

Evaluation Efficiency of Barium Sulfate Scale Inhibitors by Electrochemical Impedance Spectroscopy

Karima Labraoui-Djallal*, Moussa Bounoughaz

Fibrous Polymers treatment and forming Laboratory, University of M'Hamed Bougara, Boumerdes, Algeria.

E-mail: karimalab@yahoo.fr and moussa_bounoughaz@yahoo.fr

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The electrochemical behaviour of carbon API 5L X70 grade steel electrode towards barium sulfate scaling and scaling inhibitors is investigated in this paper. A study of the carbon steel/injection water interface, with and without inhibitor, was carried out using electrochemical impedance spectroscopy (EIS). The scanning electron microscopy (SEM) and the X-ray diffraction study, in the absence of scale inhibitors, revealed the formation of a thick layer on the surface mainly composed of barium sulfate BaSO_4 . The barium sulfate scale is formed naturally and evolves with the immersion time. EIS spectra, in uninhibited medium, present three capacitive loop corresponding to transfer charge resistance, deposit resistance and porous resistance. The effectiveness of scale inhibitors used in oil fields pressure maintaining systems is evaluated. The EIS spectra in the presence of the inhibitors show the decrease of the resistances reveal that the scaling inhibitors effect is a tendency to form low amounts of barite solid precipitated on the electrode surface and their inhibiting efficiency increases with concentration rise.

Keywords: Scale inhibitor, Barium sulfate, incompatible Water, EIS

1. INTRODUCTION

The scaling problem is widespread and common for all worldwide of the oil and gas industry. Water injection into oil reservoirs is used to maintain pressure and improve the increase secondary recovery from reservoirs that have low natural energy [1-10]. Nevertheless, often, the injected water is incompatible with the formation water. As a consequence the deposition of scale minerals in the injection well, production wells and production facilities cause considerable losses to oil and gas production. However, an expensive works are required to remove the scale and prevent its

reappearance. The build-up of barium sulfate mineral scale in oil and gas fields have a damaging effect on the flow of fluid in reservoir rocks and in wells in the production of oil fields.

The value of effective scale treatment during field exploitation estimated in millions of US dollars per year has a considerable economical impact.

Pressure maintaining system in “Tin Fouyé Tabankort”, an oil fields in Algeria is generally provided by water injection. The contact between the injection water “LIAS” rich in sulfates (SO_4^{2-}) and the formation water “ORDOVICIEN” containing barium ions Ba^{2+} , calcium Ca^{2+} and strontium Sr^{2+} causes a dangerous degradation by encrusting deposits of BaSO_4 , SrSO_4 and CaSO_4 .

A breakthrough causes the formation of deposits, mainly composed of barium sulfate, insoluble even with strong mineral acids [1-5]. The scale formation begins in the wells and lead to almost a total blocking of production and surface facilities tubing. The wells affected by barium sulfate deposits are downright abandoned because of the impossibility of their recovery. This situation cause, as already mentioned, a significant economic losses due to unrecoverable downtime. As a remedy to the clogging phenomenon caused by the barium sulfate scales in the tubing and pipelines in the oil production facilities, use of the most effective scale inhibitors remain the only alternative [10-20]. The addition of scale inhibitors helps maintaining the BaSO_4 particles in suspension during the fluid transfer (water and oil).

Scaling and inhibition scaling have been well studied by many researchers using the electrochemical investigations and surface characterization techniques [21-29]. Barium sulfate scaling onto carbon steel in the presence and absence of scaling inhibitors used the spectroscopy electrochemical impedance EIS, is the objective of this research. As a starting point, we considered that it important to study the effect of immersion time on barite scaling on surfaces of electrode. In addition, the effect of scale inhibitors was also investigated such as the phosphonate and polyacrylate-phosphate-ester. The impact of these inhibitors on the precipitation behaviour of barium sulfate on the substrate is determined. The development of an electrochemical EIS experimental procedure to determine the performance of barium sulfate scale inhibitors on the ordinary steel surface has provided original electrochemical data that need further consideration.

