

## Effect of Absorbed Hydrogen on Active Dissolution of Carbon Steel in Near-Neutral pH Electrolyte

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### Abstract

The dissolution kinetics of hydrogen-charged carbon steel in environments simulating the electrolyte under a delaminated coating on underground pipelines has been studied. It has been shown that the active dissolution of iron is considerably accelerated by hydrogen absorption by the metal. This effect can result in local corrosion, in particular, stress corrosion cracking of steel structures.

**Key words:** carbon steel, soil electrolyte, anodic dissolution, hydrogen absorption

### Introduction

Currently, the majority of failures that occur on high pressure buried pipelines result from local corrosion, primarily stress corrosion cracking (SCC) of the metal under delaminated insulating coatings [1~3]. In view of this, systematic studies carried out in many countries all over the world deal with the corrosion behavior of low-alloy and carbon steels in environments simulating the so-called subfilm electrolyte, i.e., solution in the corrugated parts of an underground pipeline coating.

To study the SCC of pipe steels, the NS4 solution is often used as the test environment; this solution was formulated on the basis of analyses of liquids found under delaminated underground pipeline coatings [4]. It has been shown that the corrosion potential of low-alloy and carbon steels in this environment corresponds to the active dissolution region of such steels [4~6] and hence the metal should corrode rather uniformly.<sup>1</sup> However, it has been noted that a local corrosion site (pit or crevice) is formed on the steel surface upon a small cathodic shift of potential from the corrosion potential; this effect is believed to result from hydrogen absorption by the metal [4~10].

In fact, hydrogen absorption by iron, carbon steels and stainless steels increases their corrosion rates in rather concentrated bicarbonate solutions, thus decreasing

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<sup>1</sup> This can involve selective dissolution of steel phase components and nonmetal inclusions [7].

their pitting resistance [11, 12]. The effect of atomic hydrogen on the active dissolution rate of steel in these environments is ambiguous and depends on the content of activating ions (chloride and sulfate) [12]. Adsorbed hydrogen atoms inhibit the anodic dissolution of iron in acidic sulfate solutions [13].

The purpose of this work was to study the effect of atomic hydrogen on the kinetics of active dissolution of mild steel in electrolytes with near-neutral pH.

## Experimental Setup

The experiments were carried out in a Devanathan – Stachurski electrochemical cell [14] on St3 steel, with composition as specified in Table. Thickness of the samples - 100  $\mu\text{m}$ , with a work area of 4.25  $\text{cm}^2$ . The foil for the membranes was annealed for 1 h at 850°C in argon. Prior to the experiments, the electrode was degreased with ethanol, then chemically etched for 2 min in an  $\text{HCl} : \text{H}_2\text{O} = 1 : 1$  solution.

**Table. Chemical composition (wt. %) of the St3 steel used in the study.**

C	Si	Mn	Ni	S	P	Cr	Cu	Al
0.05	0.03	0.38	0.09	0.04	0.035	0.05	0.15	0.16

The following working electrolytes were used:

- NS4 solution, i.e., the following mixture: 1.64 mM  $\text{KCl}$  + 5.75 mM  $\text{NaHCO}_3$  + 1.23 mM  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  + 0.74 mM  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , pH 8.2;
- borate buffer (0.4 M  $\text{H}_3\text{BO}_3$  + yM  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), pH 5.0; 6.0; 7.36; 8.3;
- NS4 solution acidified with hydrochloric acid to pH 5.0; 6.0 or 6.7;
- NS4 mixtures with borate buffer, pH 5.0; 5.8; 6.0; 6.7; 7.36; 8.3.

Chlorides or sulfates were added as concentrated aqueous solutions of sodium salts. All solutions were prepared from reagent grade chemicals using double distilled water. Experiments were carried out at room temperature ( $20 \pm 2$  °C) in solutions deaerated with argon.

The theoretical background of the method involving a bipolar membrane electrode have been reported previously [15, 16]. The polarization conditions of the hydrogen-generating membrane side required to create a particular rate of hydrogen penetration into the metal ( $i_p$ ) are reported elsewhere [15]. The membrane working side was pre-polarized for 10 min at  $E = -0.75$  V. After that, either a constant potential corresponding to the active dissolution of the metal in the test environment was established, or polarization of the membrane's working side was

disconnected and the variation of current (or free corrosion potential) *versus* time was recorded.

