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Optimization of Functional Compositions in Spreading Inhibition

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The concentration ratio between a selected spreading agent and a selected corrosion inhibitor was optimized to effectively mitigate bottom-of-the-line (BOL) and top-of-the-line (TOL) corrosion under sour gas and aerated conditions. This was performed with electrochemical polarization measurements, electrochemical noise diagnosis and mass loss measurements at low alloy steels in oil field formation brine (i) saturated with 1 bar H_2S, (ii) exposed to air and (iii) de-aerated with hydrazine dihydrochloride ($N_2H_4{\cdot}2HCl$) and in the presence of N_2 atmosphere above solution. It appeared that the functional system worked well in sour environment at an optimized concentration ratio, however, could not prevent pitting in the air-saturated medium. A new functional system has to be developed for such conditions.

Key Words: Spreading inhibition, Low alloy steel, Electrochemical polarization, Electrochemical noise, Pipeline corrosion.

INTRODUCTION

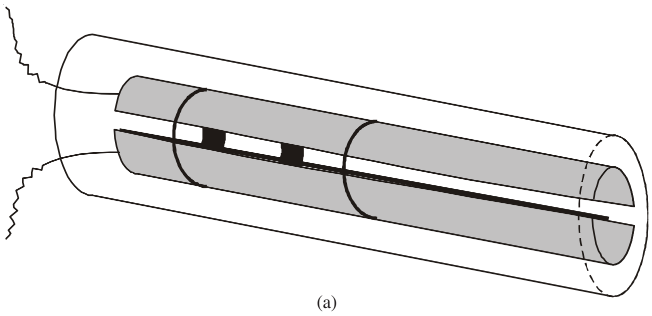
Inhibition of top-of-the-line (TOL) corrosion in wet natural gas pipelines is difficult to achieve under stagnant or stratified flow conditions.

A new method to bring corrosion inhibitors from the bottom-of-the-line (BOL) up to the top-of-the-line even under such difficult conditions has been introduced based on the principle of spreading inhibition[1,2]. A spreading agent (a specially selected surfactant compound) is added to the pipeline liquid at the bottom-of-the-line together with a corrosion inhibitor. If the spreading agent and the corrosion inhibitor[3-5] have been selected well with respect to chemical structure and concentration ratio, then the spreading agent causes a liquid film to climb up the pipe wall against the gravity up to the top-of-the-line. The spreading film contains the corrosion inhibitor compound(s) and by spreading, transports it to the top-of-the-line[1,2]. To reach a sufficiently high inhibitor concentration at the top-of-the-line even under condensation conditions, it is crucial to select the right combination of spreading agent and corrosion inhibitor and to use it at optimized concentration ratios. Not all the inhibitors can be transported with every spreading agent at all concentration ratios. This paper reports on studies on the influence of mixtures of inhibitor and spreading agent on the efficiency of corrosion protection.

EXPERIMENTAL

Potentiodynamic polarization and electrochemical noise (ECN) measurements were performed with carbon steel electrodes in sour gas environments. Mass loss experiments with carbon steel coupons were carried out in aerated and de-aerated natural brine solutions. All experiments were performed at room temperature under stagnant conditions in order to simulate stagnant or laminar flow conditions encountered in pipelines where the presence of condensate, H_2S and temperature gradients can cause very corrosive environments favouring pitting and hydrogen embrittlement in the top-of-the-line parts of a pipeline[6-8].

Low alloy steel coupons (Table-1) were pre-coated with electrophoretic coating to avoid influence of crevice corrosion in electrochemical measurements. For the potentiodynamic and ECN measurements the specimens (a steel rod and two half cylindrical steel rods) were then fixed inside a glass tube with epoxy resin as shown in Fig. 1. The mass loss experiments were performed with coupons of the low alloy steel 2 (Table-1).

