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LABORATORY INVESTIGATION OF ENVIRONMENTALLY INDUCED CRACKING OF API-X70 AND X80 PIPELINE STEELS

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ABSTRACT

Carbon steels, used in pipelines for the transport of oil and its derivatives, are frequently exposed to fluids.

This can result in stress induced corrosion cracking (SCC) and/or hydrogen embrittlement (HE).

The present paper evaluates the susceptibility of pipeline steels (API-X70 and API-X80) to SCC and HE, using a slow strain rate test (SSRT) based on the National Association of Corrosion Engineers' (NACE) norm and a traditional standard NACE test. The (SSRT) method used, employed a sodium thiosulphate solution to evaluate susceptibility to HE, thereby offering a simpler experimental procedure than the standard NACE test. The results confirm the efficacy of the sodium thiosulphate as an H_2S – SCC susceptibility test solution when utilised in SSRT testing. Though no secondary cracks were detected in the materials investigated, both steels were observed to suffer a ductility loss upon exposure to this solution. In NACE type tests, the test pieces were subjected to constant loading at 80% of σ_y. Fracture did not occur for these samples.

INTRODUCTION

The Brazilian national oil pipeline network has been expanded progressively in the last few years and the tendency is that this will continue in the short-medium term. In parallel with this expansion, nearby communities have continued to grow, thereby approaching the pipeline installations. Consequently, the effective guarantee of pipeline integrity has thus assumed an even higher level of importance, since the risks associated with any catastrophic failure, would not be limited to purely environmental factors. Practical safety and quality guarantees, in this situation, depend upon a wide range of activities, which will include all stages, from steel production to pipe fabrication, as well as subsequent pipeline construction, operation and maintenance.

Oilfield service conditions involving high-pressure oil and gas with high CO_2, H_2S and chloride contents demand pipeline steels of not only high mechanical strength, but also high resistance to corrosion and to hydrogen embrittlement (HE) phenomena. The nucleation and growth of cracks in pipelines constructed of plain carbon and of low alloy steels, when exposed to fluids containing H_2S have resulted in catastrophic failures. Furthermore, in practice, adequate formability and good weldability are, of course, also critical factors. Theoretically, three basic conditions must be fulfilled for SCC to occur; a corrosive medium, a tensile load and the inherent susceptibility of the alloy in question Patel (2001), Psaila (1997), National Energy Board (1996).

The slow strain rate test has been widely exploited as a laboratory technique to evaluate the susceptibility of metallic materials to SCC and HE. In the case of candidate steels for service in the petrochemical industry, the SSRT is of particular interest since the relative speed of the high-load test permits suitably wide-ranging appraisals, involving the generation of a significant number of results in a relatively short period. By contrast, the NACE 0177-96 - Method A - Standard Tensile Test (1996) is used to evaluate SCC resistance according to a fracture/no fracture criterion, and the degree to which internal cracks are provoked in test pieces subjected to constant uniaxial elastic strain in the standard NACE solution, at ambient temperature and pressure.

The objective of the present work is to evaluate the SCC and HE behaviour of API-X70 and API-X80 class pipeline steels, using SSRT and NACE 0177/96 - Method A testing.

EXPERIMENTAL METHODS

MATERIALS

The materials studied, API-X70 and API-X80 grade steels, were received in tube form. The chemical compositions are shown in Table 1.

Steel	Composition (wt%)							
	C	Mn	Si	Nb	Ti	Cr	Mo	N
API-X70	0,06	1,55	0,18	0,055	0,017	0,02	-	0,0071
API-X80	0,04	1,85	0,18	0,073	0,016	0,32	0,03	0,004

Table 1 – Chemical Composition of the Steels

HYDROGEN PERMEATION TESTS

Hydrogen permeation tests were carried out using flat specimens of both steels (sample thickness 5,9 mm) and a Devanathan permeation cell containing sodium thiosulphate solution in the cathodic side and 1N NaOH solution in the anodic side. The permeation current was registered by using a potentiostat attached to the anodic side using a platinum counter electrode and a saturated calomel electrode as reference. The results obtained are indicated in Figure 1.

