

The Influence of Hexamethylenetetramine on the Corrosion and Hydrogen Permeation of Type API 5L-X52 Steel

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Abstract

The inhibitive effect of hexamethylenetetramine on the corrosion and hydrogen permeation behaviour was evaluated on a type API 5L-X52 steel in 1N H₂SO₄ solution. Potentiodynamic polarization curves were employed to determine the electrochemical behaviour of the steel, while the Devanathan–Stachurski technique was used to estimate the hydrogen permeation rate. Optical and scanning electron microscopies and energy dispersive X-ray analysis were used for surface analysis. Additionally, to detect the hydrogen damage in the steel, an ultrasonic technique based on the sound wave attenuation was employed. The obtained results clearly indicate that Hexamethylenetetramine inhibits efficiently the corrosion of the steel but increase the quantity of absorbed hydrogen in the bulk metal. The organic compound seems to have a specific influence on the hydrogen evolution reaction, reducing the active site numbers where hydrogen could be reduced and partially blocking the recombination of atomic hydrogen to molecular hydrogen on the steel surface. Apparently, this effect leads to a larger hydrogen absorption into the metal lattice. In the samples that were tested in solutions containing inhibitor, considerable superficial damages such as blistering and hydrogen induced cracking were observed. Moreover, the higher inhibitor concentration, the larger is the mechanical damage observed in steel.

Keywords: corrosion inhibitor, hexamethylenetetramine, API 5L-X52 steel, hydrogen permeation, hydrogen induced cracking, blistering, ultrasonic testing, attenuation.

Introduction

Metallic materials may absorb considerable amounts of hydrogen in practical conditions such as electroplating, cathodic protection and corrosion, but especially in industrial processes that involve production, transport and crude oil refining. Atomic hydrogen may diffuse through a metal lattice because of its smaller size, and then it can recombine to form molecular hydrogen within structural defects such as inclusions, voids and microcracks among other places. Hydrogen embrittlement occurs as a result of hydrogen adsorption on the metal surface, with its consequent absorption within the metal lattice. The irreversible hydrogen trapping into metals lead to a progressive degradation of their mechanical properties and increases the probability of cracking. The above described phenomena could occur in a higher extent when the hydrogen sulphide concentration is high in the aqueous environments where the metal is immersed [ref1–5].

Corrosion inhibitors have been widely used to decrease hydrogen penetration in steels. Previous studies [ref4,6,7] have already demonstrated the effectiveness of several organic compounds to reduce the corrosion rate and hydrogen absorption in metals exposed to sour environments, inhibiting the hydrogen evolution reaction by means of physical isolation of metal surface and/or modifying the electrical double layer. Amines are well know by their inhibiting effect on the corrosion in carbon and low alloy steels, specially in systems containing H₂S. The presence of nitrogen in the organic compound with unsaturated bonds allows the adsorption of the organic compound on the metal surface, therefore hindering the metal dissolution [ref8]. However, it also have been found that some organic compounds can effectively inhibit the corrosion of metals but stimulate the hydrogen absorption within the metal lattice, because the recombination reaction of atomic adsorbed hydrogen on the metal surface is partially blocked [ref9].

Ultrasonic inspection of metallic materials is an adequate technique that could help to reduce and prevent catastrophic failures in pipelines systems and industrial equipments. Conventional techniques have not exhibited good detectability for hydrogen damage in steels, but very good results have been obtained using non-conventional methods like attenuation, backscattering signal, spectral analysis and ultrasonic velocity change [10,11]. The damage caused by hydrogen changes the way in which ultrasonic waves are propagated. The presence of dissolved hydrogen into the metal bulk may affect the elasticity modulus reducing the longitudinal and shear ultrasonic waves.

The objective of this study was to investigate the inhibitive action of hexamethylenetetramine on the corrosion and hydrogen permeation behaviour of type API 5L-X52 steel, which is commonly used in the oil industry for production and transportation of natural gas and crude oil.

Experimental

Materials Preparation

The metallic material used in the present work was an API 5L grade X52 steel. The chemical composition of the steel is presented in table 1.

Table 1. Chemical composition of the API 5L-X52 steel.