The formation of barium sulfate scale on a carbon steel surface in solution and under ordinary conditions is so difficult because of the antagonist phenomenon of corrosion and scaling which occurs at the metal surface. This study shows that a barium sulfate scale can form naturally on the carbon steel surface in particulars conditions. It forms a protective layer for the electrode and can be considered a natural coating enduring and efficacious against corrosion. The barium sulfate scaling can change significantly the electrochemical properties of the electrode increasing resistance and reduced the corrosion rate. The saturation of solution by Ba^{2+} and SO_4^{2-} ions induced nucleation and particle growth of BaSO_4 [14,15,30]. In this study, it has been found that the unsaturated solution is an ideal environment to form the BaSO_4 on the surface while the saturated solution does not promotes the deposition of barium sulfate on the substrate.

Study of the formation and/or inhibition of barium sulfate scale according the literature is often carried out by simulating systems include the reservoirs and pumps [4,30]. In this study, the working electrodes are immersed in the mixture solution of injection water and formation water under static

conditions at various times. The inhibition efficiency of scale inhibitors of barium sulfate is determinate by using EIS method.

2. EXPERIMENTAL

The study was carried out in a standard three-electrode cell. The reference is saturated calomel electrode (SCE), the counter electrode is a graphite bar and the working electrode is an ordinary carbon steel API 5L X70 disc with surface active area of 0.57 cm^2 . The surface of electrode is prepared by polishing with a series of emery paper from 400 to 1200, washed in distilled water and finally dried. The specimens are immersed in beakers which contained a mixture of reconstituted solutions of injection water (rich in SO_4^{2-}) and formation water (rich in Ba^{2+}). Its composition represents the concentration of salts present in the waters used in injection systems and the formation water of Algerian oilfield. All experiments were carried out using 200 ml of injection water as electrolytic solution.

The injection water and formation water are reconstituted according to the concentrations given in Table 1.

Water incompatibility is usually determined by gravimetric method (not given here) in different ratios mixture of injection water (IW) and formation water (FW). The solution mixture ratio at 50:50 provides the maximum precipitate of BaSO_4 in the solution. In contrast, there is almost no precipitate formed at 50:5 (IW:FW) because the Ba^{2+} and SO_4^{2-} ions are present in the solution. However, the ions in the solution can interact with the metal to form the BaSO_4 precipitate on the surface. For this reason, this ratio mixture is chosen as immersion solution.

The working electrodes are immersed separately in water mixtures solutions (injection water / formation water) for 12h, 24h and 48h. After that, the specimens are taken out and EIS measurements are performed accurately. The deposit is obtained after the prior immersing of the electrodes in the mixture solution.

In the second part, the working electrodes are immersed in the mixture solution in the presence of scale inhibitors at various concentrations. After 48h of immersion, the electrodes are taken out and introduced into the electrolyte solution for electrochemical measurement.

Commercial scale inhibitors used in this study are:

Inhibitor A: Aqueous solution of Ammonium Phosphonate; supplied by Baker Petrolite

Inhibitor B: Phosphonate polymer, supplied by Clariant

Inhibitor C: Ester phosphate and neutralized polyacrylate, supplied by Baker Petrolite

Table 1. Chemical composition of the waters.

Concentration [mg/l]	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	Ba^{2+}	Fe^{2+}
Injection Water	763	37	269	64	3	204	558	1300	-	-
Formation Water	39039	1779	33924	5408	851	129	140410	-	1 051	108

The electrochemical impedance spectroscopy (EIS) measurements were performed using a FRA module (Frequency Response Analyzer) AUTOLAB PGSTAT 20, with a small amplitude signal (10 mV) over a frequency domain from 100 kHz to 1 mHz with 5 points per decade. The electric parameters for the impedance plots were obtained by analyzing the experimental data by the ZView software Solartron. XRD analysis was performed using a diffract meter PHILIPS RD-binary model and the scanning electron microscope used is Philips brand and type XL30 ESEM.

3. RESULTS AND DISCUSSION

3.1. Scale formation onto the carbon steel electrode in the absence of inhibitors

3.1.1. Electrochemical impedance spectroscopy measurement

After immersion, the electrochemical measurements (EIS) are performed on the working electrode. Figure.1 shows the EIS diagrams as Nyquist plots obtained at various time of immersion.

