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The Application of Electrochemical Impedance Spectroscopy (EIS) in Studying the Synergistic Behavior of Oilfield Chemicals for a Tubular Alloy under down hole Conditions in a Kuwait Formation Water

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ABSTRACT

A bubble cell test was used with an electrochemical impedance spectroscopy (EIS) system to study the synergistic effects of scale and biocide inhibitors on the performance of a corrosion inhibitor for L-80 tubular steel under simulated down hole conditions in one of Kuwait oil fields formation water. The EIS scan range of the frequency for the impedance tests was fixed between 0.1 to 20,000 Hz for all conditions and measurements were carried out at open circuit potential. The EIS results are in the form of Nyquest plots which indicated that all chemicals and their combinations show reduction of corrosion rate of L-80 in a simulated down hole condition. The levels of reduction vary for the chemicals and their combinations indicating different metal surface interaction mechanisms. The synergism between 250 ppm of biocide and 5 ppm corrosion inhibitor in the formation water exhibited the best protection of L-80 against corrosion.

Keywords: Nyquest plots, formation water, tubular alloys, inhibitors.

INTRODUCTION

The application of electrochemical impedance spectroscopy (EIS) as a tool in corrosion research has resulted in a wealth of information concerning methods of corrosion protection which were difficult to study with traditional direct current (DC) techniques. This includes corrosion protection by corrosion inhibitor which takes into account the in-homogeneities of most real surfaces.

Evaluation of corrosion inhibitors for tubular steels such as L-80 is of practical importance due to the large scale use of these alloys in oil production industries. One important application area is the protection of these alloys during the production of oil from oil producing wells [1]. The ability to quickly screen and evaluate inhibitors for this type of application is important in order to choose an effective inhibitor in a short period of time.

Several investigators [2-18] have demonstrated that the EIS technique can be applied successfully to elucidate the behavior of corrosion inhibitors in acid solutions and in near neutral pH aqueous solutions. In the evaluation of steel in an inhibited waste stream, the EIS was shown to be a very powerful tool for predicting corrosion in the absence of a definitive understanding of the corrosion mechanism [5].

In this research work, AC impedance tests in a bubble cell were carried out for three chemicals (scale inhibitor, corrosion inhibitor and a biocide) to study the individual and interactive effects from the chemicals for L-80 alloy steel under simulated downhole conditions of one of the Kuwaiti oilfields. Using the AC impedance technique, the material loss under different conditions was calculated using electrochemical laws.

EXPERIMENTAL PROCEDURE

BUBBLE CELL

The conditions for the tests were as specified at the start of the study as described below:
The water composition was prepared according to specification provided by Kuwait Oil Company (KOC) as shown in Table 1. The testing conditions are as follows:
Temperature: 60^oC
CO_2: Saturated, bubbled throughout the tests
Test duration: 2 hours
Number of Replicate Tests: 3
Surface finish: 400 grit
Material: L-80 Steel

Electrochemical Parameters

The scan range of the frequency for the AC impedance tests was fixed (20,000 – 0.1 Hz) for all the conditions. The EIS measurements were conducted using an ACM Gill-8 system, and impedance experiments were performed at above mentioned frequency range. The excitation amplitude for these experiments was 5 mV. Nyquest plots were obtained for uninhibited and inhibited brine solutions under down-hole conditions. Tests were conducted in an oxygen-free environment. Only CO_2 gas was used in the experiments.

Rod shaped coupons (38 mm length x 6 mm diameter) of carbon steel were used in this study. The surface of each coupon was first cleaned with 5% HCl to remove mill scale (rust), mechanically polished to 1200 silicon carbide paper and finally degreased in acetone and dried with hot air. The measurements were carried out at the open circuit potential.

Chemical Dosage

To study the synergism of the chemicals, AC impedance measurements were carried under various conditions with different concentrations of the chemicals as shown in Table 2 according to the requirement. The samples were immersed in the test solutions for two hours before the tests carried out. Eight conditions were assessed in total.

