



*Dedicated to Professor Alexandru T. Balaban
on the occasion of his 80th anniversary*

THE STUDY OF CORROSION REACTIONS BY MEANS OF A RADIOMETRIC TECHNIQUE

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This paper deals with a kinetic study of the corrosion reactions of two steels immersed in aggressive solutions of HCl and HNO₃. The corrosion reactions in very strong acid media follow a first order kinetic, as was found in other similar papers. By means of a radiometric method based on the β rays absorption in the layers of iron ions passed into acid media through the anodic dissolution of the steels, the values of the global constant of rate corrosion can be determined. From cyclic voltamograms it was established that in HNO₃ media, the corrosion process is developed in two stages, instead of one as in HCl solutions. This statement corresponds to the results obtained from the kinetic study, when the 2 global constants of corrosion rate were found.

INTRODUCTION

There are series of monographs which deal with the use of radioisotopes in investigating the corrosion of metals and alloys.¹⁻²

Thus, Hohorst³ researched the corrosion of some alloys by using marked atoms. In this respect, firstly a Kr-85 radionuclide was immersed into a matrix made from the investigated material, and afterwards the corrosion was started placing the metallic sample into an aggressive medium. Corrosion was monitored based on the radioactivity of the Kr-85 which was distributed through the reactant system.

Focusing on the irradiation of a corroded zone with γ - rays, Bochinin and Kulikov⁴ found the corrosion degree of some metallic parts inside of industrial plants. Through different penetration by Cl-36 of metallic surfaces, Naqvi and others⁵ researched the corrosion of various types of steels incorporated in industrial equipments. Other authors⁶⁻⁹ used various research techniques: Mössbauer spectroscopy, X-ray diffraction, γ -spectrometry, surface spectroscopy, etc., for identifying corrosion

products (radioactive or stable) which appear inside of nuclear power plants.

For the kinetic characterization of the complex corrosion process several papers were published. They present mathematical equations with some physico-chemical parameters which are varying *versus* the solid sample – aggressive media contact time.

In this respect, Mathur and Vasudevan¹⁰ studied the iron corrosion in HCl, H₂SO₄ and H₃PO₄ at various temperatures. From experimental data, they established that between the reaction rate (r) and the acid concentration (C) the following kinetic equation can be written:

$$r = k \cdot \exp(B \cdot C) \quad (1)$$

where k is the rate constant, and B represents another constant which takes into account the geometry of the corroded probe.

On the other hand, Khadom and others¹¹ established that the effect of temperature and HCl concentration on the reaction rate, which has been described above by Mathur formula, can be calculated using the following equation:

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$$r = A \exp\left(-\frac{E}{RT}\right) \cdot \exp(BC) \quad (2)$$

Vettegren *et al.*¹² showed that the variation in time of the concentration of corrosion products, which result out of the contact between steel sample and sea water, can be expressed by a first-order kinetic equation:

$$B_t = B_\infty [1 - \exp(-k_c \cdot t)] \quad (3)$$

Here $B(t)$ and B_∞ represent the concentration of iron ions passed into the corrosive medium at a given time t and at the end of experiment, while k_c refers to the reaction rate constant.

The corrosion reaction of the carbon steel in a 3% NaCl solution has been researched from a coulometric method by Kuzmak și Kozheurov¹³ who have found that both the gravimetrically determined concentrations of Fe^{2+} and Fe^{3+} which have passed into solution ($q_{Fe^{2+}}$ and $q_{Fe^{3+}}$), and the measured current intensity, which corresponds to these species, $I_{Fe^{2+}}$ and $I_{Fe^{3+}}$, can be kinetically expressed by the following relations:

$$\begin{aligned} I_{Fe^{2+}} &= I_{0a} \exp(-k_a t) \text{ and} \\ I_{Fe^{3+}} &= I_{0c} \exp(-k_c t) \end{aligned} \quad (4)$$

Here, I_{0a} and I_{0c} refer to the initial values of these intensities, while t is the contact time between the solid sample-aggressive medium and k means the effective rate constant of the corrosion reaction.

Popova *et al.*¹⁴ have studied the corroding of a mild steel in HCl solutions in the absence and in the presence of some inhibitors. It has been found that, in the absence of the inhibitor, the corrosion process can be rendered through self accelerating reactions, described by the following kinetic equation:

$$x = -\frac{I}{a} \ln(1 - abt) \quad (5)$$

where x stands for the weight loss after a given contact time t between reactants, a is a inhomogeneity parameter for the solid-solution interface, while b is a constant.

