

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

USE OF β -RAYS ABSORPTION IN THE STUDY OF STEEL CORROSION

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Received May 18, 2009

In this paper the corrosion of 5 types of API steel samples, immersed in aggressive solutions of HCl and H₂SO₄ was studied. An investigation method based on the absorption of the β rays emitted by ²⁰⁴Tl radionuclide by the layers of the iron ions, which appear in the aggressive solutions through the corrosion of those steel samples was used. There is a dependence between the β rays intensity measured from above the corrosion medium, and the concentration of the iron ions passed into solution. Out of the experimental data the values of the constant global rate of corrosion were accounted. The corrosion process is faster in HCl than in H₂SO₄ for each steel sample.

INTRODUCTION

The use of the labelled atoms in order to elucidate the process of chemical and electrochemical corrosion is mentioned by more authors, and the results of the scientific studies are presented in a series of monographs and important articles.¹⁻⁵

Lohberg⁶ labelled with ²¹⁴Pb the Zn/Al/Pb alloy so as to search the process of the corrosion released by the water vapours, with the help of the distribution of the respective radionuclide in that aggressive solution. Simnad and Ruder⁷ immersed in different aird and desaired solutions, which contained ⁶⁰Co²⁺ and ⁵¹Cr³⁺ radionuclides, different samples of iron. The corrosion process was observed based on the distribution of those radionuclides upon the surfaces corroded through radiographic techniques.

The turning into passive of the iron alloyed with chrome was studied by Powers and Hackerman⁸, using ⁵¹CrO₄²⁻ solution, with different pH values. They noticed that when pH \geq 11, chromate anions are not absorbed upon the surface of steel, being prevented by hydroxide ions which previously formed a monomolecular layer protector and lasting on that solid sample.

Some combined methods of study – electrochemical and radiochemical – were used by Kolotykin⁹ when monitored the slow corrosion process of some steels and other alloys without iron.

Vogg and others¹⁰ studied the corrosion of Incaloy-825 in HNO₃ solutions (1, 2 ... 4.75M) in different experimental conditions, determining the loss of Fe, Cr and Ni from the solid samples through the approach of activating with neutrons coupled with γ nuclear spectrometry. As a source of neutrons there were used those in the nuclear reactor which resulted in nuclear fission of ²³⁵U, but also those spontaneously emitted by ²⁵²Cf.

Kiss et co¹¹ observed the corrosion process through the absorption of stable ¹⁸O nuclide upon different surfaces corroded by the used aggressive mediums.

Hohorst¹² used ⁸⁵Kr ($\Lambda = 7.4 \times 10^6$ Bq) fission product which resulted as waste in reprocessing of spent nuclear fuel elements, and also to determine the tightness of some hermetically closed metal vessels, which contained different corrosion solutions.

Naqvi and the others¹³ have investigated the steel corrosion in some aggressive mediums, watching the penetration of the corroded surfaces by chlorine (labelled as ³⁶Cl) in the gas phase.

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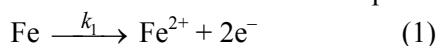
The kinetics of the steel corrosion was observed through more approaches with radioactive tracers, such as the inner isotopic dilution, γ rays transmission, the β rays absorption or retro-diffusion and others.¹⁴⁻¹⁹ There have been established correlations between the amount of iron ions, which passed into corrosion solution through the anodic dissolution of the solid samples and the intensity of the nuclear radiations measured by means of the proposed experimental devices.

In this paper the kinetics of the corrosion of some API steel samples, in HCl and H₂SO₄ corrosion solutions, using a radiometrical approach based on the β rays absorption by the iron ions released within time in the corrosion medium was studied.

