Bringing new functionalities to Rotating Cage Autoclave Assembly

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Abstract

The standard Rotating Cage (RC) is a very useful comparative method for screening materials, crude oils and corrosion inhibitors. Thinking of reduce costs and time expended in laboratory tests, mainly to evaluate inhibitors by RC and electrochemical techniques tests; we developed an Electrochemical Rotating Cage Autoclave assembly (ERCA). Herein we present the ERCA system and the electrochemical response validation using a well-known redox system. Additionally, we compared the impedance diagrams of bare carbon steel in a 0.16% NaCl brine at 500 RPM with 1 and 100 bar of CO2. Preliminary results of inhibitors electrochemical evaluation during the RC test showed the film formation and growth. With ERCA is possible to use electrochemical techniques to monitor the corrosion process or inhibitor action during the RC laboratory test. Electrochemical results can be compared with standard weight loss performed after the test using the standard RC samples tested in the same batch. The aim is to show that even with the modifications made to include those new functionalities, the system presented here reproduces the standards already known for tests in conventional RC and in addition, it is possible to obtain reliable electrochemical data, bringing new functionalities to RC standard test.

Keywords: Electrochemical Rotating Cage Autoclave, Corrosion Inhibitors, Impedance.

Introduction

In the last thirty years, Rotating Cage (RC) system has being widely used to evaluate materials and corrosion inhibitors performance (1-12). Despite of being a very conservative test methodology, the laboratory results are in good agreement with those obtained from field. The costs to perform a Rotating Cage Autoclave tests (with CO_2 and H_2S) are low when compared to flow loops and Jet Impingement tests. Additionally, it is possible to replicate oil and gas field conditions in terms of brine and gas composition, temperature, pressure and flow regime (8, 13 ,14). Concerning the last point, the flow distribution and cage geometry were the main RC discussion focus in the last decade (15-22).

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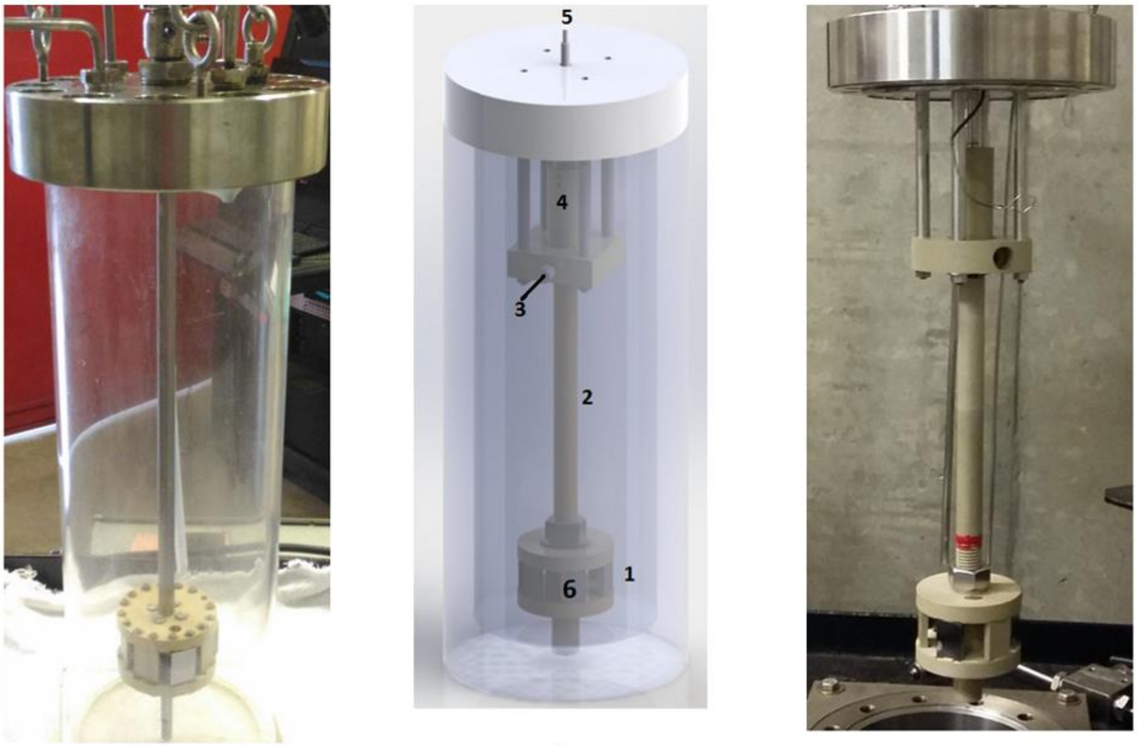
The studies of Delouis (16, 17) and Chaal (17, 18) with the microelectrodes and recently by Vera (10), to evaluate the distribution of shear stress along the specimen surface, were carried out at atmospheric pressure and temperature. However, those publications inspired us to develop an RC assembly capable to perform electrochemical measurements on ordinary RC steel specimens in autoclaves conditions (high-pressure/high temperature, HPHT) (23, 24). The idea was to overcome the main Rotating Cage technique limitation described by Schmidt and Bakalli (25): do not perform electrochemical measurements, specifically under HPHT conditions. It is a consensus on literature (17, 18, 20-22) that more studies are necessary to propose a better correlation between field wall shear stress and RC velocity. Therefore, in this paper we are going to report only the cage velocity. The results are associated with cage speed and we did not present it as shear stress. It is worth to mention that the ERCA can perform test in an oxygen free environment and saturated with CO_2 or other gas mixtures containing even H_2S, at high pressure and temperature.
This work presents the ERCA assembly, the tests performed to prove the reliability of the electrochemical measurements and preliminary results of corrosion inhibitor evaluation. The aim is to show that even with the modifications made to include those new functionalities, the system presented here reproduces the standards already known for tests in conventional RC and in addition, it is possible to obtain reliable electrochemical data, including electrochemical impedance, bringing new functionalities to RC standard test.

