

Characteristics Analysis and Corrosion Inhibition in Typical Produced Water of Jidong Oilfield

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Abstract. The composition of oilfield water is complex and diverse. The development and application of corrosion inhibitors can effectively inhibit the corrosion of pipelines and equipment by oilfield water. The ions in produced water of Jidong Oilfield were determined by instrumental analysis and chemical analysis. Triazine prepared from ethanolamine and formaldehyde as corrosion inhibitor was evaluated by weight loss method. The corrosion inhibition experiments were carried out in ancient water samples, and the effects of concentration and temperature on corrosion inhibition were investigated. Finally, corrosion inhibitors were applied to the corrosion inhibition of produced water with different compositions in Jidong Oilfield, the corrosion inhibition of steel sheet was evaluated under different salinity conditions, and the effects of various ion contents in typical water samples and salinity on corrosion inhibition were analyzed. The experimental results show that the corrosion inhibition effect of triazine is better, and the product can be used in various water samples in oilfield with the inhibition efficiency above 85%.

Keywords: Corrosion inhibition; weight loss method; water analysis.

1 Introduction

In the process of oil and gas field oil production, the produced water is of poor quality and complex composition [1]. It generally has high salt content, high COD value, large polymer content, and large oil content [2,3]. Some also contain small amounts of heavy metals and bacteria [4]. Direct discharge will cause irreversible damage to the surrounding environment and a great waste of water resources. In oil and gas fields, it is generally considered to reinject the produced water after treatment [5]. If the water quality conditions do not meet the injection requirements, scaling, blockage, and corrosion will occur [6,7], which will inevitably cause corrosion on the oil layer [8], water injection pipelines and equipment [9]. In order to ensure that the water quality meets the technical requirements of the industry, oilfield water detection and analysis is required [10]. On the one hand, it can ensure that the water quality requirements for reinjection are met, and scaling and corrosion are reduced [11], and on the other hand, the recovery factor cannot be reduced [12]. In addition to using corrosion-resistant materials, corrosion inhibitors must be selected according to the specific water environment and added to the produced water [13]. However, research on the cost-effective, low-toxicity and environmentally friendly corrosion inhibitors with high corrosion inhibition efficiency for steel is urgently needed [14-16]. As a new corrosion inhibitor, triazine, a synthetic product of

ethanolamine and formaldehyde, has excellent corrosion inhibition properties. With the stable spatial structure and inhibitory properties [17,18], triazines are suitable for oilfield produced water containing complex ions.

2 Experimental

2.1 Materials

Ethanolamine was supplied from Tianjin Kermel Chemical Reagent Co., Ltd. Formaldehyde was purchased from Tianjin Tianli Chemical Reagent Co., Ltd. Anhydrous calcium chloride was purchased from Tianjin Shengao Chemical Reagent Co., Ltd. Magnesium chloride hexahydrate was supplied from Chengdu Kelong Chemical Reagent Factory. Sodium bicarbonate was purchased from Tianjin Baishi Chemical Co., Ltd. Anhydrous sodium sulfate was purchased from Tianjin Tianli Chemical Reagent Co., Ltd. Sodium chloride and Potassium chlorid were purchased from Tianjin Shengao Chemical Reagent Co., Ltd. Methyl orange and Phenolphthalei were supplied from Tianjin Kermel Chemical Reagent Co., Ltd.

2.2 Characteristics analysis method

At present, the main methods of water quality analysis are instrumental analysis and chemical analysis. The contents of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , F^- , Cl^- , NO_3^- , NO_2^- ,

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PO₄³⁻ and SO₄²⁻ in typical water samples of Jidong Oilfield were determined by ion chromatography. The flow rate controlled by chromatographic conditions was 1.200mL/min, and the injection volume was 20 L. The content of Fe³⁺ in typical water samples of Jidong Oilfield was determined by spectrophotometry. And the contents of CO₃²⁻ and HCO₃⁻ in water samples were determined by titration analysis. 0.5% phenolphthalein solution as indicator, CO₃²⁻ in water samples was determined by sulfuric acid standard solution. 0.1% methyl orange solution as indicator, HCO₃⁻ in water samples was determined by sulfuric acid standard solution.

