On the estimation of fatigue crack growth in a contaminated H_2S environment by interrupted cyclic tests

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Abstract

Regular and jumbo cylinders are often used for compressed natural gas (CNG) transportation and storage. CNG is a mixture of mostly methane (up to 98%) with a small amount of other minor hydrocarbons and can contain impurities such as hydrogen sulphide (H_2S), carbon dioxide (CO_2), and condensed water. For automotive applications, where CNG is used as fuel for vehicles, the natural gas is properly treated and filtered to remove such corrosive contaminants, however this might not be the case of CNG used for industrial applications, especially in newly fast growing countries. These impurities can promote the formation of an acid environment with low pH values and the well know hydrogen embrittlement (HE) phenomenon due to adsorption and entry of hydrogen into the steel.

The present paper shows a methodology developed to estimate fatigue crack propagation rate for a low alloy steel grade in case of a contaminated CNG environment, where certain amount of impurities such as H_2S, CO_2 and condensed water are present.

The methodology is presented together with preliminary experimental tests in a selected contaminated CNG environment. Further experimental verifications are in progress.

1 Introduction

The use of CNG as a fuel is continuously growing worldwide especially in newly fast developing countries where it provides a way to reduce emissions and pollutants typical of conventional fuels. Type I steel cylinders are nowadays the most widespread way of storing natural gas on vehicles, typically at a working pressure of 200 bar. Natural gas is a mixture of mostly methane (up to 98%) with a small amount of other minor hydrocarbons (ethane, propane and buthane) and can contain impurities such as H_2S, CO_2, and water. Before natural gas can be used as a fuel, it has to be properly filtered and cleaned to remove all the impurities, in order to meet the specifications of marketable natural gas and to ensure that CNG does not compromise the structural integrity of the cylinder. These impurities, in fact, can promote the formation of an acid environment with low pH value, therefore leading to a corrosion fatigue phenomenon occurring due to the combined actions of cyclic pressurization and the corrosion impurities present in the CNG.

This problem was well known since 1980’s and several efforts were spent to determine the limits of the natural gas contaminants to ensure safety of CNG cylinders against possible internal corrosion occurring during its lifetime.

Results reported in ([1]) obtained with slow strain rate tests were used to establish the limits of H_2S and CO_2 to ensure that internal corrosion of CNG cylinders could not represent a hazard over the cylinders lifetime. According to these results, maximum admissible H_2S partial pressure was 0.0035 bar while maximum CO_2 partial pressure was 0.49 bar.

These data were adopted by the NFPA (National Fire Protection Association) and in terms of H_2S partial pressure they are coherent with the standards currently in use ([2]) while the CO_2 partial pressure requirement of 0.49 bar is more stringent.
In the present paper, tests on precracked samples were carried out at high pressure (20 MPa) within an autoclave reproducing a very severe environment with a H_2S content much higher than the one admitted in [2]. Since it was not possible to use a crack opening displacement (COD) gage within the autoclave due to the high pressure and the harsh environment, a methodology was developed in order to estimate crack propagation rate within such environment. The methodology was initially verified in air showing a very good agreement with fatigue crack growth rates available on the same steel and obtained according to ASTM E647 standard ([3]). Later, the methodology was applied in the autoclave with CNG at the target pressure and the desired amount of impurities. Preliminary tests results obtained in such environment are presented and discussed with data available in the literature. Further tests are currently in progress.

2 Case Study

Table 1 shows the composition of the environment selected for the present study. Compared to wet gas composition admitted by standard ISO 11439 ([2]) it is much more severe in terms of H_2S content.
Such environment was reproduced inside an autoclave operating at 20 MPa total pressure. Liquid water was placed in the bottom of the autoclave ensuring that moisture was present, however the samples were not immersed in the aqueous solution.

Table 1: Target environment used in the present study

Chemicals	Levels
H_2S	330 ppm
CO_2	4%
H_2O	Present
CH_4	Up to 20 MPa

The investigated grade was a low alloy Cr-Mo steel in a quenched and tempered (Q&T) condition.

3 Methodology

The proposed methodology involves carrying out fatigue tests on precracked samples at different stress levels and at predefined number of cycles. At the end of the test the sample is fractured at liquid nitrogen temperature for observing fracture surface.
The flow chart of the methodology is reported in Table 2. The methodology was successfully applied in air and later applied in the autoclave environment reported in Table 1.

Table 2: Proposed methodology for the estimation of crack propagation rate

Sample preparation and machining of the artificial EDM notch (0.2mm x 2mm).

↓

Precracking for $N=10^7$ cycles.

↓

Fatigue tests at different load levels and different number of cycles ΔN.

