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DETERMINATION OF SUBSURFACE HYDROGEN CONTENT IN THE API X52 AND API X65 PIPELINE CARBON STEELS

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ABSTRACT

Subsurface content of electrochemically charged hydrogen in the API X52 and API X65 pipeline carbon steels was determined using the hydrogen electrochemical oxidation method in 0.2 M oxygen free *NaOH* solution. Samples of both grades of carbon steel were subjected to cathodic polarization in a oxygen free soil simulating solution with neutral pH. Electrochemical hydrogen oxidation determines the total electric charge involved in the Faradaic hydrogen oxidation process. The subsurface hydrogen content (C_H) in *mol/cm^3* assessed by electrochemical hydrogen oxidation was a function of the cathodic polarization time which was in agreement with the maximum hydrogen penetration depth as determined by electrostatic Van de Graaff type ion accelerator measurements conducted on samples after different hydrogenation periods. Ion accelerator results indicated that hydrogen electrochemically charged on steel reached a depth of 20 *μm*. For the studied API steels the resistance to hydrogen absorption decreases with decreasing of steel strength (yield stress). The hydrogen electrochemical oxidation technique was a reliable method to assess quantitatively hydrogen subsurface concentration on steels subjected to cathodic polarization, from soft to total cathodic protection conditions.

KEY WORDS: *hydrogen concentration, Hydrogen absorption, electrostatic Van de Graaff ion accelerator.*

INTRODUCTION

Carbon steels along with other alloys are susceptible to hydrogen absorption which may lead to degradation in physical and mechanical properties. Hydrogen permeation through metals has been extensively studied in order to establish the mechanism of hydrogen entry, the hydrogen diffusivity through the material, and hydrogen trapping as well as the sub-surface hydrogen concentration [1-3]. Long-term exploitation of buried carbon steel pipelines promotes the steel hydrogenation process. Moreover, external environmental conditions cause free corrosion processes, where hydrogen can evolve on metal surface as result of cathodic counterpart of the metal dissolution. The majority of buried pipelines are subjected to cathodic protection to reduce corrosion degradation. This protection system is by its nature an important promoter of hydrogenation on the external face of steel pipelines.

The impending synergy of hydrogenation and mechanical loading, (sustained or cyclic) can lead to an increase in the risk of damage and unexpected fracture of pipelines during long-term exploitation [4-6]. Therefore, the characterisation of hydrogen in metals is important for the understanding, prediction and prevention of hydrogen related failures of engineering structures.

The whole picture of the interaction processes metal-hydrogen can be described considering three stages: (1) the entry of hydrogen from the surrounding environment into the metal, (2) the transport (diffusion) of hydrogen inside the metal and (3) the trapping of hydrogen at structural defects and/or formation of hydrides phases. The efficiency of hydrogen entry is characterised by the concentration of hydrogen dissolved in the metal just beneath its surface. Once absorbed, hydrogen makes a component of the interstitial solid solution, i.e. hydrogen atoms randomly distributed among metal atoms in the metal lattice [7]. The absorbed hydrogen refers to the total hydrogen concentration in the material comprising hydrogen in solution and hydrogen at trapping sites [7-10].

It is worth mentioning that a number of reported works were conducted with using of cathodic charging of hydrogen under high current density polarisation. Such charging is not truly representative

of the hydrogen entry conditions in real operating pipelines, where different situations can be present, from free corrosion, to complete cathodic protection. This fact was pointed out in work [11] in which the authors proposed a hydrogen oxidation current method to investigate the absorbed hydrogen concentration in hydrogen pre-charged pipeline steels. This method is easy to use with an adapted electrochemical monocell, especially in field, as a sensitive and convenient tool for determining the sub-surface hydrogen concentration in metallic structures under service conditions. Results from this method show that hydrogen concentration increase with increasing pre-charging current density, which is approximately consistent with the Sieverts law and also it was found that hydrogen concentration increases linearly with the logarithm of hydrogenation time [11].

Capelle et al., assessed the ability of three API grade pipeline steels to absorb hydrogen under hydrogenating in special solution NS4 with *pH* 6.7, which simulates the soil in contact to buried pipelines [12, 13]. In these conditions i.e., in deoxygenated, neutral pH solution, hydrogen atoms are generated on the steel surface by the electrochemical reduction of water molecules [14, 15].