Table 1: Formation Water Composition

	Units	Formation Water
Sodium	mg/l	51343
Calcium	mg/l	10232
Magnesium	mg/l	2361
Potassium	mg/l	2264
Strontium	mg/l	281
Barium	mg/l	2.4
Iron	mg/l	46.9
Lithium	mg/l	3.1
Silocon	mg/l	0.8
Boron	mg/l	19.0
Chloride	mg/l	104534
Bicarbonate	mg/l	299
Sulfate	mg/l	25
Fluoride	mg/l	4
Carbonate	mg/l	<0.1
Hydroxyl	mg/l	<0.1
Phosphate	mg/l	1.15
(NO_2 + NO_3)	mg/l	0.2
NH_3^-N	mg/l	52.5
TDS calculated	gm/l	171
Density @25^oC	gm/cm^3	1.108

Table 2: The concentration of corrosion inhibitor, scale inhibitor, and biocide used with the formation water

Test No.	Corrosion inhibitor (ppm)	Scale inhibitor (ppm)	Biocide (ppm)
1	0	0	0
2	5	0	0
3	0	5	0
4	0	0	250
5	5	0	250
6	5	5	0
7	0	5	250
8	5	5	250

RESULTS AND DISCUSSION

Nyquest plots for all test conditions are shown in Figures 1 (a-h). The test results are based on 3 replicates and in some cases more replicates were performed where spurious test results were obtained.