Potentiodynamic (1 or 100 mV/s) and potentiostatic (potential step 20 mV, exposure time 10~20 min) polarization curves were recorded starting from  $E = -0.8$  V, using an IPC-Pro-MF potentiostat.

Electrode potentials are reported against SHE.

## Results and discussion

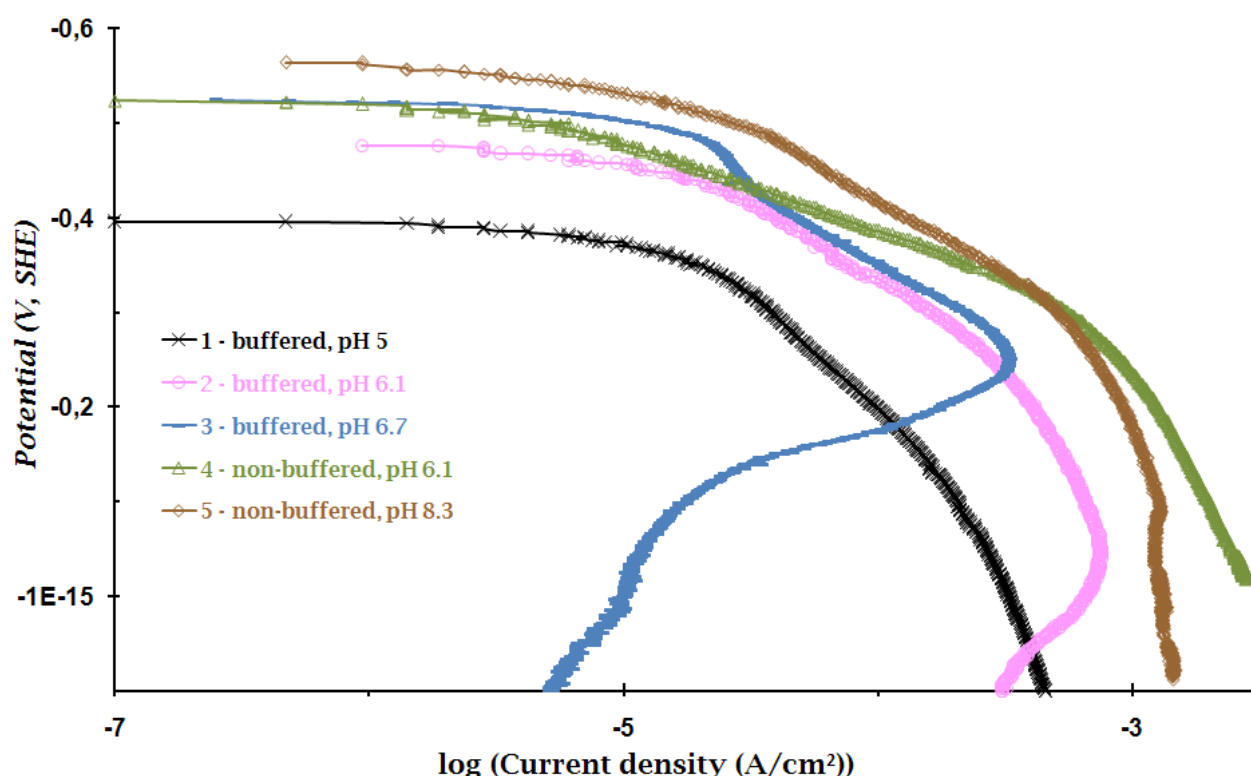
The corrosion-electrochemical behavior of iron and carbon steels in neutral media is traditionally studied using borate buffer as the supporting electrolyte, since it has been shown that variation of borate ion concentration does not affect the metal active dissolution kinetics [17]. Sulfate and chloride anions added to a borate solution accelerate iron dissolution [18].