The curves present three time constants clearly observed by three semicircles. This capacitive loops indicate that the deposition on the steel is controlled by different process. This curve is observed on the impedance diagrams obtained for carbon steel and conventionally interpreted as, at high frequencies, a charge transfer resistance, and at low frequency a diffusion loop linked to the reaction of reduction of dissolved oxygen [24-28]. This curve indicates also that the deposit on the electrode is covered with a porous layer and generally encountered in the case of heterogeneity of the interface metal/solution. This heterogeneity is also detected through the low “n” values found [24].

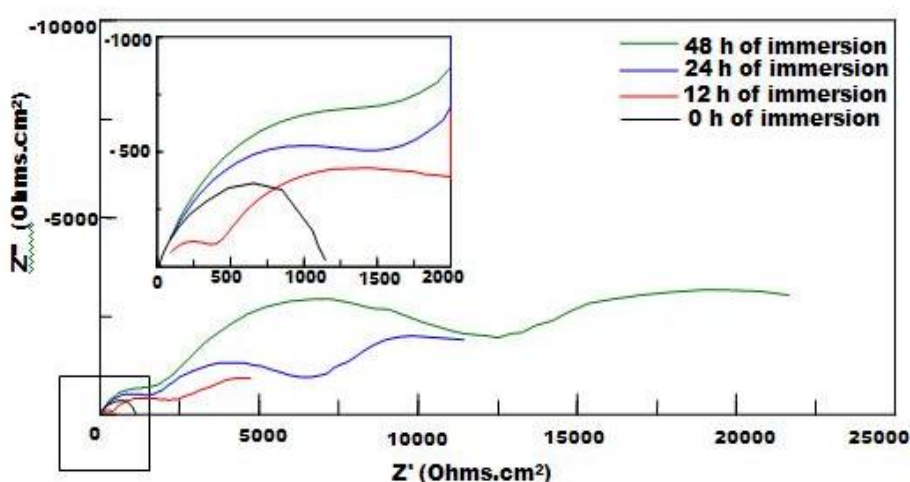


Figure 1. EIS spectra obtained on the electrodes of API X70 5L carbon steel at different immersion time.

The semicircle observed at high frequencies is assigned to the charge transfer resistance R_{ct} and the double layer capacitance C_{dl} corresponding. The resistances R_{ct} increases and C_{dl} values decreases with increasing time of immersion; this means that the charge transfer process is hampered by the

formation of barium sulfate deposits which causes the reduction of the active surface of the electrode work.

The capacitive loop appearing at medium frequency can be attributed to the formation of protective layer on the metal/solution interface and provides information on the evolution of the thickness of the coating layer. The resistance of deposit R_{deposit} increases with increasing time of immersion whereas the deposit capacity decreases.

At low frequencies, the capacitive loops are assigned to the resistances of the pores R_{pores} related to the transport phenomena of the electro-active species. Increasing of this resistance with the immersion time is explained by the narrowing of the pores formed in the deposit and it is difficult about the species to penetrate or diffuse through the pores. The parameters associated with the impedance diagrams determined from Nyquist plots are summarized in Table 2.

Table 2. Parameters values for circuit fitting data of EIS at various immersion times

	Immer sion time	R_e (Ω)	R_{tc} (Ω)	n	C_{dl} (μF)	R_{deposit} (Ω)	n	C_{Deposit} (μF)	R_{Pores} (Ω)	n	C_{Pores} (μF)
Bare electrode	0h	13,3	1150	0,70	277	-	-	-	-	-	-
Electrode with deposit	12h	22	380	0.58	0.4	1650	0,58	100	5000	0.42	3000
	24h	20	1400	0.70	0,06	5000	0.61	25	10000	0.60	800
	48h	19	1325	0,80	0,028	8117	0.67	13	22000	0,48	250

The equivalent circuit of the interface electrode/deposit/solution, without inhibitor, is presented in Fig. 2 (a), the fit of data shows the superposition of the simulated impedance spectrum with that obtained experimentally in Figure 2 (b).