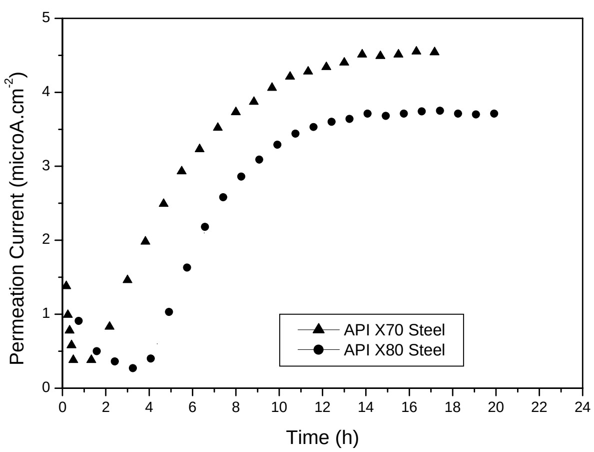

Figure 1 – Hydrogen permeation current obtained for API-X70 and API-X80steels in sodium thiosulphate solution.

The permeation tests demonstrated the difference in hydrogen permeation current between the steels. The steady state current measured for API-X70 steel was higher than that for API-X80, for the same sample thickness, while the incubation period before hydrogen oxidation initiated in the anodic compartment of the permeation cell was about 1,5 h for API-X70 steel and 4 h for X80.

SLOW STRAIN RATE TEST (SSRT)

The SSRT was carried out using uniaxial loading of cylindrical test pieces of the two steels. Results obtained for tests in air were compared with those obtained for testing with the testpiece immersed in a hydrogen-generating solution Lima (2001). Table 2 shows the chemical composition of the test solution. The production of H_2S in this thiosulphate-based solution occurs at the surface of the sample due to the local chemical reactions which occur when it is immersed in the medium.

Composition of the Solution	
Component	Content
Sodium Thiosulphate ($Na_2S_2O_3$)	10^{-3} mol/l
Sodium Chloride (NaCl)	5%vol
Acetic Acid (CH_3COOH)	0.5%vol

Table 2 – Chemical composition of the sodium thiosulphate solution

The comparative analysis of the stress-strain curves was undertaken on the basis of the following parameters; Yield Strength (σ_y); Ultimate Tensile Strength (σ_{UTS}); Rupture Strength (σ_f); Elongation at Rupture (El%); Reduction in Cross Sectional Area at Rupture (RA%); and Time to Rupture (TR). The fractographic analysis was carried out using scanning electron microscopy (SEM) and the microstructural characterisation by both optical microscopy (OM) and SEM.

NACE TM 0177/96 –METHOD A (STANDARD TENSILE TEST)

SCC tests were undertaken according o the NACE TM 0177/96. Method A (Standard Tensile Test) norm, NACE INTERNATIONAL (1996) using solution B according to NACE, the chemical composition is given in Table 3.

Composition of the Solution	
Component	Content
Glacial Acetic Acid (CH_3COOH)	0.23%vol
Sodium Chloride (NaCl)	5%vol
Sodium Acetate ($CH_3COOHNa$)	0.4%vol

Table 3 – Chemical Composition of the NACE solution used.

After the test, the surfaces of the testpieces which had been exposed to the NACE solution were cleaned in accordance with the ASTM G-1-95 norm, permitting a metallographic examination to determine whether or not surface cracks had been produced Lima (2001).

DISCUSSION

As can be seen from Figure 1a and 1c the API-X70 steel exhibited a Ferrite-Pearlite microstructure, whereas the API-X80 grade had a microstructure composed of granular Bainite with 3.4vol% of AM constituent (Austenite-Martensite) as shown in Figure 1b and 1d.

The API-X70 steel exhibited ductile characteristics when SSRT tested in air as shown in Figures 2a-c. This ductile characteristic changed to cleavage when tested in thiosulphate based solution, indicating some degree of embrittlement as shown in figure 2d-f, where few plastically deformed regions were found.