Methodology

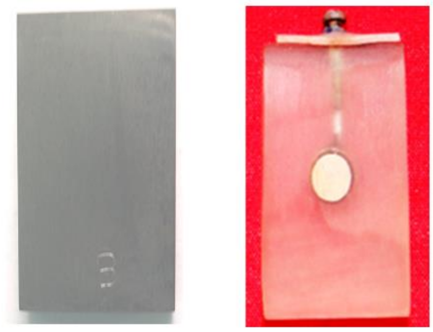
Conventional RC vs. Electrochemical RC
In a conventional RC, the rotating shaft is in contact with test solution (see fig. 1a). To the ERCA PEEK gloves were built to electrical insulate the shaft from test solution. This insulation was necessary to ensure that the electrochemical response is only from the specimen under test and not from the stainless steel shaft.
The crucial point of ERCA (fig. 1b) project was to set an insulated electrical contact from the specimen (item 6), in the cage (item 1), with a point outside the autoclave (made from item 3), to connect in a potentiostat. The electrical contact of the specimen was possible by a screw threaded directly at specimen, which was in contact with other stainless steel screw embedded in the cage (item 6) and threaded the central shaft (item 2). Comparing the conventional RC (fig. 1a) with ERCA (fig. 1b and 1c) is clear the central shaft insulation by a peek glove, necessary to avoid the solution electric contact. To stablish the electric contact from a rotating shaft to a static point, among the viable options, we decided to use an electrical contact of graphite pressed by a spring to the rotation shaft (item 3 on fig.1b), as it is traditionally done in rotating disk/cylinder electrode systems.



a b c

Figure 1 – a) Conventional Rotating Cage b) Electrochemical Rotating Cage assembly schematic drawing and c) ERCA picture. From fig. 1b) 1 - Cage with 6 specimens, 2 - main shaft with peek gloves, 3 - external electric contact with internal spring and graphite electric contact, 4 - insulated connection between magnetic shaft and cage main shaft. 5 - Connection to magnetic shaft, 6 - specimen.

On ERCA, the cage and specimens' size are the same used on conventional RC presented on figure 1a. It is possible to test six specimens, five to ordinary weight loss test and one to electrochemical measurements. The weight loss coupons are 30 mm x 20 mm x 3 mm, the electrochemical coupon has the same size in width and length, but is thicker to fit the electric contact screw. Figure 2 presents the ERCA specimens type 1, to weight loss tests and type 2, to electrochemical measurements. All tests were carried with three specimens in the cage: two destined to WL test and one to electrochemical measurements. The other three specimens' places in the cage were filled with peek coupons.



