The study of hydrogen permeation in carbon steel and inhibitors impact

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Abstract: *The hydrogen permeation, the effect of Na_2S as a promoter to hydrogen permeation, and the effect of inhibitors was evaluated in carbon steel in 12% HCl. In this study the electrochemical technique developed by Devanathan was employed. The experiments were performed in a special design and built two compartment-measuring cells separated by the samples made from carbon steel. The samples were first coated with Palladium to one side. The electrolytes on the cathodic and anodic side of the cell were 12 % HCl and 1M NaOH respectively. By means of a potentiostat in a three electrode arrangement where our sample was the working electrode, a calomel electrode was the reference electrode and a platinum disk served as the counting electrode was first investigated the hydrogen permeation rate in the medium of HCl 12 %. Then crystals of Na_2S were added in order to study the effect of promoters on the hydrogen permeation. To investigate the effect of inhibitors toward hydrogen permeation in HCl 12% and HCl + Na_2S, five different organic compounds were selected: Aniline, Formaldehyde, Benzonitril, Urotropine and p-Toluidine. Their concentration on the medium was 2 g / l.*

The obtained results clearly indicate that Na_2S strongly promotes the hydrogen permeation in carbon steel. Among the organic compounds, Urotropine shows the most inhibitive effect on the Na_2S action. It is the best inhibitor also of the hydrogen permeation in HCl medium. Aniline in contrary to Urotropine increases the quantity of absorbed hydrogen in the bulk metal. This organic compound seems to have a specific influence on the hydrogen evolution reaction, reducing the active site numbers were hydrogen could be reduced and partially blocking the recombination of atomic hydrogen to molecular hydrogen on the steel surface. The other organic compounds seem to have no effect on hydrogen permeation and on the Na_2S action.

INTRODUCTION

In general, the hydrogen presence on the metals' surface is very dangerous because hydrogen can penetrate in the metal and cause different actions that ruin mechanic and chemical properties of the material, creating in this way the so-called hydrogen break. Hydrogen can penetrate in metal only in an atomic circumstance, for this reason the breakage occurs anytime the conditions favor the creation and preservation of atomic hydrogen in contact with metallic surface. This breakage of metals happens during the surface treatment processes, metals production, shaping or transforming and welding. This makes their usage more difficult, by decreasing homogeneity and their field of use. Hydrogen breakage is found in a variety of materials, although a special interest is dedicated to ferroze materials, because of their wider use. This breakage is very damaging because often it is found in materials with high mechanic resistance, which are greatly required in modern technology.

Every chemical or electrochemical reaction combined with the release of atomic hydrogen on the surface of a metal causes the insert of some gas in metallic net that can be considerable enough to produce hydrogen breakage.

The purpose of this report was the study of hydrogen permeation in carbon steel. This permeation occurs as a result of the atomic hydrogen development on the surface of steel sample through corrosion processes. For this reason, the Devanathan measuring cell is used. Through this cell, the study of hydrogen permeation in different aggressive environments, the influence of the substances that encourage permeation of hydrogen on metals, and the study of inhibitors that decrease hydrogen permeation, is made possible.

The device measuring hydrogen permeation

The device for measuring hydrogen permeation in carbon steel samples consists of:

A steel tile, 1mm thick and covered with palladium on one side

A measuring double Devanathan cell
12% HCL solution, 1M NaOH solution
Potentiostat of the type Tacussel PJT-24-1
Recorder
Reference calomel electrode with Haber-Lugin capillary
Assistant platinum electrode in a disc shape
The device scheme is depicted in Figure 1.

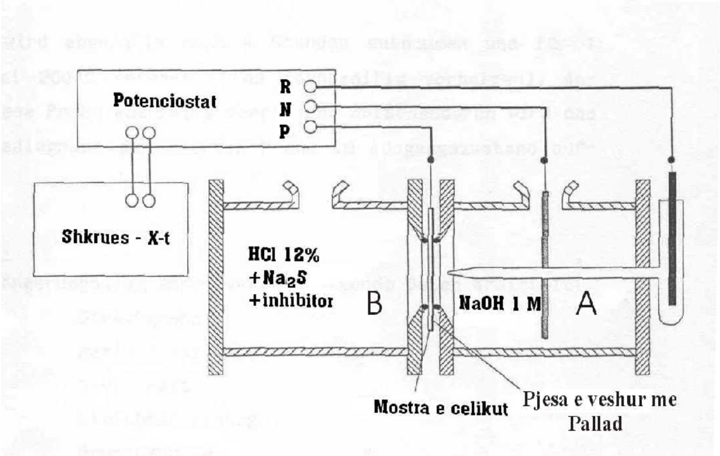


Fig 1. Schematic depiction of the device for measuring hydrogen permeation in a carbon steel sample. P- working electrode, N- assistant platinum electrode, R- reference electrode (calomel electrode).