The absorbed hydrogen atom concentration will increase continuously with the cathodic polarisation potential. The role of cathodic polarisation is to generate hydrogen atoms and also to recombine hydrogen atoms. The hydrogen-charging process will be controlled by recording the cathodic polarisation current I_{cath} *(t)*. Hydrogen concentration in metal can be determined on the base of hydrogen discharging process under anodic polarization using the hydrogen electrochemical oxidation method used successfully in works [12, 15-17].

EXPERIMENTAL

Materials. The metals under study were two API grade pipeline steels manufactured in Mexico with chemical composition as presented in table 1.

Table 1. Chemical composition of pipeline steels grade API manufactured in Mexico

Steel		C	Mn	Si	Cr	Ni	Mo	S	Nb	Al	V
API X65		0.07	1.34	0.3	-	0.005	-	0.002	0.048	0.036	0.05
API X52		0.08	1.09	0.284	0.017	0.020	0.03	0.004	0.038	0.041	0.051

Metallographic Analysis. In order to determine the effect of microstructure on the hydrogen absorption of the carbon steels under study, samples were prepared and subjected to metallographic analysis. Sample surfaces were grinded with SiC paper grit 400, 800 and 1200. After grinding, samples were polished with a diamond paste of 1 μm particle size. The surface was subjected to etching with nital 5%.

Electrochemical characterization of the steels. Potentiodynamic polarization tests were conducted in NS4 neutral pH solution (electrolyte for hydrogenation) and in 0,2 M NaOH solution (for electrochemical hydrogen oxidation) in order to determine the electrochemical behavior of the 2 pipeline steels under study. Electrolytes were prepared with analytical degree chemicals and distilled water according to the concentrations used by Yan [11] and Capelle [12] and listed in tables 2 and 3.

Table 2. Chemical composition of neutral pH NS4 solution for hydrogenation tests

Chemical	NaHCO3	KCl	CaCl2·6H$_2$O	MgSO4·7H$_2$O
Quantity (g/l)	0.483	0.122	0.268	0.131

Table 3. Electrolyte for electrochemical hydrogen oxidation

Chemical	NaOH	H$_2$O
Quantity (g/l)	8.0	1000

The NS4 neutral pH solution and the NaOH 0.2 *M* (*pH* = 12.5) solution were deaerated with N_2 for 30 minutes prior to the tests maintaining a lower nitrogen flow during the polarization period. Steel Cylindrical samples of 6 mm diameter x 5 mm length were attached to a conducting wire at one end for electronic connection and embedded in resin resulting in a working electrode surface area of 0.28 *cm^2*. The surface area was grinded with SiC abrasive paper grit 1200, washed with distilled water, cleaned with acetone and air dried before tests.

A conventional three electrode electrochemical cell was used for the evaluation of the electrochemical behavior of the steels in both electrolytes with a saturated calomel electrode as

reference electrode, a graphite bar as auxiliary electrode and the embedded steel samples as working electrodes. Potentiodynamic polarisation tests were conducted in both electrolytes at room temperature ($T = 24$ $^{\circ}$C). A cathodic overpotential of 300 mV was applied to the steel samples in the NS4 solution from which the potential scanning was carried out at a rate of 10 mV/min. The polarisation finished at a potential of 100.00 mV vs SCE. The polarisation tests of steel samples in the 0.2 M NaOH solution involved the application of a cathodic overpotential of 200 mV and anodic polarisation to a potential value of 400 mV vs SCE using a scan rate of 10 mV/min.

Hydrogenation of pipeline steels. The specimens were immersed into the deaerated NS4 solution and subjected to cathodic potentiostatic polarisation by applying a cathodic overpotential of 200 mV, (E_{cath} = $const$). From the potentiodynamic polarisation tests the value of the corrosion potential (E_{Corr}) for the steels was determined as indicated in table 4 as well as the potential at which the samples were potentiostatically polarised (E_{cath}) for hydrogenation tests.

Table 4. Values of open circuit potential and cathodic polarisation potential

Steel	(E_{OCP}, mV vs SCE)	(E_{Cath}, mV vs SCE)
API X52	-740	-940
API X65	-710	-910

Electrochemical hydrogen oxidation. According to the procedure reported in work [15], the hydrogen discharging of metals can be carried out by applying potentiostatic anodic polarisation (E_{anodic} = +170 mV vs SCE) during some defined time t_{dis}. At this potential level the three pipeline steles present a passive behaviour in the NaOH solution as demonstrated by the potentiodynamic polarisation tests.