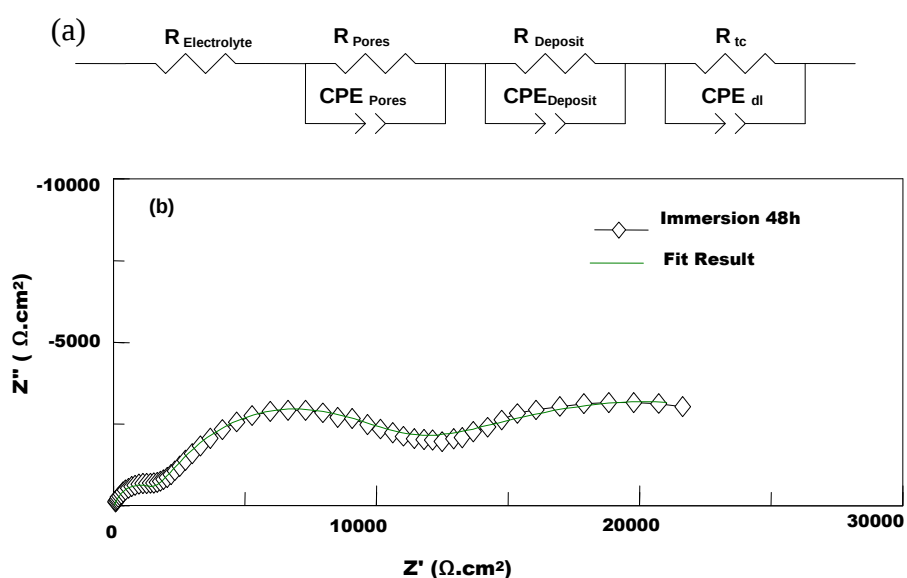


Figure 2 a) Equivalent electrical circuit of the interface electrode/depot/solution and **b)** Experimental pedance spectra of electrode immersed for 48 h and the corresponding simulated spectrum.

3.1.2. XRD analysis

The diffractograms relate to the ordinary carbon steel substrate with and without the deposit formed after 48 hours of immersion is represented in Figure. 3. The XRD spectrum (Fig. 3 in blue) contains two intense peaks located at $2\theta = 20^\circ$ and 29.17° attributed to barium sulfate BaSO_4 compound [30].

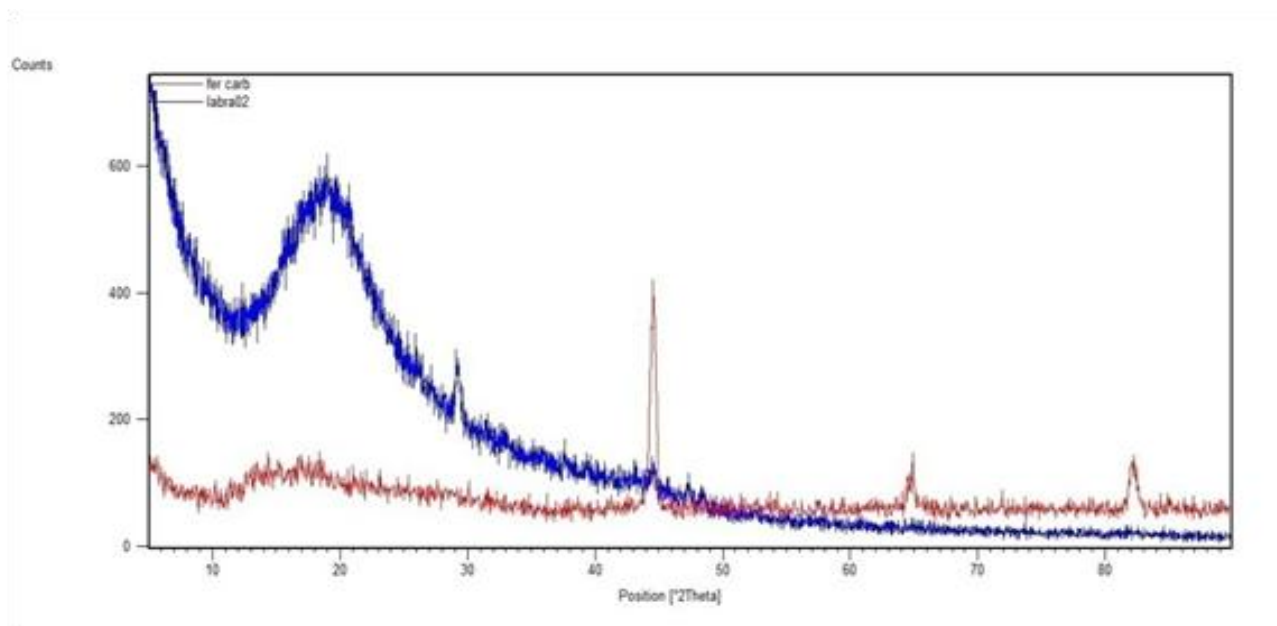
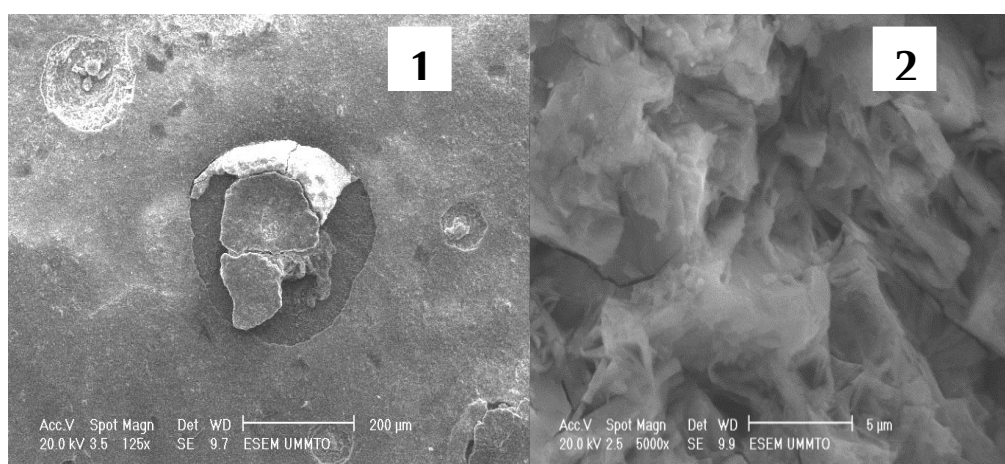