In the presence of the inhibitor the kinetic equation is a zero-order one.

Moraru and others¹⁵ have studied the corrosion of two steels in solutions of 3% NaCl și KCl,

showing that this process can be kinetically characterized by a formula like this:

$$x = -\frac{a}{b} [1 - \exp(-at)] \quad (6)$$

where a and b are the coefficients resulted through a linear regression (Levenberg-Marquard), and t is steel-solution contact time.

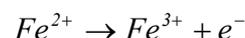
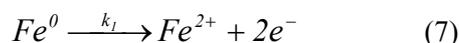
Similar exponential formulae are presented by Bujak and Varga¹⁶ when "thin gap method" is used for studying ion reduction $^{51}CrO_4^{2-}$ on a platinum electrode.

The present paper is a new sequence of some previous studies¹⁷⁻²² concerning the investigation the corrosion of certain steels in different experimental conditions, based on the radioactive tracers methods.

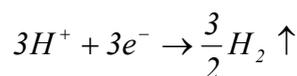
RESULTS AND DISCUSSION

In an acid medium, the metal and alloy corrosion can be rendered by a sequence of reactions

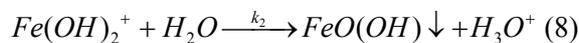
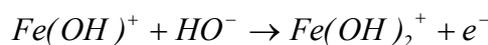
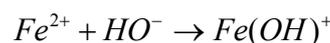
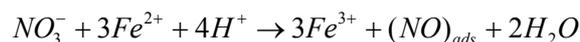
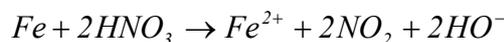
i) anodic dissolution of the sample:



ii) the reduction of ions H^+ , with a depolarizing role in that corrosive medium, owing to the capture of electrons which were freed before:



In the presence of nitric acid, the corrosion can go on through a sequence of intermediary reactions²³⁻²⁴ due to anions NO_3^- being reduced to NO_2^- or even to NO (gas):



In fact, the involvement of the Fe^{2+} ions in the reduction of NO_3^- , but also the participation of Fe^{3+} species suggested from the intermediary reactions, were proved by cyclic voltammetry.

Concretely, through these studies, the presence of Fe^{2+} and Fe^{3+} ions has been proven in the different corrosion reactions described above, a fact that confirms the truthfulness of the proposed mechanisms.

Taking into consideration the sequences of the above mentioned reactions (7-8), it can be stated

$$-\frac{d[Fe(OH)_2^+]}{dt} = k_2 [Fe(OH)_2^+] \cdot [H_2O] \quad \text{or} \quad (11)$$

$$\ln[Fe(OH)_2^+] = -k_2 t, \text{ or } [Fe(OH)_2^+] = [Fe^{3+}] = e^{-k_2 t}. \quad (12)$$

These kinetic equations resemble those formerly presented (1-6) by other authors, being rendered likewise through an exponential term.

By means of experimental data, it has been deduced that, as the concentration of iron ions increases in the acid solution, the intensity of β -rays measured, as counting rate R , decreases, and therefore the relations above written can be rendered in the following way:

$$\ln R = -k_1 t \quad \text{and} \quad (13)$$

$$\ln R = k_2 t \quad (14)$$

If the experimental data are plotted in the coordinate $\ln R = f(t)$, a series of straight lines with several slopes, were obtained. From these slopes can be determined the values of the global rate constants of the investigated corrosion reactions.

The practical results are shown in Figs. 1 and 2 and Table 1.

Hence, it can be observed, in case of HCl, for each reactant system, it get only a descending straight line, whereas, for the HNO_3 case, two straight lines result: a descending one and an ascending one.

The explanation resides in the fact that the corrosive medium represented by HCl did not favor the appearance of less soluble reaction products (salts), because the corresponding chlorides, formed with the iron ions and with those belonging to other elements, have a high degree of solubility.

