

Use of the β -Rays Absorption for the Study of Corrosion Reactions

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Abstract: This work deals with a radiometric method proposed for the study of metal and alloy corrosion, based on the absorption of the β rays emitted by an external source ^{90}Sr - ^{90}Y . These radiations which are passing through the corrosive medium are absorbed partially by the iron ions appeared inside by the anodic oxidation of a steel sample. The concept of the 'constant of global reaction rate' has been introduced to describe the dissolution of the 3 steel samples in aggressive solutions: HCl, H_2SO_4 and CH_3COOH , from a kinetic point of view. The corrosion process takes place in different ways in reactions studied, being influenced both by the characteristics of the steel and of the aggressive medium, decreasing as: $\text{HCl} > \text{H}_2\text{SO}_4 > \text{CH}_3\text{COOH}$

Keywords: β -rays absorption, Corrosion, Kinetics, Radiometric method, Steel

Introduction

There are a series of papers and monographs which describe the use of marked atoms in explaining the corrosion processes in different experimental conditions¹⁻⁴.

In this context, Varga et al⁵ have investigated the accumulation of the radioactive corrosion products, Co-60, Mn-54, Cr-51, Fe-59, etc, inside of cooling agent steel pipes, within the VUER nuclear plant, applying some tracer techniques, in 'situ' together with other methods based on Moessbauer spectroscopy, X-rays diffraction, etc. Navqi and his collaborators⁶ have studied steel corrosion in aggressive solutions by analysing the degree of penetration of marked chlorine $^{36}\text{Cl}_2$ through corroded surfaces.

The present paper presents another approach proper to investigate the corrosion process kinetics than that outlined in previous studies⁷⁻²⁰. These former investigations were based on the absorption of β - or γ -rays in corroded surfaces, or in aggressive media, β -rays backscattering, isotopic internal dilution, or γ rays transmission.

A lot of international research studies should be mentioned concerning to the kinetically characterization of the corrosion process²¹⁻²⁴. These shown the way in which

corrosion reactions in different experimental situations can be defined by different mathematical equations:

$$\text{- linear } x = k \cdot t \quad (1)$$

$$\text{- parabolic: } x^2 = k \cdot t \quad (2)$$

$$\text{- exponential: } x = \exp(k \cdot t) \quad (3)$$

regarding to the variation in the time (t) of anodic dissolution of a metallic sample (x) in aggressive medium.

For example, Vettegren et al²⁵ have researched the steel corrosion in sea water proposing a mathematic expression to describe this first-order kinetic reaction:

$$B(t) = B(\infty) \cdot [1 - \exp(-k_c \cdot t)] \quad (4)$$

Here, $B(t)$ and $B(\infty)$ are the iron ion concentrations for a specific time t and, respectively, at the end of the experiment (∞), while k_c is the rate constant for this process.

Experimental

A series of rectangular samples (3x2cm) from 3 different steel samples were used. Their composition is presented in Table 1.

Table1. The chemical composition of steel samples

% steel sample	C	Si	Mn	Cr	Mo	Ni	Al	Cu	V
XII	0.3700	0.2700	1.0200	0.0600	0.0300	0.1100	0.0050	0.1800	0.0040
XIII	0.1900	0.2700	0.8300	0.1000	0.0400	0.1100	0.0200	0.2200	0.0050
XIV	0.3200	0.2000	0.7100	0.5400	0.1900	0.0400	0.0250	0.1400	0.0050

These have been faced with emery paper, degreased with acetone and washed with water, and then placed in cylindrical 50 ml glass vials.

Acid solutions were prepared, containing: HCl, H₂SO₄ and CH₃COOH with 3 concentrations: 1; 0.5 and 0.1 M. From each of these solutions, 30 ml were poured into the glass vials having inside the steel samples, obtaining 27 reactant systems. Then, the cylindrical glass vials were hermetically closed in order to avoid water evaporation. From this moment the corrosion reactions were considered as started.

