THE EVALUATION OF THE CORROSION INHIBITOR PERFORMANCE IN HOT HCl SOLUTIONS BY THE IMPEDANCE TECHNIQUE

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ABSTRACT

Some considerations on corrosion inhibitors are given and their use in specific applications such as the acid cleaning of steam generators is shortly reviewed. The performance evaluation is based on the differential capacitance of the metal–solution interphase, the polarization resistance in the low–frequency region and the area method that are introduced in an intuitive way using a simplified electric network to represent the behaviour of the metal–solution interphase and Kramers–Kronig's relations. The behaviour of iron and two low alloy steels in 5 wt% HCl solutions containing a commercial product at different concentrations and temperatures of 65, 75, 80 and 90°C has been examined. Electrochemical measurements were performed over the frequency interval $[0.08, 2 \times 10^4]$ Hz under current control and using suitable software so as the RMS value of potential difference between the working and reference electrodes is always inside the interval [4, 6] mV. Experimental results show that this procedure provides corrosion workers a valid aid to evaluate the performance of corrosion inhibitors. The experimental data are very promising for iron because there is a tight link between the double–layer capacitance and polarization resistance, and the mean corrosion rate. In the case of the two low alloy steels, however, the situation is slight different as a consequence of the influence of chromium on the chemical stability of the examined inhibitor.

INTRODUCTION

It is well–known that corrosion inhibitors used to perform the acid cleaning or pickling of ferrous materials with hot HCl solutions are generally made from mixtures of nitrogen–containing organic compounds /1,2/ and can hinder electrode kinetics through a great variety of physicochemical mechanisms /3/, even if the prevailing opinion is that protection of a metal is mainly achieved through adsorption of organic molecules on its surface.

As regards nitrogen–containing compounds, the opinion of Hackerman /4,5/ is that their chemisorption on the metal surface is mostly due to the unpaired electrons of the π bonds of the nitrogen atoms. At any rate the basic aspects of corrosion inhibition have been thoroughly reviewed, for instance, by Riggs /6/ and Trabanelli /7/. However, it is convenient to recall that the physicochemical characteristics of the base metal, such as purity, surface state and charge, may influence the performance of an organic compound.

An interesting aspect of the corrosion inhibition concerns the definition of proper procedures for evaluating their effectiveness /8/ in restraining a corrosion process. The choice of procedures that have to be adopted to carry out electrochemical tests has a noticeable importance because, in principle, the efficiency of organic compounds cannot be evaluated in an absolute manner. On the other hand, one of the main objectives of a specific test is to simulate the true operating conditions as faithfully as possible.

The last observation is important because corrosion rates of metals and alloys in acid solutions containing proper corrosion inhibitors depend also on their hydrodynamic conditions. To this end reference can be made to Gardner's work /9/ dealing concisely with the effect of the flow rate of the fluid on the dissolution of a metal. At any rate it is right to emphasize that the choice of the static or dynamic conditions to be adopted to perform tests is of fundamental importance as concerns the evaluation of the inhibitor effectiveness, the quality control and acceptance criteria.

The evaluation of the inhibitor effectiveness needs careful determinations of corrosion rates. The direct method, based on the specimen weight–loss or solution analysis, has the advantage of providing reliable data but is time consuming. Moreover, the weight loss technique gives only the mean corrosion rate so that it is not possible to determine whether anomalies have occurred during the test.

Electrochemical methods, which can use direct current as well as alternating current, provide almost instantaneous corrosion rates so that it is possible to detect anomalous behaviours that impair the resistance to corrosion of the material under investigation. However, the trend of electrode kinetics obtained from electrochemical measurements is not always faithful.

As regards the acid cleaning of steam generators of thermal power plants the main aim of this operation is to remove from the internal surface of the tubes the protective film /10,11/, constituted by oxides and deposits from corrosion products and containing mostly magnetite /12,13/, in order to improve thermal exchange and reduce the fuel consumption and power demand for compensating hydraulic losses.

The need for acid cleaning of a steam generator is determined by several factors, such as the quality of feedwater, the effectiveness of the magnetite film in protecting bare alloys, and the transport of corrosion products. As a rule of thumb, the degree of inorganic fouling of the internal surface of the tubes cannot be predicted in a reliable way because it is rather hard to define *a priori* the length between two consecutive operations that will suit any type of steam generator.

The acid cleaning technology should satisfy two contrasting requirements. On the one hand, the acid solution should be aggressive enough to remove the magnetite layer from the internal surface of the tubes in the shortest possible time. On the other hand, the mechanical integrity of boiler tubes has to be preserved as long as possible and the reduction in their thickness during the performance of this operation should be as negligible as possible.

The previous requirements are compatible if use is made of proper corrosion inhibitors. The essential characteristics of inhibitors are to not interfere with kinetics of magnetite dissolution and restrain the corrosion of bare alloys where protective film has been removed from the tube surface. However, experience shows that, in principle, inhibitors are not able to hinder corrosion due to the galvanic coupling between magnetite and carbon steel.