Yet, for the nitric acid, it is initially noticed an ever-increasing accumulation of Fe^{2+} ions (so called the active zone with descending curve), and

that the corrosion process develops according to a first order kinetics, that is:

$$\frac{d[Fe^{2+}]}{dt} = k_1 [Fe^{2+}], \text{ or} \quad (9)$$

$$\ln[Fe^{2+}] = k_1 t, \text{ or } [Fe^{2+}] = e^{k_1 t}. \quad (10)$$

The reaction (8) follows a "pseudo first order" kinetics, which means:

after reaching a highest point (the passive zone, with a minimum value of $\ln R$), a decrease of concentration in Fe^{2+} species produced. These Fe^{2+} ions started a reduction of NO_3^- anions, resulting nitrogen species slower oxidation numbers (IV and II), together with the appearance of less soluble products of Fe^{3+} , such as $FeO(OH)$, Fe_2O_3 etc. (the post passive zone).²⁵ Similar results, which include the corrosion reactions zones, have been reported by other authors.²⁶⁻²⁷

On the other hand, the results of the electrochemical study described are shown both in the cyclic voltammograms (Figs. 3-5) and also in Table 2.

The reduction reaction of NO_3^- ions is observed in these 3 cyclic voltammograms, in cathodic zone, both in the absence (Fig. 3a) or in presence of steel samples (Fig. 3b and 3c). If the acid concentration is higher, the peak intensity in the reduction zone increases, which can be explained by the reduction of NO_3^- ions to NO_2^- or NO.

The appearance of the Fe^{2+} and Fe^{3+} ions is proved by two maxima in the voltammograms in the part of anodic oxidation due to their reactions with nitric acid. It is observed a direct dependence between the values of rate constants k_1 and k_2 (Table 1) from kinetic study and the values of the maxima anodic intensities for the same iron species (Table 2) passed into solution through corrosion process.

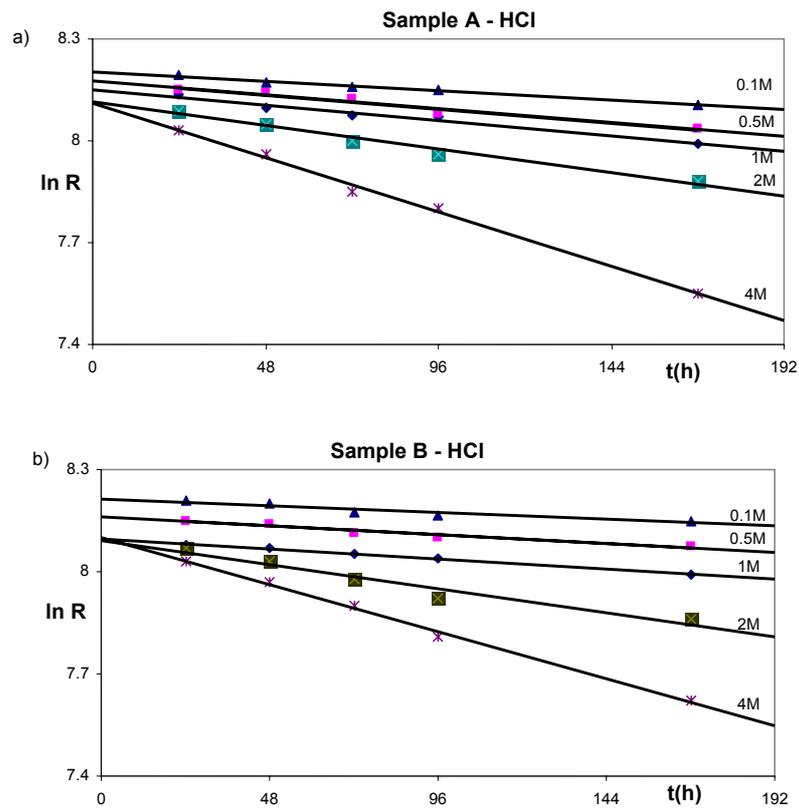


Fig. 1 – Variation in time of the intensity of β -rays (as logarithms) for steel sample A and B immersed in different HCl aggressive media.

Table 1

The constant values of global corrosion rate for of the studied systems

Sample	Reaction medium	Concentration (M)	$k_1(\text{h}^{-1}) \times 10^3$	$k_2(\text{h}^{-1}) \times 10^4$
A	HCl	4	3.33	-
		2	2.46	-
		1	0.94	-
		0.5	0.81	-
		0.1	0.59	-
B	HCl	4	2.89	-
		2	1.48	-
		1	0.63	-
		0.5	0.53	-
		0.1	0.42	-
A	HNO ₃	4	3.29	10.01
		2	2.02	4.16
		1	0.92	2.50
		0.5	0.58	2.29
		0.1	0.20	0.83
B	HNO ₃	4	2.71	6.45
		2	1.33	3.95
		1	0.56	0.62
		0.5	0.45	2.71
		0.1	0.18	4.16

