A critical review and experimental analysis of the equation recommended by ASTM G148-97 and ISO 17081: 2004 for the calculation of the hydrogen diffusivity in metals and alloys

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ABSTRACT

Since its discovery in 1864 by Cailletet [1], hydrogen embrittlement of metals has been the target of several investigations. In 1962 Devanathan and Stachurski [2], developed an electrochemical technique for hydrogen permeation. There are now three methods to produce hydrogen: galvanostatic, potentiostatic and under open circuit potential in an acid medium (OCPAc). Regulations in Refs. [3] and [4] standardized hydrogen permeation only by the potentiostatic method. In the present work an experimental methodology for OCPAc procedure was developed. The authors conclude that the equation of diffusivity proposed by ISO 17081 and ASTM G148-97 [3] and [4] can lead to underestimated diffusivity values. The authors conclude the mathematical model proposed for the OCPAc method presented a satisfactory fit to the experimental data. Diffusivity values were calculated not only for this case but also for all other methods. However, to evaluate and explore the limits of the proposed methodology, the authors recommend its use with other metals and alloys.

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Introduction

API grade steels API5L X70 and X65 are widely used for the transportation of oil and natural gas. Their lifespan is affected by the transport of fluids and operating conditions. One of the causes of embrittlement and the deterioration of the mechanical properties of steel is exposure to hydrogen [1,5—7]. The hydrogen evolution reaction can occur even with cathodic protection as well as in other electrochemical plating processes [8—12]. Due to the small size of the hydrogen atom, it can diffuse rapidly in the metal matrix, concentrating on microcavities, or grain boundaries, or simply by forming metal hydrides. These phenomena cause microstructural damage and modify the mechanical properties of steel, causing structural failures and the propagation of cracks [13,14].

The electrochemical hydrogen permeation technique was introduced by Devanathan and Stachurski [2]; this technique consists of the symmetrical arrangement of two cells—one for

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Nomenclature

API	American Petroleum Institute
BC	Background current density, Table 3
CE	Counter Electrode
DP	Potentiostatic-potentiostatic (double-potentiostatic) permeation method
GP	Galvanostatic-potentiostatic permeation method
NACE	National Association of Corrosion Engineers
OCPAc	Open circuit potential in an acid medium
PAR	Princeton Applied Research
RE	Reference Electrode
SCE	Saturated calomel electrode
WE	Work Electrode (Sample)

Symbols

D_{app}	apparent diffusivity, $cm^2 \, s^{-1}$
i	Current density, $\mu A \, cm^{-2}$
$i(t)$	Transient current density, $\mu A \, cm^{-2}$
i_{ss}	Current density on steady state, $\mu A \, cm^{-2}$
t	Time, s
t_b	Breakthrough time, s
t_L	Time-lag, s
t_h	Half time [when $i(t)/i_{ss} = 0,5$], s
A_1, A_2, x_0, p	Parameters of the logistic sigmoid function, Eq. (3)
L	Membrane thickness, mm
$Q(C)$	Total charge from the hydrogen oxidation, Coulombs

hydrogen production and another for hydrogen detection. The detection cell is maintained at a constant oxidation potential. Another cell is used to generate hydrogen by the galvanostatic-potentiostatic method (GP), constant potential, the double-potentiostatic method (DP) or the open circuit in acid medium (OCPAc) method. Over recent years there have been important advances in this field; however, questions about the mathematical models used to calculate the apparent hydrogen diffusivity have been raised. This methodology is currently being used to study the hydrogen diffusivity phenomenon in metal matrices [15].

Consistent with the ASTM G148-97 and ISO 17081: 2004 standards, the diffusivity of hydrogen in numerous publications is estimated only by the DP method, even if the GP and OCPAc methods were used. The work in Refs. [16–19] showed that the first two methods have different boundary conditions and thus different solutions from Fick's second law. It is noted that these standards do not justify the use of only one equation regardless of the method used to generate hydrogen.

This paper aims to clarify this issue by calculating the apparent hydrogen diffusivity according to the method employed. Our results were evaluated by electrochemically testing permeation using API 5L X65 and X70 alloys. These API 5L grade steels were manufactured by TMCP process (Thermomechanical Controlled Rolling) and received the additions of Niobium and Vanadium to acquire desired mechanical properties.

Experimental

The experiments were performed with API 5L X65 and X70 steel (40 mm diameter and 1 mm thick) abraded with SiC paper (200, 400, 600, 1200) and polished with alumina suspensions (1, 0.3 and 0.005 μm). The steels were then cleaned using ethanol and acetone in an ultrasonic bath. No Pd coating was applied to the samples. The nominal compositions are shown in Table 1.

The potential and current relating to hydrogen generation were determined by potentiodynamic polarization. Fig. 1 shows the experimental setup.

Electrochemical hydrogen permeation test

Permeation measurements were conducted using the cell developed by Devanathan and Stachurski [2] as shown in Fig. 2. A 0.1 mol L^{-1} NaOH solution was used in the anodic semi-cell. The samples were passivated for 24 h. The oxidation potential in the detection cell was +300 mV vs SCE. The cathodic cell was filled with a 0.1 mol L^{-1} NaOH solution once the background current density was approximately 0.2 $\mu A/cm^2$. Hydrogen was then produced by either DP or GP. All experimental control and measurements were performed using the PAR (Princeton Applied Research) Model VMP3 multi-channel potentiostat. All electrochemical experiments were performed at ambient temperature in the range 24–26 °C. Fig. 2 shows the experimental setup. Permeation tests were made in triplicate, i.e., a test for each of the three fresh sample of API 5L X65 and X70 class. Fig. 5(a–f) shows the average results of these permeations.

In open circuit potential assay (OCPAc), hydrogen can be produced in an acid medium by bubbling H_2S in the production semi-cell. However, due to the toxicity of this gas [21], we used sodium thiosulfate. This gas inhibits the coalescence of hydrogen molecules and therefore stresses the diffusive effect.

Once the background current (0.2 $\mu A \, cm^{-2}$) was achieved, the load cell was filled with a NACE solution TM0284-96[a] [22] (0.5% glacial acetic acid and 5% NaCl with 10^{-3} (mol L^{-1})) of $Na_2S_2O_3$; pH = 3.1–3.4 [21].

Data analysis using the classic method

The apparent diffusivity was calculated from the time-lag method, as shown in Table 2. This table shows Eqs. (1) and

Table 1 — API 5L X70 and X65 nominal composition in % wt (Usiminas) [20].

Steel	C	Si	Mn	P	S	Nb	Ti	Cr	V	Mo	Cu
API 5L X70	0.1	0.24	1.58	0.013	0.004	0.05	0.04	0.022	0.037	0.002	0.029
API 5L X65	0.07	0.18	1.37	0.019	0.004	0.05	0.04	0.021	0.048	0.0009	0.026