Both parts of the cell that are filled with solution have a volume of 400 ml. They communicate with each other through two circular spaces with 2,8 cm diameter. The carbon steel sample is placed exactly between these spaces of the cells and it is used to for experiment to study hydrogen permeation in the conditions of an aggressive environment. Palladium covers one side of the steel tile because it has the ability to absorb hydrogen. The side with palladium is exposed to cell A, while the other steel side is exposed to cell B. Our sample is used as work electrode. Potentiostat polarizes this sample on a constant value of the potential E_H = + 380 mV

The job principle and procedure

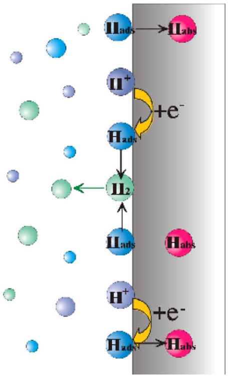
Cell B is filled with 12% acid hydrochloric. In this cell, on steel sample's surface atomic hydrogen will be produced, as a result of the reaction of steel and acid hydrochloric. A part of this hydrogen will be absorbed on sample's surface. The discharge of hydrogen ions occurs according to Volmer's reaction.

$$H_3O^+ + e^- \rightarrow H_{ad} + H_2O \qquad (1)$$

Some of hydrogen atoms absorbed on the metal's surface can be recombined in a second phase which is describe by Tafel's reaction:

$$H_{ad} + H_{ad} \rightarrow H_2 \qquad (2)$$

In this way, H_2 molecule can be moved away as a gas, meanwhile atomic hydrogen part can penetrate in the metal. Every increase of hydrogen absorbed leads to an increase of hydrogen permeated in the metal. This is because there exists equilibrium between hydrogen absorbed on the surface and hydrogen atoms absorbed in the metal. The permeation process of hydrogen in steel sample is depicted in a schematic way in figure2.



The superficial concentration of hydrogen atoms does not depend only on the quantity formed per time unit. It can also depend on the components that encourage the formation of hydrogen atoms as according to equation (1) or obstruct recombination as according to equation (2). Sulfurs, hydrogen sulfurs, cyanides etc. are the substances that encourage hydrogen permeation. Hydrogen that permeates in steel sample is oxidized anodic ally on acidthe other side of the sample. This oxidation occurs on the surface of steel covered with palladium on cell A which is filled with 1M NaOH. For this reason, steel tile by means of a potensiostat is kept under a constant potential passivity condition of EH = +380 mV and atomic hydrogen oxidation in hydrogen ions occurs in it. The current running between steel sample and platinum electrode is registered in a timing scribe. This stream is a mass of hydrogen quantity that penetrates into steel tile in the time unit.

The study of the inhibitors' effect on acid hydrochloric reaction in hydrogen permeation

The inhibitors' effect on aggressive environment such as acid hydrochloric in hydrogen permeation on steel sample with carbon is studied in this experiment.
The experiment procedure is as follows:
After the scheme is connected in a circuit as figure 1 shows, the cell A, confined by the palladium surface, is filled with NaOH 1M. In this moment, the recording of current *I* in timing terms starts.

a) When the current reaches an approximately constant value, cell B is filled with 12% hydrochloric acid. During this time, the current is recorded constantly.
b) When another constant value is reached in acid solution, the inhibitor is added in a 2 g/l concentration.

The hydrogen quantity that permeates in steel in time and surface unit is calculated from current values in:
12% hydrochloric acid
Hydrochloric acid + inhibitor
This is done supposing that all hydrogen reaching the steel/NaOH surface is oxidized in a quantitative manner according to the following equation:

$H_2 = 2H^+ + 2e^-$ (3)

Five different kinds of organic inhibitors were included in our study: Urotropine, Aniline, Formaldehide, Benzonitrile, and p-Toluidine. A new sample was used for every experiment. Figure 3 depicts stream density graphics in timing terms for these samples.

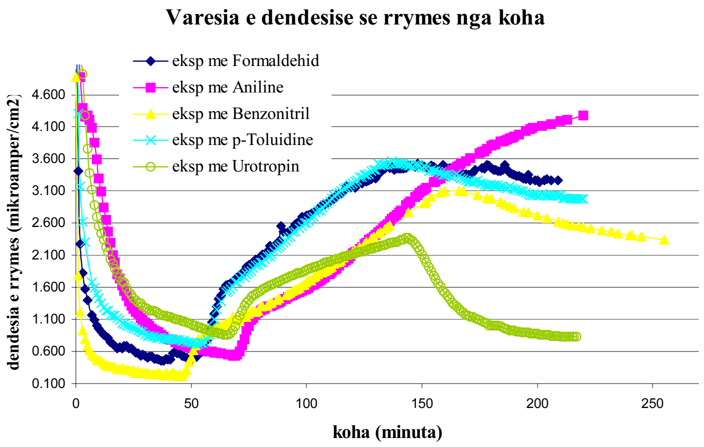


Fig 3. “The stream density relation with time” graphic for hydrogen permeation in carbon steel study experiment.

Chart 1 shows values of stream density and hydrogen volume in constant current moments. On the basis of these values we can judge on the inhibited effect of selective organic substances.

Tab 1.