↓

Sample opening in liquid nitrogen and SEM observation of precracking length and crack propagation (Δa).

↓

Calculation of average ΔK based on initial and final crack length using the crack shape function (section 5);

↓

Plot of $\Delta a/\Delta N$ vs. ΔK value.

4 Experimental tests

4.1 Interrupted Fatigue Tests in Air

Figure 1 shows an example of the specimen used for the interrupted fatigue tests in air and in autoclave environment. In all the specimens an electro discharge machining (EDM) notch was transversely machined, perpendicular to the load application. The notch dimensions were 0.2 mm x 2 mm (depth x length), corresponding to a square root area of approximately 630 μm.

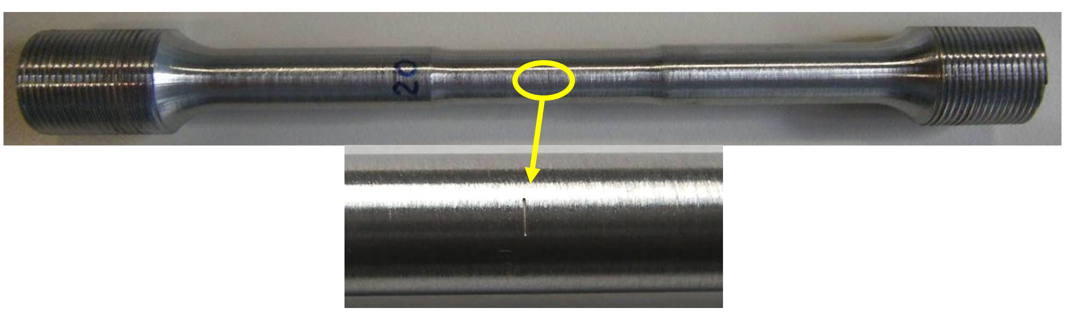

Figure 1: Sample used for interrupted fatigue tests

Initially the fatigue limit on these samples with the artificial notch was estimated using a stair-case test sequence at a stress ratio R=-1. Based on this fatigue limit a precracking technique with a stress ratio R=-2 was used to precrack the specimens. All the samples were tested in air for $N=10^7$ cycles using a resonant machine and then observed in a SEM (scanning electron microscope) in order to verify the presence of non-propagating cracks at the bottom of the defect.
Once precracking was completed, interrupted fatigue tests were carried out in air using a 100 kN servo-hydraulic commercial test frame, under constant amplitude loading conditions. Four load levels were employed as reported in Table 3. The load levels and the number of cycles were estimated based on the available crack propagation rate (Paris law) which was then used to verify the goodness of the proposed approach. Load levels are reported in terms of nominal stress acting on the area of the notch.

Table 3: Load levels used for fatigue tests in air

Load Levels	ΔS [MPa]	Number of cycles ΔN
1	796	4,000
2	676	7,000
3	497	16,000
4	318	20,000

All the tests were carried out at stress ratio R=0.1. Two samples were fatigue tested for each of the load levels. After fatigue tests samples were cooled down to liquid nitrogen temperature and then statically loaded to failure for exposing the fracture surface. Samples were then examined in a SEM for observation of fracture surface and crack growth measurement.

4.2 Interrupted Fatigue Tests in Autoclave Environment

The same approach was used for fatigue tests in autoclave. Due to the limitations of the autoclave equipment, tests were carried out at a different stress level compared to air and with a slightly higher stress ratio, R=0.3. At the beginning of the test the sample was positioned in the loading frame and, after autoclave sealing, the target environment was introduced by pressurizing the gases (H_2S, CO_2 and CH_4). A small quantity of liquid water was also placed at the bottom of the autoclave to ensure moisture conditions.

Only one load level was employed as reported in Table 4. Three tests were carried out under constant amplitude loading conditions at a frequency of 4 min/cycle using a trapezoidal waveform with one minute hold at the maximum pressure.

Table 4: Load level used for fatigue tests in autoclave environment

Load level	ΔS [MPa]	Number of cycles ΔN
1	239	4000
		2000
		2000

Figure 2 shows an example of surface appearance after fatigue interrupted test in autoclave environment. The original notch, the precracking area and the crack propagation surface are visible. The crack propagation area is covered with iron sulphide typical of exposure to H_2S contaminated environment.