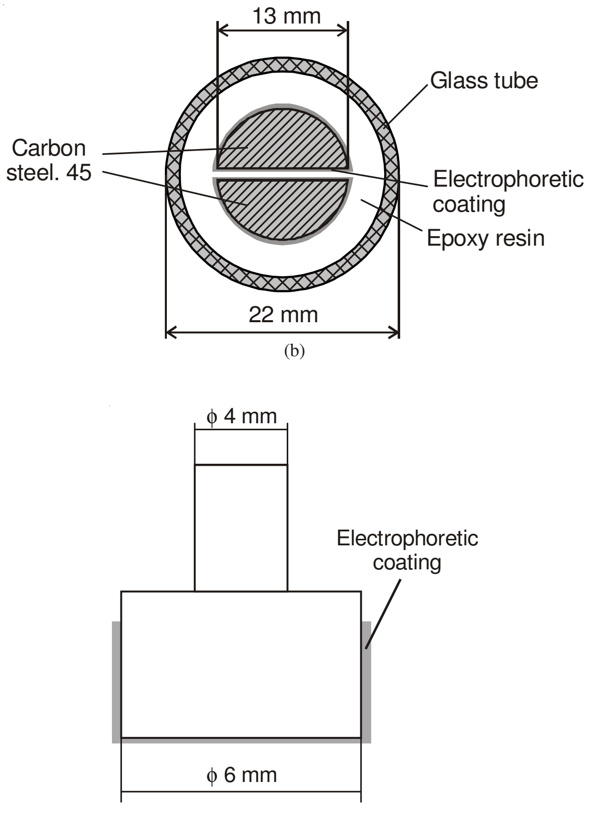


(a)

TABLE-1
COMPOSITION OF LOW ALLOY CARBON STEELS TESTED

Element [mass %]	C	Si	S	P	Mn	Ni	Cr	Mo	Ti	Cu	W	Al
Low alloy steel 1	0.49	0.30	0.035	0.020	0.69	0.10	0.14	0.02	0.002	0.28	0.001	–
Low alloy steel 2	0.25	0.17	0.043	0.021	0.60	0.60	0.05	0.07	0.03	0.12	0.05	0.17

Pre-treatment of the working electrode surfaces included.



(b)

(c)

Fig. 1. Scheme of electrochemical noise sample (a) and the cross-section (b). The scheme of potentiodynamic coupons (c)

TABLE-2
EXPERIMENTAL MATRIX FOR ELECTROCHEMICAL SCREENING MEASUREMENTS*

Test No.	Surfactant concentration (g/L)		Inhibitor concentration (mg/L)					
	0.5	1.0	250	375	500	750	1000	1250
1	–	–	–	–	–	–	–	–
2	–	+	–	–	–	–	–	–
3	+	–	+	–	–	–	–	–
4	+	–	–	+	–	–	–	–
5	+	–	–	–	+	–	–	–
6	–	+	+	–	–	–	–	–
7	–	+	–	–	+	–	–	–
8	–	+	–	–	–	+	–	–
9	–	+	–	–	–	–	+	–
10	–	+	–	–	–	–	–	+

*Stock solution: 0.1 M NaCl.

TABLE-3
COMPOSITION OF OILFIELD BRINE (FORMATION WATER)

pH	Fe^{++} (mg/L)	(H_2S) as total S (mg/L)	Chloride (mg/L)	Alkalinity (mg/L)
6.5-7.4	0.18	200	88.7	3.8

Wet grinding subsequently with 120, 240, 320, 600, 1000 grade emery paper. Rinsing with distilled water. Drying with warm pressurized air. Degreasing subsequently with petrol-ether, acetone and methanol. Rinsing with distilled water and drying with warm oil-free pressurized air.

After each electrochemical measurement the working electrode was treated with a solution of HCl (1:1) + 2 g/L hexamethylenediamine (urotropine).

Media: The electrochemical measurements were performed in 0.1 M NaCl with addition of a selected surfactant compound and a selected commercial inhibitor generally used in sour environments.

The experimental matrix with the variation of inhibitor/surfactant concentrations and ratios is given in Table-2. All test solutions were first de-aerated with N_2 for 0.5 h and then saturated for 0.5 h at room temperature with H_2S at 1 bar.