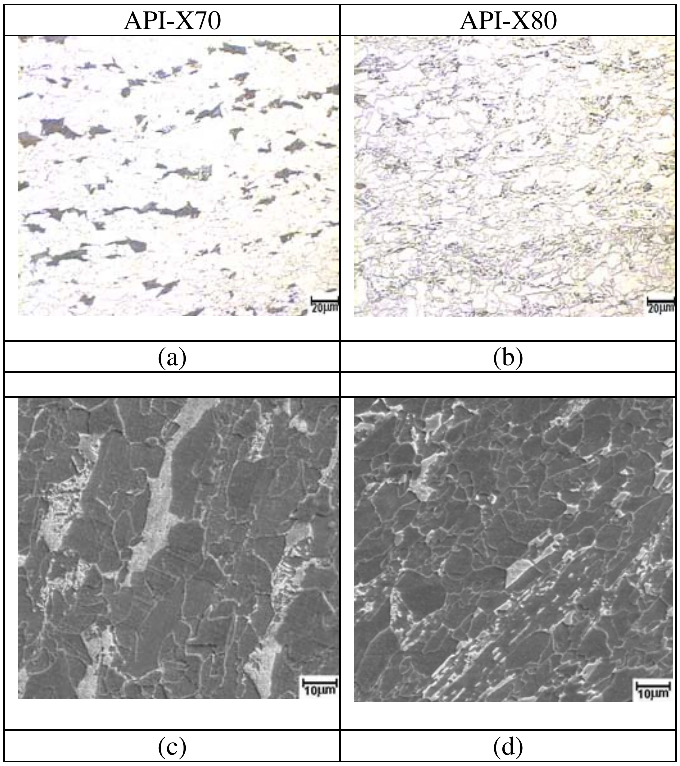

Figure 2 – Optical Micrographs (a,b) and Scanning Electron Micrographs (c, d)

These observations are sustained by the observation of the elliptical fracture surface (Figure 2b) and the ductile mode of fracture (Figure 2c) accompanied by a reduction in cross sectional area of 68% during the test in air while this reduction is 17% when tested in thiosulphate-based solution.

The same tests were repeated for the (API-X80). For the SSRT in air the fracture was characteristically ductile (Figures 3a-c), with dimples on fracture surface is clearly visible in Figure 3c and regions of extensive plastic deformation were evident, as shown in Figures 3a and 3b. In the thiosulphate-based solution, this steel also presented brittle fracture characteristics, as shown in Figure 3f.

The overall reduction in cross sectional area at fracture was 60% when tested in air and when tested in the thiosulphate-based solution, the reduction in area was only 7%, furthermore as seen in figures 3d and 3e, in this case very few regions of significant plastic deformation were found. These characteristics indicates some susceptibility to embrittlement.

Analysis of the longitudinal sections of the API-X70 and API-X80 testpieces after thiosulphate solution testing did not reveal secondary internal or surface cracks for either steel. The final fracture is associated with plastic collapse as a consequence of the small remaining area.

The relationship between σ_f (fracture strength) and time to fracture (Fig. 4) shows that the time to fracture was longer when tested in the air than in the thiosulphate-based solution, and this time was longer for the API-X80 than for the API-X70.

The differences observed in the values of σ_f (fracture strength) can be due to a reduction in plasticity as shown in figure 4b. The API-X80 steel suffered a significantly greater reduction in area in solution than the API-X70, this may indicate a presence of hydrogen, since the area reduction was smaller than that observed when tested in air and the fracture strength was higher, indicating some embrittlement. Also, as shown in figure 3d, as compared to figure 3a there was very little plastic deformation on the surface fracture.