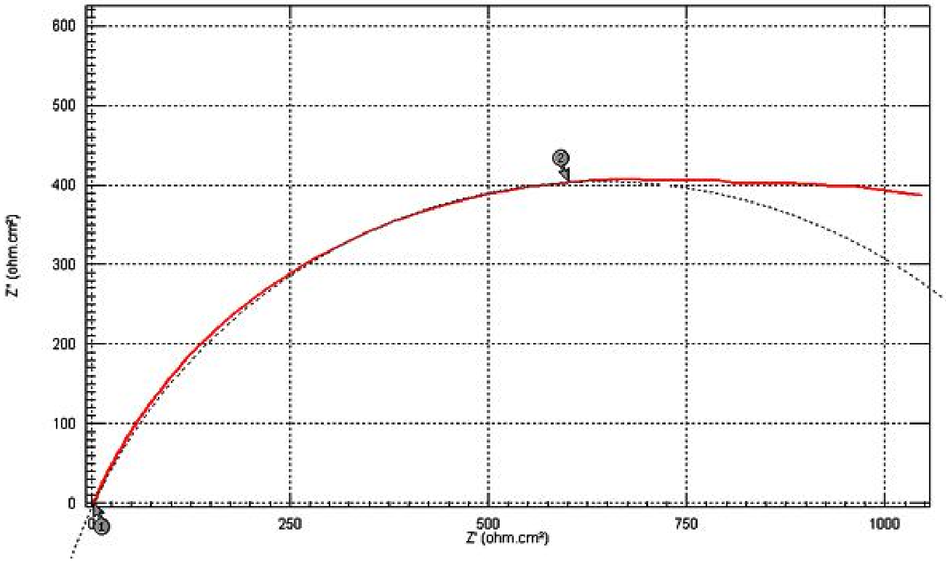

Figure 1 – a: Blank

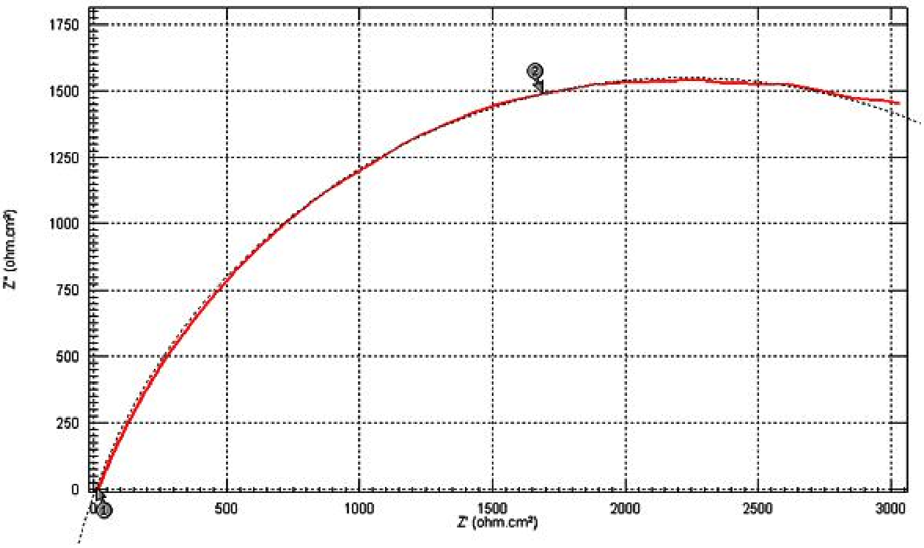

Figure 1 – b: Corrosion inhibitor 5 ppm

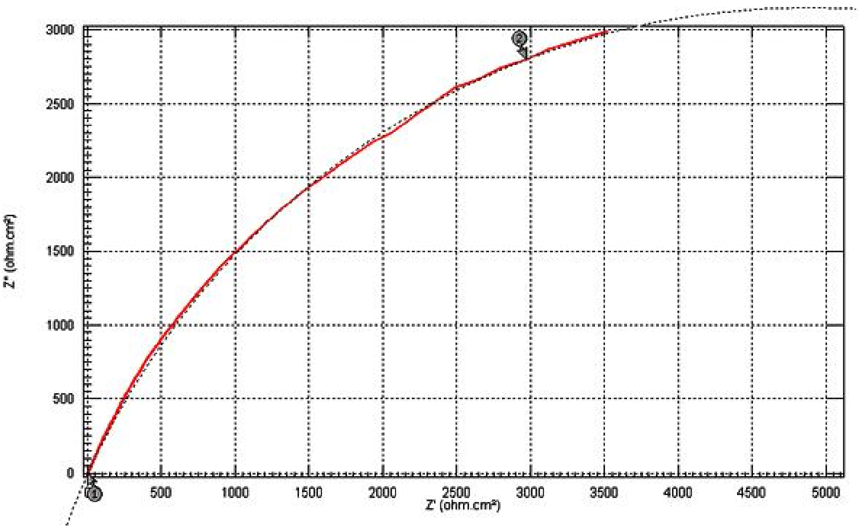

Figure 1 – c: Scale inhibitor 5 ppm

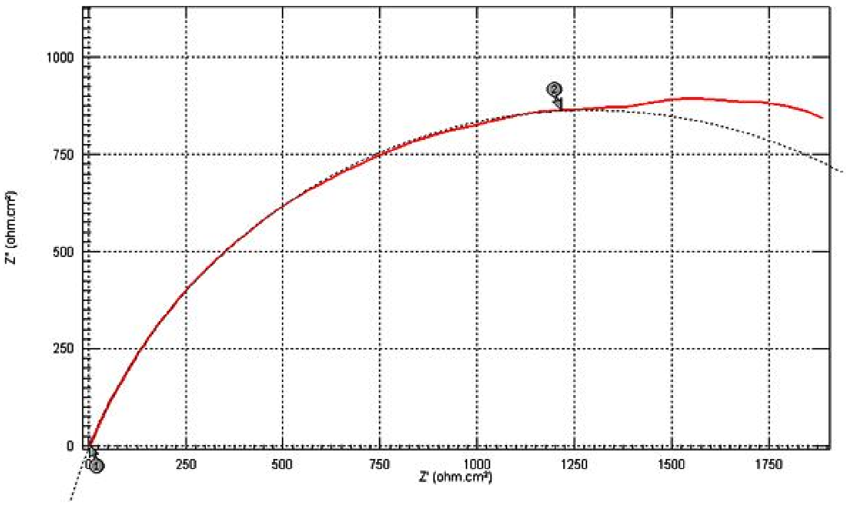

Figure 1 – d: Biocide 250 ppm

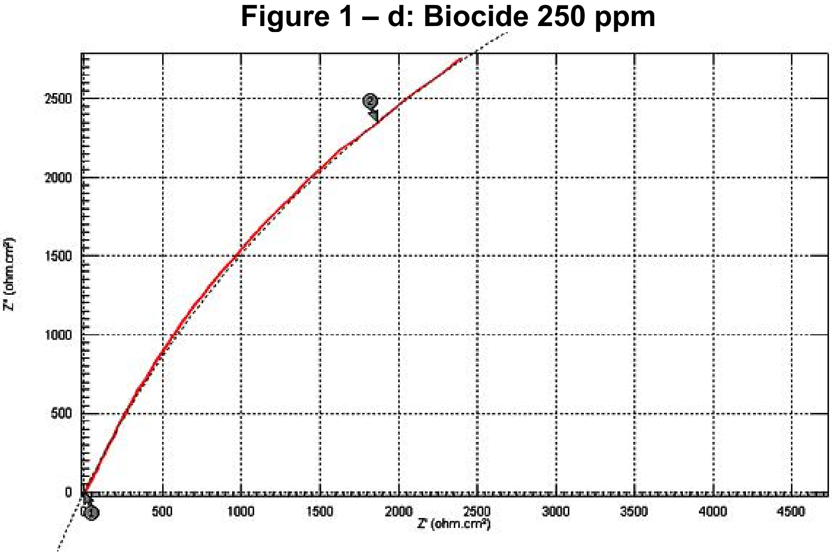

Figure 1 – e: Corrosion inhibitor 5 ppm, Biocide 250 ppm

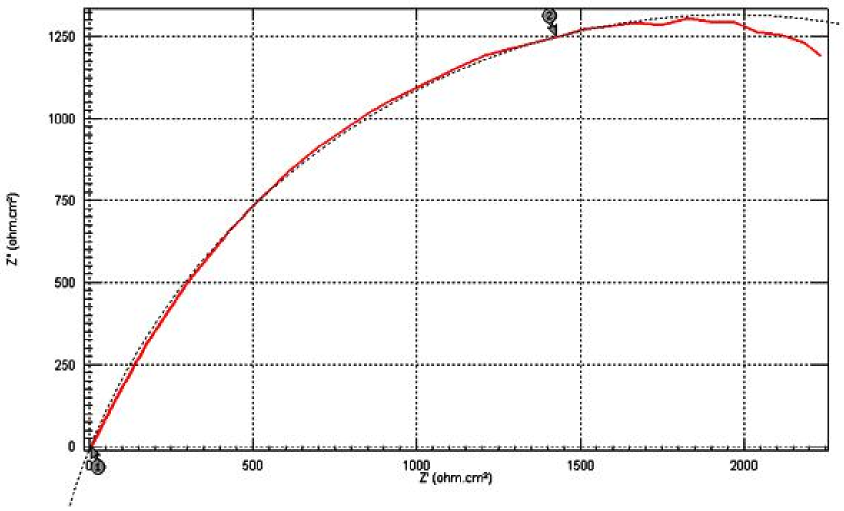

Figure 1 – f: Corrosion inhibitor 5 ppm, Scale inhibitor 5 ppm

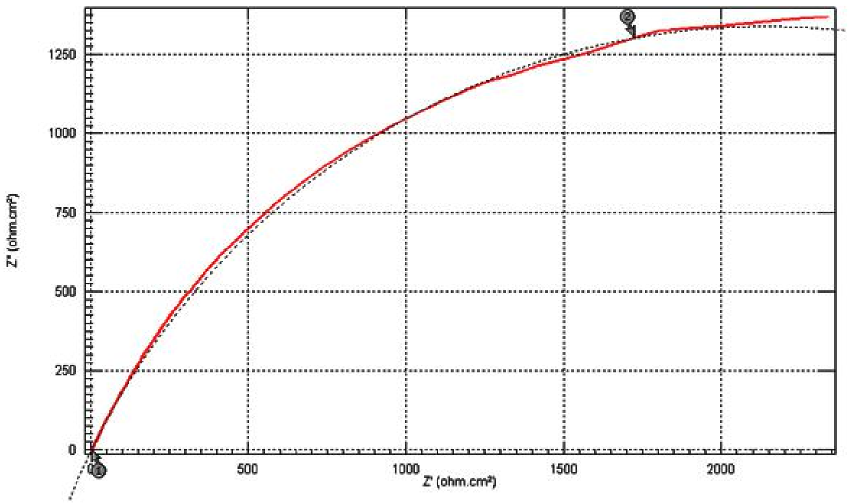