Mass loss experiments were performed in natural oil field brine (formation water, Table-3) obtained from the crude oil reservoir in Ballshi town, Albania. The exposure occurred either in open glass ware with access of air or in closed vessels under de-aerated conditions with add of hydrazine dihydrochloride ($N_2H_4{\cdot}2HCl$) and in a atmosphere of purified nitrogen above solution. The nitrogen gas was first purified with pyrogalol. To make sure that the test solutions were completely deoxygenated, hydrazine was added to the test solutions. The addition hydrazine caused a pH drop from 7.35-7.05.

Electrochemical measurements: Potentiodynamic measurements were carried out in a typical three-electrode electrochemical cell with a saturated calomel electrode *via* a Haber-Luggin capillary as reference electrode and a platinum electrode as counter (auxiliary) electrode. The measurements were performed with a type PJT 24-1 potentiostat with a potential scanning device. The potential scan rate was 900 mV/h. The cathodic potential scan range was 500 and 100-200 mV for the anodic side, according to a predetermined triangular program E0-E1-E0. Before the potential scanning the rest potential was measured for at least 0.5 h. The maximum current density (i_{max}) was 1 mA/cm^2 both in the anodic and cathodic range.

Electrochemical noise measurements have been performed because of its advantage to provide information on the activity of the corrosion processes in real time without disturbing the corrosion system. The electrochemical noise method is based on the measurement of potential and/or current fluctuations between two freely corroding electrodes immersed in the corroding medium. The properties of the pair of electrodes can be "identical" or different with respect to type of metal, surface size and/or surface quality. It only depends on the evaluation algorithm of the noise data. In present investigation the recently developed CoulCount method has been used which offers a user friendly tool for current noise data evaluation[1,2,9-11]. Basically, the software converts current noise data into lines with always positive slope. The slope correlates with the intensity of corrosion activities on the electrode surfaces. Details of the data evaluation algorithm can be found in work of Schmitt *et al.*[11,12]. The authors used the CoulCount software for the ECN experiments reported in this paper.

Evaluation of experiments: The samples were visually and microscopically (metallographic microscope NEOPHOT 21) inspected after the test runs. Corrosion current densities in [µA/cm^2] and respective corrosion rates in [mm/y] were calculated using the Tafel extrapolation of the potentiodynamic polarization curves and Faradays law (equ. 1):

$$v_{corr} = \frac{KMi}{n\rho} \qquad (1)$$

where M= the atomic weight of the metal [g-atom], i = current density in [µA/cm^2], n = number of electrons exchanged during metal dissolution, ρ = density in [g/cm^3] and K = a constant which equals to 0.00327 if v_{corr} is needed in [mm/y][4].

RESULTS AND DISCUSSION

Potentiodynamic polarization: Potentiodynamic polarization curves and the corresponding average Tafel extrapolations are given in Figs. 2-4 for the solutions with optimum surfactant/inhibitor ratio (0.5 g/L surfactant + 375 ppm inhibitor and 1.0 g/L surfactant + 750 ppm inhibitor) and for the additive-free solution. The above given additive concentrations yielded the lowest corrosion rates and the highest inhibitor efficiencies (Table-4). This was also confirmed by visual and microscopic inspection of the electrode surfaces after the experiments (Fig. 5).

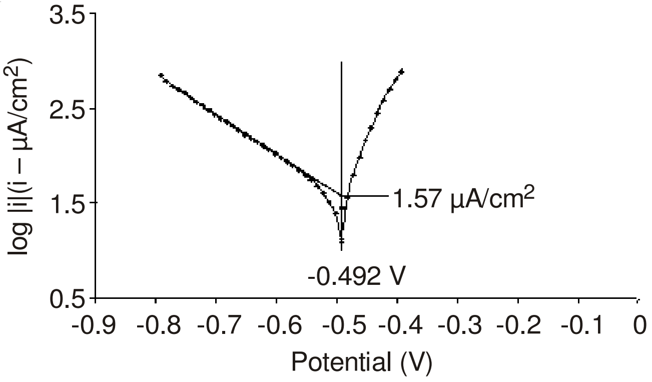


Fig. 2. Potentiodynamic curves and average Tafel extrapolation for low alloy steel 1 in de-aerated 0.1 M NaCl saturated with H_2S; no additives