In fact, according to Hoar /14/ the scale dissolution is due to the formation of local microcells between oxide and the steel that acts as an anode. Thus, the reductive dissolution of magnetite occurs through the overall reaction $Fe + Fe_3O_4 + 8H^+ \rightarrow 4Fe^{2+} + 4H_2O$, which takes place through an electrochemical path.

Another important characteristic of commercial products, which are generally made from a blend of compounds, is a high chemical stability of all the constituting species at temperatures higher than room temperature so that the formation of decay products can be considered negligible. In fact, decay products might stimulate the corrosion process. In addition, a commercial product must not react with the corrosion products of various carbon steels.

THE EVALUATION OF THE INHIBITOR EFFECTIVENESS

The definition of the inhibitor effectiveness is very easy when electrode kinetics of a corroding system are described by the law

$$I = I_{cor}\,(e^{\alpha\Delta E} - e^{\beta\Delta E}), \tag{1}$$

where I_{cor} indicates the corrosion current density and the parameters α and β are related to the anodic Tafel slope B_a ($B_a = \alpha^{-1}$ ln 10) and the cathodic Tafel slope B_c ($B_c = \beta^{-1}$ ln 10).

In all these cases the quantitative determination of the inhibitor performance can be based on the electrochemical parameters such as I_{cor} and the polarization resistance R_p /15, 16/. However, when R_p is used, it is useful to recall that the Tafel slopes might depend on the inhibitor concentration c because of the change in the double layer structure due to displacement of water molecules /6/.

For the class of electrochemical systems described by the kinetic law (1) the inhibitor effectiveness P% of a chemical compound having concentration c is defined by the relationship

$$\mathrm{P\%} = \frac{I_{cor}(0) - I_{cor}(c)}{I_{cor}(0)}100, \tag{2}$$

where $I_{cor}(0)$ is the corrosion current density in the blank solution.

When R_p is employed, the definition of the inhibitor effectiveness is immediate if one bears in mind the link between $I_{cor}(c)$ and $R_p(c)$. In this case the exact expression of the inhibitor effectiveness takes the form

$$\mathrm{P\%} = \frac{R_p(c)(\alpha(c)+\beta(c)) - R_p(0)(\alpha(0)+\beta(0))}{R_p(c)(\alpha(c)+\beta(c))}100 \tag{3}$$

The previous equation underlines that the evaluation of the inhibitor effectiveness needs the knowledge of the values of $\alpha(c) + \beta(c)$ and $\alpha(0) + \beta(0)$. Such a constraint nullifies the advantage of the simplicity of the polarization resistance method. To use the R_p scheme easily the validity of the approximate relationship

$$P\% = \frac{R_p(c) - R_p(0)}{R_p(c)} 100 \tag{4}$$

is usually assumed.

As regards corrosion inhibitors for acid environments to be used to perform acid cleaning operations, the equations (3) and (4) generally provide very close values of P%. In fact, experience shows that for a wide range of c values the inequality $R_p(c) \gg R_p(0)$ holds with a good accuracy.

The surface impedance technique allows the approximate evaluation of inhibitor effectiveness using the techniques based on the capacitance C of the metal–solution interphase, the transfer resistance, the polarization resistance and the area of the plane region bounded by the curve $Z_i = f(Z_r)$ and the Z_r axis.

As regards the scheme based on C, whose use was suggested by Hackerman /17/, the inhibitor effectiveness P% is computed using the expression /18/

$$P\% = \frac{C(0) - C(c)}{C(0) - C_l} 100, \tag{5}$$

where the quantity C_l, that accounts for the existence of a lower bound of $C(c)$ corresponding to the electrode surface totally covered by a monolayer of inhibitor molecules, is determined by setting P% = P_d%, the inhibitor effectiveness P_d% being determined by a direct method, at a prefixed concentration c.

THE ELECTRODE IMPEDANCE TECHNIQUE

It is well–known that examination of the response of an electrochemical system to a sinusoidal external signal of small amplitude needs the use of an electrical network /19/ able to represent as faithfully as possible the observed experimental trend. An in-depth treatment of this topic has been given, for instance, by Macdonald /20/. The choice of suitable electrochemical parameters will be justified on empirical considerations. This is possible because the behaviour of a wide class of electrochemical systems is described with a satisfactory approximation by fairly simple electric networks which have the advantage of defining unambiguously the physical meaning of their components.

Interphase capacitance

The double–layer capacitance *C* depends on the electrode potential, even if in the vicinity of the free corrosion potential it takes a nearly constant value. The dipolar element, which provides a simple and accurate electric representation of the metal–solution interphase in the high–frequency region, is shown in Fig. 1. The network is constituted by a parallel combination of the transfer resistor R_t and capacitor C in series with the solution resistor R_s.