Figure 1 – g: Scale inhibitor 5 ppm, Biocide 250 ppm

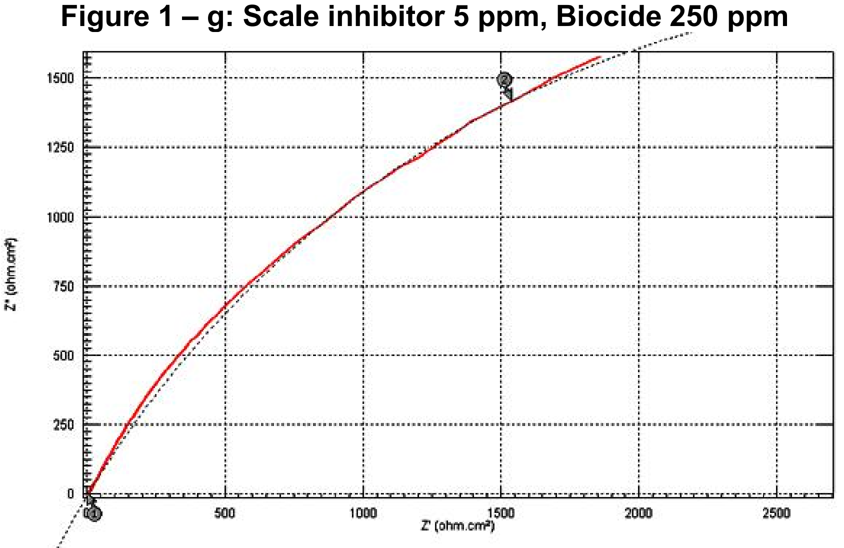

Figure 1 – h: Corrosion inhibitor 5 ppm, Scale inhibitor 5 ppm, Biocide 250 ppm

It is clear from the results that a semi-circle can be used to fit the curves in the figures suggesting that the nature of the surface layer on the pipeline material remains relatively homogeneous under all conditions. The semi-spherical curve fitting has enabled the solution resistance (R_{sol}) and charge transfer resistance (R_{ct}) to be determined. Using 120mV as the Tafel constants β_a and β_c values, the corrosion current density can be calculated and the corrosion rate in mm/year or mpy can be derived according to Faraday's Law. By plotting the data obtained from the experiments (Figure 2), the corrosion rate of L-80 steel under all conditions can be compared. It is clear that the corrosion inhibitor and biocide combination exhibits the best inhibition to corrosion for L-80 steel. The positive or negative interactions of the chemicals in terms of the effect on the corrosion rate are summarized in Table 3.