Type 1 Type 2

Figure 2 – ERCA weight loss Specimens, type 1. ERCA electrochemical coupon, type 2.

Rotating Cage Electrochemical response – validation

In order to validate the RC electrochemical response a well-known system was used: 0.05mol/L of ferri/ferrocyanide solution in 0.5 mol/L of potassium sulfate; viscosity of 1.01 mPa.s at 25ºC. We used a platinum working electrode with geometry type 2, area of 0.228 cm² (Fig. 2). The cage rotation speed varied from 100 to 700 RPM; the potential scan rate was 0.01V/s and all electrochemical were performed in an IVIUM potentiostat. The electrochemical tests on platinum electrode intend to evaluate stability and reproducibility of the measurements and the dependency of limiting current with ERCA rotation.

Electrochemical measurements on carbon steel electrodes

A specimen of API X65 carbon steel was used as working electrode (area = 0.31 cm² - type 2 geometry), the hastelloy autoclave vessel was the counter electrode and a hastelloy C-276 wire used as pseudo reference electrode. All electrochemical tests were carried out in 0.16% NaCl brine saturated with CO_2. Ivium potentiostat was used to perform electrochemical impedance measurements with the following parameters: 1000 Hz to 2 mHz, 6 points/dec, amplitude of 20 mV around the corrosion potential. For all immersion test conditions, see table 1.

Corrosion inhibitors tests

ERCA Inhibitors tests conditions were: 100 ppm of a commercial corrosion inhibitor in an oxygen free 0.16% NaCl brine saturated with CO_2, test conditions are presented on table 1.

Weight Loss test

Following ASTM G 1 (26) procedure, after the Rotating Cage Autoclave test the standard specimens, the two coupons type 1, were pickled to evaluate overall mass loss to estimate corrosion rate.

Table 1 – Summary of test conditions, 0.16% NaCl brine

Inhibitor (100 ppm)	CO_2 Pressure (bar)	Temp (ºC)	Cage rotation (RPM)	Immersion period (h)	Tests	See results
no	1	25	0	3	Impedance	Fig. 4, Table 2
no	1	25	500	3	Impedance	
no	100	25	500	3	Impedance	
Yes	1	25	400	72	Impedance + WL	Fig. 5a, Table 2
No	1	25	400	72	WL	Table 2
No	100	100	400	72	WL	Table 2
Yes, But removed after 46h	1	25	400	168	Impedance + WL	Fig. 5b, Table 2
yes	100	100	400	72	Impedance + WL	Fig. 6, Table 2

Results and Discussion

Before start to use the Electrochemical Rotating Cage Autoclave (ERCA) assembly to evaluate corrosion inhibitors or even to compare materials electrochemical response, some control tests were performed to check its accuracy. For Rotating Cylinder Electrodes (RCE), the equation that correlates limiting current and speed of rotation is empirical, constructed from experiments performed by Eisenberg (27). Since RC is similar to a RCE, when the cage is entirely filled with coupons, the equation 1 was adopted to confirm whether the ERCA electrochemical data are coherent, without distortions caused by the experimental setup.

$$i_{lim} = 0{,}0791\ nFC_0 w^{0,70} d^{-0,30} V^{-0,344} D_i^{\ 0,644} \qquad \text{eq. 1}$$