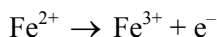
RESULTS AND DISCUSSION

The corrosion process can generally be outlined through two main reactions:

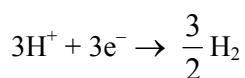
a) The anodic dissolution of the metal sample:



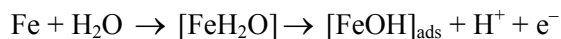
and



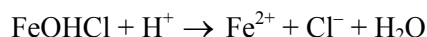
b) The reduction of H⁺ ions with depolarizing role, which fulfils through the capture of the electrons emitted by the corrosion of the metal:



But there are still other possible intermediary reactions which cause the anodic dissolution of the metal samples, where the acidifying of iron gradually takes place²⁰:



In hydrochloric acid medium (pH<3), the Cl⁻ ions have a catalysing role in the process of anodic dissolution of the metal samples, what can be shown through the following sequence:

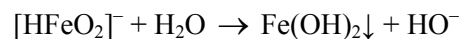
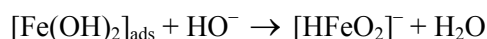
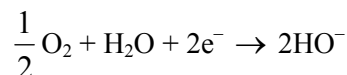


Here, the Cl⁻ ions penetrate the [FeOH]_{ads} protector layer previously absorbed on the steel

$$-\frac{d[\text{Fe}(\text{OH})_2]_{\text{ads}}}{dt} = k_2[\text{Fe}(\text{OH})_2]_{\text{ads}} \cdot [\text{H}_2\text{SO}_4]$$

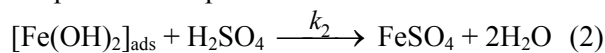
surface, leading to the acceleration of the corrosion reaction.

But when pH ≥ 3, there can be achieved the passiveness of the corrosion, to a more or less extent, through the formation on the surface of the solid sample previously immersed in an aggressive medium, of some harder soluble compounds such as oxides, hydroxides or salts of iron ions, in the case of steel or of other ions for other types of alloys, what can be suggested as follows:

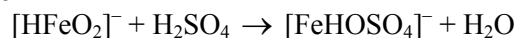


This is a pseudo I order reaction, in which the ferrous hydroxide is formed as a protector layer on the metal surface subjected to corrosion.

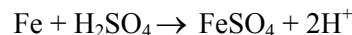
In the presence of H₂SO₄, the process can continue with the coming out of some salts or compounds with protector role²¹⁻²²:



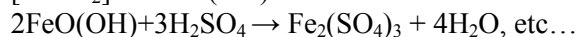
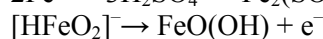
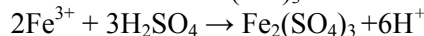
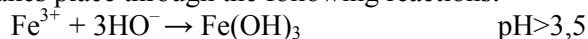
or



but also



But in the presence of Fe³⁺ the passiveness takes place through the following reactions:



Taking into consideration the main reaction of the anodic dissolution of the steel sample, the chemical reaction first order²³ is:

$$\frac{d[\text{Fe}^{2+}]}{dt} = k_1[\text{Fe}^{2+}]$$

In its integrated form it follows that

$$\ln \frac{[\text{Fe}^{2+}]_0}{[\text{Fe}^{2+}]} = k_1 t, \quad (3)$$

Knowing that the reaction (2) is possible in the presence of H₂SO₄ when pH ≥ 3, there can be ascertained that this develops process by a second order reaction, where the concentrations of the two reactants are different

By integration it results:

$$k_2 t = \frac{1}{([\text{Fe}(\text{OH})_2]_{\text{ads}0} - [\text{H}_2\text{SO}_4]_0)} \ln \frac{[\text{H}_2\text{SO}_4]_0 ([\text{Fe}(\text{OH})_2]_{\text{ads}0} - [\text{Fe}(\text{OH})_2]_{\text{ads}})}{[\text{Fe}(\text{OH})_2]_{\text{ads}0} ([\text{H}_2\text{SO}_4]_0 - [\text{Fe}(\text{OH})_2]_{\text{ads}})}, \quad (4)$$

where the indices "0" represent the concentrations of the reactants for $t = 0$.