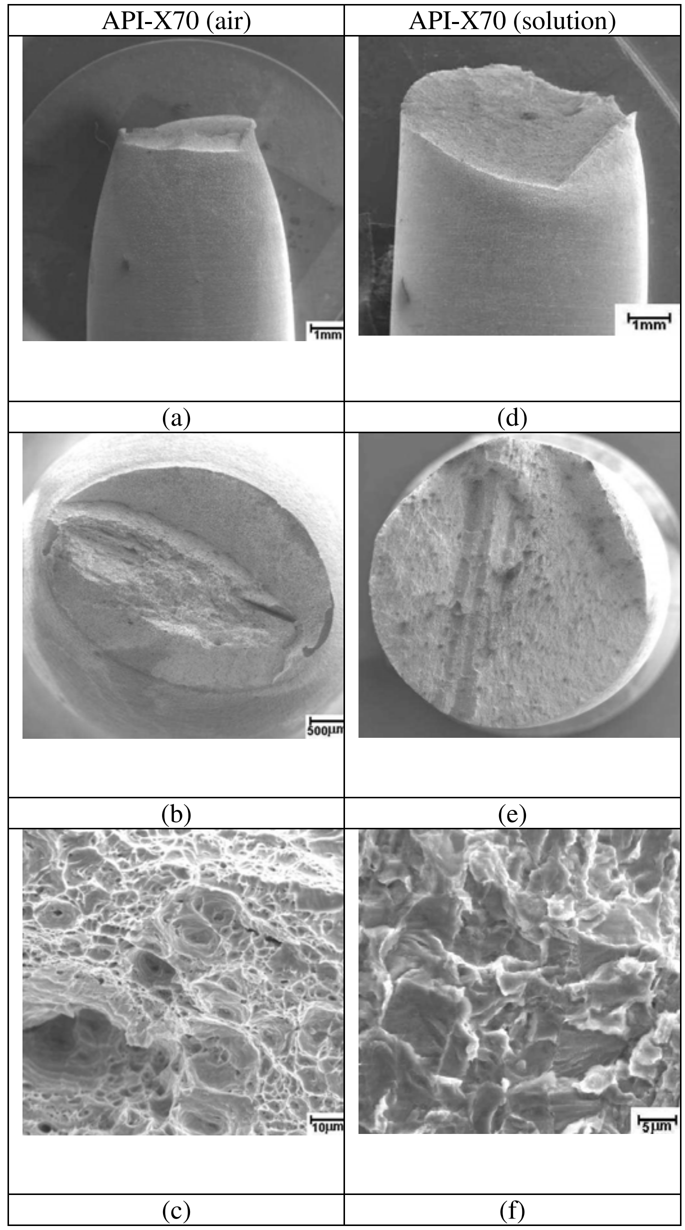

Figure 2 –SEM analysis of API-X70 testpieces tested in air (a, b, c) and in the Thiosulphate-based Solution (d, e, f)

The degree of (SCC) susceptibility, as measured in the SSRT is expressed using a relative ductility parameter. An analysis of the above parameter reveals that the effective ductility of the API-X70 and API-X80 steels was, in fact, significantly reduced presenting ratios (of results in air/results in solution) of much less than one Small (1996), indicating susceptibility to HE, Despite this fact, secondary cracks were not revealed in the fractographic analysis.