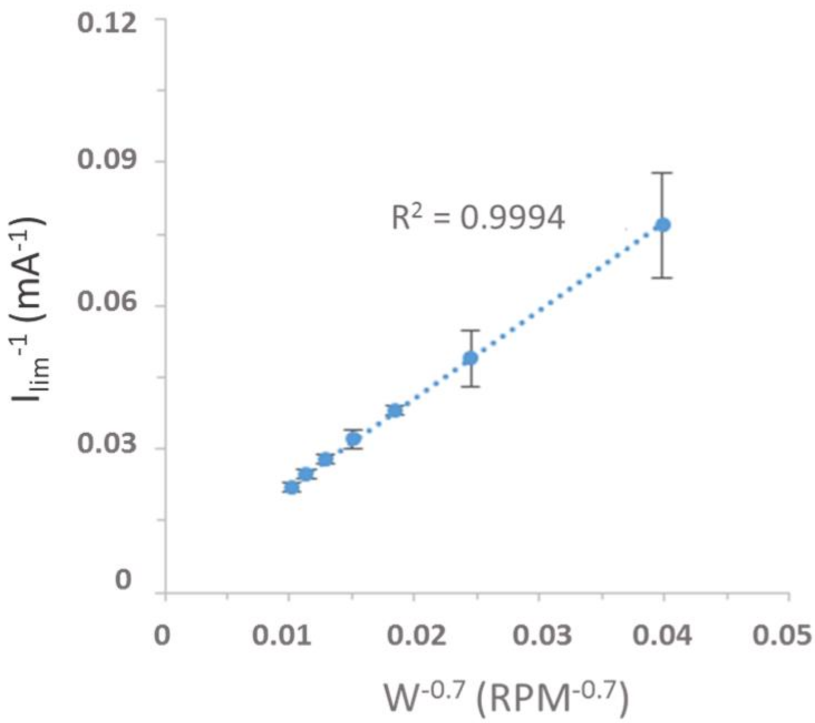


Figure 3 – Cathodic Limiting current of 0.05 mol/L $K_3[Fe(CN)_6]$ on platinum electrode vs. cage rotation speed, based on Eisenberg equation. [27] **Rotation speed: 100 to 700 RPM.**

Within the experimental error, a linear behavior was observed to $ilim^{-1}$ vs. $w^{-0,7}$. These results are in agreement with literature previous reports (16,28). Knowing that ERCA setup gives consistent electrochemical results to DC techniques, electrochemical impedance measurements (AC technique) were carried out to evaluate the response of ERCA to another well-known system. Once the corrosion behavior of carbon steel is extensively studied in our laboratory, we choose the impedance diagrams of X65 carbon steel on 0.16% NaCl brine saturated with CO_2 at static conditions and at 500 RPM to evaluate the performance of ERCA setup. The Nyquist diagrams presented on figure 4 corroborate literature results (27-29) to static measurements, showing only one time constant. At 1 bar the impedance diagrams at static and 500 RPM conditions presented quite similar behavior, with only one time constant and the same frequency to the capacitance associated with charge transfer process, but with smaller corrosion resistance to the later (flow accelerate condition). The diagram at 100 bar of CO_2 showed not only a smaller resistance but also an acceleration of corrosion process, which is noticed by the shift of time constant frequency from 1.59 Hz to 10 Hz illustrated on figure 4.