Concentration (wt %)				
Steel	C	Si	Mn	S
API 5L-X52	0.14 ±0.01	0.30 ± 0.01	1.2 ±0.1	0.004 ± 0.0001

The specimens were made from rectangular pieces of steel cut lengthwise from an 11 mm thick pipeline. Some stripes were machined to 8 mm thickness and subsequently cold rolled to 1mm thickness in several

steps with two intermediate annealings in pure nitrogen atmosphere at 600°C for 60 min. The reason for the heat treatments was to keep, as far as possible, the original microstructure. For polarization studies, samples of 1cm x 1cm were used, while for the hydrogen permeation measurements specimens of about 2cm x 5cm were employed. Another group of samples was machined to 5mm in thickness. This group was used for the ultrasonic evaluation performed after the hydrogen permeation tests.

Polarization

Polarization studies were performed according to ASTM G5-87 standard. A five electrodes corrosion cell was used. Steel specimens, with an exposed area of 1cm², were employed as working electrodes while a saturated calomel electrode (SCE) and two platinum electrodes were used as the reference electrode and counter electrodes respectively. The working electrodes were mechanically polished with different grades of emery paper (180, 240, 320, 400 and 600 grid), rinsed with double distilled water and acetone and then dried. Prior to the experiment, the samples were prepared by polishing with 1µm high purity alumina powder, degreased in an ultrasonic bath with xylene, rinsed with acetone and dried quickly by warm air blowing.

All tests were carried out in 1N H₂SO₄ solution prepared from analytical grade reagent and double distilled water. The hexamethylenetetramine (HMT) was used at 3 different concentrations, that is, 10⁻², 10⁻³ and 10⁻⁴M. This was achieved by dissolving the appropriate amount of solid HMT into the sulphuric acid solution. High purity nitrogen was bubbled through the electrolyte prior and during the experiment in order to keep the system free of dissolved oxygen. The Potentiodynamic polarization curves were obtained using a potential scan rate of 10 mV/min starting from 500mV below E_{corr} and moving in the anodic direction to 200mV above the open circuit potential. A PC4 750 Gamry potentiostat was used for polarization measurements. All experiments were performed at room temperature.

Hydrogen Permeation Studies

In order to investigate the hydrogen permeation rate through type API 5L-X52 steel, the electrochemical technique developed by Devanathan–Stachurski was employed. The experiments were performed in a specially designed and built two compartment cell separated by the hydrogen permeation test specimen. The electrolytes on the cathodic and anodic side of the cell were 1N H₂SO₄ and 0.1M NaOH respectively. On the cathodic side, the inhibitor (HMT) was added to the electrolytic solution prior to filling the compartment, at the same concentrations stated before. Both solutions were prepared from analytical grade reagents and double distilled water. In order to reduce any possible electrolyte impurities, the solutions were pre-electrolyzed in separate electrolytic cells by imposing a current density of 3mA/cm² during 3 hours. Additionally, the electrolytes were deaerated with pure hydrogen gas before placing it into the permeation cell. The transfer was made without any air contact.

The steel membranes were prepared, as described above, by conventional metallographic grinding and polished using 1μm high purity alumina powder. Specimen surfaces were rinsed with double-distilled water and ultrasonically cleaned in xylene during 15 minutes, rinsed with acetone and then dried by warm air blowing. Later on, just before the experiments, the anodic side of the membrane was coated with electroless palladium using a commercial solution (Pallamarse). An area of 0.9 cm² of the steel membrane was exposed to the solution.

The anodic side of the cell was potentiostatically maintained at 0.150mV vs. SCE using an EG&G PARC model 363 potentiostat/galvanostat to ensure that the steel was in its passivation zone and to oxidize the atomic hydrogen that diffused through the membrane. Prior to the permeation experiment, the anodic side was left polarized at that potential for 12 h. After that time has elapsed a typical passivation current of 300 nA/cm² was obtained. Then, the cathodic compartment was filled with the acid solution with or without the inhibitor and the potential was held constant at -900mV vs. SCE employing a Microstat model 1503 potencioestat. The anodic current was recorded as a function of time using a

DakBook k/216 data acquisition system. All the experiments were carried out at room temperature.