Figure 1 shows the anodic potentiodynamic curves (APC) recorded on steel in mixtures of the NS4 solution with borate buffer with various pH values (curves 1~3). One can see that as the solution pH increases, the APC shift towards negative potentials, while the critical passivation current decreases. It should be noted that if polarization curves are recorded in the potentiostatic mode, the passivation potential ( $E_p$ ) is shifted in the negative direction, but at  $E < E_p$  the variation of current in time is insignificant. APC show rather extended Tafel regions with a slope of about 100 mV. Thus, the regularities of dissolution of steel in a buffered NS4 solution qualitatively agree with the kinetics of iron anodic dissolution in weakly-acidic sulfate media (pH 4~5.5) at potentials of the so-called prepassive APC region [19, 20].

The active dissolution rate of steel in a non-buffered NS4 solution, the acidity of which was changed by adding hydrochloric acid, also depends on the pH, but no pronounced metal passivity is observed (Fig. 1, curves 4 and 5)<sup>2</sup>. Furthermore, at  $E < E_p$  the anodic current is greater in the absence of a buffer (*cf.* curves 2 and 4); hence, acidification of the near-electrode solution layer due to formation of iron hydroxide compounds is insignificant.

Apparently, borate ions partially replace activating anions from the metal surface, thus decreasing the metal ionization rate. However, steel dissolution rate at potentials near the corrosion potential does not change considerably upon addition of borate buffer to NS4, which allows this environment to be used as a test solution simulating a soil electrolyte with a predefined acidity.

<sup>2</sup> The APCs show no pronounced current decrease upon potential shift in the anodic direction, but the metal dissolution rate at  $E > -0.3$  V in the solution with pH 8.3 becomes smaller than that in the solution with pH 6 (Fig. 1, curves 4 and 5).



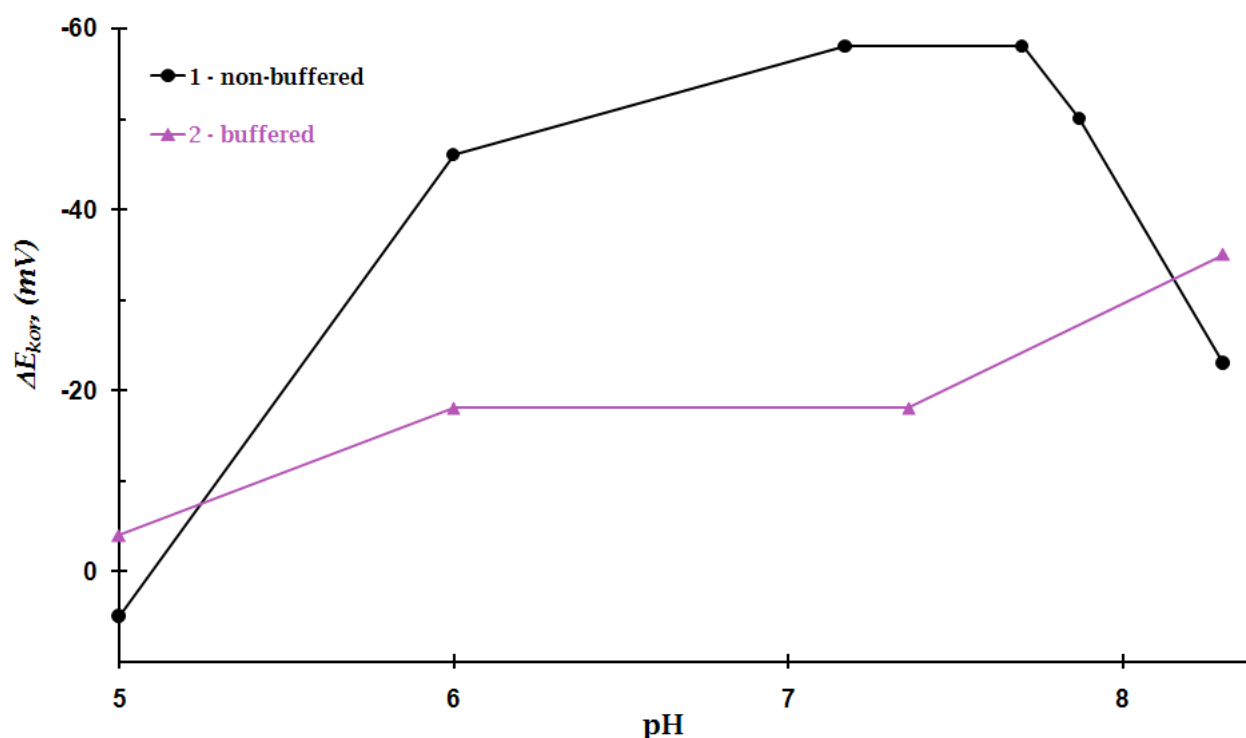
**Fig.1: Potentiodynamic polarization curves (1 mV/s) in the buffered (1~3) and non-buffered NS4 solutions (4, 5).**