The change in the value C_u, which refers to the unit area, is mainly due to the displacement from the double layer of the water molecules by those of the inhibitor which insulate the metal surface from the aggressive solution. Thus, the capacitor C can be regarded as the resultant of two capacitors in parallel, filled with dielectrics having different permittivities, and its capacitance is equal to $C_u\vartheta = C_{u1}\vartheta + C_{u0}(1 - \vartheta)$, ϑ being the surface coverage and C_{u0} indicating the contribution of water molecules to the interphase capacitance.

As regards the behaviour of electrochemical systems in the high frequency region, it is correct to assume that electrode kinetics are not able to follow the variation of the sinusoidal signal and their response depends mostly on the structure of the metal–solution interphase that the inhibitor has helped to build. Hence the resistor R_t is not necessarily related to the faradic current sustaining the electrode reactions but can account for the energy loss due to the reorganisation of the double layer more simply. From a physical point of view such a result is a direct consequence of the phase angle shift existing between the electric field and dielectric displacement.

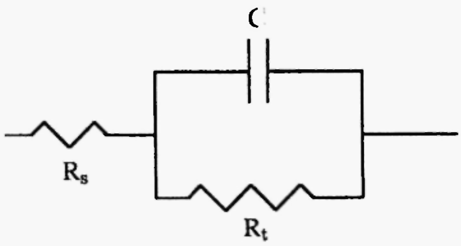

Fig. 1: Simplified electric representation of the metal–solution interphase in the high–frequency region.

Evaluation of the polarization resistance

The determination of the inhibitor effectiveness through the use of a low–frequency sinusoidal signal can be justified by a rigorous mathematical treatment dealing with a more general definition of the polarization resistance, R_p.

The impedance Z(ω) is an analytical function of ω in its upper half–plane /21/ and, on account of its physical meaning, satisfies the condition

$$Z(-\omega) = Z^*(\omega). \tag{6}$$

So between the real part $Z_r(\omega)$ and the imaginary one $Z_i(\omega)$, the two relations

$$Z_r(\omega) = \frac{2}{\pi}\int_0^\infty \frac{xZ_i(x) - \omega Z_i(\omega)}{x^2 - \omega^2}\,dx \tag{7}$$

$$Z_i(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{Z_r(x) - Z_r(\omega)}{x^2 - \omega^2}\,dx, \tag{8}$$

known as Kramers–Kronig's relations /22/, can be set. The correct use of the equation (7) needs to set $Z_i(\omega) = -Z_{ei}(\omega)$, $Z_{ei}(\omega)$ indicating the experimental values of the imaginary part of impedance.

From the definition of the differential impedance

$$Z(\omega) = \frac{\delta \Delta E(\omega)}{\delta i(\omega)}, \tag{9}$$

it follows that R_p is given by

$$R_p = \lim_{\omega \to 0} Z_r(\omega), \tag{10}$$

which is equivalent to

$$R_p = \frac{2}{\pi}\int_0^\infty \frac{Z_i(x)}{x}\,dx. \tag{11}$$

The equation (11) has been introduced to point out an easy and alternative way for evaluating corrosion rates.

In fact, the equation (8) shows that $Z_i(\omega) \to 0$ for $\omega \to 0$. Thus, for $\omega \ll 1$ the inequality

$$Z_r(\omega) \gg | Z_i(\omega) | \tag{12}$$

holds.

On the basis of the previous inequality it is correct to assume that the approximation

$$Z_r(\omega) \simeq R_p \tag{13}$$

works properly when ω takes rather small values.

Area method

If one assumes that the response of a given system to sinusoidal signals is described by the network of Fig. 1, it is easy to prove that the experimental points ($Z_r(\omega_k)$, $-Z_i(\omega_k)$) ($k = 1, 2, \ldots, N$) belong to the circumference whose equation is

$$\left[Z_r - \frac{2R_s + R_t}{2}\right]^2 + Z_i^2 = \frac{R_t^2}{4} \tag{14}$$

Thus, in the ideal case, the centre of the circle belongs to the Z_r axis. Under such an hypothesis the area $\pi R_t^2 / 8$ of the upper semicircle gives a good idea of the inertia of the corrosion process, its square root being directly proportional to R_t which is equivalent to R_p.

Finally it is useful to emphasize that experience shows that in many cases the experimental points ($Z_r(\omega)$, $-Z_i(\omega)$) belong to a circumference whose centre lies below the Z_r axis. Such a situation is explained by observing that generally the response of electrochemical systems depends on the frequency of the sinusoidal signal.

EXPERIMENTAL

The effectiveness of a commercial inhibitor, specific for ferrous materials, was determined by examining the behaviour of Armco iron and SA 182 grade F11 (steel A) and SA 182 grade F22 (steel B) low alloy steels in 5 wt% HCl solutions. The specimens were cylindrical in shape and the exposed surface was mechanically prepared using Struers emery papers up to No. 1000. The surface area of each specimen was of about 10 cm^2.