Out of the obtained experimental data there can be ascertained that in proportion as the concentration of the Fe^{2+} ions in the corrosion solution increases there is lowering the β rays intensity measured R (in cpm) due to their absorption by the layers of ferrous (and ferric) ions from the reactant system, that is:

$$R = f\left(\frac{1}{[\text{Fe}^{2+}]}\right)$$

and

$$R = f([\text{Fe}(\text{OH})_2]_{\text{ads}})$$

As such from the two integrated forms of the above mentioned kinetic equations, there results:

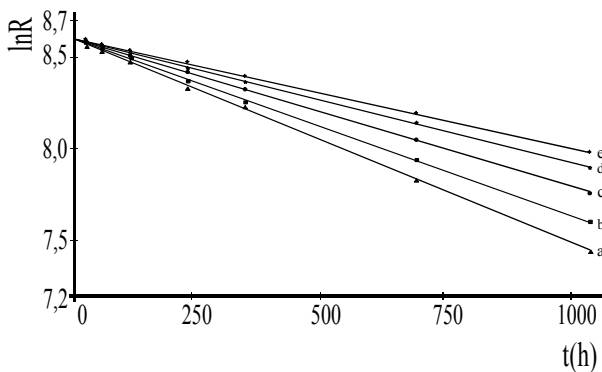
$$\ln R = f(t)$$

The experimental data obtained for the studied corrosion systems were plotted out in these coordinates: $\ln R = f(t)$ getting straight lines with several slopes (fig.1-5).

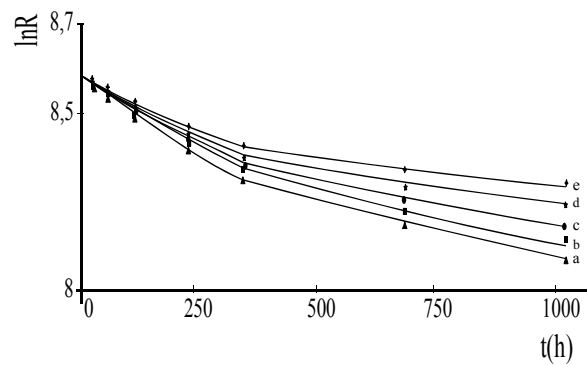
From these slopes the global rate constants of corrosion process can be calculated.

It must be mentioned that in H_2SO_4 corrosion medium, in the respective graphical representations there appeared two straight lines instead of only one, just like in the case of HCl , having two very distinct slopes. This result can be explained through the fact that in the first part of the corrosion process the anodic dissolution takes place more rapidly, and then the reaction becomes slower, probably due to the coming out of some passive-protector compounds upon the solid surfaces immersed in aggressive media:

$\text{Fe}(\text{OH})_2$, FeSO_4 , $\text{FeO}(\text{OH})$, etc.

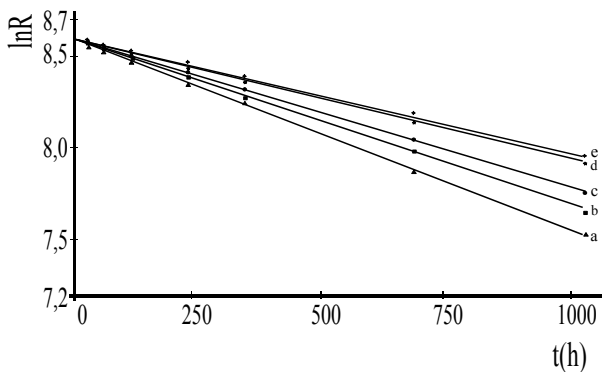


1.1.

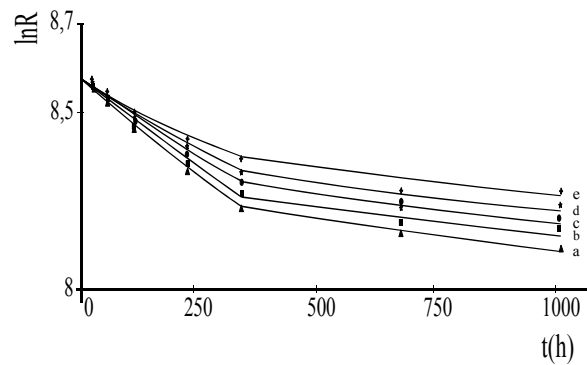


1.2.