Every 24 hours, 0.5 ml of solutions were taken out of each reactant system, in order to determine the evolution in time of the concentration of iron ions that passed through the corrosive solution through the anodic dissolution of the steel. The 0.5 ml of solution that have

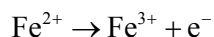
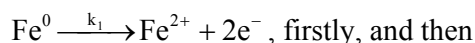
been taken out and then has been transferred into an aluminium bowl placed above a radioactive source of ^{90}Sr - ^{90}Y ($\Lambda = 2 \times 10^8 \text{ Bq/g}$) which emitted pure β rays, collimated through 2 focusing slots. Above the aluminium bowl, a Geiger-Müller β (1.5 mg/cm^2) detector was installed, connected to an electronic scaler VSP-M-14, in order to determine the intensity of β rays after they have penetrated the solution with the Fe^{n+} ions resulted through the steel corrosion processes.

Taking into account the experiment results, it has been noted that as the corrosion process develops in time, the iron ion concentration increases, $[\text{Fe}^{n+}] = [\text{Fe}^{2+}] + [\text{Fe}^{3+}]$, while the intensity of β rays measured by the GM detector decreases. In other words, with the increasing in iron ions concentration, the β rays, with different energy values, are absorbed more and more by the iron ions layers, which render a decreasing of the measured activity values, as counting rate (R).

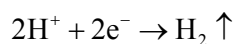
Results and discussions

The corrosion process can be illustrated through a sequence of reactions²⁶⁻²⁷, presented in two phases:

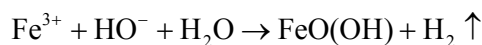
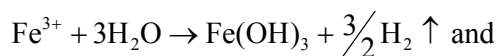
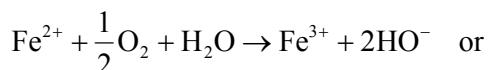
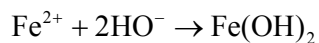
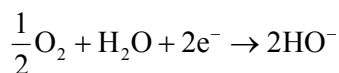
- (i) the anodic dissolution of the metallic sample



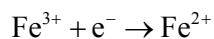
- (ii) the cathode reduction of hydrogen ions H^+ (having a depolarising role) in strong acid solutions



In the basic solution, at the cathode, it can write such as reactions:



In a neutral medium, the following transformation can take place



Taking all this into account, it can approximate that in strong acidic solutions, the anodic dissolution of steel with the appearance of Fe^{2+} ions can be described a first-order kinetic reaction, through an integrated formula, written as:

$$\ln[\text{Fe}^{2+}] = k_1 \cdot t, \text{ or } [\text{Fe}^{2+}] = \exp(k_1 \cdot t) \quad (5)$$

This proposed exponential equation, is similar to that used by other authors (mentioned above) when the pH of the corrosive medium is lower, $\text{pH} \leq 2$.

Furthermore, the rate of the corrosion process (I_{cor}), from an electrochemical perspective, can be expressed through Butler and Volmer's exponential formula²⁸, which essentially confirms the equation presented above, more exactly:

$$I_{\text{cor}} = I \cdot \exp\left(\frac{\beta n F}{RT} \cdot \eta\right) \quad (6)$$

In this case, I is the net corrosion current, η represents the over potential, while $\beta \approx 0.5$ is a symmetry factor.

According the equation presented above, and taking into consideration the dependence between the concentration and the counting rate: $[\text{Fe}^{2+}] = f(1/R)$, the experimental data can be represented graphically in the coordinates: $\ln R = f(t)$, as is shown in the figures 1-3.

From the slopes of the straight lines it can calculate the constant values of the global corrosion rate. These values are presented in Table 2.

Table2. The values of the global rate constants (k) for the studied corrosion reactions

Corrosion medium \ Steel sample		$k(\text{h}^{-1})$		
		XII	XIII	XIV
HCl (M)	0.1	2.41×10^{-4}	5.14×10^{-4}	4.55×10^{-4}
	0.5	6.80×10^{-4}	7.90×10^{-4}	7.56×10^{-4}
	1.0	8.19×10^{-4}	11.16×10^{-4}	10.63×10^{-4}
$\text{H}_2\text{SO}_4(\text{M})$	0.1	3.53×10^{-4}	3.3×10^{-4}	4.24×10^{-4}
	0.5	7.62×10^{-4}	6.52×10^{-4}	6.85×10^{-4}
	1.0	8.56×10^{-4}	8.41×10^{-4}	10.73×10^{-4}
$\text{CH}_3\text{COOH}(\text{M})$	0.1	2.83×10^{-4}	2.88×10^{-4}	4.55×10^{-4}
	0.5	3.34×10^{-4}	4.73×10^{-4}	7.56×10^{-4}
	1.0	3.57×10^{-4}	8.35×10^{-4}	10.63×10^{-4}