The acidity of the solution in the corrugated parts of the pipeline isolation coating can be supported by an electrolyte flow through the coating defects or by the production of carbon dioxide by live bacteria. However, even in these cases the buffer capacity of the subfilm electrolyte is not high, as evidenced by a considerable variation of its pH under simulated conditions of pipeline cathodic protection [21, 22]. Since the pH of the subfilm electrolyte and its variation during pipeline operation have not been exactly determined, the corrosion-electrochemical behavior of the hydrogen-charged metal was studied both in the buffer environment and in the NS4 solution acidified with hydrochloric acid.

One of the most likely growth reasons of a local corrosion site is that a potential difference appears between two areas of the metal surface, *e.g.*, between the crack tip (or pit bottom) and the remaining surface. Therefore, let us consider how hydrogen absorption of steel affects its free corrosion potential.

Figure 2 shows the dependence of the corrosion potential difference for hydrogen-charged and hydrogen-free steel ( $\Delta E = E_{\text{cor}} - E_{\text{cor},0}$ ) on the pH of the NS4 solution acidified with hydrochloric acid (curve 1). One can see that hydrogen absorption by steel in the solution with pH 5 shifts insignificantly the steel corrosion potential in the positive direction ( $\Delta E > 0$ ). The corrosion potential of hydrogen-charged steel in

environments with higher pH values becomes more negative ( $\Delta E < 0$ ), that is, the area of hydrogen-saturated metal is the anode of the galvanic couple and, in principle, can dissolve more intensely than hydrogen-free steel. The highest potential difference is observed in NS4 solutions with pH around 7 (curve 1).



**Fig. 2: Dependence of the corrosion potential difference for hydrogen-charged ( $i_p = 0.2 \text{ mA/cm}^2$ ) and hydrogen-free steel.**