Ultrasonic Evaluation and Surface Analysis

In order to detect the hydrogen damage into the steel, an ultrasonic analysis was conducted on steel samples of 5mm thickness before and after the hydrogen permeation tests. Thick specimens were selected for this study since evaluation on thin specimens (1mm thick) produced noisy signals. All the measurements were performed using a Krautkramer USM 22 ultrasonic equipment and a 10Mz frequency transducer model KBA525. The attenuation coefficient α was calculated based on the first and second backwall echoes and the test specimen thickness. On the other hand, optical and scanning electron microscopy techniques were employed to study the steel surface morphology after the hydrogen permeation tests, and energy dispersive X-ray analysis was used to characterize some inclusions observed in the metallic material.

Results and Discussion

Steel Microstructure

The steel microstructure in the as-received condition, observed by optical microscopy, was a typical banded ferrite/perlite structure (figure 1a). Elongated and rounded inclusions, mainly MnS, were observed; some aluminates, silicates and calcium inclusions were also found within the material. The cold rolled and annealed samples showed a microstructure mainly comprised by ferrite with fine pearlite and fragmented spherodized cementite (figure 1b).

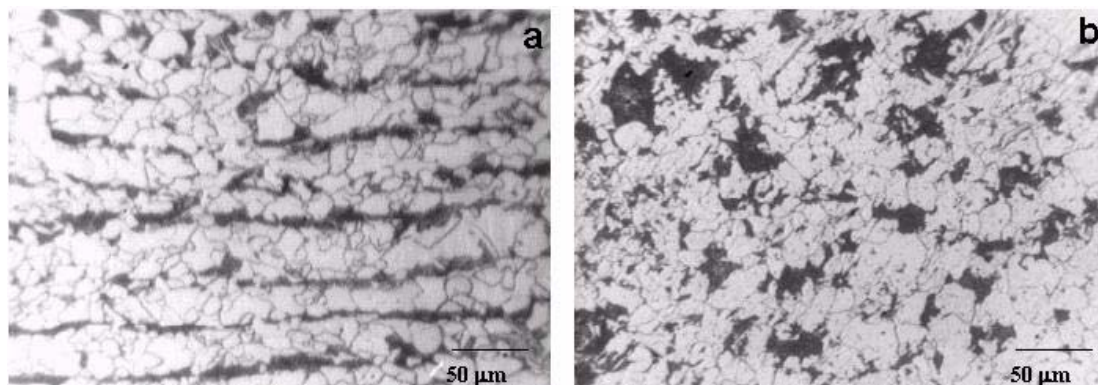


Figure 1. Microstructure of the API 5L-X52 steel in: a) as-received condition, b) cold rolled and annealed.

Polarization Studies

Figure 2 shows the potentiodynamic polarization curves of the samples at different hexamethylenetetramine concentrations. As it can be seen, the corrosion potential was only slightly affected as the concentration of HMT in the electrolyte increased from 10^{-4}M to 10^{-2}M . Additionally, the form of the curves is very similar either in the cathodic or in the anodic side, which indicates that the mechanisms of iron dissolution and hydrogen reduction apparently remain unaltered in the presence of the hexamethylenetetramine.

The main difference in the above mentioned curves is observed in the current density values. It is clear from figure 2 that for the same potential, the samples tested in presence of the organic compound showed current density values, both anodic and cathodic, lower than those samples tested without inhibitor. Moreover, for the same electrode potential, the current densities decreased with increasing inhibitor concentration. This indicates a reduction in the corrosion rate of the steel with increasing inhibitor concentration. Apparently, adsorbed molecules of the organic compound decrease the active surface area where both electrochemical reactions take place, delaying the corrosion of the steel. Based on these results, if the samples are polarized at a specific cathodic potential in presence of inhibitor, the hydrogen atoms will be produced at a lower rate.

The corrosion inhibitor efficiency and cathodic inhibitor efficiency at -900mV (SCE) were calculated from figure 2 and the results are presented in table 2. As it can be noticed, the highest inhibition effect is attained at concentrations of 10^{-3}M of HMT. If the inhibitor is added to the electrolyte at concentrations greater than this, the inhibition efficiency diminished. As a result, the corrosion rate increases again. On the other hand, when the potential value is above -350mV (SCE), the curves tend to be overlapped. This is a clear indication that the organic compound is not efficient when the steel potential is ennobled. This could be due to the repulsion between the protonated organic compound and the increasingly positive metallic surface. This result suggests that the organic molecules are adsorbed on the steel surface mainly by electrostatic forces.