Inhibitor concentrations ranged from 0.1 to 3.0 g/kg. The tests were performed at temperatures of 65, 75, 80 and 90°C and lasted seven hours. The mean corrosion rate was determined by the weight–loss method.

Electrochemical measurements began half an hour after the specimen had been immersed in the solution to allow the system to reach a steady state. They were performed under current control using a Solartron computerized system constituted by a mod. 1286 electrochemical interface and a mod. 1250 frequency response analyzer. An Ingold mod. 363 electrode was used as reference and its filling solution was changed periodically. The frequency interval [0.08, 2 × 10^4] Hz was examined and measurements were performed at the free corrosion potential.

Three electrochemical systems were examined during each run and were connected with the electrochemical interface by a three–channel scanner, each channel being of the 4–way type.

The Solartron computerized system and scanner were driven by suitable software designed to process experimental data at the end of each measurement cycle using a fixed model. This program written in *basic* provides the values of R_s, R_t, R_{pr}, C and the area, S, of the plane region enclosed by the curve $Z_i = f(Z_r)$ and the Z_r axis.

The calculations of R_{pr} and S were made by best–fitting the N pairs $(Z_r(\omega_k), -Z_i(\omega_k))$ ($k = 1, 2, ..., N$) with the relationship

$$Z_r^2 + Z_i^2 + pZ_r + qZ_i + r = 0 \tag{15}$$

where p, q and r are the unknown parameters to be determined. Under these conditions we have $R_{pr} = \sqrt{p^2 - 4r}$.

The values of R_t and C are determined by considering the points belonging to the frequency interval [10^3, 10^4] Hz using the best–fitting method given in /23/. The value of R_s is determined by processing data inside the frequency interval [6 × 10^3 , 2 × 10^4] Hz with the extrapolation method /23/.

For each frequency the current range and the current amplitude are optimized in such a way that the RMS value of the potential difference between the working and reference electrodes is between 4 to 6 mV. Usually the RMS value of the potential difference is rather close to 5 mV.

The integration time depends on the working frequency. For frequency values inside the interval [9 × 10^2, 2.1 × 10^4] Hz the integration time corresponds to 2 × 10^3 periods. The period numbers assigned to the intervals [190, 9 × 10^2] Hz, [5, 190] Hz and [0.08, 5] Hz are 200, 20 and 2 respectively.

The input channels of the frequency response analyzer use the alternating–current coupling over the frequency interval [11, 2 × 10^4] Hz because it provides the best reproducibility of two consecutive measurements. Direct–current coupling is used for frequency values < 10 Hz. In any case, the electrochemical interface eliminates the direct–current components from the current and voltage signals sent to the frequency response analyzer.

At the beginning of each measurement the offset of the oscillator is checked and the electrochemical interface compensates the electrode polarization by supplying a direct current of the opposite sign. This operation is very useful to avoid undue shifts of the free corrosion potential, whose amplitude depends, in principle, on the inhibitor concentration. During this work potential shifts higher than 10 mV were occasionally observed.

RESULTS

Tables 1, 2, 3 and 4 report the mean corrosion rates, expressed in mg $cm^{-2}h^{-1}$, of iron and steels A and B as a function of the inhibitor concentration at temperatures of 65, 75, 80 and 90°C. For comparison, it is useful to recall that the mean corrosion rate of iron, determined through 5–hour tests in 5 wt% HCl solutions without inhibitor and at 75°C, is 44.648 mg $cm^{-2}h^{-1}$.

Tables 5, 6 and 7 show the values of R_s, C, R_t, R_{pr} and S for iron and the two steels, A and B, in inhibited solutions at 65°C. All the data refer to measurements performed 3 hours after the beginning of the test.

Tables 8, 9 and 10 give the values of the electrochemical parameters

Table 1

Mean corrosion rates in some solutions at 65°C

c g/kg	iron	steel A mg cm^{-2} h^{-1}	steel B
0.1	0.124	0.258	0.181
0.2	0.098	0.227	0.183
0.3	0.114	0.161	0.164
0.5	0.115	0.186	0.151
1.0	0.102	0.173	0.167
1.5	0.093	0.181	0.131

Table 2

Mean corrosion rates in some solutions at 75°C

c g/kg	iron	steel A mg cm^{-2} h^{-1}	steel B
0.1	0.181	1.218	0.208
0.2	0.148	0.286	0.173
0.3	0.127	0.279	0.207
0.4	0.097	0.235	0.238
0.5	0.076	0.182	0.234
1.0	0.093	0.210	0.200
1.5	0.064	0.214	0.198
2.0	0.090	0.203	0.175