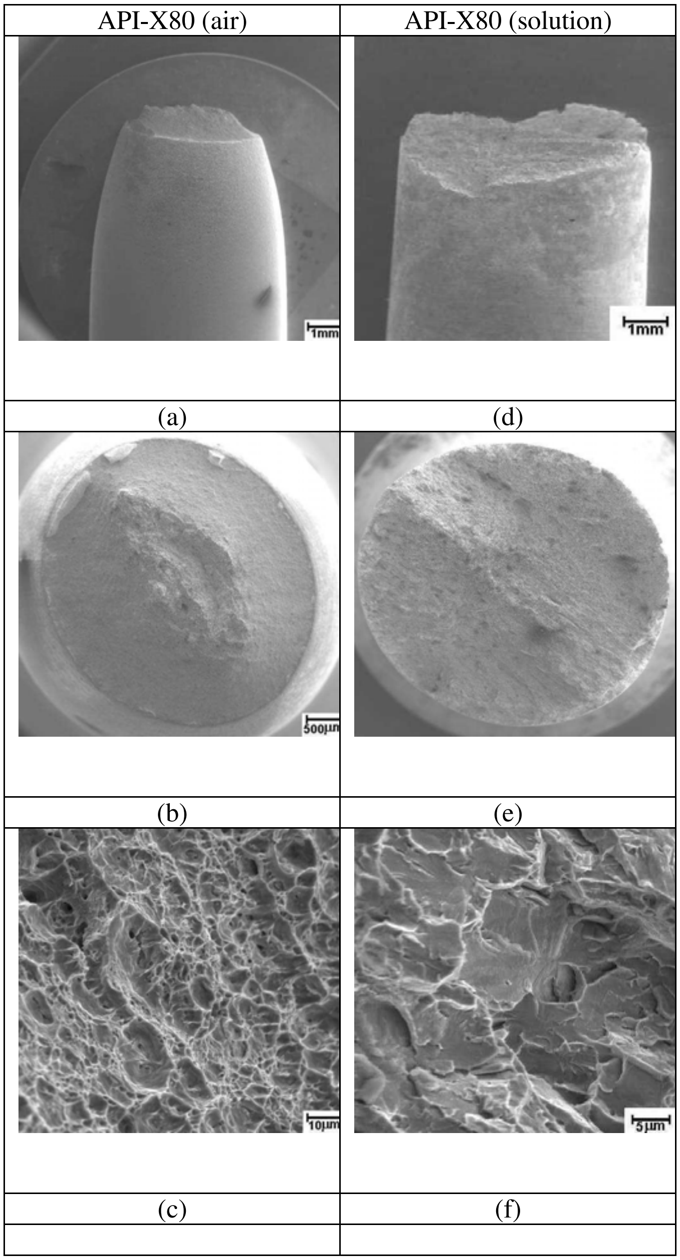

Figure 3 –SEM analysis of API-X80 testpieces tested in air (a,b,c) and in the Thiosulphate-based Solution (d,e,f)

The reduction in ductility observed, can be attributed in this case, to a loss in the intrinsic toughness of the steels when submitted to an aggressive enviroment, independent of the presence of any secondary cracks. Such cracks would normally be associated with the recombination of hydrogen atoms, previously in solid solution, to form hydrogen molecules at microscopic interfaces. This form of recombination often occurs at non-metallic inclusions. The observed loss of strength/ductility was manifested at relatively high stress levels, a condition in which even quite low concentrations of hydrogen can provoke a loss in toughness.

In the case of the tests carried out according to the NACE TM 0177/96 – Method A (Standard Tensile Test) norm, NACE INTERNATIONAL (1996) testpiece rupture occurred for neither the API-X70 nor the API-X80 grade after 720h of exposure to 80% of the YS, despite H_2S levels of the standard NACE solution, orders of magnitude higher than those present in the thiosulphate-based solution used in the SSRT.