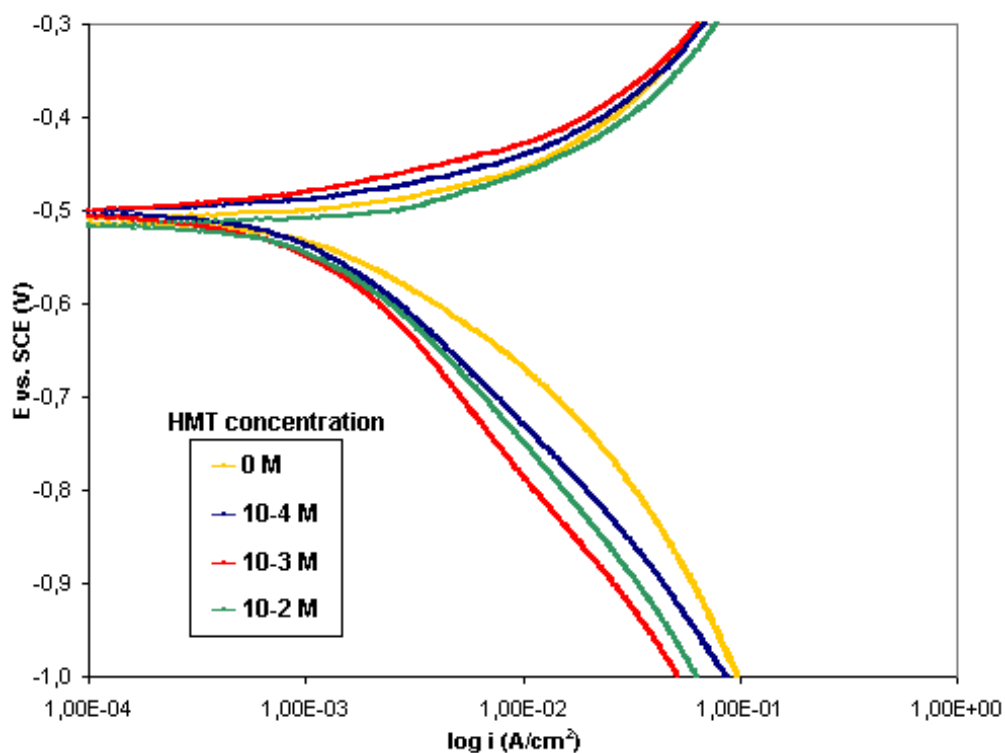


Figure 2. Potentiodynamic polarization curves for the steel in deaerated $1\text{N H}_2\text{SO}_4 + \text{HMT}$ at 25°C .

Table 2. Corrosion inhibitor efficiency.

Concentration (M)	0	10^{-4}	10^{-3}	10^{-2}
$E = E_{\text{corr}}$	0%	33%	66%	50%
$E = -900\text{mV (SCE)}$	0%	27%	57%	45%

Hydrogen Permeation Studies

The hydrogen permeation transients of the steel for the various concentrations of hexamethylenetetramine were measured as a function of time and the results are displayed in figure 3. As it can be seen from this figure the curves followed a similar pattern, that is, an increase in the permeation current density until a steady state is attained after several hours of exposure. It can also be observed that the permeation current density increases with the increase on the inhibitor concentration. Moreover, the samples tested with the highest concentration of hexamethylenetetramine, showed permeation currents four times greater than those of the samples tested without inhibitor. Opposite to what was expected, the organic compound stimulated the hydrogen permeation, even though less atomic hydrogen was produced on the steel surface. As a result, more hydrogen damage such as blistering and cracking would be expected in the samples tested in the inhibitor presence.