Figure 3. Diffractograms obtained on the samples; Red: The bare electrode of API X70 5L grade steel and Blue: Electrode covered with BaSO_4 .

3.1.3 Scanning electron microscopy (SEM)

The scanning electron microscope SEM analysis showed that the deposits completely cover the surface of the working electrode (Fig. 4). The SEM photos concern the deposit formed after 48 hours of immersion. The covering of the metal surface by barium sulfate is well illustrated in Figure 4.1. The large magnification image fig.4.3 revealed the existence of pores in the coating layer, the thickness and heterogeneity of the layer are noticed through this figure, which confirms the results obtained by EIS.



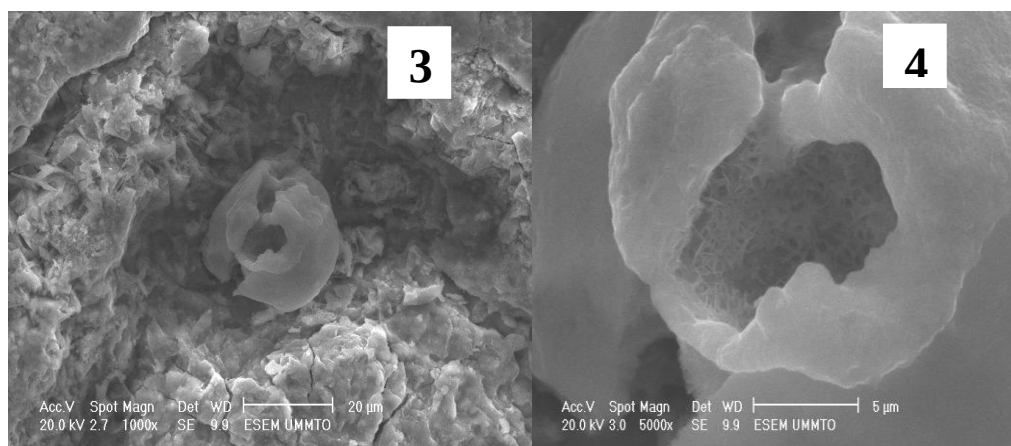


Figure 4. SEM micrographs obtained on the carbon steel electrode after its immersion for 48 h in the injection water/formation water mixture solution.