The total quantity of absorbed hydrogen into the metal can be defined as [12]:

$$Q_H^{abs} = \int_0^{t\exp} [I_H(t) - I_{ref}(t)]dt, \text{ under } E_{anod} = const;$$

where $I_H(t)$ is anodic polarisation current for hydrogen charged specimen and $I_{ref}(t)$ is anodic polarisation current for specimen without hydrogen (reference/Blank curve). Calculation of hydrogen concentration was done according to following equation

$$C_H = Q_H^{abs}/zFv,$$

where z is the number of electrons take in reaction; F is the Faraday constant; v is the effective volume of specimen.

RESULTS AND DISCUSSION

Metallographic Analysis. The maximum grain size of the API X65 steel was of approximately 25 μm and the (%) ferrite/pearlite ratio was 83/17. Figure 1 presents the micrographs of this steel at 100X. Considerable particles precipitation, (from 5 to 20 μm size range), were observed in the samples of X65 steel. The precipitated particles presented diverse morphologies with a predominance of elongated shapes and spheroidal particles. Steel API X52 presented a ferrite continuous phase with some perlite colonies distributed randomly and with an average size of 50 μm.

The presence of inclusions or precipitates in these steels has a strong influence on their mechanical properties. Thus for example, the high strength of the micro-alloyed steels is related with the grain refinement induced by small metallic particles [18].

Evaluation of the electrochemical behaviour of the pipeline carbon steels. The electrochemical behaviour of the pipeline steels in the hydrogenation electrolyte at room temperature allowed us determining the corrosion rate and the controlling rate reaction of the whole corrosion process in the N_2 deaerated NS4 solution. The two pipeline steels showed a charge transfer controlled anodic and cathodic reactions with a very similar slope for the anodic branch. These steels are susceptible to intense corrosion in the NS4 electrolyte. Tafel extrapolation method was used to determine the corrosion rate of the three pipeline steels based on the information provided from the polarisation curves as presented in table 5.
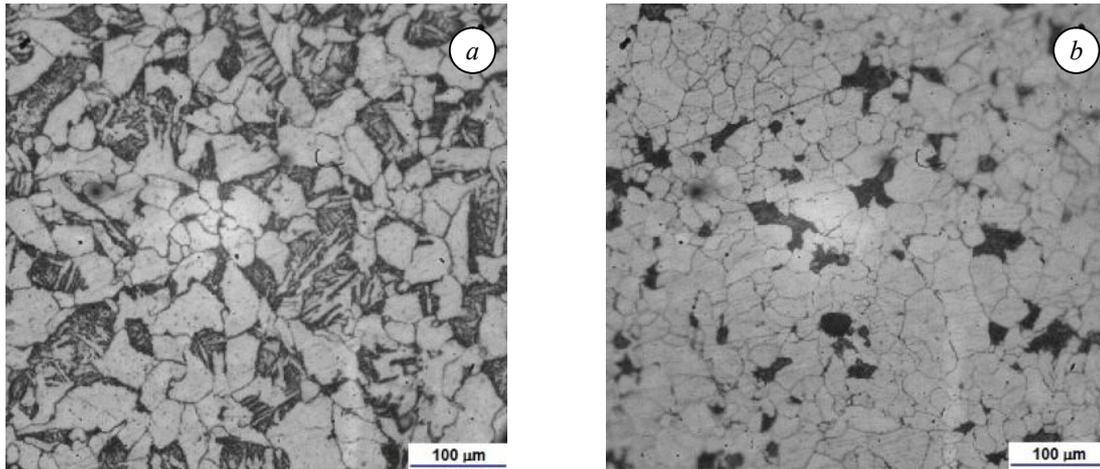
Fig. 1. Microstructure of steels API X65 (*a*) and X52 (*b*) at 100X.

Table 5. Values of corrosion potential, corrosion current density and corrosion rate

Steel	(E_{Corr}, mV vs SCE)	i_{corr} (mA/cm^2)	V_r (mm/year)
API X52	-810	6.471×10^{-5}	0.756
API X65	-850	5.687×10^{-5}	0.661

During electrochemical hydrogen oxidation, the surface of the steel samples get passive at the applied potential of 170 mV vs SCE. The passive region from - 200 to 600 mV in the polarisation curve presents the lowest anodic current density associated to dissolution of steel under this condition.