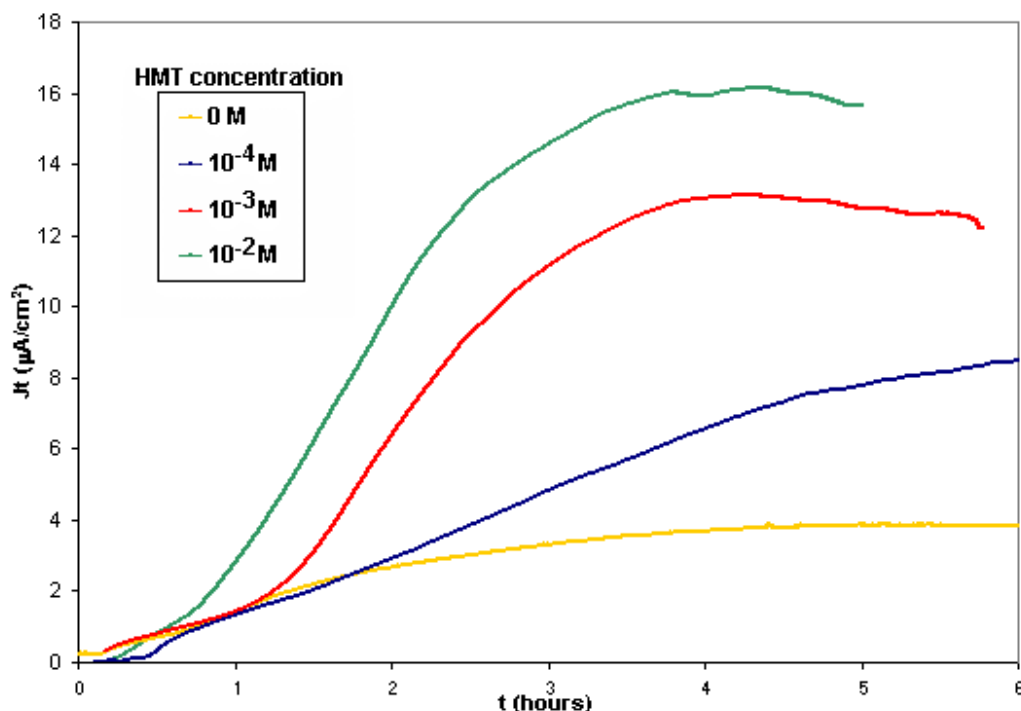


Figure 3. Hydrogen permeation curves for 1 mm thick membranes in deaerated 1N H₂SO₄ + HMT at 25°C.

Figure 4 shows the possible mechanism of hydrogen evolution and penetration in presence and absence of hexamethylenetetramine. Essentially, in absence of inhibitor, the hydrogen evolution reaction (HER) involve the hydrogen ions discharge on the steel surface, followed by two reactions which correspond to hydrogen desorption (chemical or electrochemical recombination) and hydrogen absorption within the metal lattice (figure 4a) [ref12]. Nevertheless, if there are adsorbed molecules of the organic compound in the steel surface, the recombination reaction of electrochemical reduced hydrogen could be inhibited. Therefore, adsorbed atomic hydrogen activity may increase and as a result more hydrogen penetration is promoted into the steel (figure 4b) [ref12].

The hydrogen diffusion coefficients were determined for the steel membranes by four different methods [ref6] and the results are presented in table 3. The values obtained in this work are similar to those previously obtained for similar steels by other researchers [ref2,7]. Nevertheless, diffusion coefficients values around one order of magnitude greater than

those have been reported for the same steel too [ref14]. It could be possible that the cold rolled and the annealing treatments have slightly modified the hydrogen diffusivity on the steel.