Figs. 1 – mean sample 1 in HCl (1-1) and H_2SO_4 (1-2) corrosion media.

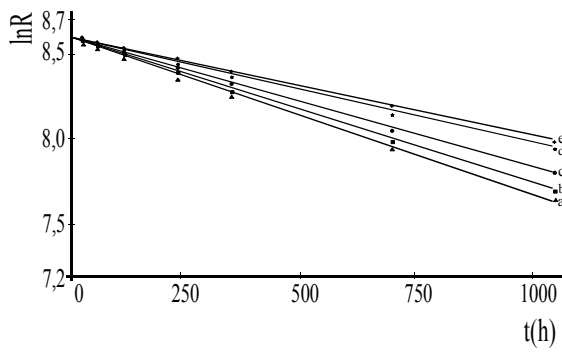


2.1.

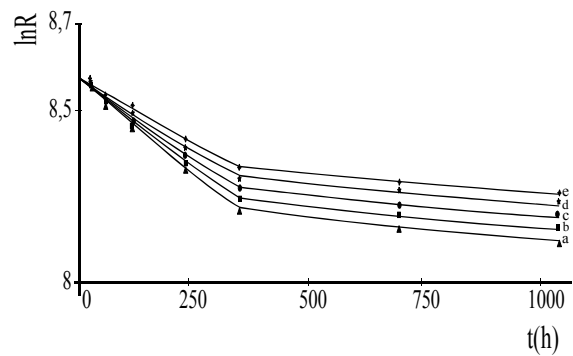


2.2.

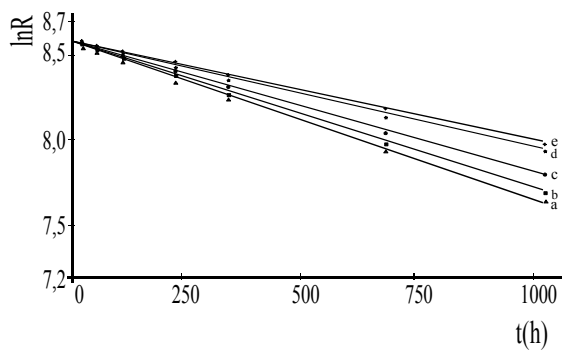
Figs. 2 – represent sample 2 in HCl (2-1) and H_2SO_4 (2-2) solution.



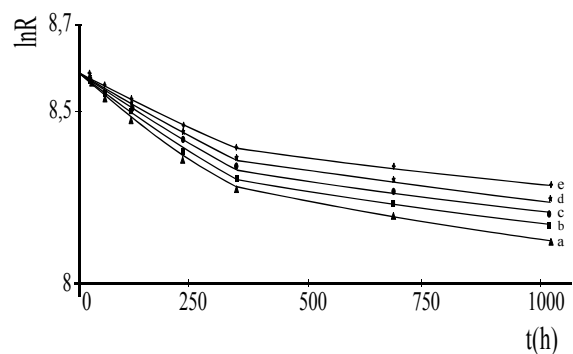
3.1.



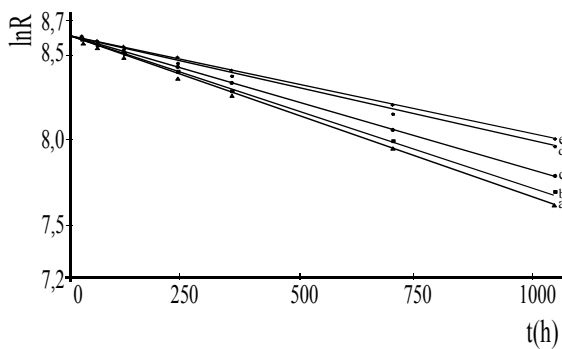
3.2.

