corrosion rate was decreased by urotropine.

### 3.4. Effect of Urotropine on SCC of Super 13Cr Steel by Hang Sheet Experiment

The test solutions were 39wt%  $\text{CaCl}_2$  brine with and

without inhibitors, and the specimens were placed in PTFE vessel. The solution was deaerated by bubbling  $\text{N}_2$  gas for 12h then bubbling  $\text{CO}_2$  for 6h before PPET vessels placed in autoclave.  $\text{CO}_2$  was purged into the autoclave and partial pressure of  $\text{CO}_2$  was maintained at 1.0MPa, the temperature was controlled at  $125^\circ\text{C}$ . The test time was 14 days. The surface corrosion crack of four-point-bend experiment was invested, and the result was shown as the figure 5.

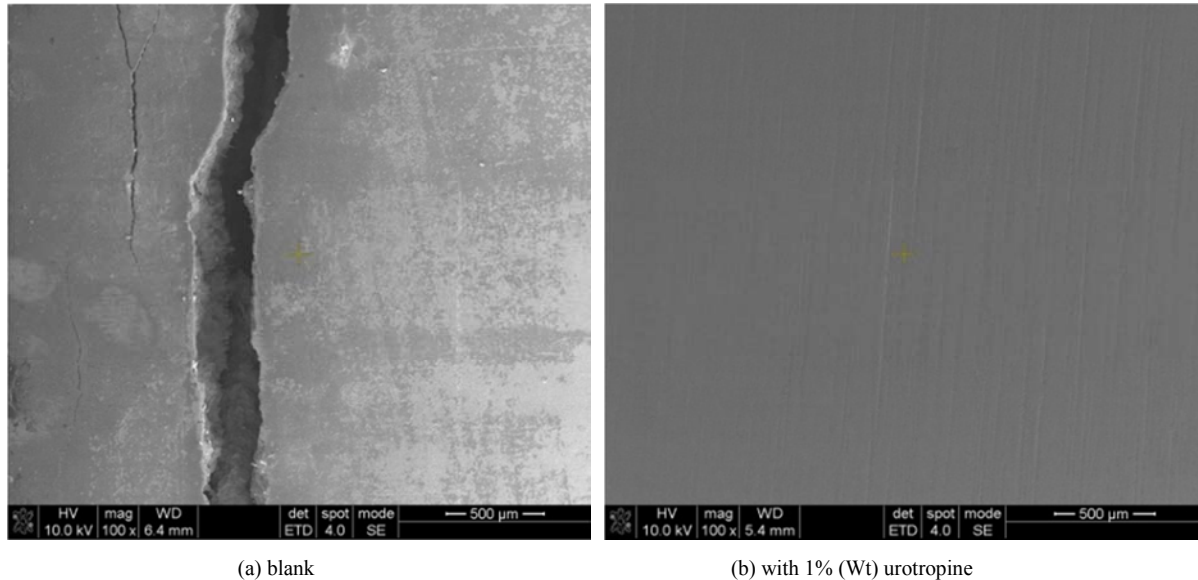


Figure 5. Hanging results of super 13Cr steel in the completion with and without 1% (Wt) inhibitor a) blank; b) with 1% (Wt) urotropine.

The results indicated that the super 13Cr stainless steel was susceptible to stress corrosion cracking without adding inhibitor, which the four-point-bend test specimen was fractured and the surface of steel had some cracks. After addition urotropine, the SCC sensitivity of super 13Cr steel was decreased, and the surface of steel had none cracks. Urotropine could prevent the SCC of super 13Cr steel in the test condition.

## 4. Conclusions

At 1.0MPa,  $125^\circ\text{C}$ , SCC of super 13Cr steel rapidly occurs in a  $\text{CO}_2$ -saturated completion fluid in the presence of 0.2% acetic acid. Urotropine has good inhibition effect on general corrosion of super 13Cr steel in  $\text{CaCl}_2$  brine. And after adding 1% inhibitors, the SCC sensitivity of super 13Cr steel decreased. The hanging results show that the SCC of super 13Cr steel is inhibited after adding 1% urotropine.

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