Hydrogenation and evaluation of sub-surface hydrogen concentration in Steel API X52. The tests were conducted using the electrochemical cell adapted for fix position of working, auxiliary and reference electrodes. The specimens were immersed into the cell with NS4 solution and exposed under constant polarisation potential E_{cath}.

The total quantity of evolved hydrogen on metal surface will be assessed as [15-17]:

$$Q_H^{Ev} = \int\limits_0^{t\,exp} I_{cath}(t)dt, \quad \textbf{under } \mathbf{E_{cathod} = const.}$$

Taking into account that for carbon steel API X52 the open circuit potential (OCP) in the NS4 deaerated solution was near -740 *mV* vs SCE, it has been chosen that E_{cath} = *-940 mV vs SCE* for the hydrogenation.

Immediately after hydrogen charging of samples for different times, in the SN4 solution, the specimen was removed from the electrochemical cell and fixed in other electrochemical cell containing the 0.2 *M* NaOH solution in order to conduct the hydrogen electrochemical oxidation for determination of the quantity of absorbed H in the steel. The calculation of hydrogen concentration was done considering an effective volume of the specimen of 0.576 *cm³*. The chronoamperometries of samples hydrogenated for different periods are as shown in figure 2.

Hydrogen electrochemical oxidation Reference current I_{ref}, was obtained a chronoamperometry and from this the electric charge involved Q_{Blank} was determined. The value of Q_{Blank} was 0.486 mA s, which was used for the calculations of the subsurface hydrogen concentration.

Hydrogenation and evaluation of sub-surface hydrogen concentration in Steel API X65. The same procedure was carried out for samples of steel API X65 subjected to hydrogenation for for different times up to 66 hours after which the electrochemical hydrogen oxidation was applied in the 0.2 *M* NaOH solution. Fig. 3 presents the chronoamperometries of the electrochemical hydrogen oxidation for the samples.

These results are directly related to the hydrogen absorption process on the specific steels and demonstrated their susceptibility to hydrogenation in deaerated, neutral pH NS4 solution under a cathodic polarisation (200 mV below the open circuit potential) that is very near to the condition of full cathodic protection for steel API X52.
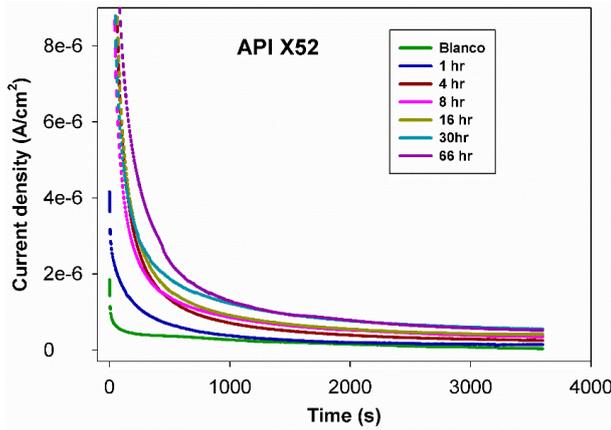
Fig. 2. Hydrogen oxidation current for steel API X52 in deareated 0.2 M NaOH solution from samples hydrogenated for different periods.
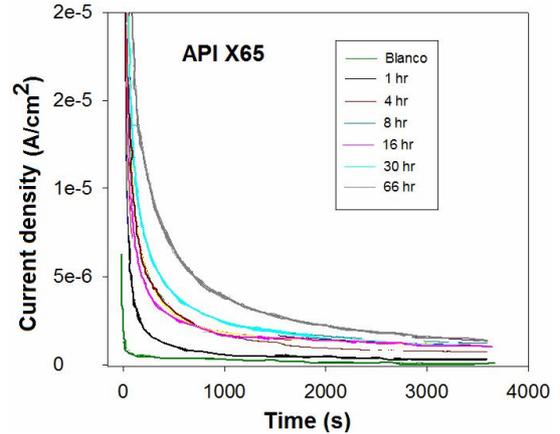

Fig. 3. Hydrogen oxidation current for steel API X65 in deareated 0.2 M NaOH solution from samples hydrogenated for different periods.