Figs. 3 – show sample 3 in HCl (3-1) and H₂SO₄ (3-2) aggressive solutions.

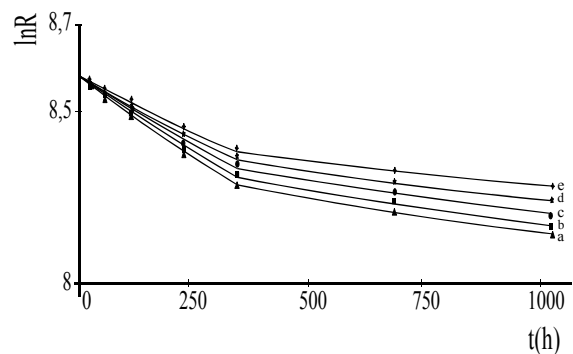
4.1.



4.2.

Figs. 4 – Point out sample 4 in HCl (4-1) and H₂SO₄ (4-2) solutions.

5.1.



5.2.

Figs. 5 – Mean sample 5 in HCl (5-1) and H₂SO₄ (5-2) corrosive solutions.

The concentrations of used acids are noted as: a): 4M, b): 2M, c): 1M, d): 0.5M, e): 0.25M.

These compounds can diminish partially the further development of the corrosion reactions.

The global rate constants of corrosion are registered in Table 1.

The resistance to corrosion depends principally on the amount of carbon, that means the more carbon in the steel the less resistant to the respective process it is.²⁴⁻²⁶

Likewise, transitional metals such as microelements in the composition of steels have an

important role in the passiveness of the corrosion. The d atomic orbitals, free or partially occupied with electrons, can catch the electrons freed from the anodic dissolution of steel, without allowing the developing of the other chemical reactions in the given corrosion medium.

Hydrochloric acid has a more intense corrosion action than the sulphuric acid.