2.3 Preparation of simulated oilfield water

According to water type and salinity, four typical water samples from Jidong Oilfield were screened out in this experiment, as shown in Table 1. The simulated water is prepared according to the salinity of oilfield water, and the calculation method is based on the calculation program of simulated water (the volume of simulated water is 1L). The preparation of simulated water for four typical Jidong Oilfield water samples are shown in the table below.

Table 1 The preparation of simulated Jidong Oilfield water

Name	Reagent	Quality (g)
ND9	CaCl ₂	1.9680
	MgCl ₂ ·6H ₂ O	0.4543
	NaHCO ₃	1.9552
	Na ₂ SO ₄	0.8220
	NaCl	9.4825
ND17-1	CaCl ₂	10.4373
	MgCl ₂ ·6H ₂ O	6.8758
	NaHCO ₃	2.0158
	Na ₂ SO ₄	0.2029
	NaCl	54.7707
ND17-3	CaCl ₂	1.9645
	MgCl ₂ ·6H ₂ O	0.6430
	NaHCO ₃	1.4017
	Na ₂ SO ₄	0.6950
	NaCl	4.6031
ND38P1	CaCl ₂	0.7417
	MgCl ₂ ·6H ₂ O	2.4216
	NaHCO ₃	0.6237
	Na ₂ SO ₄	0.1609
	NaCl	1.1840

2.4 Synthesis of triazine

Ethanolamine and formaldehyde were attained at the molar ratio of 1:1, ethanolamine was put in a 50mL three-necked flask, a small magnet was added in, the three-necked flask was fixed in the magnetic agitator of a constant temperature water bath at 60°C, the mixed liquid was stirred to add formaldehyde within 0.5h. Condensation at reflux for 3h, the synthesized product was cooled to room temperature.

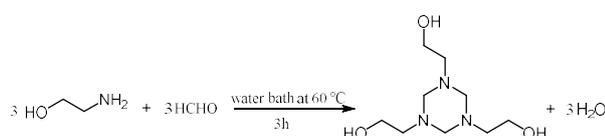


Fig. 1 Synthetic chemical equations for triazine

2.5 Preparation of corrosive solution

The preparation of ancient water samples required firstly, 21.65g CaCl₂, 1.4g MgCl₂·6H₂O, 0.09g NaHCO₃, 1.12g Na₂SO₄, 8.24g NaCl, 0.9g KCl were weighed and added in beaker, then dissolved with water and determined volume in 1L volumetric flask. 100mL of ancient water samples were added to 125mL grinding bottle, and the triazine products synthesized by ethanolamine and formaldehyde were added, respectively. Ensure that the concentration in water samples was 0, 0.1%, 0.2%, 0.5%, 1.0%, and 2.0%. Corrosion solutions for other types of water sample corrosion inhibitors are prepared in the same manner as described above.

2.6 Treatment of steel sheets

The tested material is A₃ steel sheets were abraded with a series of emery papers, and the surface area S of the steel sheet was calculated and recorded. The steel sheet was successively soaked in petroleum ether and anhydrous ethanol, and then the surface of the steel sheet was dried with a hair dryer. The mass of each steel sheet is weighed by an analytical balance and recorded as m₁. Every two pieces of steel discs are divided into a group and photographed for recording. Each group of A₃ steel sheet was hung with string into the grinding bottles containing corrosion fluids with different corrosion inhibition agents, and these bottles were put into the thermostatic water bath heated to specific temperature in advance for 48h. The steel sheets were taken out and put on the qualitative filter paper to dry naturally, then photographed for recording. The plates were put in 0.2mol·L⁻¹ dilute hydrochloric acid immersed for 30 s, made the steel rust attached to the surface drop out. The liquid on the surface of the steel sheets was blotted up with filter paper, soaked in the petroleum ether for 2 min, immersed in anhydrous ethanol for 2 min. These steel discs were taken out and placed on qualitative filter paper, dried with hair dryer. The quality of each piece of treated steel sheets were weighed by the analytical balance, noted as m₂. And compared with the m₁, Δm was obtained.