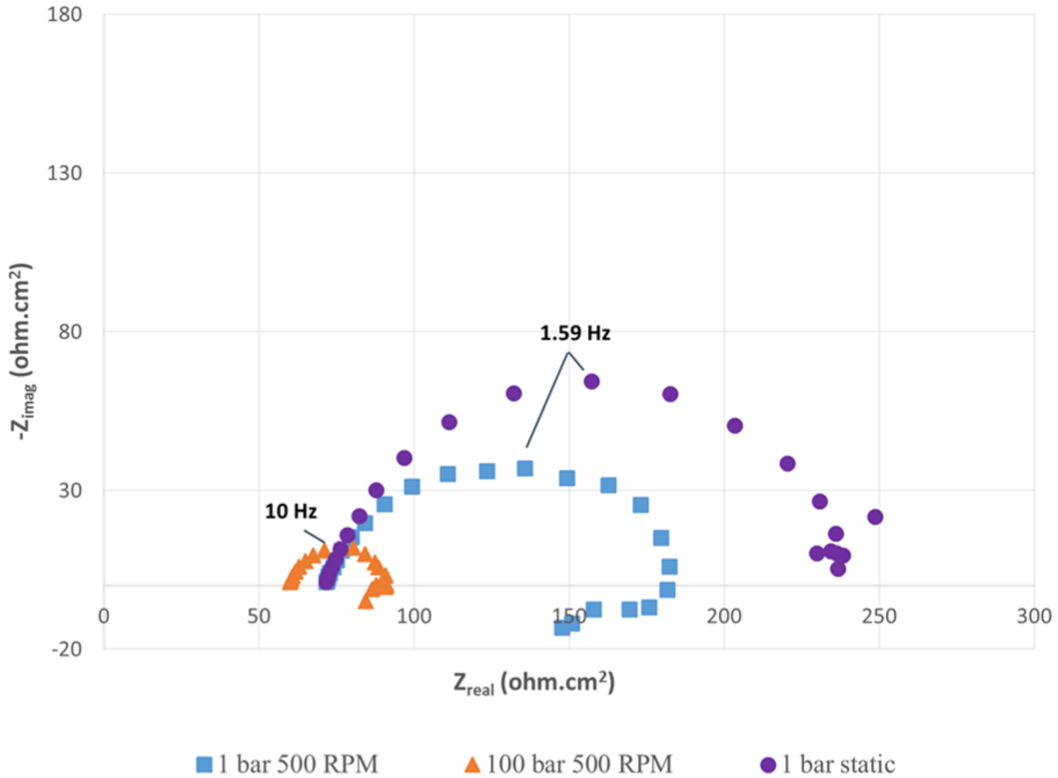


Figure 4 – Nyquist diagram to X65 carbon steel, geometry type 2 area: 0.31 cm^2, at 0.16 % NaCl, saturated with CO_2, 25°C.

The results presented on figures 3 and 4 clearly demonstrate that electrocemical measuments performed on ERCA reproduced literature results (27-29). By the diagrams at dynamic flow conditions (500 RPM) and high pressure is possible to evaluate the influence of flow conditions and pressure on X65 carbon steel corrosion process during the immersion test. It is worth to remember that the main reason to built a RC adapted to electrochemical measurements is to follow the corrosion inhibitor action along the immersion period, including HPHT conditions and also have the ordinary weight loss test from other coupons located at the same cage to estimate corrosion rate.