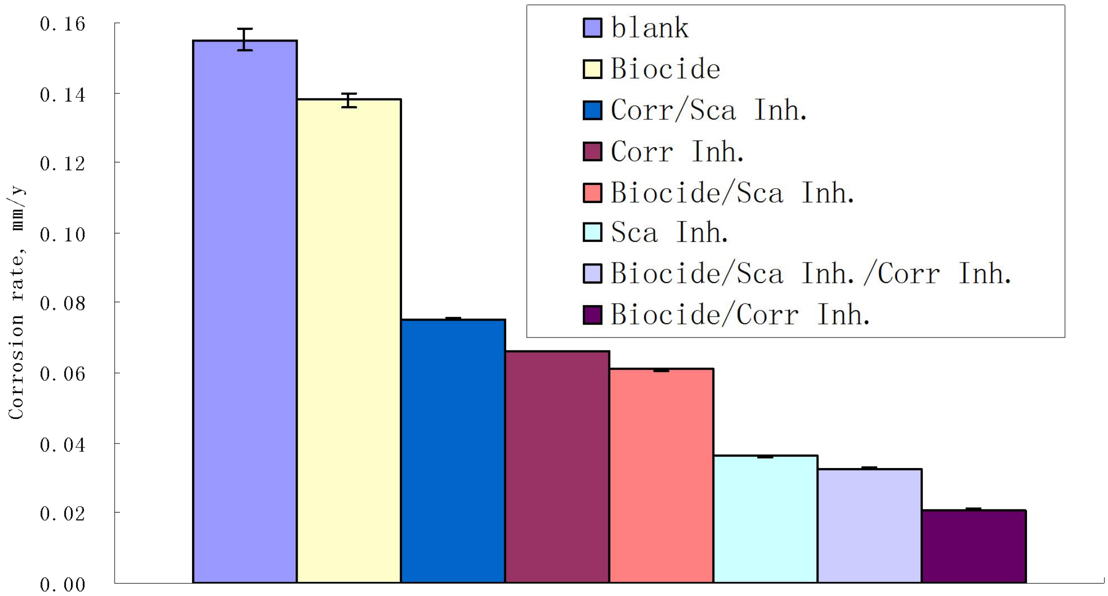

Figure 2: Corrosion rate under testing conditions in a bubble cell for L-80 steel

Table 3: Interactions of the corrosion inhibitor, scale inhibitor and biocide
positive: reduces overall corrosion rate
negative: increases overall corrosion rate

	Blank Solution		
Added Chemical	Corrosion Inhibitor	Scale Inhibitor	Biocide
Effect	positive	Positive	positive
	Corrosion Inhibitor		
Added Chemical	Scale Inhibitor	Biocide	Scale Inh./Biocide
Effect	negative	Positive	positive
	Scale Inhibitor		
Added Chemical	Corrosion Inhibitor	Biocide	Corrosion Inh./Biocide
Effect	negative	Negative	positive
	Biocide		
Added Chemical	Corrosion Inhibitor	Scale Inhibitor	Corrosion/Scale Inhibitor
Effect	positive	Positive	positive

MAIN FINDINGS AND DISCUSSIONS

1. All chemicals reduce the corrosion rate compared to the blank solution. As expected the biocide on its own has a small effect. Biocides in some instances have been shown to increase corrosion due to their oxidizing effects.

2. Scale inhibitor decreases the efficiency of the corrosion inhibitor – this has been reported previously and is expected.

3. The results indicate that biocide decreases corrosion rate of the material when combined with other chemicals which is unexpected. As, a biocide often contains compounds that usually oxidize and improves the open circuit potential of the pipeline steel. Although it could oxidize the surface to provide a more protective surface, biocide on it own is not effective. This is the most interesting synergy. One possible explanation could be that biocide could increase pH at interface and promote $CaCO_3$ and hence decrease corrosion. The understandings can be improved if the details of the chemicals can be provided.

4. Scale inhibitor on its own is effective depending on its nature. Adding corrosion inhibitor or biocide makes it less effective suggesting that the scale inhibitor is very surface active. To enable the understanding of the nature of the scale inhibitor to be improved, it is suggested to conduct tests on the change in contact angle and also to study the efficiency of the scale inhibitors as the concentration increases.

5. Tafel constants β_a and β_c values of 120mV are used in this study. However the values may vary slightly resulting in a deviation of the corrosion rate values for different conditions. Anodic polarization and Cathodic polarization measurements are suggested to be carried out to determine the Tafel constants. The corrosion rate results obtained from this study can also be confirmed by linear polarization technique.

CONCLUSIONS

1. All chemicals and their combinations show reduction of corrosion rate of L-80 in a simulated down-hole condition.

2. The levels of reduction vary for the chemicals and their combinations indicating different metal surface interaction mechanism.

3. The synergism between 250 ppm of biocide and 5 ppm corrosion inhibitor in the formation water exhibits the best protection of material from corrosion.

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