2.7 The method of corrosion inhibition performance evaluation

The weight loss experiments were performed in several kinds of water samples in the absence and presence of various concentration of triazine corrosion inhibitor. The corrosion inhibition performance was mainly evaluated by calculating uniform corrosion rate and corrosion inhibition rate. The mass loss is determined after removing from the corrosion solution. The uniform corrosion rates (W_{corr}) have been obtained as suggested in equation (1):

$$W_{corr} = \frac{\Delta m}{St} \quad (1)$$

Δm—the weight loss, g; S—the exposed area of steel sheet, cm²; t—the period of immersion of corrosion, h.

The inhibition efficiency ($E_w\%$) was determined by following equation(2):

$$E_w \% = \frac{\Delta m_0 - \Delta m}{\Delta m_0} \times 100 \quad (2)$$

Δm_0 —the weight loss of the steel sheet in the absence of triazine in the corrosion solution, g; Δm —the weight loss of the steel sheet in the presence of triazine, g.

3 Result and Discussion

3.1 Water samples analysis results

The ions in typical water samples of Jidong Oilfield were determined by ion chromatography and chemical analysis. The results are shown in the Table below.

Table 2 The mass concentration of ions in some water samples of Jidong Oilfield

N o.	Name	Cationic concentration (mg/L)					Anion concentration (mg/L)		
		Na ⁺ +K ⁺	Ca ²⁺	Mg ²⁺	Ba ²⁺ +Sr ²⁺	Fe ³⁺	Cl ⁻	SO ₄ ²⁻	HC O ₃ ⁻
1	ND8	5940.5	319.2	32.9	116.9	0	4014.9	126.3.8	336
2	ND9	7972.8	710.6	54.4	98.9	0	7167.8	555.8	142.0
3	ND17	2063.3	449.0.2	124.0.6	285.4	1.	3780.2	116.0.3	680.4
4	ND17-1	2494.2	376.8.7	823.4	203.1	2.	4229.2.3	137.2	146.4
5	ND17-3	4655.3	688.4	77.0	3.3	0	4234.6	469.9	101.8
6	ND23	4791.3	637.4	38.0	70.5	0.	3654.3	724.4	118.0
7	ND26	7203.9	483.1	33.7	7.4	0	1198.4.2	0	990
8	ND105	4807.5	225.9	39.1	110.7	0	4528.2	353.8	320
9	ND38P1	1007.7	267.8	2.9	11.9	0.	1200.4	108.8	453
1	ND38P64	3887.7.0	817.1.1	248.1.8	3492.1	0	7848.3.2	113.8	560

The measured results in Table 2 were processed to calculate the total alkali content, total hardness and salinity of the water sample, and the type of the water sample was determined.

Table 3 Analysis of some water samples in Jidong Oilfield

No.	Name	Total base quantity (mg/L)	Total hardness (mg/L)	Salinity (mg/L)	Water type
1	ND8	336	352.1	12024.2	NaHCO ₃
2	ND9	1420	765	17980.3	NaHCO ₃
3	ND17	680	5730.8	65246.1	CaCl ₂
4	ND17-1	1464	4592.1	73633.7	CaCl ₂
5	ND17-3	1018	765.4	11146.5	Na ₂ SO ₄
6	ND23	1180	675.4	11096.0	NaHCO ₃
7	ND26	990	516.8	20702.3	CaCl ₂
8	ND105	320	265.0	10385.2	Na ₂ SO ₄
9	ND38P1	453	270.7	3053.2	CaCl ₂
10	ND38P64	560	10652.9	132178.8	CaCl ₂

It can be seen from Table 3 that the salinity, hardness and chloride ion content of produced water samples in Jidong Oilfield vary greatly, with the salinity span ranging from thousands to tens of thousands, and the salinity and chloride ions have a great influence on the corrosion rate. Therefore, ND38P1, ND17-3, ND17-1 and ND9 were selected to study the corrosion of steel sheet under different salinity conditions.