3.2. Impact of scale inhibitors

3.2.1. EIS measurement

The electrochemical impedance spectroscopy (EIS) is used to determinate the electrode ordinary steel behavior in the presence of scale inhibitors at the same previous environment. Fig.5 illustrates the EIS spectra recorded after 48 hours of immersion in presence of scale inhibitors at various concentrations.

Results obtained from EIS measurements show that the diameter of the capacitive loop decreased after the addition of scale inhibitors into medium solution.

The inhibitors affect the interface electrode/depot/solution characterized by giving two time constants represented by two capacitive loops shown in Fig. 6a. The values of the resistances R_{ct} , $R_{deposit}$ and R_{pores} decreases when the inhibitor concentration increases, this is explained by the fact that the scale inhibitors act on the crystal growth and germination of the sulfate barium on its surface and prevents deposition [29-30]. Therefore, the high values of the capacitances are due to the increase of the electrode active surface. This behaviour shows that the impedance of inhibited substrate decreases with increasing of inhibitors concentration and lead to excellent scale inhibitive performance.

Accordingly, the solutions at low concentrations of scale inhibitors, molecules act on the first nuclei of barium sulfate formed and thereby block the growth active sites.

However, when the surfactant (inhibitor B) concentration increases, its molecules are adsorbed on the surface, this is true until there is no more space available to the interface and the surfactant molecules begin to form micelles. The inhibition efficiency of scale inhibitors depends of the critical micelle concentration (CMC) [31]. These types of surfactants may form a layer of inhibitor molecules that protects the surface of the electrodes and increases the resistance of the charge transfer [28]. The capacitance values of the electrical double layer (C_{dl}) and layer deposit ($C_{deposit}$) which decrease with the concentration of scale inhibitors, are found in line with the resistance values.

The parameters associated with the impedance diagrams such as resistances and capacitances are determined from Nyquist plots and summarized in Table 3.