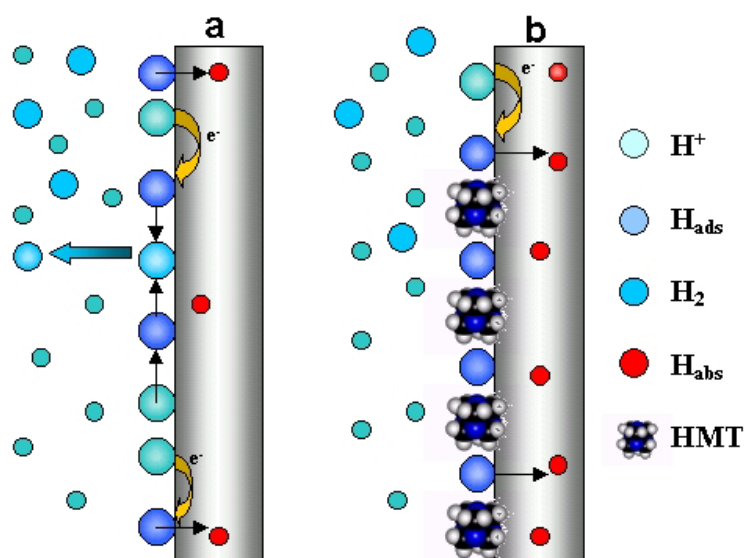


Figure 4. Schematic representation of the HER: a) in the absence of HMT, b) in the presence of HMT.

Table 3. Hydrogen diffusion coefficients attained by different analytical techniques for the API 5L-X52 steel in deaerated 1N H₂SO₄.

Method	D [cm ² /s]
Time Lag	3,48x10 ⁻⁷
Laplace method: slope	3,48x10 ⁻⁷
Laplace method: intercept	3,17x10 ⁻⁷
Fourier method	4,05x10 ⁻⁷

Surface Analysis

The microstructural analysis made after the samples were exposed to the 1N H₂SO₄ solution did not show any evidence of hydrogen damage, neither at the surface nor into the metal. These results seem to indicate that, under these conditions, the hydrogen concentration within the metal was insufficient to promote the formation of blisters and cracks. However, the plates exposed to the acid solution in the presence of inhibitor were susceptible to hydrogen induced cracking and blistering at all concentrations. Moreover, the higher the inhibitor concentration, the larger the mechanical damage observed in the steel. Figure 5 shows several micrographs obtained by scanning electron microscopy for the sample tested with the highest inhibitor concentration. As it can be seen from these figures, large blisters as long as 300μm, were seen on the steel surface. Most of them, as shown in figure 5a, are aligned in the cold rolled direction. Figures 5b and 5c are another micrographs showing cracking propagation around the blisters. This result is a clear indication of the high hydrogen pressures generated inside the blisters. Figure 5d is a detail of a crack growing on the steel surface. Cracks propagation seems to be intergranular. Nevertheless, transgranular propagation of cracks was also observed.

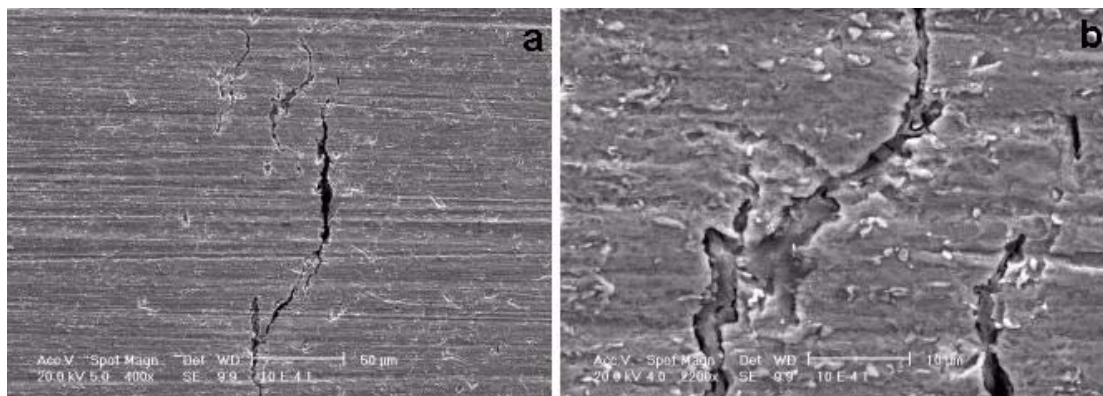


Figure 6. SEM micrographs of a sample exposed to 1N H₂SO₄ + 10⁻⁴M HMT.
a) microcracks developing near the largest crack. b) cracks detail.