NaOH		**HCl**		**Inhibitor**		
i (μA/cm^2)	**V (H_2) cm^3**	**i (μA/cm^2)**	**V (H_2) cm^3**	**Lloji i Inhibitorit**	**i (μA/cm^2)**	**V (H_2) cm^3**
0.862	2.001E-07	2.374	5.511E-07	Urotropinë	0.829	1.925E-07
0.537	1.246E-07	3.382	7.852E-07	Anilinë	4.276	9.928E-07
0.455	1.057E-07	3.447	8.003E-07	Formaldehid	3.268	7.588E-07
0.244	5.662E-08	3.089	7.172E-07	Benzonitril	2.341	5.436E-07
0.715	1.661E-07	3.528	8.154E-07	p-Toluidinë	2.976	6.908E-07

The study of the effect of Na_2S in hydrogen permeation and the impact of inhibitors on this effect.

The experimental procedure is the same as the first experiment, besides the Na_2S added to the acid.
From the current values, we can calculate hydrogen quantity that permeates into steel in terms of time and surface unit in:

a) 12% Hydrochloric Acid
b) Hydrochloric acid + Na_2S
c) Hydrochloric acid + Na_2S + inhibitor

Current density and H_2 volume are expressed graphically in terms of time *t*. (Figure 13 and 14)

Organic inhibitors like: Urotropine, Aniline, Formaldehyde, Benzonitrile, and p-Toluidine were studied even in this experiment. A new sample was used for every experiment. Figure 4 depicts current's density in terms of time graphics for these samples.

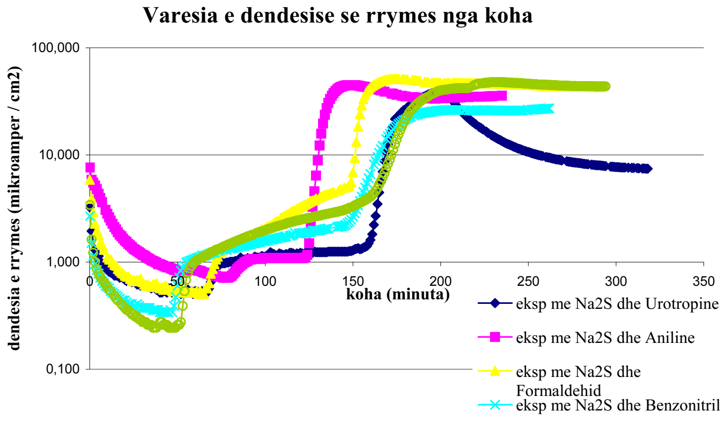


Fig 4. Dependency of current's density to time curve in the experiment for the study of hydrogen permeation and stimulating substances reaction with this permeation into carbon steel.

Chart 2 shows current density values and hydrogen volume values at the moment of constant current values.

NaOH		**HCl**		**Na_2S**		**Inhibitor**		
i (μA/cm^2)	**V (H_2) cm^3/ (cm^2 s)**	**i (μA/ cm^2)**	**V (H_2) cm^3/(cm^2 s)**	**i (μA/cm^2)**	**V (H_2) cm^3**	**Lloji Inhibitorit**	**i (μA/cm^2)**	**V (H_2) cm^3/(cm^2 s)**
0.520	1.208E-07	1.415	3.284E-07	37.951	8.811E-06	Urotropin	7.447	1.729E-06
0.715	1.661E-07	1.089	2.529E-07	34.683	1.043E-05	Anilin	33.577	7.795E-06
0.504	1.170E-07	5.138	1.193E-06	47.089	1.197E-05	Foramaldehid	43.089	1.000E-05
0.341	7.927E-08	2.374	5.511E-07	26.114	6.062E-06	Benzonitril	27.154	6.304E-06
0.244	5.662E-08	3.154	7.323E-07	42.065	9.766E-06	p-Toluidin	43.740	1.015E-05

Conclusions of the experiments

From the above experiments we can conclude that:
Urotropine is the most effective inhibitor of all organic components studied so far. Its inhibitor impact on hydrogen permeation into steel sample with carbon in a 12% hydrochloric acid environment is quite clear. As we can see from the curves in Figure 3, its presence allows hydrogen quantity that permeates into metal to decrease to 100% of the mass.

Urotropine is the most effective inhibitor and has priority to other components (aniline, formaldehyde, benzonitril, p-toluidine) as regards to stimulating reaction of Na_2S in hydrogen permeation into metal (Figure 4).

It is important to mention the opposite effect of aniline concerning hydrogen permeation in hydrochloric acid environment. This component not only does not inhibit hydrogen permeation, but on the contrary it stimulates it. During its absorption in metal surface, aniline can block partially recombination of atomic hydrogen with molecular hydrogen. This effect is very fundamental in its use as inhibitor. Even though it can be used as inhibitor for general corrosion of carbon steel, we need to be careful in using it in environments where atomic hydrogen can be developed. Its presence can cause hydrogen breakage of the machineries. Benzonitrile has only few inhibitor abilities towards hydrogen permeation in 12% HCl and no effect on Na_2S stimulating action.

Formaldehyde and p-toluidine have no inhibitor effect on hydrogen permeation in 12% HCl and also on Na_2S reaction in this permeation.

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Докладът е рецензиран