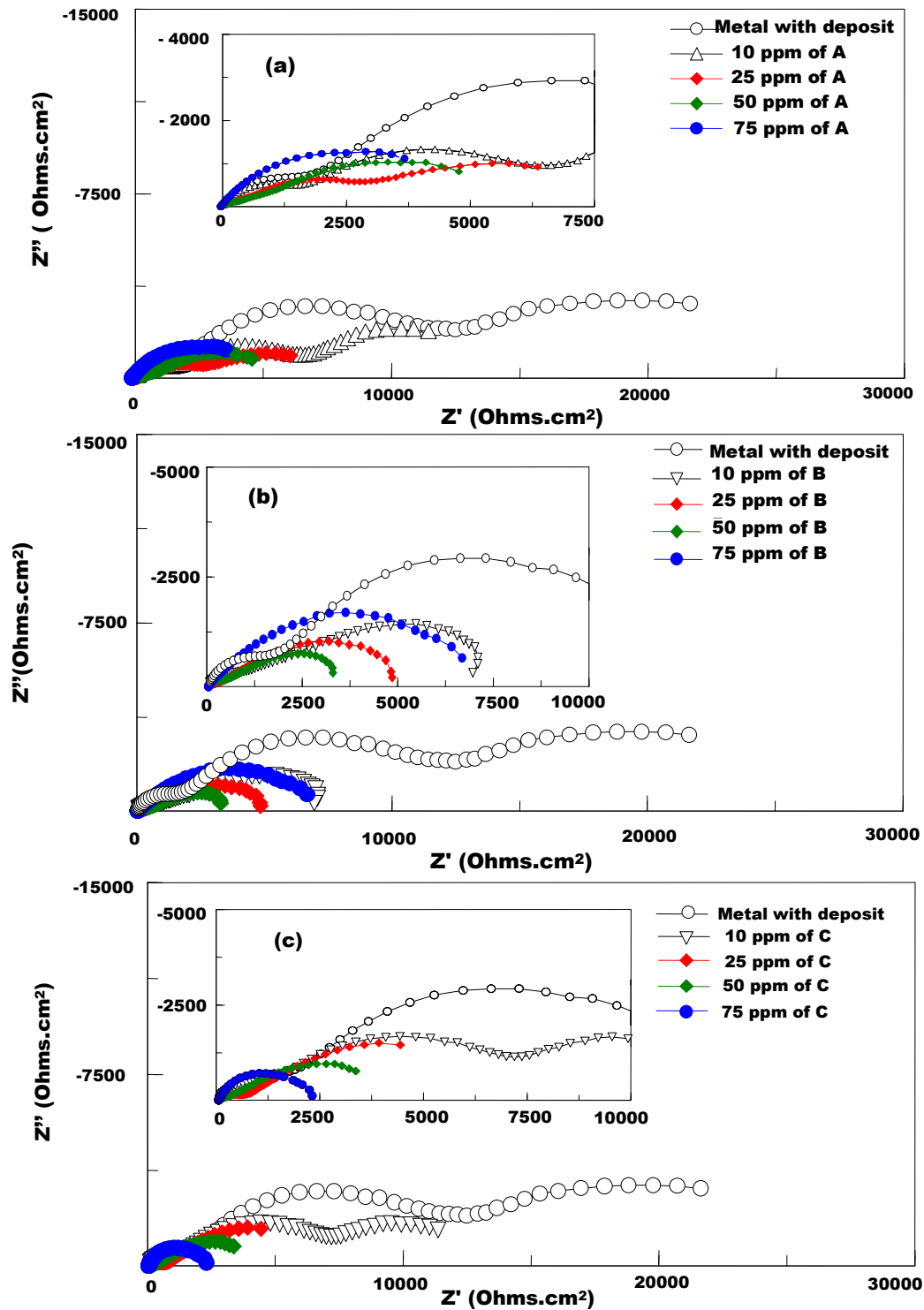


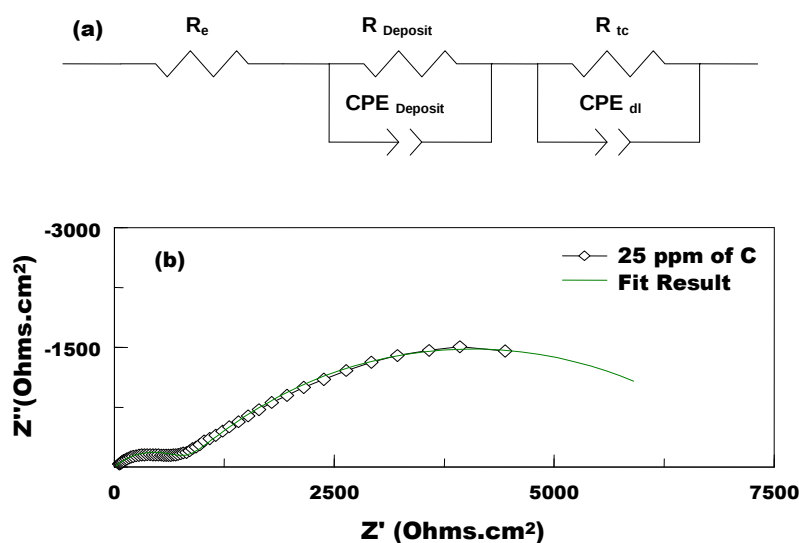
Figure 5. EIS Nyquist plots for the electrode in the presence of scale inhibitors at various concentrations after 48 hours of immersion (a) Inhibitor A; (b) Inhibitor B and (c) Inhibitor C.

The impedance spectra simulated and experimental, in the presence of inhibitor C at 25 ppm are shown in Figure 6.b. The two spectra are superimposed and are scalable to the selected circuit.

Deposit inhibitors affect the interface electrode/deposit/solution and the impedance spectra are characterized by two time constants giving the equivalent electrical circuit shown in Figure 6a.

Table 3. Parameters extracted from EIS diagrams of Figure 5.