Absorbed hydrogen concentration by RBS. The Ion Beam Analysis Techniques, such as Elastic Recoil Detection Analysis (ERDA) and Rutherford Backscattering Spectrometry (RBS) give a very precise measurement of the concentration of hydrogen and oxygen, respectively. In the present case samples of steels API X52 and X65 were hydrogenated up to 48 hours after which were immediately subjected to RBS measurements. The results of hydrogen concentration are presented in Fig. 4 for the different hydrogenation times. This analysis indicated that the hydrogen penetrated up to 20 μm into the steels. The results of sub-surface hydrogen concentration in both steels measured by electrochemical and RBS methods are summarised in table 6.
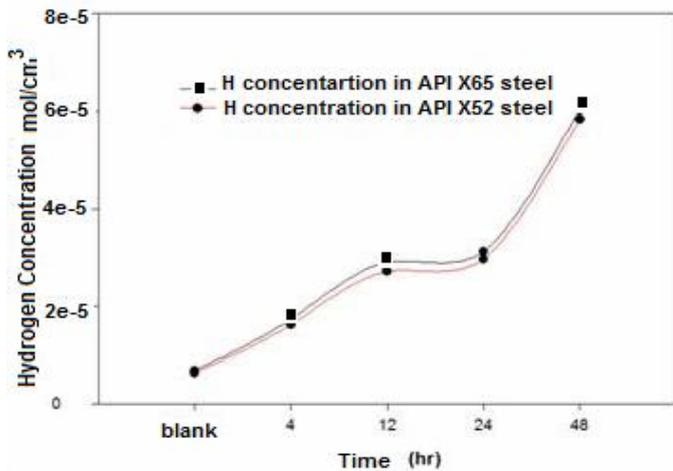

Fig. 4. Hydrogen concentration measured by RBS as a function of hydrogenation time.

Table 6. Values of hydrogen concentration as a function of hydrogenation time obtained from electrochemical and RBS methods

Electrochemical measurements			RBS measurements		
Hydrogenation	API X65	API X52	Hydrogenation	API X65	API X52
Time, (hrs)	C_H, (mol/cm^3)	C_H, (mol/cm^3)	Time, (hrs)	C_H, (mol/cm^3)	C_H, (mol/cm^3)
0.5	138.143×10^{-9}	22.805×10^{-9}	Blank	163.44×10^{-9}	151.92×10^{-9}
1	282.013×10^{-9}	70.527×10^{-9}	1	-	-
2	299.554×10^{-9}	132.372×10^{-9}	2	-	-
4	330.534×10^{-9}	215.284×10^{-9}	4	415.2×10^{-9}	388.8×10^{-9}
8	447.507×10^{-9}	322.145×10^{-9}	8	-	-
12	466.259×10^{-9}	386.228×10^{-9}	12	698.4×10^{-9}	650.4×10^{-9}
16	573.198×10^{-9}	523.854×10^{-9}	16	-	-
24	613.290×10^{-9}	581.449×10^{-9}	24	748.8×10^{-9}	711.14×10^{-9}
30	695.029×10^{-9}	599.511×10^{-9}	30	-	-
48	845.841×10^{-9}	695.749×10^{-9}	48	1444.8×10^{-9}	1396.8×10^{-9}
66	951.275×10^{-9}	791.987×10^{-9}			

Considering that the two methods for determination sub-surface hydrogen concentration are completely different in nature, the sub-surface concentration found in both carbon steels is of the same order of magnitude being in all cases higher the one obtained from the RBS measurements because this technique counts all hydrogen in sample, the solved hydrogen, trapped and that in hydrides whereas the electrochemical oxidation only measures the solved hydrogen and possible that trapped in sites very near to the surface.

CONCLUSIONS

1.   The steels API X52 and API X65 are susceptible to hydrogen absorption in deaerated electrolyte of neutral pH when subjected to low cathodic polarisation.

2.   For short hydrogenation periods the hydrogen concentration C_H (mol/cm^3), increased as a function of the time of electrochemical charging in both steels.

3.   The Bainitic microstructure of API X65 steel facilitated hydrogen absorption compared to the ferritic one of steel APT X52 which presented lower hydrogen concentration.

4.   RBS method allows determining the total hydrogen concentration considering its dissolved, trapped and second phase precipitation condition.

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