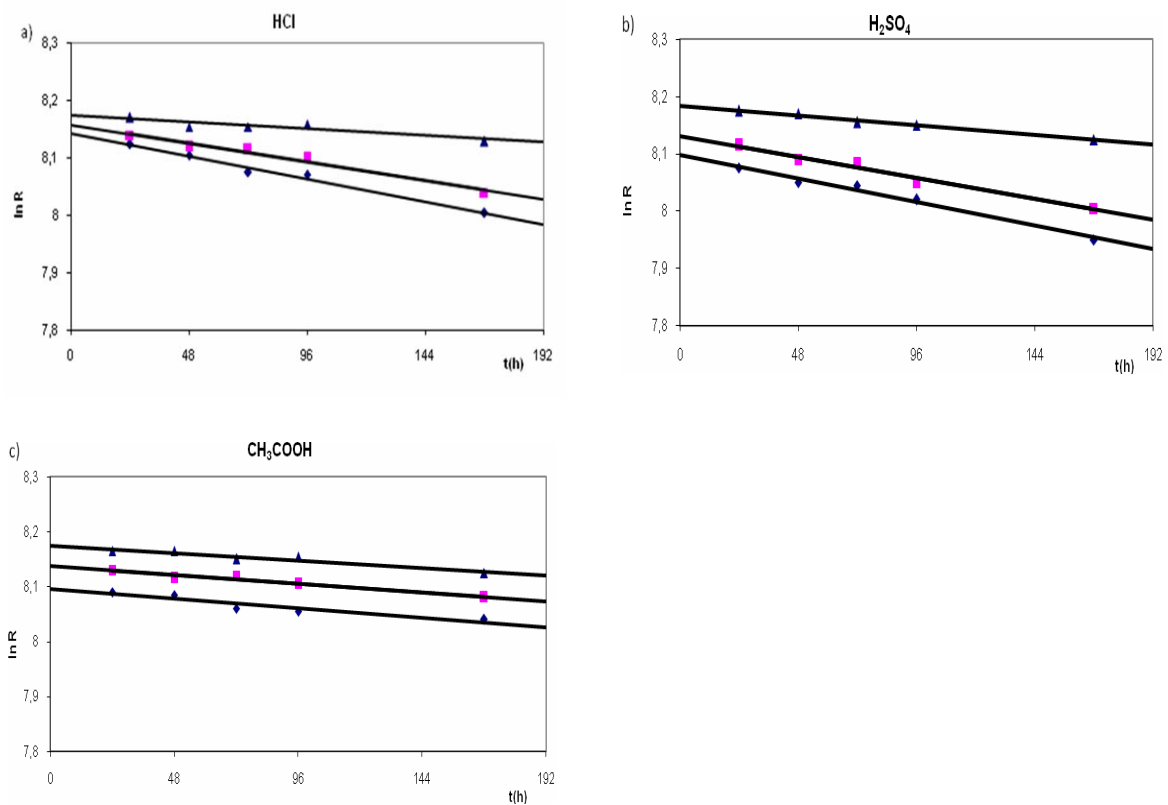
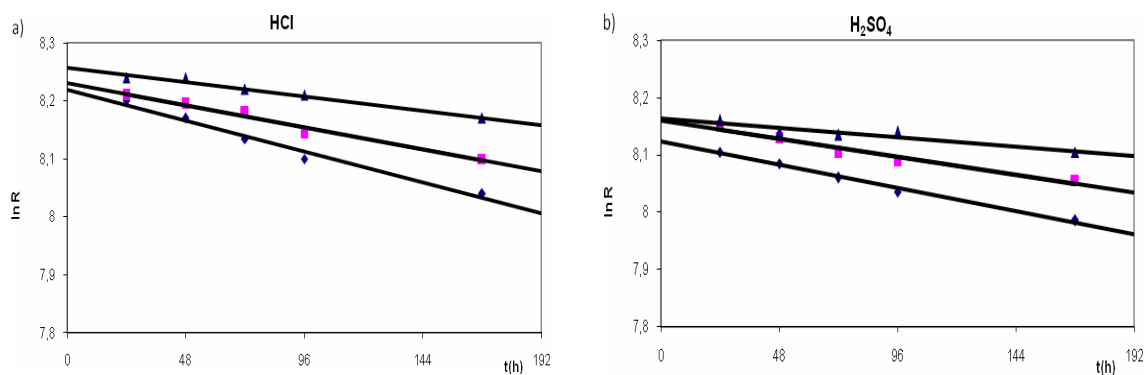


