

Kinetic Investigation of the Corrosion Process by Means of the β Rays Absorption

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This paper deals with an approach of the investigation of the corrosion reactions, which is based on the absorption of β rays emitted by Tl-204 radionuclide by the iron ions, which pass into the aggressive solution through anodic dissolution of a metal sample. There can be noticed a decreasing of the activity β rays, reduction which is measured while the concentration of the iron ions in the corrosive solution increases. Out of the experimental data, there can be calculated the constant of the global corrosion rate, which accurately characterizes the development of this complex process. There was experimentally investigated the corrosion of three types of steel: H-12, MoCN-15 and W-85 in aggressive media of HCl and NaCl solutions. The values of the global rate constants vary depending on the steel composition and the corrosion medium.

Keywords: aggressive media, corrosion, kinetics, radioisotopes, steel samples

There are known a lot of papers which largely deal with the investigation of the corrosion process using the labelled atoms, showing at the same time different experimental devices or original techniques applied for this reason [1-3].

The inhibiting effect of the solutions of chromium labelled with Cr-51 upon the metal samples in some corrosive mediums [4] and, the distribution of Fe-59 and Cr-51 radioisotopes which resulted from the intensifying with neutrons of the steel samples subsequently put to corrosion in different experimental conditions were studied [5].

The rate of the corrosion process of the same metal samples considering the quantity of O-18 labelled oxygen which is absorbed on those solid surfaces was determined [6]. Co-60 and Pb-210 radioisotopes [6] was used to explain the pitting corrosion mechanism of the aluminium plates in different aggressive media [7].

There is mentioned the building of some experimental devices for the continuous observation of the corrosion reactions, either through β rays absorption [8] or through the distribution of some radioisotopes in the corrosive medium [9]. β rays diffusion through steels, as well as the reflection of deuterium and helium by the metal samples put to corrosion, was another approach of investigation of this process [10-11].

Others researchers [12] used the neutron activated analysis connected to γ nuclear spectrometry in order to determine the concentration of iron as well as of some microelements occurred from the corrosion of the metal samples in different aggressive media.

This paper is a continuation of previous studies regarding the use of some tracer techniques concerning the investigation of the corrosion process through internal isotopic dissolution, or β rays absorption [13-16].

Experimental part

Firstly some steel samples H-12, MoCN-15 and W-85 in the form of a bar, being 2cm long and 1.5cm in diameter

were selected for investigations. These samples were cleaned with emery and degreased with methanol and acetone and then washed with water.

Then there were prepared, as corrosion media, some solutions of 0.1M and 0.5M HCl as well as NaCl 0.5M, out of which there were poured by 20mL in 9 cylindrical glasses of 50mL each, that means 3 glasses for each of the corrosive medium. Then a steel sample, previously prepared, was put in each of the glasses and the corrosion process started.

To observe the time development of the corrosion of the 3 metal samples, there was used a technique of investigation based on the absorption of pure β rays emitted by Tl-204 radionuclide by the iron ions which pass into the aggressive solution through anodic dissolution of the respective types of steel.

The beam of β rays sent forth by Tl-204 ($\Lambda=6 \cdot 10^5$ Bq) was collimated through a slit ($\Phi=0.10$ cm) in lead plate, which was centered on a fixed pedestal settled under the cylindrical glass with the metal sample put to corrosion. Part of many-energetically β rays ($E_{\max}=0.76$ MeV) has penetrated the bottom of the cylindrical glass 0.3mm thickness and was selectively more and more absorbed by the iron ions delivered by the corrosive medium through anodic dissolution of those types of steel.

It is mentioned that the position of the metal sample in the glass remained the same, so that it did not influence the geometry of the detection system. The decreasing in time of the radioactivity measured during the development of the corrosion of the steel was much more conspicuous regarding the radioactive decay of β radioisotope Tl-204 ($T_{1/2}=3.5$ years) fact that was established through a parallel determination, without corrosion.