Table 1

The constant values of global corrosion rate for the studied steel samples

Steel sample	Reaction medium	k_1 (h^{-1})	k_2 ($L \times \text{mole}^{-1} \times h^{-1}$)
1	HCl (4 M)	1.92×10^{-3}	-
	HCl (2 M)	1.83×10^{-3}	-
	HCl (1 M)	1.66×10^{-3}	-
	HCl (0.5 M)	1.45×10^{-3}	-
	HCl (0.25 M)	1.24×10^{-3}	-
	H ₂ SO ₄ (4 M)	1.16×10^{-3}	6.54×10^{-5}
	H ₂ SO ₄ (2 M)	1.14×10^{-3}	6.25×10^{-5}
	H ₂ SO ₄ (1 M)	1.12×10^{-3}	5.82×10^{-5}
	H ₂ SO ₄ (0.5 M)	1.08×10^{-3}	4.76×10^{-5}
	H ₂ SO ₄ (0.25 M)	9.7×10^{-4}	3.86×10^{-5}
2	HCl (4 M)	1.93×10^{-3}	-
	HCl (2 M)	1.85×10^{-3}	-
	HCl (1 M)	1.68×10^{-3}	-
	HCl (0.5 M)	1.25×10^{-3}	-
	HCl (0.25 M)	1.22×10^{-3}	-
	H ₂ SO ₄ (4 M)	9.85×10^{-4}	9.07×10^{-5}
	H ₂ SO ₄ (2 M)	9.52×10^{-4}	7.74×10^{-5}
	H ₂ SO ₄ (1 M)	9.28×10^{-4}	5.35×10^{-5}
	H ₂ SO ₄ (0.5 M)	8.98×10^{-4}	4.46×10^{-5}
	H ₂ SO ₄ (0.25 M)	8.83×10^{-4}	3.27×10^{-5}
3	HCl (4 M)	1.86×10^{-3}	-
	HCl (2 M)	1.78×10^{-3}	-
	HCl (1 M)	1.61×10^{-3}	-
	HCl (0.5 M)	1.31×10^{-3}	-
	HCl (0.25 M)	1.19×10^{-3}	-
	H ₂ SO ₄ (4 M)	9.36×10^{-4}	9.67×10^{-5}
	H ₂ SO ₄ (2 M)	8.61×10^{-4}	7.62×10^{-5}
	H ₂ SO ₄ (1 M)	7.66×10^{-4}	6.10×10^{-5}
	H ₂ SO ₄ (0.5 M)	6.87×10^{-4}	4.56×10^{-5}
	H ₂ SO ₄ (0.25 M)	6.62×10^{-4}	3.57×10^{-5}
4	HCl (4 M)	1.89×10^{-3}	-
	HCl (2 M)	1.80×10^{-3}	-
	HCl (1 M)	1.64×10^{-3}	-
	HCl (0.5 M)	1.35×10^{-3}	-
	HCl (0.25 M)	1.22×10^{-3}	-
	H ₂ SO ₄ (4 M)	1.09×10^{-3}	9.37×10^{-5}
	H ₂ SO ₄ (2 M)	1.06×10^{-3}	8.03×10^{-5}
	H ₂ SO ₄ (1 M)	1.03×10^{-3}	7.89×10^{-5}
	H ₂ SO ₄ (0.5 M)	9.88×10^{-4}	6.44×10^{-5}
	H ₂ SO ₄ (0.25 M)	8.75×10^{-4}	4.86×10^{-5}
5	HCl (4 M)	1.95×10^{-3}	-
	HCl (2 M)	1.87×10^{-3}	-
	HCl (1 M)	1.71×10^{-3}	-
	HCl (0.5 M)	1.38×10^{-3}	-
	HCl (0.25 M)	1.27×10^{-3}	-
	H ₂ SO ₄ (4 M)	1.09×10^{-3}	9.37×10^{-5}
	H ₂ SO ₄ (2 M)	1.06×10^{-3}	9.07×10^{-5}
	H ₂ SO ₄ (1 M)	1.01×10^{-3}	7.82×10^{-5}
	H ₂ SO ₄ (0.5 M)	9.79×10^{-4}	5.86×10^{-5}
	H ₂ SO ₄ (0.25 M)	9.31×10^{-4}	4.38×10^{-5}

EXPERIMENTAL

Firstly HCl and H₂SO₄ corrosion solutions with concentrations: (0.25, 0.5, 1, 2 and 4) M have been prepared.

Then were cut more samples out of the 5 types of API steels, being almost of the same size, after which these were polished with emery paper, washed with water and cleaned in acetone.

The chemical composition of the 5 types of API steels used in these experiments is presented in Table 2.

Further on, in 50ml cylindrical vials ($\Phi = 3$ cm), was placed a metal sample each, over which there was poured 30ml from given corrosion solution each and 5ml ²⁰⁴TiNO₃ solution, having 1.13×10^6 Bq/kg specific activity. The starting of the corrosion process was considered from this time on.

Table 2

The chemical composition of the 5 types of API steels

Steel composition	Fe	C	Mn	Si	Cu	Sn	Ni	Mo	Cr	Pb	< 0.1%
1	98.10	0.13	0.71	0.35	-	-	-	0.07	0.09	0.110	S, B, Zn, Pb, V, Al
2	98.00	0.23	0.84	0.24	0.11	0.083	0.05	0.02	0.13	0.090	S, Sb, Nb, Al, Ti
3	98.90	0.11	0.33	0.02	0.12	0.160	0.08	0.02	0.10	0.090	S, Nb, V, Ti
4	97.30	0.23	-	0.25	-	-	0.24	0.16	0.63	0.009	S, B, As, Ti
5	98.10	0.20	0.66	0.24	0.30	0.146	0.10	0.02	0.06	0.010	S, Nb, Al

In addition there was prepared also a "blank" sample which contained only the corrosion medium and the radioactive solution, without the steel sample.