Figure 1. Sample XII



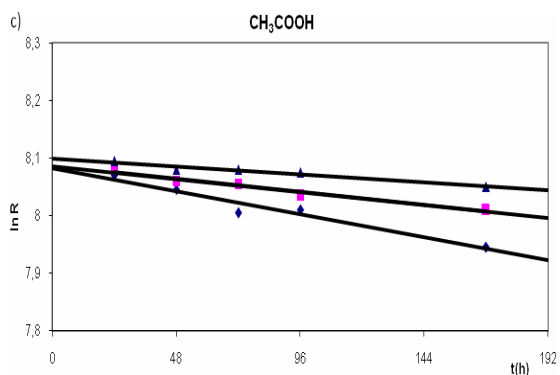


Figure 2. Sample XIII

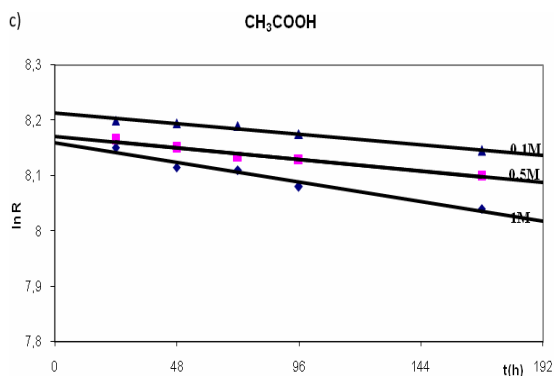
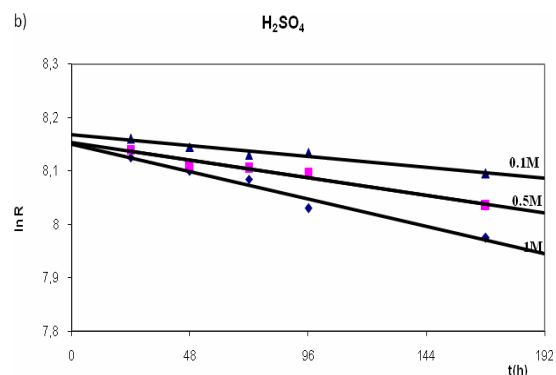
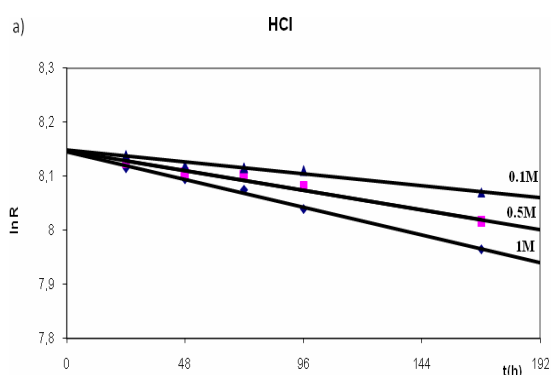
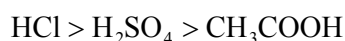


Figure 3. Sample XIV

Figures 1-3. The dependence of the measured intensities (as $\ln R$) of β rays which penetrated the corrosion medium, on the contact time steel sample – acid solution: HCl (a), H_2SO_4 (b), CH_3COOH (c):

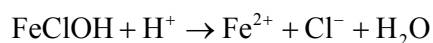
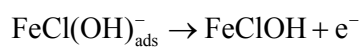
From these values, it can conclude that for a given steel or acid concentration, the corrosion rate decreases in the following order:



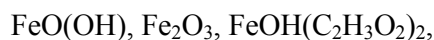
On the other hand, for a given acid, the corrosion process is more intense for the steel XII versus the other two types studied:



The explanation for these observations resides in the fact that in a HCl medium, the corrosion process is higher as the Cl^- ions play a catalyzing role through the series of possible chemical reactions that can take place, more specifically:



On the other hand, in the presence of H_2SO_4 and CH_3COOH it could obtain oxides or less soluble salts on the steel surfaces, thus reducing the reaction rate significantly in those solutions:



Moreover, it know that the higher percent of C in the steel, the smaller its resistance to corrosion.