Inhibitor	Conc. ppm	R_e (Ω)	R_{ct} (Ω)	n	C_{dl} (μF)	$R_{Deposit}$ (Ω)	N	$C_{Deposit}$ (mF)	R_{Pore} (Ω)	n	C_{Pore} (μF)
A	10	12,5	1390	0,70	0,06	5000	0,61	25	10000	0,60	800
	25	13	500	0,49	13	2300	0,55	50	5250	0,46	1000
	50	28	410	0,50	16	600	0,60	150	4950	0,52	1000
	75	34	5000	0,58	500	500	0,8	900	-	-	-
B	10	20	800	0,67	250	8200	0,40	150	-	-	-
	25	25	400	0,40	750	5400	0,65	350	-	-	-
	50	19	500	0,50	750	3500	0,50	790	-	-	-
	75	54	6800	0,54	200	450	0,8	9000	-	-	-
C	10	-	1236	0,68	1	6490	0,60	880	6060	0,68	20
	25	20,0	810	0,52	20	6520	0,54	826	-	-	-
	50	19,0	700	0,26	800	3814	0,55	2000	-	-	-
	75	68,9	2050	0,75	60	350	0,81	2500	-	-	-

**Figure 6** a) Equivalent circuit model used to fit the EIS experimental data obtained in the presence of inhibitor b) Nyquist plots obtained for the electrode after its immersion for 48 hours in solution with 25 ppm of scale inhibitor C, and his simulated spectrum.

3.2.2. Inhibition efficiency of scale inhibitors.

The inhibition efficiencies E (%) of scale inhibitors are calculated from the following equation:

$$E \% = \frac{R_d - R_{inh}}{R_d} \cdot 100$$

Where, R_d and R_{inh} are the resistances of the electrode with deposit and scale inhibitors, respectively. The resistance R_d concerned the total resistance of the electrode that found after 48 hours of immersion, its value is $31500 \Omega \cdot cm^2$. Table 4 gives the inhibition efficiencies E (%) for different

concentrations of scale inhibitors.

Table 4. Inhibition efficiency of scale inhibitors at different concentrations

Inhibitor	Conc. (ppm)	R_{inh} ($\Omega.cm^2$)	E %
A	10	16402	47,86
	25	8063	74,37
	50	5988	80,96
	75	5534	82,40
B	10	9020	71,33
	25	5825	81,48
	50	4019	87,22
	75	7304	76,78
C	10	13786	56,18
	25	7350	76,64
	50	4533	85,59
	75	2468,9	92,15

The efficiency values calculated from the previous equation can give an estimate of the inhibiting power of the tested product. According to this study, the inhibitors containing phosphonates are a potential inhibitor towards barium sulfate precipitation [13,15,16] but it should be noted that it has a limit of efficiency due to the micelle formation so it is impotent at a concentration called “critical micelle concentration” CMC. The inhibitor B is the most powerful inhibitor of barium sulfate scaling but here the EIS study shows that it is already much effective at a low dose (10 ppm). However, at 75 ppm the efficiency decreases because of the micelles appearing.

However, the polyacrylate combined to phosphate-ester (inhibitor C) has a satisfying inhibiting effect which increases with increasing of inhibitor concentration. This compound is considered the most powerful scale inhibitor of these series because it acts on the nucleating and crystal growth of Barium Sulfate and prevents its adhesion surface.

4. CONCLUSION

The electrochemical impedance spectroscopy is used to study the behavior of the ordinary API X70 5l steel electrode covered with barium sulfate scale. It has been found that after the immersion of the electrodes in the mixture of unsaturated solution containing the injection water (SO_4^{2-}) and formation water (Ba^{2+}), a deposit is naturally formed on the surface. The X-ray diffraction and scanning electron microscopy MEB analysis confirmed that it is the Barium sulfate $BaSO_4$ compound.

The electrochemical impedance spectra in the absence of inhibitors give three capacitive loops corresponding to the charge transfer resistance R_{ct} , deposit resistance $R_{deposit}$ and pores resistance R_{pores} respectively. Increasing resistances with immersion time reveals that the active surface of the electrode

is totally blocked by the deposit layer. However, it can be considered as mineral coating against corrosion. The EIS results obtained are in good agreement with those obtained by the surface characterization analysis (MEB and DRX).

The inhibition efficiency of scale inhibitors of barium sulfate is determinate by using parameter extracted from EIS spectra. Its value depends on global resistances obtained in the absence and presence of scale inhibitors. The phosphonate is one of the most powerful inhibitors of barium sulfate scaling. This study shows that the inhibitor B (phosphonate) is much effective at low dose and at high concentration its efficiency is limited because of apparition of the micelles. However, the polyacrylate combined to phosphate-ester (inhibitor C) has a satisfying inhibiting effect which increases with increasing of inhibitor concentration.

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