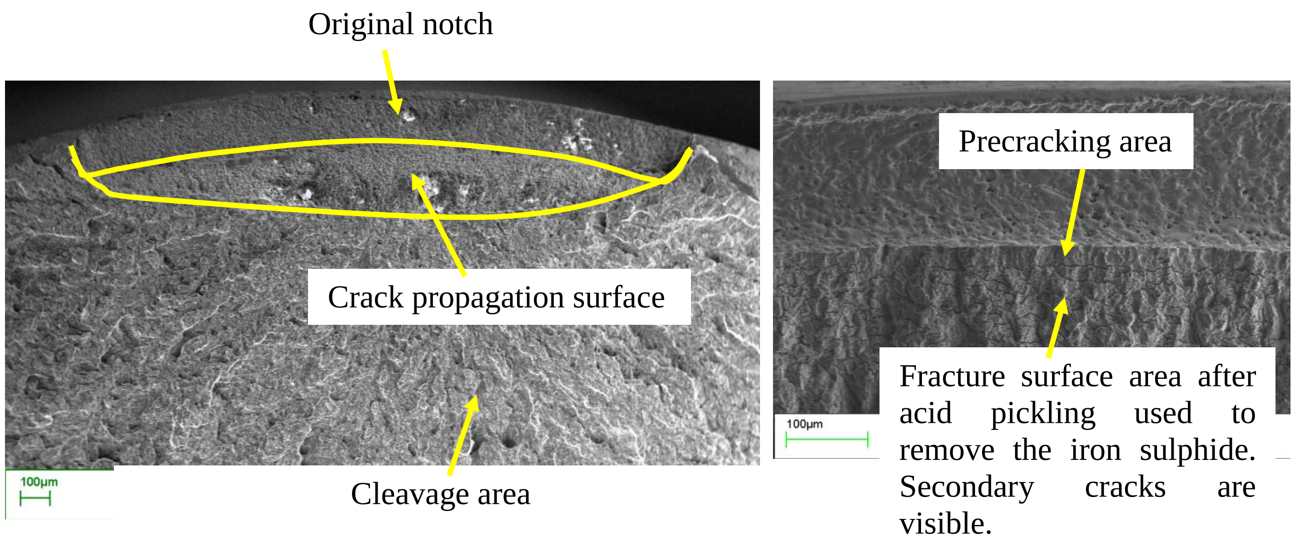

Figure 2: Example of fracture appearance after test in autoclave environment

5 Finite Element (FE) Analysis

By looking at several pictures of crack shapes at the end of the tests, a FE model was implemented as reported in Figure 3. FE analyses were carried out with Abaqus FE software for estimation of stress intensity factor (K) at the crack tip based on the J-integral value. In particular 10 cracks were modeled with depth in the range 0.41 mm<a<0.52 mm. The K values were interpolated with:

$$K = Y(a/D)\sigma\sqrt{\pi a} \qquad (1)$$

where Y(a/D) is the geometric factor expressed by a fourth order polynomial.

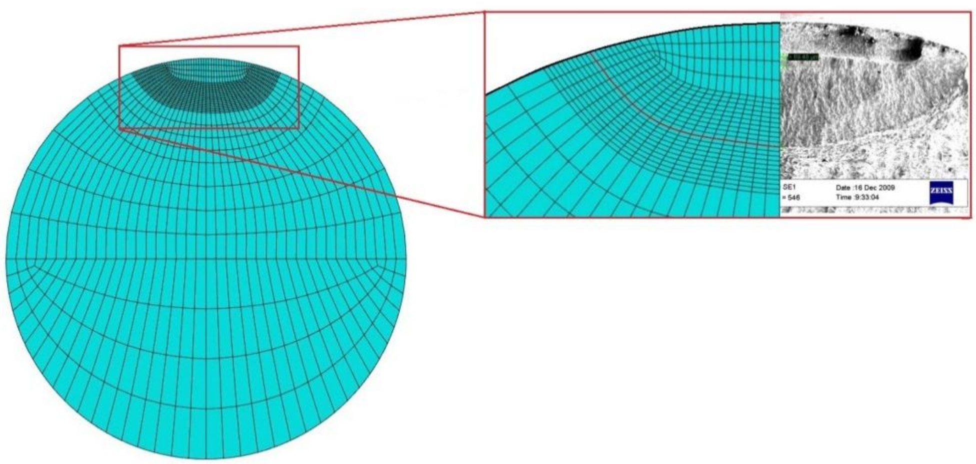

Figure 3: FE model used to calculate J-integral and derive the correspondent K-value

6 Results

The proposed approach was first verified in air conditions based on the tests reported in Table 3. The results were plotted on a typical da/dN vs. ΔK diagram using the average ΔK between the initial and the final value, while crack propagation rate was estimated by the ratio between measured crack length and number of cycles. The same approach was used for the results of the autoclave tests.