Above the cylindrical glass, there is a G.M.- β (1.5mg/cm²) detector connected to a VSP-14M scaler, by means of which there is determined the activity of β rays after they penetrated the absorbant medium.

The chemical composition of the three types of steel is shown in table 1.

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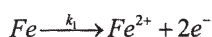
Table 1
THE CHEMICAL COMPOSITION OF H-12, MoCN-15 AND W-15 STEEL

Steel composition	H-12	MoCN-15	W-85
C	2.2	0.60	0.34
Si	0.35	0.35	0.30
Mn	0.45	0.80	0.75
P	0.03	0.03	0.03
Cr	1.1	0.80	1.5
Mo	-	0.30	1.0
Ni	0.30	0.36	-
Cu	0.30	0.36	-
W	-	-	6,0

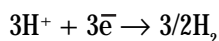
Results and discussion

As it is known, the corrosion reactions can be expressed in many ways:

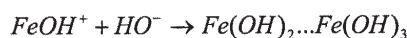
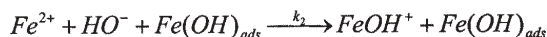
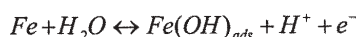
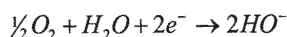
- the anodic dissolution of iron in a corrosive medium:



- the reduction of hydrogen ions with a depolarizing role based on the electrons capture:



- there can take place other chemical reactions [17-21] in the presence of oxygen and at a pH > 3.5:



Here, $Fe(OH)_{ads}$ plays a catalyst role in the corrosion process.

$Fe(OH)_2$ or $Fe(OH)_3$ appear in the neighbouring of the metal samples as a forming brown-russet solid mass, at pH > 3.5 as in the case of NaCl corrosive solution. At pH < 3.5 the reactions (iii) do not take place.

Considering the reactions mentioned above, the global rate of the corrosion process can be expressed by the differential equations:

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

$$\frac{d[Fe^{2+}]}{dt} = k_2 \cdot [Fe^{2+}] \cdot [HO^-], \text{ where } [Fe^{2+}] \neq [HO^-].$$

In the integrated forms, it results:

$$k_1 = \frac{1}{t} \ln \frac{[Fe^{2+}]_0}{[Fe^{2+}]}, \text{ if pH} < 3.5$$

$$k_2 = \frac{1}{t([Fe^{2+}] + [HO^-])} \ln \frac{[Fe^{2+}]_0 [HO^-]}{[HO^-]_0 [Fe^{2+}]}, \text{ if pH} > 3.5$$

By "0" index there were written the respective initial concentrations of the ions.

Since the activity of absorbed β rays (R) decreases as Fe^{2+} ions concentration increases, results: $R = f \frac{1}{[Fe^{2+}]}$.

Taking into account the above mentioned integrated expressions and the dependence of activity on the iron ions concentration, it can be written: $\ln R = f(t)$.