3.2 Evaluation of corrosion inhibition of triazine

The corrosion inhibition performance of triazine in ancient water quality was evaluated by weight loss method. The results are shown in Table 4. As seen, the uniform corrosion rate decreases with the increase of inhibitor concentration. When the concentration of inhibitor is 2%, the uniform corrosion rate is the lowest 0.0240 g·cm⁻²·h⁻¹. The inhibition efficiency increases to 84.7953%, which has an excellent corrosion inhibition effect on steel sheet.

Table 4 Evaluation of corrosion inhibition of triazine

No.	Inhibitor concentration(%)	W_{corr} (g·cm ⁻² ·h ⁻¹)	E_w %
1002	0.0	0.1751	/
1003		0.1789	/
1092	0.1	0.0467	72.92
1093		0.0470	75.00
1097	0.2	0.0432	75.00
1098		0.0434	77.08
1105	0.5	0.0414	76.04
1106		0.0387	78.12
1111	1.0	0.0340	80.21
1112		0.0311	82.29
1114		0.0269	82.46
1115		0.0240	84.80

It can be seen from Fig. 2 that the corrosion inhibition effect on the steel sheet is the best when the corrosion inhibitor concentration is 2.0% at 343K. The surface of the steel sheet is attached with reddish brown corrosion products, indicating the presence of Fe₃O₄. Black corrosion products are also attached to the surface of the steel sheet, and the specific phase composition needs to be further analyzed by XRD. When the concentration of corrosion inhibitor reached more than 0.5%, spot corrosion was observed, mainly because of the uneven adsorption of corrosion inhibitor, a small anode/large cathode activation - passivation battery system is formed [19,20].

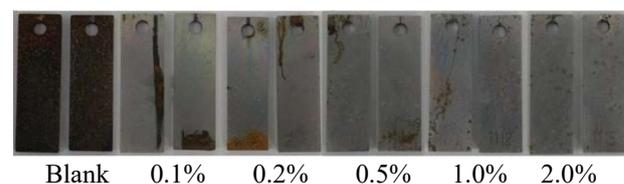


Fig. 2 Comparison of corrosion inhibition effect of different concentrations of triazine

3.3 Effect of temperature on corrosion inhibition of triazine

The value of uniform corrosion rate (W_{corr}) and inhibition efficiency (E_w %) were summarized from the weight loss measurements with and without the addition of various concentration of triazine in ancient water at 323K, 333K, 343K and 353K, respectively. The results were shown in the tables below.

Table 5 Corrosion inhibition evaluation of triazine at 323K

No.	Inhibitor concentration(%)	W_{corr} ($\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	$E_w\%$
1126	0.0	0.0840	/
1127		0.0850	
1213	0.1	0.0144	82.42
1214		0.0109	86.81
1215	0.2	0.0111	86.81
1216		0.0146	82.42
1217	0.5	0.0091	89.01
1218		0.0129	84.62
1219	1.0	0.0109	86.81
1220		0.0129	84.62

Table 6 Corrosion inhibition evaluation of triazine at 333K

No.	Inhibitor concentration(%)	W_{corr} ($\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	$E_w\%$
1181	0.0	0.1309	/
1182		0.1397	
1123	0.1	0.0294	78.38
1124		0.0256	81.08
1125	0.2	0.0217	83.78
1126		0.0255	81.08
1127	0.5	0.0239	82.43
1128		0.0201	85.14
1129	1.0	0.0218	83.78
1130		0.0220	83.78