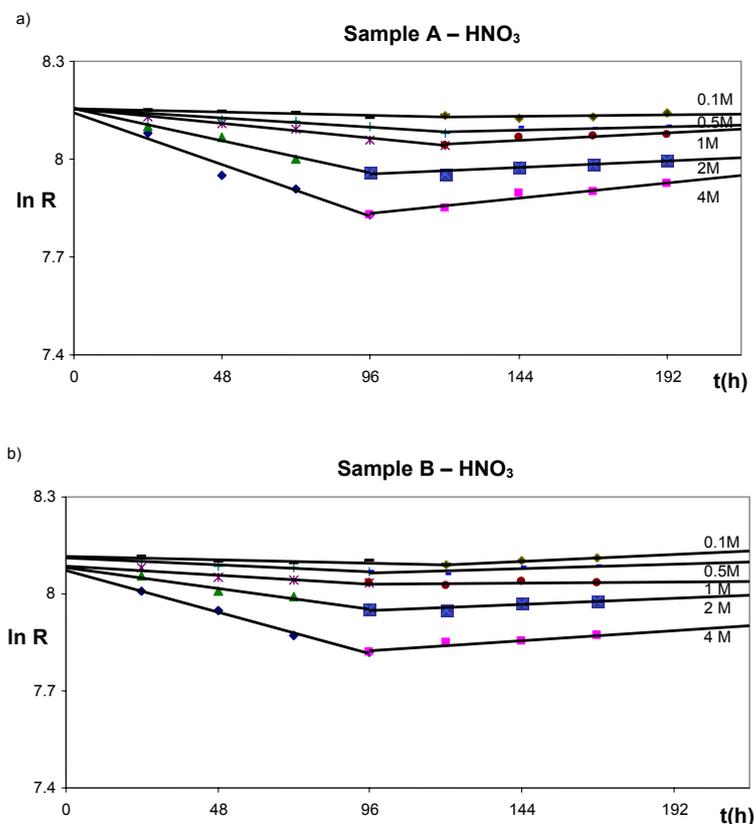


Fig. 2 – Dependence of β -rays intensities (as logarithms) and the contact time for steel samples A and B put in several HNO_3 corrosive media.

From the given results it can be observed that the corrosion process is more intense (with higher values of the global rate constants) when the concentration of the aggressive medium of a given steel is higher.

At the same time, the corrosion process is faster in HCl than in HNO_3 for a given steel sample. However, for the given aggressive solution, corrosion is more intense in the case where the steel has a higher percent of carbon.

On the other hand the presence of transitional metals (as Cr, Ni, Cu) from steel composition can hinder the development of corrosion process because the electrons freed through anodic dissolving of solid sample, are captured by the

“3d” atomic orbitals. In this way these electrons cannot participate afterwards in the reduction of H^+ ions, thus passing the corrosion reaction.

From these reasons the corrosion is stronger for A as for B steel species, as was found in this radiokinetic study.

Furthermore, it can be noticed a proportionality between the rate constants values of the corrosion reactions of the two steels in HNO_3 solutions and the intensity values of anodic current for the two peaks corresponding to Fe^{2+} and Fe^{3+} ions, pointed out in the shown voltammograms, which confirms the validity of the proposed method in the approach of that particular study.