Table 3

Mean corrosion rates in some solutions at 80°C

c g/kg	iron	steel A mg cm^{-2} h^{-1}	steel B
0.1	0.115	0.510	0.330
0.2	0.066	0.383	0.314
0.3	0.127	0.307	0.561
0.4	0.118	0.372	0.441
0.5	0.104	0.292	0.421
1.0	0.090	0.463	0.319
1.5	0.043	0.216	0.382
2.0	0.059	0.205	0.493

Table 4

Mean corrosion rates in some solutions at 90°C

c g/kg	iron	steel A mg cm^{-2} h^{-1}	steel B
0.3	0.096	0.812	1.308
0.4	0.093	1.262	2.018
0.5	0.061	0.765	1.099
1.0	0.083	0.696	1.409
1.5	0.067	1.115	1.073
3.0	0.040	0.522	2.215

Table 5

Values of the electrochemical parameters for iron in some solutions at 65°C after 3 hours

c g/kg	R_s Ω	C μF cm^{-2}	R_t Ω cm^2	R_{pr} Ω cm^2	S Ω^2 cm^4
0.1	0.24	2.0	53	444	41661
0.2	0.25	2.7	38	527	55589
0.3	0.30	2.9	36	509	52012
0.5	0.35	2.5	46	530	62765
1.0	0.26	2.7	50	730	124282
1.5	0.28	2.7	54	747	144002

Table 6

Values of the electrochemical parameters for the steel A in some solutions at 65°C after 3 hours

c g/kg	R_s Ω	C μF cm^{-2}	R_t Ω cm^2	R_{pr} Ω cm^2	S Ω^2 cm^4
0.1	0.23	14.9	6	226	12983
0.2	0.24	11.2	7	269	16547
0.3	0.89	6.8	8	339	23748
0.5	0.29	5.9	12	386	27133
1.0	0.32	4.9	15	441	34640
1.5	0.67	6.9	8	442	43897

Table 7

Values of the electrochemical parameters for the steel B in some solutions at 65°C after 3 hours

c g/kg	R_s Ω	C μF cm^{-2}	R_s Ω cm^2	R_{pr} Ω cm^2	S Ω^2 cm^4
0.1	0.22	16.9	11	228	12231
0.2	0.29	5.7	15	346	22315
0.3	0.36	4.2	17	412	30607
0.5	0.39	5.4	15	394	31790
1.0	0.32	4.8	15	441	34639
1.5	0.36	5.1	35	448	42846

Table 8

Values of the electrochemical parameters for iron in some solutions at 75°C after 5 hours

c g/kg	R_s Ω	C μF cm^{-2}	R_t Ω cm^2	R_{pr} Ω cm^2	S Ω^2 cm^4
0.1	0.36	1.7	53	387	31507
0.2	0.28	3.9	27	314	20484
0.3	0.28	2.6	45	525	53474
0.4	0.27	2.7	47	545	63184
0.5	0.20	3.1	56	561	73870
1.0	0.22	3.1	61	488	55473
1.5	0.22	3.1	61	564	74188
2.0	0.18	3.2	49	615	84656

Table 9

Values of the electrochemical parameters for the steel A in some solutions at 75°C after 5 hours

c g/kg	R_s Ω	C μF cm^{-2}	R_t Ω cm^2	R_{pr} Ω cm^2	S Ω^2 cm^4
0.1	0.23	12.2	5	31	163
0.2	0.23	17.2	3	119	2941
0.3	0.23	11.9	5	191	7432
0.4	0.36	8.9	7	214	9318
0.5	0.23	5.3	16	193	7518
1.0	0.26	5.4	12	358	19867
1.5	0.23	5.2	15	307	14833
2.0	0.29	5.6	18	408	30276

Table 10

Values of the electrochemical parameters for the steel B in some solutions at 75°C after 5 hours

c g/kg	R_s Ω	C μF cm^{-2}	R_t Ω cm^2	R_{pr} Ω cm^2	S Ω^2 cm^4
0.1	0.21	17.6	5	158	5655
0.2	0.38	6.4	9	178	6574
0.3	0.32	6.3	9	183	6870
0.4	0.32	7.7	9	178	6614
0.5	0.20	18.1	8	87	1868
1.0	0.23	13.2	8	215	9749
1.5	0.24	9.9	10	304	19044
2.0	0.23	8.2	17	313	20905

Table 11

Time behaviour of the interphase capacitance, expressed in μF cm^{-2}, for some solutions at 80°C

Materials	c	time [h]					
	g/kg	0.5	1.5	2.5	3.5	4.5	5.5
iron		2.6	2.2	2.0	1.8	1.7	1.6
steel A	0.2	10.0	10.6	12.4	14.8	16.8	18.9
steel B		6.6	7.7	9.8	11.8	14.5	16.3
iron		3.9	3.4	3.3	3.3	3.3	3.3
steel A	1.5	6.8	6.8	6.5	6.2	6.0	5.8
steel B		14.6	13.6	13.1	15.0	19.7	19.4
iron		4.1	3.5	3.4	3.3	3.3	3.3
steel A	2.0	6.4	6.2	6.2	6.1	5.9	5.8
steel B		22.1	19.0	17.9	17.4	17.0	17.8