Table 7 Corrosion inhibition evaluation of triazine at 343K

No.	Inhibitor concentration(%)	W_{corr} ($\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	$E_w\%$
1002	0.0	0.1751	/
1003		0.1789	
1092	0.1	0.0467	72.92
1093		0.0470	75.00
1097	0.2	0.0432	75.00
1098		0.0434	77.08
1105	0.5	0.0414	76.04
1106		0.0387	78.12
1111	1.0	0.0340	80.21
1112		0.0311	82.29

Table 8 Corrosion inhibition evaluation of triazine at 353K

No.	Inhibitor concentration(%)	W_{corr} ($\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	$E_w\%$
1101	0.0	0.2223	/
1102		0.2259	
1103	0.1	0.1198	46.28
1104		0.1145	47.93
1105	0.2	0.0920	58.68
1106		0.0884	60.33
1107	0.5	0.0747	66.12
1108		0.0724	67.77
1109	1.0	0.0624	71.90
1110		0.0575	73.55

The effect of temperature on the inhibition efficiency of triazine was studied in the temperature range from 323 to 353 K. As seen in Table 6 and 7, the corrosion rate in the brine environment is low under the conditions of 323K and 333K, and the addition of 0.1% triazine can achieve a good corrosion inhibition effect. As the concentration of corrosion inhibitor continues to increase, the corrosion inhibition rate increases in a gentle trend. However, under the temperature of 343K and 353K, the corrosion rate was relatively high while inhibition efficiency was low. And the inhibition efficiency increased slowly as the concentration of triazine increased. Therefore, under the simulated water environment of this brine, the corrosion inhibition requirement could be met by adding 0.1% corrosion inhibitor at low temperature, while the corrosion inhibition rate could reach 82.29% only when the concentration of triazine was 1.0% at high temperature.

3.4 Effects of ions in produced water on corrosion inhibition performance

The water samples were chosen as ND38P1, ND17-3, ND17-1 and ND9 by weight loss method to study the corrosion of steel sheet under different salinity conditions at 323K.

Table 9 Evaluation of corrosion inhibition of triazine in different typical water samples

Name	No.	Inhibitor concentration(%)	W_{corr} ($\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	$E_w\%$
ND38P1	14	0	0.1976	/
	1003		0.2202	
	1075	2.0	0.0152	92.89
	1076		0.0114	94.67
ND17-3	1078	0	0.2336	/
	1079		0.2183	
	15	2.0	0.0501	95.59
	1093		0.0420	96.70
ND17-1	16	0	0.1343	/
	1117		0.1535	
	17	2.0	0.0072	94.94
	1121		0.0036	97.47
ND9	18	0	0.1635	/
	1123		0.1511	
	1124	2.0	0.0223	86.05
	1125		0.0205	87.21

It can be seen from Table 9 that the corrosion rate of steel sheet is different in different water quality environments. After comparison in the same environment, it is found that the corrosion rate of steel sheet is lower in water quality of CaCl_2 and NaHCO_3 than in water quality of NaSO_4 . The water quality is less than 75000mgL^{-1} , and the corrosion inhibitor can have better corrosion inhibition effect. The inhibition efficiency is all above 85%, which can be applied to the water quality system of oil field to delay the corrosion of steel pipe.

4 Conclusion

The corrosion inhibition effect of triazine on steel sheet was efficient. The inhibition effect was the best when the concentration was 2.0%, and the inhibition efficiency was up to 84.80%. The corrosion rate decreased with the increase of inhibitor concentration and the inhibition efficiency increased with the increase of inhibitor concentration. Some produced water samples in Jidong Oilfield have high salinity and high hardness, which is easy to cause steel pipe scaling and aggravating corrosion. The results showed that when the salinity reached tens of thousands, the corrosion rate increased significantly, and the appropriate addition of triazine corrosion inhibitor had obvious corrosion inhibition effect, with the inhibition efficiency above 85%.

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