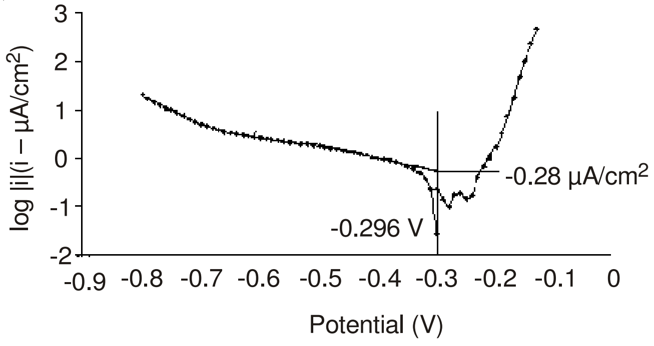


Fig. 3. Potentiodynamic curves and Tafel extrapolation for low alloy steel 1 in de-aerated 0.1 M NaCl saturated with H_2S; 0.5 g/L surfactant + 375 ppm inhibitor

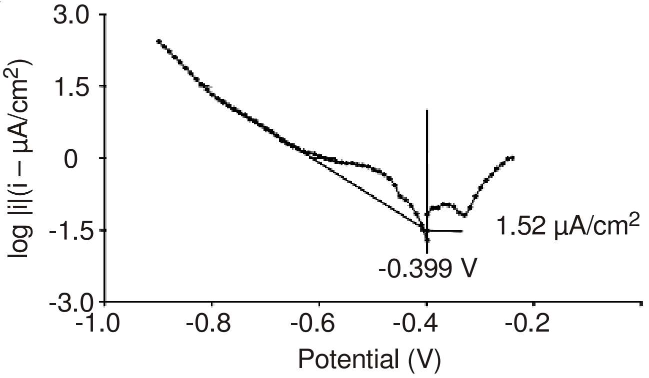


Fig. 4. Potentiodynamic curves and average Tafel extrapolation for low alloy steel 1 in de-aerated 0.1 MNaCl saturated with H_2S; 1.0 g/L surfactant + 750 ppm inhibitor

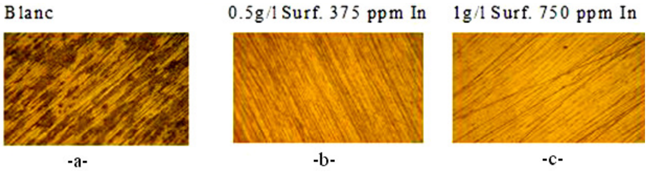


Fig. 5. Surface views of working electrode surfaces after poentiodynamic measurement (× 250), (a) sample in blank solution, (b) protected sample in presence of 0.5 g/L surfact. -375 g/L inhibitor, (c) protected sample in presence of 1 g/L surfact. -750 g/L inhibitor

Electrochemical noise measurements: The time-related total amount of noise charges exchanged between freely corroding steel sensor electrodes in different environments (solutions No. 1-10 in Table-2) are plotted in Fig. 6. The evaluations of these electrochemical noise data are in good agreement with the polarization data (Table-4, Fig. 7). The optimum of additive ratios could be already deduced from the slopes of the noise charge *vs*. time curves. The results given in Table-4 are average values from two parallel measurements with each surfactant/inhibitor ratio.