Ultrasonic Evaluation

Figure 7 shows the backwall echoes spectra for 5mm thickness samples exposed to the 1N H₂SO₄ and 1N H₂SO₄ + 10⁻²M HMT solutions for over 24 hours. In addition, the backwall echoes spectrum for the samples before the hydrogen permeation test is also presented in the same figure as reference. All measurements were carried out using a 10MHz transducer and a 46dB gain. As it can be noticed, the ultrasonic spectrum remains unaltered after the samples were cathodically charged in 1N H₂SO₄ solution (figure 7b). This could mean that the backwall echoes have the same amplitude than those echoes registered before the hydrogen permeation test. This result suggests that the material under the experimental conditions did not show any susceptibility to hydrogen induced cracking or blistering, which is consistent with the results previously discussed for similar specimens in the microstructural analysis. However, the ultrasonic spectrum of the steels tested in solutions containing hexamethylenetetramine showed higher attenuation levels than that of the samples exposed to the acid solution without inhibitor (figure 7c). Since the samples evaluated with the highest concentration of inhibitor exhibited the larger mechanical damage such as blisters and cracks, it could be possible to relate these changes in the attenuation levels with the hydrogen damage produced in the steel. Some researchers [10,11] have previously demonstrated that the backwall echoes spectrum changes with hydrogen attack is due to the presence of extra scatterers. Higher

attenuation levels are observed in attacked samples because hydrogen damage can be considered itself as an additional scatterer. This is especially certain at high ultrasonic frequencies.

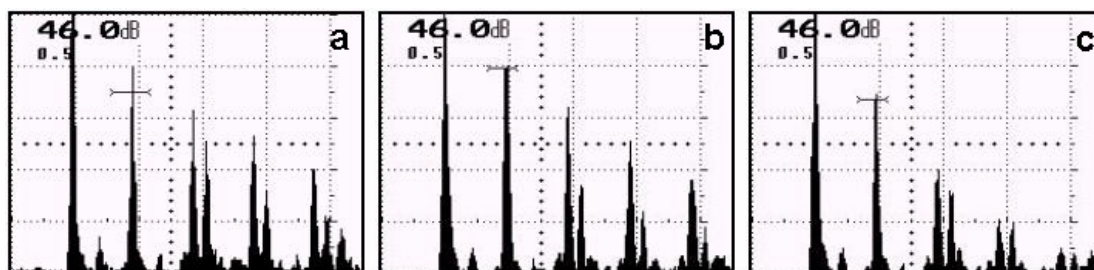


Figure 7. Pulse-echo signal for steel samples: a) before hydrogen permeation test, b) after testing in H_2SO_4 solution and c) after testing in $\text{H}_2\text{SO}_4 + 10^{-2}\text{M}$ HMT solution.

Attenuation measurements were taken on the samples at an ultrasonic frequency of 10MHz and the results are presented in table 4. As it can be seen, there are no appreciable changes in the sound wave attenuation of those samples exposed to the 1N H_2SO_4 solution. This means that the hydrogen effect within the metal is not large enough to produce appreciable changes in the ultrasonic waves propagation. Nevertheless, for those samples exposed to the solution containing inhibitor, a significant increase in the attenuation coefficient was registered. Once again, the obtained results allow drawing the conclusion that the organic compound increases the steel susceptibility to hydrogen damage.

Table 4. Attenuation coefficients measured with an ultrasonic frequency of 10MHz.

Condition	Ultrasonic attenuation coefficient α [dB/cm]
Before hydrogen permeation test	1.938
Tested in H_2SO_4 solution	1.938
Tested in $\text{H}_2\text{SO}_4 + 10^{-2}\text{M}$ HMT solution	3.223

Conclusions

The hexamethylenetetramine inhibits efficiently the corrosion of the steel but increases the quantity of absorbed hydrogen into the metal lattice. The organic compound seems to have a specific influence on the hydrogen evolution reaction, apparently diminishing the active sites where hydrogen can be reduced and therefore, partially blocking the recombination of atomic hydrogen to molecular hydrogen on the steel surface.

In the absence of inhibitor, the hydrogen that diffused through the metal did not induce considerable damages such as blisters or hydrogen induced cracking.

The susceptibility to hydrogen damage of the API 5L-X52 steel in sulphuric acid increases in the presence of hexamethylenetetramine. Moreover, the higher inhibitor concentration, the larger the mechanical damage observed in the steel.

Ultrasonic analysis of the samples showed that the height of the backwall echoes decrease and the sound wave attenuation coefficient is greater when the quantity of hydrogen in the sample increases.

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