Table 12

Time behaviour of the interphase capacitance, expressed in μF cm^{-2}, for some solutions at 90°C

Materials	c	time [h]					
	g/kg	0.5	1.5	2.5	3.5	4.5	5.5
iron		3.5	3.2	3.2	3.1	3.1	3.1
steel A	0.5	7.9	7.9	7.6	7.3	7.4	6.5
steel B		11.8	12.6	17.3	22.0	25.3	27.5
iron		3.6	3.4	3.3	3.3	3.3	3.3
steel A	1.0	7.9	8.5	8.4	8.2	8.5	9.2
steel B		12.4	11.4	10.1	19.8	60.3	61.3
iron		4.6	4.0	3.8	3.7	3.7	3.6
steel A	3.0	7.9	8.5	8.4	8.2	8.5	9.2
steel B		19.9	21.3	36.1	56.9	60.7	60.6

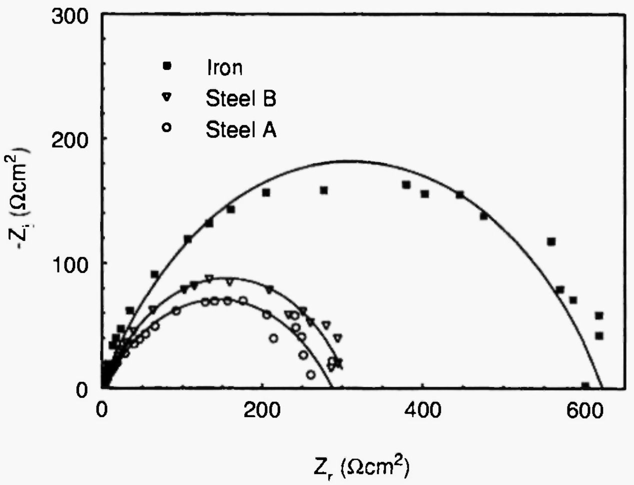

Fig. 2: Behaviour of the function $Z_i = -Z_i(Z_r)$ for iron and steels A and B in a 5 wt% HCl solution containing 1.5 g/kg of inhibitor at 75°C.

obtained from measurements performed five hours and a half after beginning of the tests for iron and steels A and B in the inhibited solutions at 75°C.

Finally, Tables 11 and 12 refer to some inhibited solutions at 80 and 90°C and show the variation of *C* as a function of time.

DISCUSSION

The first comment regards the choice of the procedure of performing sinusoidal current measurements because the main aim of this work was to assess the validity and accuracy of the impedance technique in providing reliable information on the performance of corrosion inhibitors. This point deserves careful examination because to understand properly corrosion processes it is mandatory to collect data free from systematic errors.

Examination of the network of Fig. 1 indicates that $Z_r(\omega)$ must always take values > 0 for $\omega \gg 1$ when the reference electrode does not introduce important distortions in the system response. During the present work it was observed that measurements performed under the current control permit to comply with the previous constraint over the frequency interval $[0.08, 2 \times 10^4]$ Hz. On the contrary the potentiostatic mode usually produces meaningless data close to 2 × 10^4 Hz, $Z_r(\omega)$ being < 0 or $Z_i(\omega) > 0$.

This observation has a noticeable practical importance as concerns the experimental methodology to be used to rank the efficiency of various products in restraining corrosion rates of metallic materials and define proper acceptance criteria based on data obtained from electrochemical measurements.

From this point of view the interphase capacitance, whose value depends on the surface coverage ϑ, seems to be a valid parameter to assess the effectiveness and chemical stability of corrosion inhibitors. In fact, the values of C can be easily determined by performing sinusoidal current measurements in the high frequency region. From a practical point of view, interesting advantages of such a procedure are that measurements are not time consuming and do not perturb the free corrosion state.

This remark also stresses the usefulness of developing suitable software to perform measurements under equivalent conditions so that the system response changes in a continuous way over a broad frequency interval. To this end it is mandatory to impose that the potential difference between the reference and working electrodes takes a nearly constant value over the examined ω interval. Furthermore, such a constraint is essential to operate inside the ΔE interval where the current–voltage characteristic can be approximated by a linear trend with good accuracy.

The continuous change in the system response is particularly important for the present work because the use of C is proposed on an empirical basis and its validity is justified by comparison to the trend of R_{pr} which plays the same role as the traditional polarization resistance R_p.

To this end and aiming at providing a clear explanation of the tight link between R_p and R_{pr} some considerations on the transform of Kramers and Kronig were made to point out the correctness of considering the polarization resistance as a limiting case for $\omega \rightarrow 0$. The main value of this approach is to demonstrate that in the low-frequency region the relationship $Z_r(\omega) \simeq R_p$ is a satisfactory approximation.