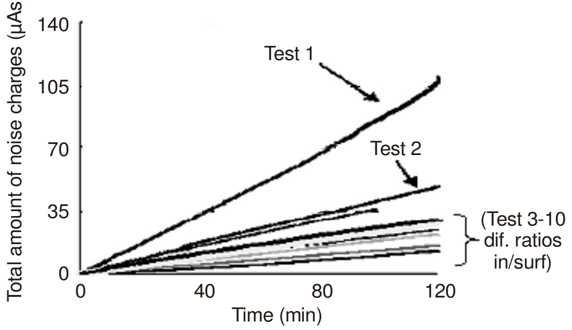


Fig. 6. Total amount of noise charge *vs*. time for low alloy steel 1 in H_2S saturated 0.1 M NaCl with different additive ratios. (Test 1: blank solution; test 2: 1 g/L surfactant; tests 3-10: different concentration and ratios surfactant/inhibitor (Table-2)

Mass loss measurements: Mass loss measurements were performed with low alloy steel 2 (composition Table-1) in natural brine solution containing H_2S (formation water) both in open vessels with access of air to the test solution and in closed vessels under de-aerated conditions with add of hydrazine dihydrochloride and in a atmosphere of purified nitrogen above solution. The effect of different surfactant/inhibitor ratios was tested to find out, if this additive mixture in the given concen-

TABLE-4
COMPARISON OF RESULTS FROM ELECTROCHEMICAL NOISE AND POTENTIODYNAMIC POLARIZATION MEASUREMENTS

Test No.	ECN measurements (average values)		Potentiodynamic polarisation data (average values)		
	Slope (tgα)	In. eff. (%)*	(i)** (μA/cm^2)	$V_{corr.}$*** (mm/y)	In. eff. (%)
1	0.876	0	38.20	0.440	0
2	0.404	53.9	7.40	0.086	80.6
3	0.238	72.3	3.30	0.038	91.4
4	0.128	85.4	0.52	0.006	98.6
5	0.235	73.2	0.78	0.009	98.0
6	0.354	59.6	1.20	0.014	96.8
7	0.179	79.6	0.43	0.005	98.9
8	0.106	98.9	0.03	0.004	99.9
9	0.202	76.9	0.40	0.005	98.9
10	0.243	72.3	0.72	0.008	98.2

*Inhibitor efficiency, **Current density, ***Corrosion rate.

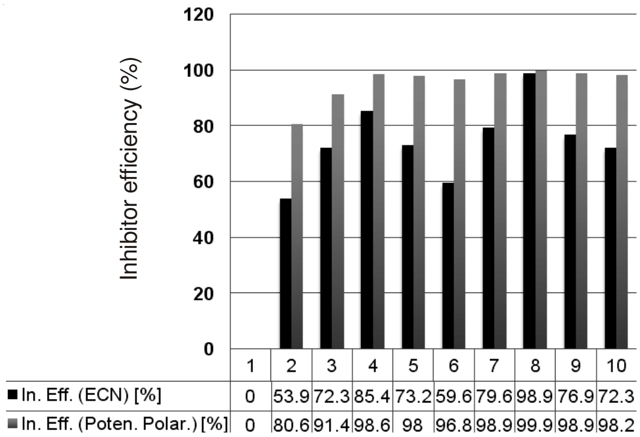


Fig. 7. Comparison of protection efficiencies obtained for the solutions 1-10 (Table-2) from potentiodynamic polarization and electrochemical noise measurements

tration ratios would be effective also in presence of dissolved oxygen.

In one set of experiments two parallel coupons of steel 2 (0.3 × 2.8 × 5.6) cm were immersed for 312 h in open vessels filled with formation water which contained surfactant/inhibitor mixtures in different concentration ratios. Another set of experiments included 11 days coupon exposure in closed vessels under de-aerated conditions. In each case, the corroded samples were inspected microscopically (× 160) with and without corrosion products. The corrosion rates measured in both sets of experiments are summarized in Table-5. It appeared that severe pitting was observed in all additive-containing experiments while no pitting was observed under de-aerated conditions.

In aerated conditions it appeared that severe pitting was observed in all additive-containing experiments. In case of air contact to the H_2S-containing natural oilfield water, formation of elemental sulphur was observed, which cause the increase of the medium corrosivity so decreasing the additive package inhibition efficiency. For such conditions more effective additive packages should developed.