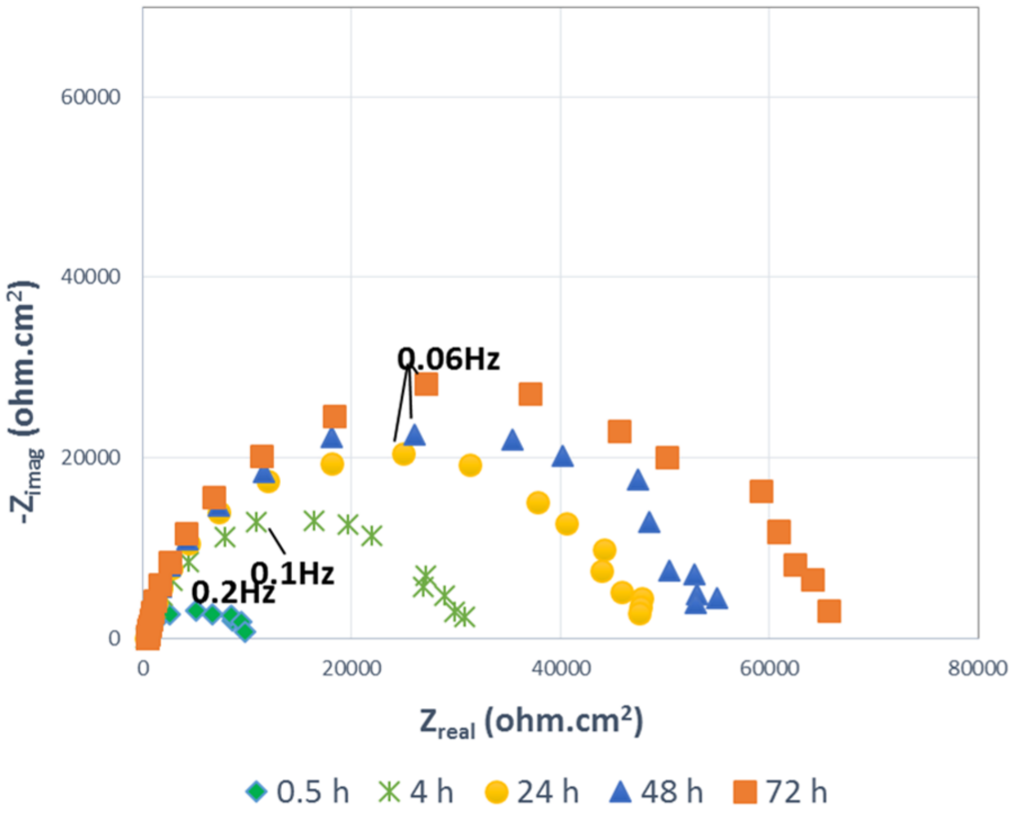


Figure 5a – Nyquist diagram to X65 carbon steel, 0.16 % NaCl, 1 bar CO_2, 25°C with 100 ppm of corrosion inhibitor, 400 RPM, 72 hours of test.

To illustrate the ERCA viability to monitor insitu the corrosion inhibitor behavior three different test were carried out. Figure 5a present the impedance diagrams of X65 carbon steel on 0.16% NaCl with 100 ppm of commercial corrosion inhibitor, at 25°C, 1 bar CO_2 and 400 RPM. The corrorion inhibitor was added in the first 20 minutes of immersion period. The semicircle diameter, from the nyquist plots, increased with immersion time. These results shows that due to inhibitor presence the X65 carbon steel corrosion resistance increased progressively within the test period. Suggesting inhibitor film thickening on X65 carbon steel. On figure 5b the experimental condition was the same as the one presented on figure 5a, but the test solution was completely removed after 46h of test and replaced by another with the same composition without inhibitor.

It was possible to follow the corrosion resistance behavior in situ by the impedance diagrams. Even after removing the inhibitor, the corrosion resistance remained higher than the one observed to bare X65 carbon steel on 0.16% NaCl (see figure 4). In the first hours after inhibitor removal one may argue the increase on corrosion resistance may be due to inhibitor trace amount left on autoclave, wich is possibly true. Another possibility is that inhibitor film formed on steel surface is somehow dameged along the test and there is no inhibitor in solution to renew it, therefore the corrosion resistance decreased.