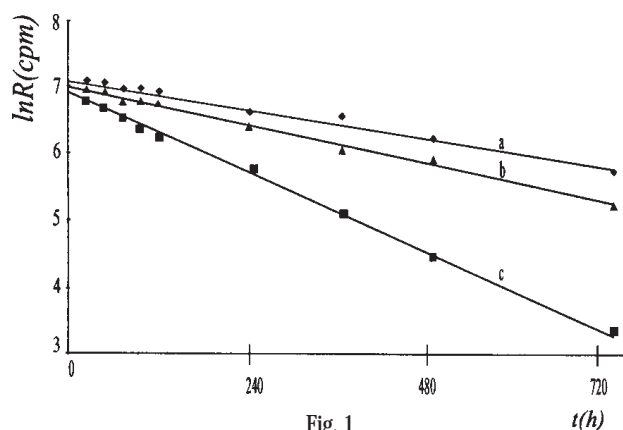


Fig. 1

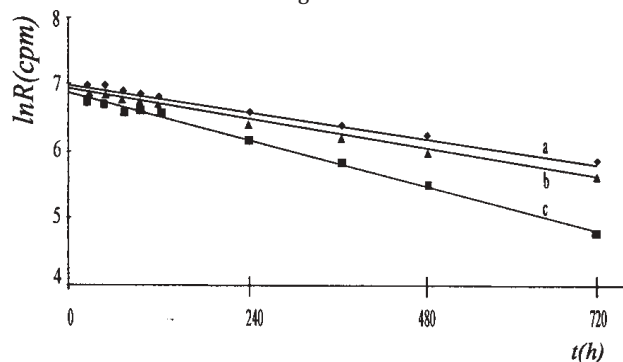


Fig. 1

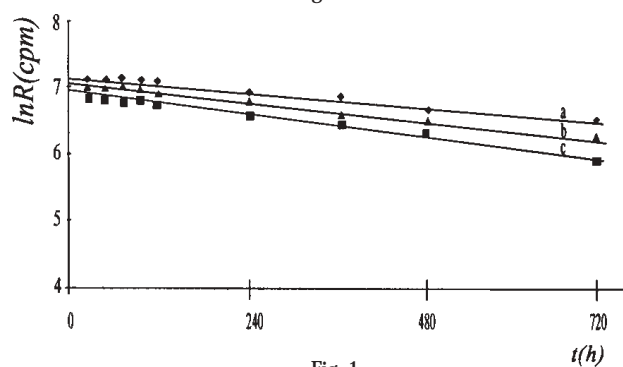


Fig. 1

Fig. 1-3

Dependence of the activity (as logarithms) of absorbed β rays vs. contact time of the the steel samples: W-85 (a), MoCN-15(b) and H-12 (c) with aggressive media : 0.5M HCl (fig. 1), 0.1M HCl (fig. 2) and 0.5M NaCl (fig. 3)

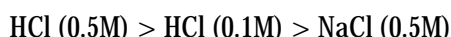
By plotting the experimental data in these coordinates, straight lines arise (figs.1-3) out of whose slopes the values of the global corrosion rate constants can be calculated. These values are shown in table 2.

Taking into account the obtained values, it can be observed that the corrosion of the metal samples depends on the H^+ ions concentration, with a depolarizing role in

Table 2
THE CONSTANT VALUES OF GLOBAL CORROSION RATE FOR THE STUDIED STEEL SAMPLES

Steel samples	Reaction medium	$k(h^{-1})$
H-12	HCl (0.5 M)	$5.50 \cdot 10^{-3}$
	HCl (0.1 M)	$2.75 \cdot 10^{-3}$
	NaCl (0.5 M)	$1.84 \cdot 10^{-3}$
MoCN-15	HCl (0.5 M)	$3.34 \cdot 10^{-3}$
	HCl (0.1 M)	$1.91 \cdot 10^{-3}$
	NaCl (0.5 M)	$1.54 \cdot 10^{-3}$
W-85	HCl (0.5 M)	$1.46 \cdot 10^{-3}$
	HCl (0.1 M)	$1.04 \cdot 10^{-3}$
	NaCl (0.5 M)	$0.71 \cdot 10^{-3}$

the development of this process. For a given metal sample, the global rate constants decrease:



Furthermore, the presence of some transitional metals with partial free d atomic orbitals can furnish an inhibitory effect on the corrosion of studied samples. The electrons emitted from the anodic dissolution of the steel samples immersed in the aggressive medium will be "captured" by the free atomic orbitals of these transitional metals, and therefore, the corrosion action can be slowed down. In this way, for a given aggressive medium, the values of the global rate constants varies the series:



The carbon concentration of the steel composition affects the corrosion process. The smaller the carbon contents in the steel, the bigger the corrosion resistance of the respective samples.

Conclusions

It was proposed a radiochemical method for investigation of the corrosion reactions in 3 aggressive solutions of HCl and NaCl.

The corrosion reactions were described kinetically by the global rate constants much more exactly than the known methods used in these studies.

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