The influence of additives under de-aerated conditions was observed reduce of the pitting. No pitting was observed in the case of the following combinations: 0.5 g/L surfactant: 375 mg/L commercial inhibitor, 1 g/L surfactant: 750 mg/L commercial inhibitor. Under de-aerated conditions, the cathodic reaction is driven only by the hydrogen sulphide naturally dissolved in the delivered formation brine. Due to the limited amount of H_2S present in the constant containment the corrosion rate was not very high in the additive-free system. Nevertheless, the additive package proved to reduce the corrosion attack and to develop inhibitive efficiency.

Results of both types of experiments under aerated and de-aerated conditions are visualized in Fig. 8 for the different media A, B, C, D, F, G (Table-5).

Conclusion

Optimization of a spreading inhibition system for mitigating of top-of-the-line corrosion of carbon steel in wet sour gas pipelines was performed using potentiodynamic polarization measurements and a newly developed electrochemical noise diagnosis method called CoulCount. The spreading system consisted of a mixture of a selected surfactant and a selected corrosion inhibitor. Both electrochemical methods selected the same concentration ratios for the compounds of the spreading system 0.5 g/L surfactant/375 ppm commercial sour gas inhibitor. Efficiencies of 98.6 % (potentiodynamic polarization) and 85.4 % (ECN diagnosis), respectively, were found for the above combination of surfactant and inhibitor.

TABLE-5
EFFECT OF SURFACTANT/INHIBITOR MIXTURES ON CORROSION OF CARBON STEEL
2 IN DE-AERATED AND AERATED FORMATION WATER AT ROOM TEMPERATURE

Medium	Additives		De-aerated solution		Aerated solution	
	Surfactant (g/L)	Inhibitor (mg/L)	$v_{corr.}$ (mm/y)	In. eff. (%)	$v_{corr.}$ (mm/y)	In. eff. (%)
A	0	0	0.054	0	0.098	0
B	1	0	0.009	82.9	0.057	41.8
C	1	250	0.007	87.0	0.083	15.3
D	1	500	0.006	88.5	0.082	16.3
E	1	750	0.005	90.7	0.074	24.5
F	1	1000	0.007	86.5	0.072	26.5

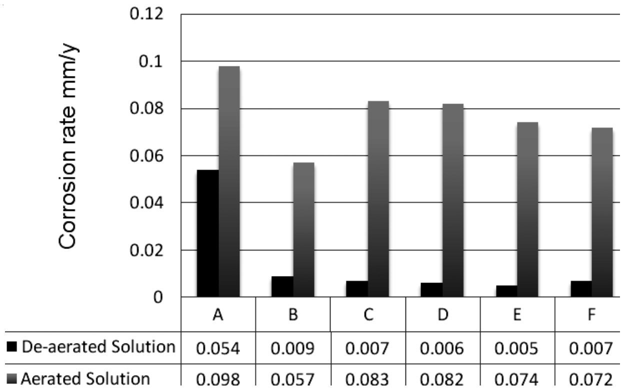


Fig. 8. Comparison of corrosion rates of carbon steel 2 (Table-1) in aerated and de-aerated oilfield formation water at room temperature in the absence and presence of additives (composition of media A-F: Table-5)

The corrosion rates went down to 7 µm/a for this combination (0.5 g/L surfactant/375 ppm inhibitor).

With a combination of 1 g/L surfactant and 750 ppm inhibitor the inhibitor efficiency could be increase to 99.9 % (potentiodynamic polarization) and 87.9 % (ECN diagnosis), respectively, with corrosion rates below 1 µm/year.

Mass loss measurements with carbon steel in H_2S-containing oilfield formation brine revealed that the inhibitor package is effective if oxygen is excluded from the system and the dissolved H_2S is the only cathodically active component. Access of air produced elemental sulphur which increased the corrosivity of the system considerably in form of deep and shallow pitting and impaired the inhibitive efficiency of the additive package. For such conditions more effective additive packages with any kind of the oxygen removers has to be developed.

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