At any rate, the ω value relating to R_{pr} falls in the low-frequency region. From this point of view there is no real need to carry out measurements at $\omega \ll 1$ in order to obtain a more accurate evaluation of R_p.

As regards the inhibitor performance in restraining corrosion processes, the data given in Tables from 1 to 4 show that the mean corrosion rates are very small and depend on the chemical composition of the three materials. The comparatively high value exhibited by the steel A in the solution containing 0.1 g/kg of inhibitor at 75°C is explained by observing that in this case localised attacks were observed in small zones near the two bases of the cylindrical specimen.

Furthermore, from the examination of the previous Tables it follows that for each temperature the inhibitor is more effective in restraining the corrosion of iron. Moreover, the value of the mean corrosion rate observed in the blank solution at 75°C indicates that the addition of small amounts of this product to HCl solutions drastically reduces the corrosion rate of iron, the lowest bound of P% being 99.6.

On the other hand, the presence of chromium in steels A and B seems to stimulate the corrosion process. In particular this observation refers to the data relating to the steel B in solutions at 90°C. In fact, the mean corrosion rate of these low alloy steels rises as temperature increases and is rather different from that of iron also when the inhibitor concentration is inside the interval of the optimum performance. In fact, as regards iron it can be underlined that its mean corrosion rate seems to be insensitive to the inhibitor concentration when $c \geq 0.4$ g/kg.

This result has a noticeable practical importance as concerns acid cleaning operations of low carbon steels because it stresses that inhomogeneities of inhibitor distribution in the solution bulk do not affect corrosion rates until local values of c are not too far from the recommended one.

Examination of Tables from 5 to 10 shows that the transfer resistance, R_t, is not a valid parameter to monitor corrosion rates. This result underlines that the behaviour of a corroding system is not changed by high–frequency sinusoidal signals when electrode reactions are not able to follow fast variations. Under such hypotheses only displacement current is flowing through the metal–solution interphase.

In contrast, the polarization resistance, R_{pr}, is a valid parameter to obtain reliable information on the performance of an organic inhibitor. The values of R_{pr} have the same order of magnitude as those quoted in /24/ where the product performance was examined by performing polarization measurements of the potentiostatic type over the [–20, 20] mV ΔE interval. This observation supports the validity of the equation (13), the value of ω relating to R_{pr} belonging to the low–frequency region.

In particular examination of Tables 5, 6 and 7 shows that the value of R_{pr} increases as the mean corrosion rate decreases, even if in some cases this trend is not strictly observed. This slight discrepancy can be explained by observing that electrochemical measurements are sensitive to instantaneous corrosion rates.

The previous considerations apply also for the area method which provides an accurate and reliable evaluation of the performance of corrosion inhibitors. This result is not surprising because in the present case the relationship $S \propto R_{pr}^2$ holds. Furthermore, it is useful to underline that the performance of sinusoidal current measurements over a broad frequency interval permits to detect any slight difference in the inhibitor behaviour. Thus, this method can be considered of the global type.

However, it should be noted that S could, in principle, depend on the centre angle subtended by the circumference arc which in its turn might change with inhibitor concentration. Thus, it is useful to consider the centre angle when S does not exhibit the same trend as R_{pr}.

As regards the interphase capacitance it is important to stress that when the values of R_{pr} are high, the values of C are usually small. This observation is the basis to establish an empirical relationship between corrosion rate and double–layer capacitance and to state that this quantity is an interesting parameter to evaluate the efficiency of corrosion inhibitors even if corrosion rates do not depend only on electrode coverage which usually is the prevailing factor /18/. In fact, it can be stated, in principle, that small values of C correspond with moderate corrosion rates.

To this end it is useful to recall that in the case of iron in uninhibited 5 wt% HCl solutions at 35 and 45°C, C took values of 23.8 and 43.3 μF cm^{-2}, respectively. These values refer to measurements performed half an hour after the specimen immersion in the test solution. Experience shows that for iron in 5 wt% HCl solutions C is usually a monotonic increasing function of time and that it is quite hard to obtain reliable values when the solution temperature is higher than 45°C.

Examination of the data in Table 5, concerning iron, shows that for concentration values from 0.1 to 1.5 g/kg C takes nearly constant values lower than 3 μF cm^{-2}. This result seems to indicate that C is not very sensitive to the inhibitor concentration when ϑ takes values close to 1.

It should be noted, however, that in the case of the steel A in the solution at 75°C and containing 0.1 g/kg of inhibitor, the value of C is rather small, although the mean corrosion rate is not negligible. This discrepancy is explained by observing that the prevailing contribution to the corrosion rate was given by localized attacks on very small zones having a negligible area. In fact, experimental data have shown that the changes in the C value throughout the test were not appreciable. At the beginning C took a value of about 9 μF cm^{-2}, while R_{pr} was equal to 107 Ω cm^2.