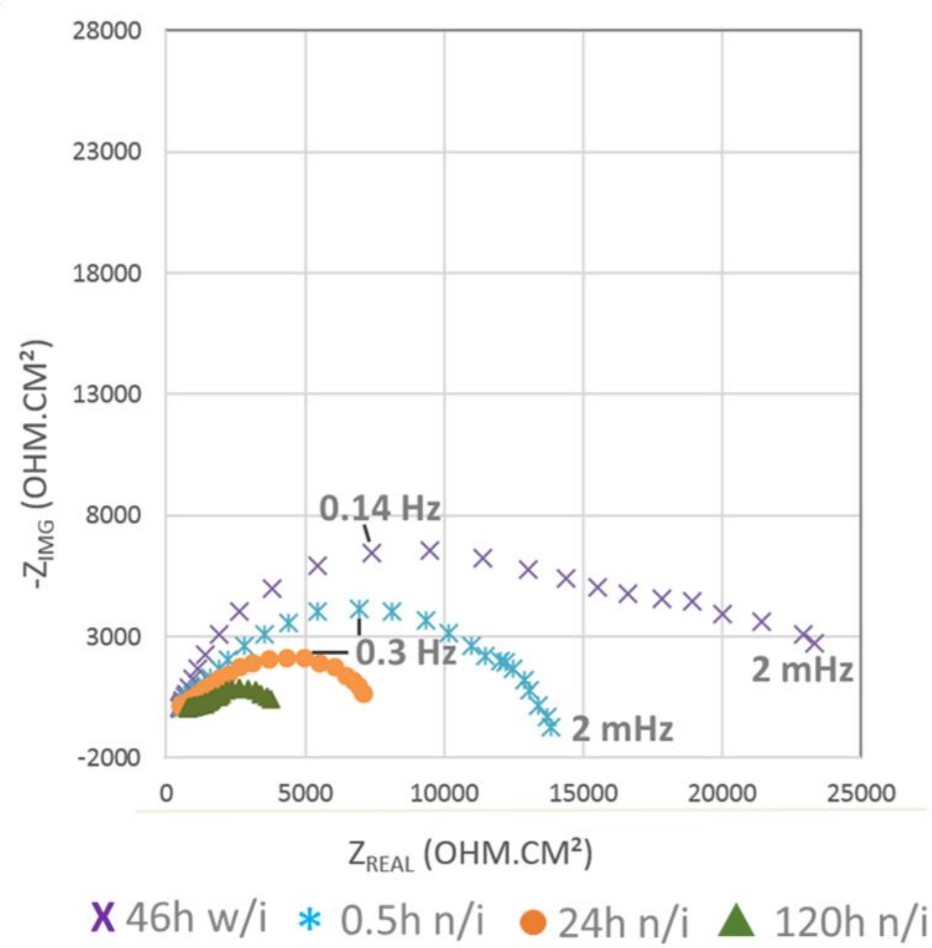


Figure 5b – Nyquist diagram to X65 carbon steel, 0.16 % NaCl, 1 bar CO_2, 25°C with 100 ppm of corrosion inhibitor, 400 RPM, 168 hours of test. Solution containing inhibitor removed after 46h and replaced by a 0.16 % NaCl saturated with CO_2. w/i: with inhibitor; n/i: no inhibitor.

From data presented on figure 6, it is demonstrated the feasibility of ERCA to monitor inhibitor action at HPHT conditions. The X65 carbon steel impedance diagrams at HPHT showed only one time constant only during the first hour of immersion, to longer test periods at least two time constants can be assigned to Nyquist diagrams presented on figure 6. The blank test impedance diagram presented on fig. 6 inset also shows even more active corrosion process than the one presented on figure 4 to 100 bar of CO_2 but at 25ºC. The high temperature favors the $FeCO_3$ film formation and therefore the impedance diagrams are more complex to evaluate than those at lower temperature are. Additionally, it has to be considered the inhibitor influence on $FeCO_3$ film formation. All these features seen on impedance diagrams were expected, but they will not be discussed here once the focus of this paper is only to demonstrate the new functionalities that electrochemical measurements can add to rotating cage test.

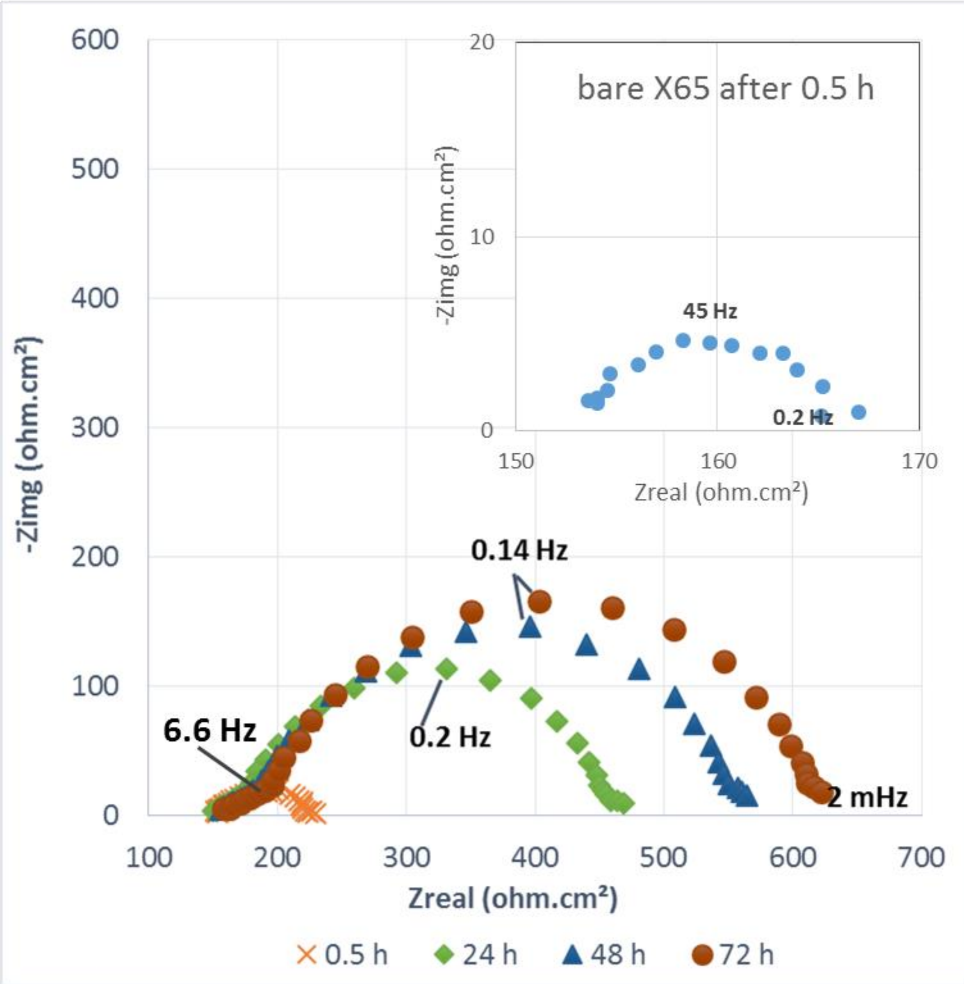
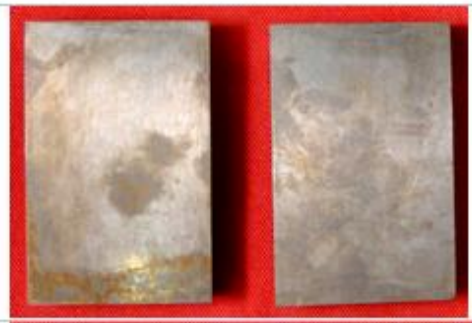
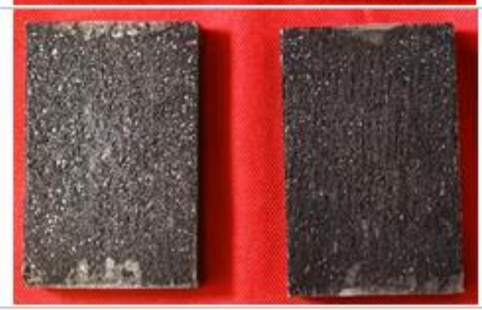