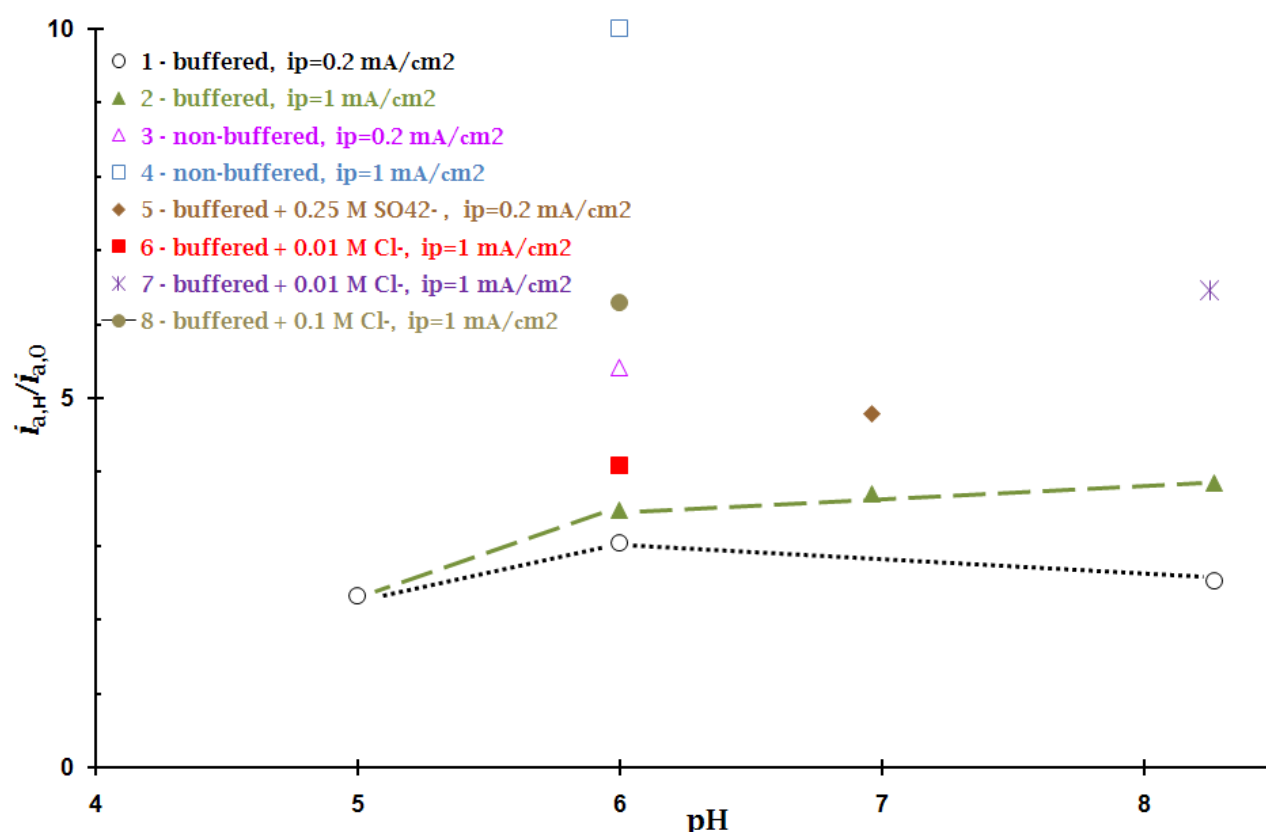
The magnitude of  $\Delta E$  in buffer environments (both in pure borate solution and in its mixtures with NS4) has a maximum at pH 8.3, whereas the potential shift at near-neutral pH values is smaller than in a non-buffered electrolyte (Fig. 2, curve 2). This obviously results from an increase in pH of the near-electrode layer of a non-buffered electrolyte due to corrosion with hydrogen depolarization. The pH of the solution bulk also increases during the experiment (this required that the solution composition be adjusted once in a while); the maximum pH variation is observed in NS4 solutions with nearly-neutral pH. Furthermore, it is possible that molization of a fraction of hydrogen atoms that are desorbed from the metal in these environments involves  $\text{H}^+$  ions (*i.e.*, the electrochemical desorption mechanism is involved), which should also increase the near-electrode pH.

Thus, hydrogen charging of steel in solutions with  $\text{pH} > 5$  results in a negative corrosion potential shift, which may be due to activation of metal dissolution or inhibition of the cathodic reaction.



The effect of hydrogen absorbed by the metal on the dissolution rate of steel in buffered NS4 solution was studied at a constant potential. We recorded the variation of anodic current as a function of time in the absence of polarization of the hydrogen-generating membrane side and at hydrogen penetration currents through the membranes ( $i_p$ ) equal to 0.2 and 1 mA/cm<sup>2</sup>. It was found that hydrogen absorption by steel accelerates dissolution of the latter, but the magnitude of this effect depends on the electrolyte pH. Figure 3 shows the ratios of quasi-steady-state dissolution currents of hydrogen-charged ( $i_{a,H}$ ) and hydrogen-free metal ( $i_{a,0}$ ) measured at constant potentials and rates of hydrogen penetration into the metal. In the solution with pH 5, the  $i_{a,H}/i_{a,0}$  ratio has the smallest value, whereas in solutions with high pH the anodic current increases with an increase in  $i_p$ . The  $i_{a,H}/i_{a,0}$  ratio measured at  $i_p = 0.2$  mA/cm<sup>2</sup> decreases (Fig. 3, points 1), whereas the ratio measured at  $i_p = 1$  mA/cm<sup>2</sup> increases (point 2) with an increase in pH.

The anodic behavior of the metal observed after the end of hydrogen charging also depends on the acidity of the corrosive environment. The anodic current in the solution with pH 5 slowly decreases with time, whereas it abruptly decreases in the solution with pH 8.3 to the value characteristic of the dissolution rate of the hydrogen-free metal.