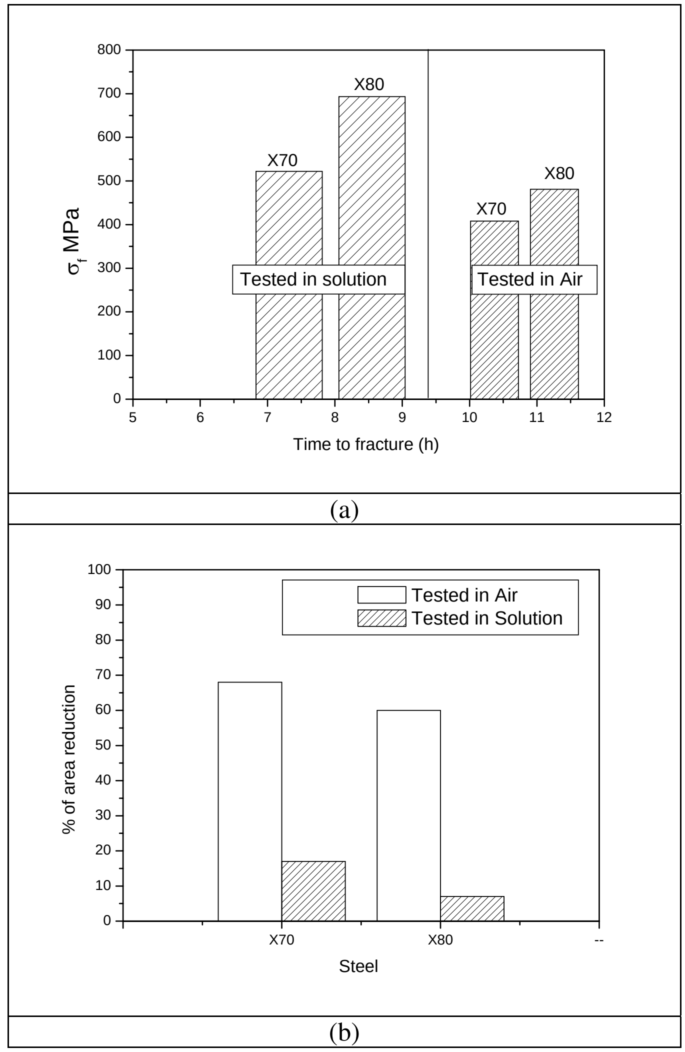

Figure 4- Behaviour of API-X70 and API-X80 when tested in air and in thiosulphate solution, (a) time to fracture and (b) % of area reduction.

The NACE test samples were also examined metallographically, and in this case, no cracks were observed to have formed as a result of the test. These results for both steels can be interpreted as being due to the elevated resistance of the microstructures of these materials to the nucleation of defects resulting from hydrogen recombination-induced damage. The apparent absence of the embrittlement effect previously detected in the SSRT would be due to lower imposed stress levels and the static nature of the NACE test loading as compared with the dynamic, high stress regime SSRT.

Loss of ductility in sodium thiosulphate solutions was attributed to the effect of hydrogen absorption as proposed by Moraes (2005). This author carried out SSRT tests using a duplex stainless steel and a high strength low alloy steel. In this paper, the effect observed in API grade steels, seems to follow the same trend.

From the permeation tests it was possible to observe a difference in hydrogen permeation current between the steels. The steady state current measured for API-X70steel was higher for the same thickness and the incubation period before hydrogen oxidation was about 1,5 h for API-X70 steel and 4 h for API-X80. These differences can be attributed to the microstructural factors, which deserve more investigation.

Another important discussion derived from permeation tests was that the magnitude of the hydrogen permeation detected in sodium thiosulphate solution. It is important to point out that the material was kept at the free corrosion potential. This result confirms the assumption of effect of hydrogen on environmentally induced cracking.

Thiosulphate solution has been used in hydrogen embrittlement tests in which this solution generates H_2S from a reaction occurring at the metallic surface. Slow strain rate tests were performed at the free corrosion potential in the case of the steels studied in the present work. This environment produces very low H_2S concentration but the effect of hydrogen was evident and is enhanced by the dynamic strain imposed during SSRT tests and the loss of ductility, can be compared to the same effect obtained in NACE solution.

It is important to point out that the H_2S content is considered low if compared to the H_2S concentration in standard solutions saturated with H_2S. The effect of thiosulphate on hydrogen reduction, has been observed by Horowitz (1983) and Jambo (2001), from the results presented by the these authors, and from the results obtained here it is possible to conclude that the steady state hydrogen permeation current obtained is comparable to the permeation values obtained in H_2S saturated environments. This behaviour is probably due to the H_2S generation reaction only occurs at the metallic surface.

Environmentally induced cracking of both steels are promoted by hydrogen. The deterioration mechanism observed under static load in NACE solution and under SSRT in sodium thiosulphate solution presented different characteristics. In NACE the most important determinating factor would be the hydrogen accumulation in the steel. In sodium thiosulphate solution the predominant effect of hydrogen would be the same intrinsic thoughness reduction of the material enhanced by the plastic straining imposed during SSRT. The results for both steels can be interpreted as being due to the elevated resistance of the microstructures of these materials to the nucleation of defects resulting from hydrogen recombination-induced damage.

CONCLUSIONS

The loss in ductility of the API-X70and API-X80steels which was observed to result from SSRT in H_2S–generating thiosulphate-based solution, indicates potential hydrogen embrittlement susceptibility

Both of the steels investigated exhibited good levels of SICC resistance as measured by the standard NACE test, showing no loss of strength under the specified conditions.

In neither of the tests were secondary cracks detected after loading in H_2S-containing mediums. This is probably due to the very low non-metallic inclusion levels in the materials studied

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