Figure 6 – Nyquist diagram to X65 carbon steel, 0.16 % NaCl, 100 bar CO_2, 100°C with 100 ppm of corrosion inhibitor, 400 RPM, 72 hours of test. Inset: Nyquist diagram from blank test (without inhibitor)

The weight loss results performed according to ASTM G1 (26) reccomendation are presented on table 2. In order to estimate inhibitor efficiency, blank tests (without inhibitor) were performed and the results are presented on table 2. The inhibitor efficiency was calculated based on weight loss rate. At this point only qualitative comparison is recommended between electrochemical and weight loss data therefore, no inhibitor efficiency was estimated based on electrochemical data. Thus, qualitatively the impedance diagrams corroborate the weight loss data, once the polarization resistance (semicircle diameter of nyquist plots) was higher to test conditions with lower weight loss. Table 2 presents also the images of all coupons after the WL pickling cycles.

Table 2 – Weight loss results, 0.16% NaCl at 400 RPM

ERCA test conditions	WL rate (mg/h)	Inhibitor efficiency (%)	Coupons' image after the WL
72h with inhibitor, 1 bar CO_2, 25°C	0.30	96.62	
168h but only 46h with inhibitor, 1 bar CO_2, 25°C	0.61	93.15	
72h **without** inhibitor, 1 bar CO_2, 25°C	8.90	--	
72h with inhibitor, 100 bar CO_2, 100°C	14.10	87.98	
72h **without** inhibitor, 100 bar CO_2, 100°C	117.28	--	

Conclusion

Based on linear behavior of limiting current x RC rotation ($ilim^{-1}$ vs. $w^{-0.7}$) observed to potassium ferricyanide reduction on platinum electrode installed on RC, we can assume the ERCA provide reliable electrochemical data.

The ERCA main advantage is to perform electrochemical and weight loss tests in the same experiment but on distinct coupons. Therefore, ERCA is a useful tool at low cost, when compared to flow loops and jet impingement setups to study corrosion inhibitors effect on steel surface.

From ERCA impedance measurements, it was possible to monitor the carbon steel corrosion and/or inhibitor action during the HPHT test. The impedance diagrams showed clearly the inhibitor effect even at trace amounts.

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