**Fig. 3: The  $i_{a,H}/i_{a,0}$  ratios at different pH values of buffered (1, 2) and non- buffered (3, 4) NS4 solution. Same values in buffered NS4 solution with additions (5~8).**

These results can be explained as follows. At potentials of iron active dissolution in environments with near-neutral pH, the metal surface is partially covered with adsorbed oxygen or a surface oxide [17, 23]. The coverage of iron surface with oxide ( $\theta_{\text{FeO}}$ ) increases with an increase in the solution pH; in particular, this results in a negative shift in the steel passivation potential. Atomic hydrogen that is desorbed from hydrogen-charged iron can reduce the surface oxide (adsorbed oxygen):

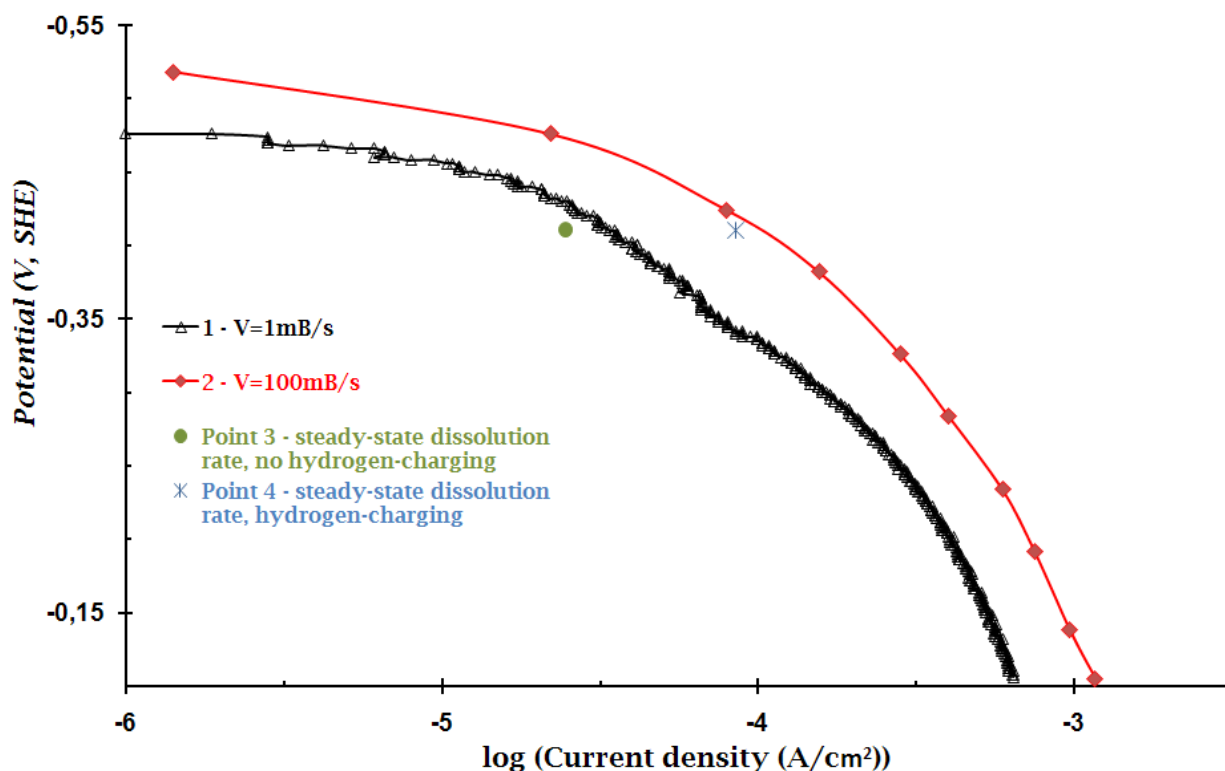


thus activating the metal dissolution. Obviously, the accelerating effect of atomic hydrogen should depend on its amount and on the  $\theta_{\text{FeO}}$  on hydrogen-free metal. Since  $\theta_{\text{FeO}}$  is higher in alkaline media, reduction of the surface oxide in these media requires a greater number of hydrogen atoms, which is characterized by  $i_p$  under steady-state conditions. However, the maximum accelerating effect of hydrogen (*i.e.*,  $i_{a,H}/i_{a,0}$ ) should also be higher in these solutions. After hydrogen absorption of the metal is stopped, its surface is covered with the oxide again:



the rate of this process is the higher the larger the amount of  $\text{OH}^{-}_{\text{ads}}$ , which is determined by the solution pH.