This "blank" sample has proved that the decreasing in time of the measured β radioactivity emitted by ^{204}Tl ($T_{1/2} = 3.5$ years and $E_{\beta_{\max}} = 0.76$ MeV) radionuclide is due to the investigated corrosion process and not to the natural radioactive decay of the respective radioisotope.

At given contact time intervals, the metal sample – the corrosion medium, there have been measured the values of the intensity of the β rays, which penetrated the respective solutions, ascertaining their lowering to the extent of the corrosion process.

The radioactivity measurements were achieved by means of a β -Geiger-Müller counter (1.5 mg/cm^2) connected to an electronic scaler/VSP-14M.

CONCLUSIONS

It is possible to follow the kinetic of the corrosion reactions using a method based on the absorption in time of the β rays by the layers of iron ions with passed into solution due to anodic dissolution of the steel sample.

The corrosion process is described kinetically by means of corrosion rate constants more exactly as in the classical methods.

REFERENCES

- M. Haissinsky, "Nuclear Chemistry and its Applications", Addison Wesley, Reading, 1964, p. 575.
- J.G.N. Thomas, *Werkstoff Korros.*, **1968**, 19, 957.
- A. Merz, "Dissertation", T.H. Karlsruhe, **1973**.
- W. Vehlow, *KfK Nachrichten*, **1983**, 15, 31.
- xxx, *Dachema Corrosion Handbook*, vol. 5, VCH Weinheim, 1989, p. 28.
- K. Lohberg, *Metallforsch.*, **1949**, 2, 230.
- M.T. Simnad and R.C.Ruder, *J. Electrochem. Soc.*, **1951**, 98, 301.
- R.A.Powers and N. Hackerman, *J. Phys. Chem.*, **1953**, 57, 139.
- Y.A. Kolotyrykin, *Electrochim. Acta.*, **1973**, 18, 593.
- H. Vogg, H. Brawn, R.Löffel, A. Lubecki, A. Merz, J. Schimitz, R. Schneider and J. Vehlow, *J. Radioanal. Nucl. Chem.*, **1976**, 32, 495.
- L. Kiss, A.I. Mohodov, L.M.Vassony and N.G. Markosyan, *Zaschita Met.*, **1980**, 16, 94.
- F.A. Hohorst, U.S. Patent NO. 5473643, **1995**.
- A.A. Naqvi, M.M. Nagadi and O.S.B. Al-Amoudi, *Appl. Rad. Isotop*, **2006**, 64, 283.
- Al. Cecal and D. Ciobanu, *Radiochim. Acta*, **1981**, 28, 283.
- Al. Cecal, *Electrochim. Acta*, **1983**, 28, 681.
- Al. Cecal, *Isotopenpraxis*, **1984**, 20, 259.
- Al. Cecal, N. Palamaru and A. Spac, *Rev. Roum. Chim.*, **1997**, 42, 180.
- Al. Cecal, K. Popa and C. Drăghici, *Radiochim. Acta*, **2005**, 93, 115.
- Al. Cecal, F. Ionică and K. Popa, *Rev. Chim. (Bucharest)*, **2008**, 59, 1234.
- J.O.M. Bockris and S.U.M. Kahn, "Surface Electrochemistry. A Molecular Level Approach", Plenum Press, New York, 1993, p. 556.
- K.C. Tripathi and K. Schwabe, *Rev. Chim. (Bucharest)*, **1962**, 7, 599.
- S.A. Opreșan and P.T. Frangopol, *Rev. Roum. Chim.*, **1999**, 44, 313.
- R. Ebisch, E. Fanghaenel, W.-D. Habicher, R. Hahn and K. Unverferth, "Chemische Kinetik", VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1971, p. 196.
- M.G. Fontana and R.W. Staehle, "Advances in Corrosion Science and Technology", Plenum Press, New York, 1970, p. 254.
- L.Oniciu, "Physical Chemistry-Electrochemistry", EDP-Bucharest, 1977, p. 319.
- M. Lakatos-Versany and M. Meiser, *J. Radioanal. Nucl. Chem.*, **2002**, 251, 75.