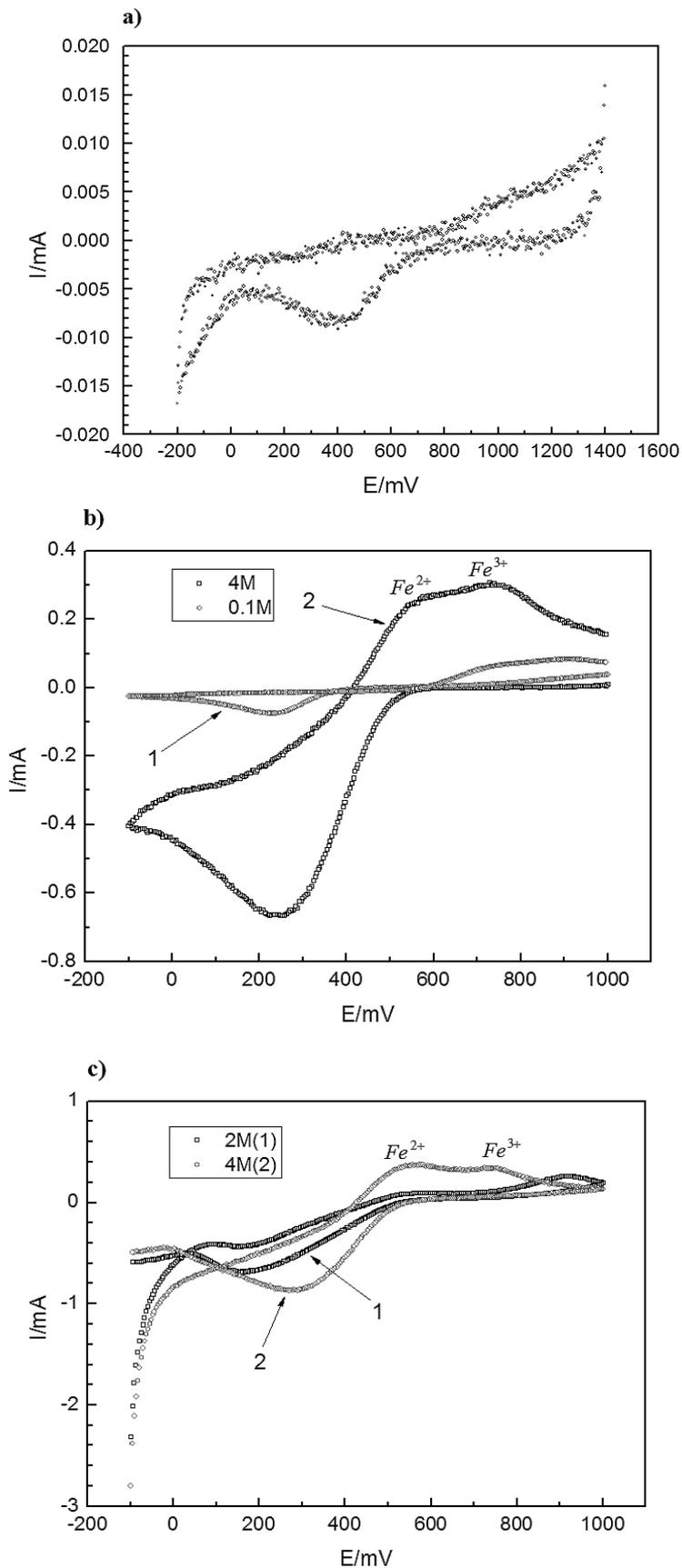


Fig. 3 – The cyclic voltammograms investigate systems: for HNO_3 (4M) without steel samples (a), or in the presence of steels: A immersed in HNO_3 (0.1 and 4 M) (b) and B put in HNO_3 (2 and 4 M) (c).

Table 2

Values of electrode potential E (mV) and current intensity I (μA) from cyclic voltammograms, with a scanning rate of 50 mV / sec, double range: -100 ÷ 1200 mV

Peak type	Sample	Peak features	Solution concentration HNO_3 (M)				
			0.1	0.5	1	2	4
Reduction peak	A	E(mV)	228	220	148	152	253
		I(μA)	-76	-410	-582	-578	-668
	B	E(mV)	204	227	127	164	286
		I(μA)	-42.1	-133	-546	-691	-889
Oxidation peak	A	E(mV)	565	550	917	574	581
		I(μA)	63.9	58.2	569	849	862
		E(mV)	711	880	1100	925	732
		I(μA)	81.1	222	245	270	303
	B	E(mV)	240	266	526	534	547
		I(μA)	74.0	67.0	69.5	80.8	390
		E(mV)	330	522	780	922	946
		I(μA)	61.1	63.6	197	254	338

EXPERIMENTAL

Radiometric determinations

At first 10 samples of the two studied steels were prepared. They had rectangular shapes and close measures (3x2cm). The steel samples were faced with emery paper,

cleaned with acetone and washed with water, after which they were introduced, separately in 20 cylindrical glass vials of 50 mL capacity.

The chemical composition of the two steels (A and B) is shown in Table 3.