In order to check the above considerations, we recorded APC with various potential ( $V$ ) scanning rates in buffered NS4 solution with pH 6.1. The dissolution rate of hydrogen-free iron increases with an increase in  $V$  (Fig. 4, curves 1 and 2); in this case, the steady-state anodic current at a constant potential (point 3) corresponds to a “slow” ( $V = 1$  mV/s) anodic curve (curve 1). The steady-state dissolution rate of the hydrogen-charged membrane (point 4) corresponds to a “fast” APC ( $V = 100$  mV/s) for hydrogen-free metal (curve 2). Hence, a steel surface undergoing hydrogen absorption acquires the same properties as it acquires upon fast transition from cathodic to anodic potentials, *i.e.*, it becomes free from passivating species.



**Fig. 4: Potentiodynamic polarization curves (1, 2) and steady-state dissolution rate of steel at  $E = -0.41$  V (3, 4) in buffered NS4 solution (pH 6.1).**

The anodic curves obtained in an NS4 solution acidified with hydrochloric acid to pH 6.1 support this conclusion (Fig. 5, curves 1~3). However, the anodic currents obtained on hydrogen-free steel in this solution with “fast” potential scanning (curve 2) are higher than the quasi-steady-state dissolution rates in the case of hydrogen absorption (curve 3). Perhaps, this results from an increase in the pH of the near-electrode non-buffered electrolyte; as a result, reaction (2) occurs rather quickly. Then, under steady-state conditions, the metal surface will be partially covered with an oxide, despite the flux of hydrogen atoms that are desorbing from the metal. This assumption is supported by the following: first, a considerable acceleration of dissolution of hydrogen-charged iron at “fast” potential scanning (Fig. 5, curve 4); and second, a strong dependence of the accelerating effect of hydrogen ( $i_{a,H}/i_{a,0}$  ratio) on the flux of hydrogen atoms in the membrane (Fig. 3, points 3 and 4).