Furthermore, the presence of certain transitional metals (Cr, Mn, Ni, Cu) in the composition of the steel hinder the corrosion process. In this situation the electrons freed through the anodic dissolution of the iron tend to be captured by the free or partially free 3d atomic orbitals, thus inhibiting their participation in the corrosion process by reducing hydrogen ions.

Conclusions

A radiometric method was applied to investigate corrosion reactions of certain steels in acids: HCl, H_2SO_4 and CH_3COOH

It was pointed out that there is a proportional ratio between the β -rays intensity measured after the passing through the corrosive medium and the concentration of iron ions obtained through the anodic dissolution of steel.

The “constant of global reaction rate” concept was introduced to illustrate kinetically the anodic dissolution of a steel in a corrosive medium.

References

1. Thomas, J.G.N., *Werkstoff Korros.*, **19**, 957 (1968).
2. Boloshova, A.N. and Kazerininov, K.E., *Corrosion*, edited by Bord, A.J., III, Marcel Dekker Inc., New York, 1969.
3. Reinhard, G., *Isotopenpraxis*, **18**, 41 (1982).
4. Vehlow, J., *KfK – Nachrichten*, **15**, 31 (1983).
5. Varga, K., Hirschberg, G., Nemeth, Z., Myburg, G., Schunk, J. and Tilky, P., *J. Nucl. Mat.*, **298**, 231 (2001).
6. Naqvi, A.A., Nagadi, M.M. and Al-Amoudi, O.S.B., *Appl. Radiat. Isotop.*, **64**, 283 (2006).
7. Cecal, A., *Radiochim. Acta*, **28**, 171 (1981).
8. Cecal, A., *Isotopenpraxis*, **17**, 328 (1981).
9. Cecal, A. and Stan, V., *Z. Phys. Chem (Leipzig)*, **263**, 117 (1982).
10. Cecal, A. and Ciobanu, D., *Radioanal. Letters*, **51**, 9 (1982).
11. Cecal, A., *Rev. Roumanie Chim.*, **28**, 91 (1983).
12. Cecal, A., *Electrochim. Acta*, **28**, 661 (1983).
13. Cecal, A., *Isotopenpraxis*, **20**, 9 (1984).
14. Cecal, A., *Isotopenpraxis*, **20**, 259 (1984).
15. Cecal, A., Sunel, V. and Matei, F., *Z. Phys. Chem (Leipzig)*, **267**, 762 (1986).
16. Cecal, A., Palamaru, M.N. and Spac, A., *Rev. Roumanie Chim.*, **42**, 99 (1997).
17. Cecal, A., Popa, K. and Cozma, D., *Rev. Chim. (Bucharest)*, **54**, 500 (2003).
18. Cecal, A., Popa, K. and Draghici, C., *Radiochim Acta*, **93**, 112 (2005).
19. Cecal, A., Ionica, F. and Popa, K., *Rev. Chim. (Bucharest)*, **59**, 1234 (2008).
20. Cecal, A., Ionica, F., Nemtoi, Gh. and Popa, K., *Rev. Roumanie Chim.*, **54**, 1127 (2009).
21. Tomescu, M. and Consantinescu, M., *Chemistry and Corrosion*, ED. Bucharest, 1979.
22. Alowitz, M.J. and Scherer, M.M., *Environm. Sci. Tech.*, **36**, 299 (2002).
23. Balasubramaniam, R., *Corros. Sci.*, **82**, 1357 (2002).
24. Teng, L., Nakatomi, D. and Seetharaman, S., *Proc. Metallurgy and Mat. Processing Sci.*, **38**, 477 (2007).

25. Vettegren, V.I., Bashkarev, A.Y., Danchukov, K.G. and Morozov, G.I., *Technical Phys. Letters*, **29**, 64 (2003).
26. Kaesche, H., *Die Korrosion der Metalle*, Springer, Berlin, 1979.
27. M'Bockris, J.O. and Kahn, S.U.M., *Surface Electrochemistry. A Molecular Level Approach*, Plenum Press, New York, 1993.
28. Lister, D.H., *Corrosion for Engineers*, New Brunswick Univ. Press, 2005,
Google, <http://canteach.candu.org/library/20053213.pdf> .