Table 3

Chemical composition of the two studied steels (A and B)

Element	Composition %	
	Sample A	Sample B
C	0.19	0.14
Si	0.21	0.23
Mn	0.61	0.63
P	0.021	0.01
S	0.008	0.004
Cr	0.05	0.09
Mo	0.02	0.02
Ni	0.03	0.07
Al	0.036	0.025
Cu	0.04	0.17
V	0.003	-
B	-	0.0005

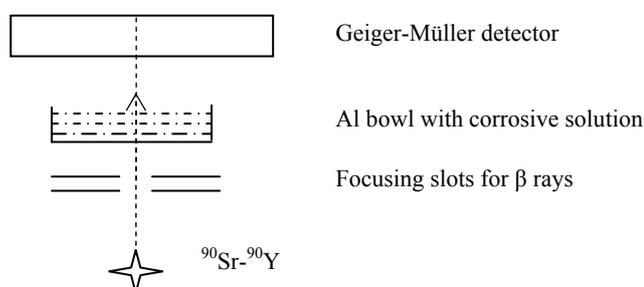


Fig. 4 – The experimental device for the determination of the β -ray intensity which penetrated the corrosive solution.

Then, the glass vials were filled with 30 mL of corrosive solution which contained, correspondingly, HCl or HNO_3 of different concentrations (4; 2; 1; 0.5 and 0.1M) obtaining 20

reactant systems. The vials were hermetically sealed in order to avoid the evaporation of the corrosive solution during the reaction time.

At given periods of time, after 24 hours, out of each vials, were taken out 0.3 mL of corrosive solution. This amount of solution contained iron ions resulting from anodic dissolution of steel was put into a 1 mL capacity aluminum bowl.

In order to determine the concentration of the iron ions, a method based on the absorption of β rays emitted by an external radioactive source of ^{90}Sr - ^{90}Y ($\Lambda=2 \times 10^8 \text{Bq/g}$), placed on the base of experimental device (outlined in Fig. 4) was employed.

It was noted that, as the steel-solution contact time increases due to the corrosion reactions, the concentration of iron ions passed through the corrosive medium by anodic dissolving of the given sample increases as well, while the intensity of β -rays measured (R) by a Geiger-Müller (1.5mg/cm^2) connected to a electronic scaler VSP-14M, decreases.

It is known that the β -rays, emitted from a radioactive nuclide, have a continuous energy spectrum and therefore are absorbed progressively more and more by the iron ions when their concentrations become higher and higher inside of the acid media.

Taking into account the interdependence between the values of the measured β -rays intensity (R) and the concentration of the iron ions inside of a corrosive solution, this method could be used to study the kinetics of the corrosion process.

Electrochemical determinations

For the purpose of the voltammetric characterization of the behavior of the two steels dissolved in HCl și HNO₃, in different concentrations, a VoltaLab32-Radiometer, Copenhagen device was used. It consisted of two parts: DEA 332 Digital Electrochemical Analyzer and IMT-102 Electrochemical Interface, to which a 3-electrode electrochemical cell was attached. The working electrode was a platinum disc one (EDPt) with $\phi = 2 \text{mm}$, while the reference one was represented by a saturated calomel electrode (ECS), whereas, for the auxiliary one, a platinum wire electrode was chosen.

Before the experimental determinations, the solutions in the electrolytic cell were desaired by inert gas (nitrogen) for 5 minutes at a room temperature.

It should be mentioned that such as cyclic voltammograms (CV) could be obtained only for the solutions HNO₃, but not for HCl.

In this respect, at first the cyclic voltammogram was drawn for the solution of 4M HNO₃ (without steel samples) on EDPt, at a scanning rate of 50 mV/sec on the entire domain: 1400-2000 mV, in both senses. From the oscillations of the measured current, represented by the distribution of the experimental points, a 408 mV cathodic peak was revealed, having an current of $I_c = -8.6 \mu\text{A}$, which was attributed to the reduction of NO₃⁻ la NO₂⁻ ions, a fact that was confirmed by scientific literature.²⁴⁻²⁵

Afterwards, other cyclic voltammograms were drawn, at different scanning rates, for the solutions containing the two steels, in different corrosive HNO₃ media. Each time, two peaks of anodic oxidation of Fe²⁺ and Fe³⁺ ions and one only for the cathode reduction of anions NO₃⁻ appeared.

CONCLUSIONS

The corrosion reactions were studied by means of a radiometric method, based on the absorption of β -rays by the layers formed from the iron ions which passed into aggressive medium through anodic dissolution of a steel sample.

This process can be characterized kinetically by means of the rate global constants, much more exactly as "classical" methods: titrimetric or gravimetric analysis, etc.

The cyclic voltammograms proved that the oxidation of iron ions in nitric acid occurred in two steps, as is found using this radiometric technique too.

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