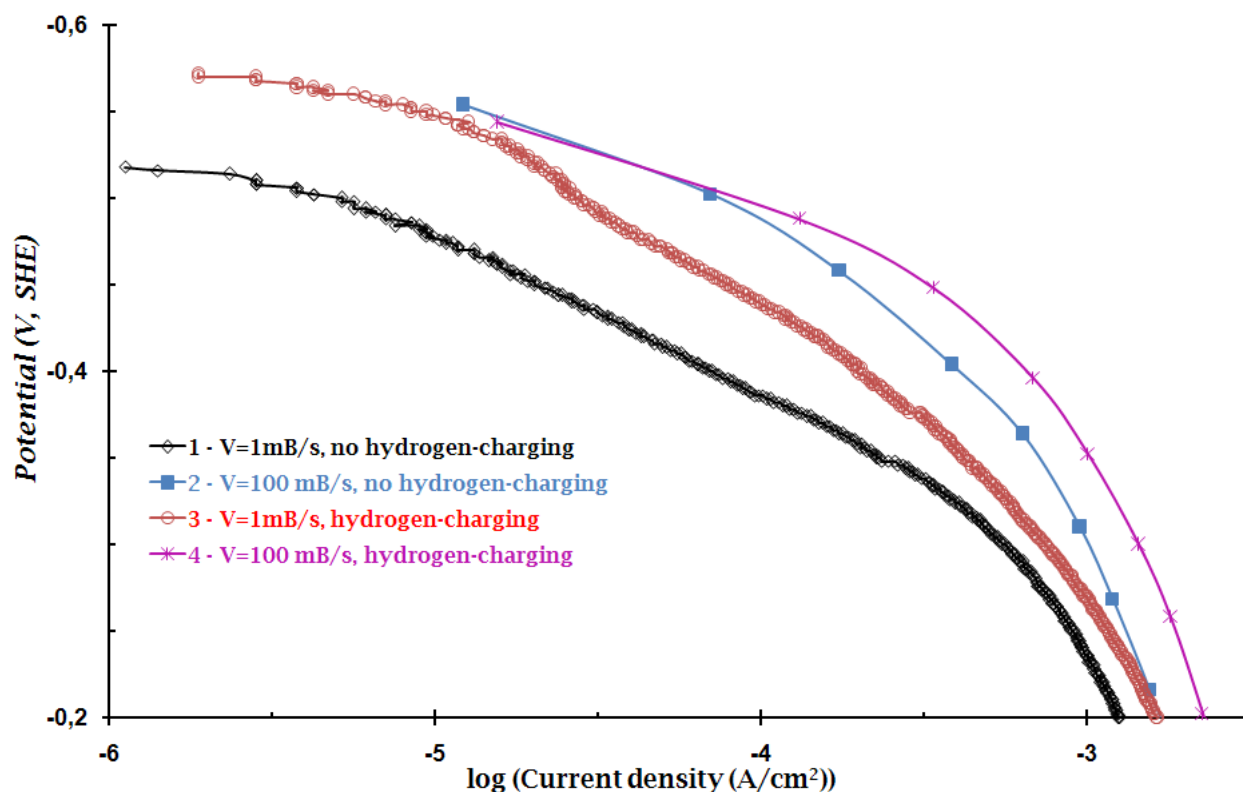


Fig. 5: Potentiodynamic polarization curves in non-buffered NS4 solution (pH 6.1)  $i_p = 0$  (1, 2) and 0.2 (3, 4) mA/cm<sup>2</sup>.

Due to an increase in the near-electrode pH, the  $i_{a,H}/i_{a,0}$  ratio at  $i_p = 1$  mA/cm<sup>2</sup> is much higher in non-buffered NS4 solution than in a buffered environment (*cf.* curve 2 and point 4 in Fig. 3). This agrees with the high shift of the corrosion potential in the negative direction upon hydrogen absorption in a non-buffered electrolyte (Fig. 1).

Thus, competition of reactions (1) and (2) may govern the crack growth in a mechanically stressed steel structure. If SCC of steel involves the local dissolution mechanism, the crack growth rate determines the amount of iron that undergoes ionization; the anodic current at the crack pit is the strongest on the juvenile surface and decreases in time due to the passivation of the metal surface (reaction 2). Due to reaction (1) occurring on a hydrogen-charged metal area, the metal passivation occurs more slowly or ceases completely. It is known that the concentration of incorporated hydrogen at a crack tip is much higher than in the metal bulk (at crack edges) [24]. Hence a crack tip can dissolve at a higher rate (no smaller than the steady-state  $i_{a,H}$  value) than its edges. Then, at first approximation, the difference in the dissolution rates of the tip surface and crack edges can be characterized by the  $i_{a,H}/i_{a,0}$  ratio.

Let us consider the effect of the concentrations of sulfate and chloride that are

among the major components of the soil electrolyte. The addition of these ions to the NS4 solution increases the  $i_{a,H}/i_{a,0}$  ratio (Fig. 3, points 5~8); even in the presence of a large amount of sulfate (0.25 M), it increases insignificantly (point 5), whereas chloride ions present in the solution can increase the dissolution rate of hydrogen-charged steel much more strongly (points 6~8). One can see that the  $i_{a,H}/i_{a,0}$  ratio increases with an increase in solution pH (points 6 and 7) and in chloride concentration (points 6 and 8); the latter fact agrees with the accelerating effect of atomic hydrogen on iron dissolution in acidic electrolytes and is presumably due to differences in the adsorption rates of  $\text{OH}^-$  and  $\text{Cl}^-$  ions on the metal surface [25].

## Conclusions

1. The dissolution kinetics of hydrogen-charged carbon steel in environments simulating the electrolyte under a delaminated insulating coating on underground pipelines has been studied using the bipolar membrane electrode method. It has been shown that hydrogen absorption by iron accelerates considerably the active dissolution of the metal in environments with near-neutral pH. Apparently, this effect is due to the surface oxide reduction with hydrogen atoms that are desorbing from the metal.
2. It has been shown that the dissolution rate is affected by the flux of hydrogen atoms through the membrane. The maximum accelerating effect of atomic hydrogen increases with an increase in solution pH from 5 to 8.3 and an increase in the concentration of anions that activate iron corrosion (chloride and sulfate).
3. Hydrogen absorption by carbon steel shifts the corrosion potential in the negative direction, which may result in local corrosion (primarily, stress corrosion cracking) of underground steel structures.

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