The quite small value of the polarization resistance R_{pr} (31 Ω cm^2) confirms the validity of the previous remark because localized attacks determine a significant decrease in this quantity.

At 75°C C is a valid parameter to rank the performance of corrosion inhibitors if sinusoidal current measurements are performed using iron electrodes. The value of C does not exhibit any anomalous behaviour and for iron is always less than 4 μF cm^{-2}. Furthermore, for the three materials the trends of R_{pr} are very regular.

From the cases examined it can be inferred that the inhibitor is very effective in restraining iron corrosion. During all the tests relating to iron inhibitor also proved to be thermally stable, the value of C remaining practically constant.

The same comment applies to the behaviour of the steel A, except for the solution at 80°C and containing 0.2 g/kg of inhibitor, in which case C is a monotonic increasing function of time.

In contrast, in the case of the steel B, C increases with time, except for the solution at 80°C and containing 2.0 g/kg of inhibitor. In this last case C seems to be a decreasing function of time.

The effect of the inhibitor in restraining the corrosion of the steel B, which contains about 2.25% of chromium, in solutions at 90°C is hard to explain. The significant increase in the C value could be justified by assuming that close to the electrode surface the inhibitor concentration takes values lower than those in the solution bulk.

Such a situation could be due to the formation of decay products which are favoured by the accumulation of Cr^{6+} ions, which are strongly oxidant, close to the electrode surface as a consequence of the oxidation of Cr^{3+} ions. Experimental data seem to support this hypothesis because C increases as the amount of corrosion products entering the solution augments. The validity of this hypothesis seems to be supported by the observation that the solution bulk is very effective in restraining iron corrosion.

At any rate the decay products of the corrosion inhibitor due to its oxidation by Cr^{6+} ions are present at all the examined temperatures even if the inhibitor–molecule depletion at the metal–solution interphase does not affect the trend of C as a function of time when the solution temperature takes values < 75°C. From this point of view C is a useful quantity to detect any anomalous condition where Cr^{6+} ions play an important role.

CONCLUSIONS

The surface impedance technique permits a good evaluation of the corrosion–inhibitor performance when measurements are performed under current control and over frequency intervals such as [0.08, 2 × 10^4] Hz. The double–layer capacitance, the polarization resistance R_{pr} and the area of the plane region bounded by the curve $Z_i = -Z_i(Z_r)$ and the axis Z_r seem to be the most promising electrochemical parameters for a reliable evaluation of the efficiency of the inhibitor in restraining a corrosion process in acid environments.

Suitable software for performing measurements and processing experimental data through appropriate mathematical models of the metal–solution interphase permits corrosion workers to select carefully corrosion inhibitors to be employed for specific applications and is a valid tool to check the effectiveness of new compound blends. In particular, in opposition to the traditional polarization resistance technique the area method is able to detect very small differences in the inhibitor performance as a function of concentration. Of course, the area of the region enclosed by the curve $Z_i = -Z_i(Z_r)$ and the Z_r axis can be computed using the most suitable best–fitting function for the case under examination.

The trend of C seems to indicate that the performance of a corrosion inhibitor may depend on the chemical composition and the microstructure of materials. This remark stresses that the efficacy of an organic compound in restraining corrosion processes cannot be determined in an absolute way and highlights the usefulness of performing tests simulating as faithfully as possible the operating conditions that will be meet during each application.

Finally, experimental data obtained for iron and the two low alloy steels point out that the chemical stability of corrosion inhibitors in hot 5 wt% HCl solutions depends mainly on the physicochemical characteristics of metals and alloys. In fact, the trend of C as a function of time at 90°C shows that the inhibitor performance in the case of iron is very different from that observed for the steel B. On the basis of this experimental observation and the well–established consideration that the value of C depends on the adsorption of the inhibitor molecules on the electrode surface, it is correct to assume that the presence of chromium may impair the chemical stability and favour the appearance of decay products.

LIST OF SYMBOLS

i	current density
I_{cor}	corrosion current density
α	reciprocal of the slope of the anodic Tafel straight line on a natural logarithm basis
β	reciprocal of the slope of the cathodic Tafel straight line on a natural logarithm basis
ΔE	potential difference referred to the free corrosion potential
P%	inhibitor effectiveness
c	inhibitor concentration
R_{p}	polarization resistance
C	differential capacitance of the metal–solution interphase
C_{I}	differential capacitance of a monolayer of adsorbed inhibitor molecules
ϑ	surface coverage
R_{s}	solution resistance
ω	angular frequency of a sinusoidal signal
$Z(\omega)$	surface impedance
Z_{r}	real part of the surface impedance
Z_{i}	imaginary part of the surface impedance
R_{t}	transfer resistance
RMS	root mean square

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