In Figure 4 the circle points represent results obtained in air according to the proposed methodology and compared with available crack propagation rate data obtained in air at the same stress ratio R=0.1 (two tests) according to ASTM E647 standard [3]. A good agreement was obtained at all the

stress levels used, showing that the proposed approach could be applied to estimate crack propagation rate in corrosive environment.
The square red points represent the experimental results obtained in autoclave environment. This crack propagation rate appears to be one order of magnitude higher compared to data in air with a very steep increase, showing a different slope from the typical values reported for air.

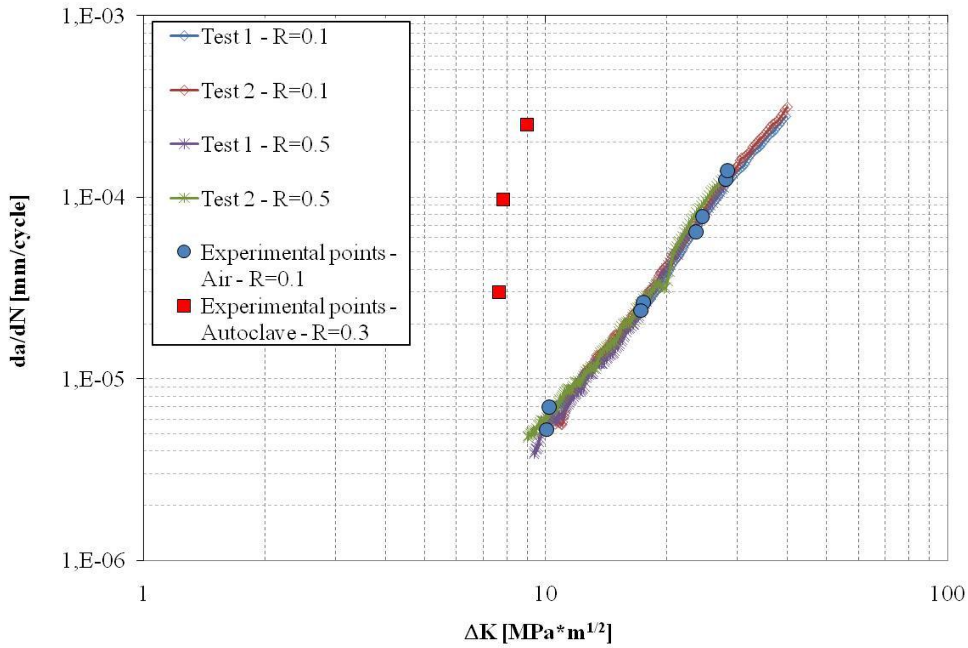

Figure 4: Results obtained in air and in the autoclave environment (preliminary tests)

7 Discussion

The proposed methodology was first verified in air showing a good agreement with fatigue crack propagation rate data obtained according to ASTM E647 standard.
The interrupted fatigue tests reported in the present work were carried out on samples with small EDM notches, therefore cracks nucleating from them can be considered as *physically small cracks* ([4]). Short cracks are known to propagate faster compared to long cracks due to a different closure mechanism.
However, for the investigated material, a significant crack closure effect was not observed since results obtained with the proposed methodology at R=0.1 well fit the data obtained according to the standard ASTM E647 procedure (Figure 4). Moreover fatigue crack propagation rate data obtained according to ASTM E647 at stress ratio R=0.1 and R=0.5 (Figure 4) do not show significant differences, therefore supporting this finding.
When dealing with different hydrogenating environments (pure gaseous H_2 and aqueous solution with H_2S), Figure 5 gives a schematic behavior of the different fatigue crack propagation rate curves:

- In a sour environment, with different H_2S partial pressure (from 0.02 MPa to 1.65 MPa) and stress ratio up to R=0.3, threshold values between ΔK=8 MPa*m$^{1/2}$ and ΔK=13 MPa*m$^{1/2}$ are reported. This phenomenon is the result of a closure mechanism due to the build-up of corrosion products at the crack tip. In the linear region of the crack propagation rate diagram the increase in the fatigue crack growth rate can be up to two orders of magnitude compared to air data ([5], [6], [7], [8]);

- In a pure gaseous H_2 environment a non linear crack propagation rate diagram is reported with the existence of a threshold ΔK value (known as ΔK^{T}_{H2}) above which a steep increase in the crack propagation rate is observed (Figure 5). However such ΔK^{T}_{H2} value is not unique depending from several factors among which H_2 partial pressures and stress ratios ([9], [10]). In the linear region of the crack propagation rate diagram the increase in the fatigue crack growth rate can be up to 30 times compared to air data ([10], [11]).

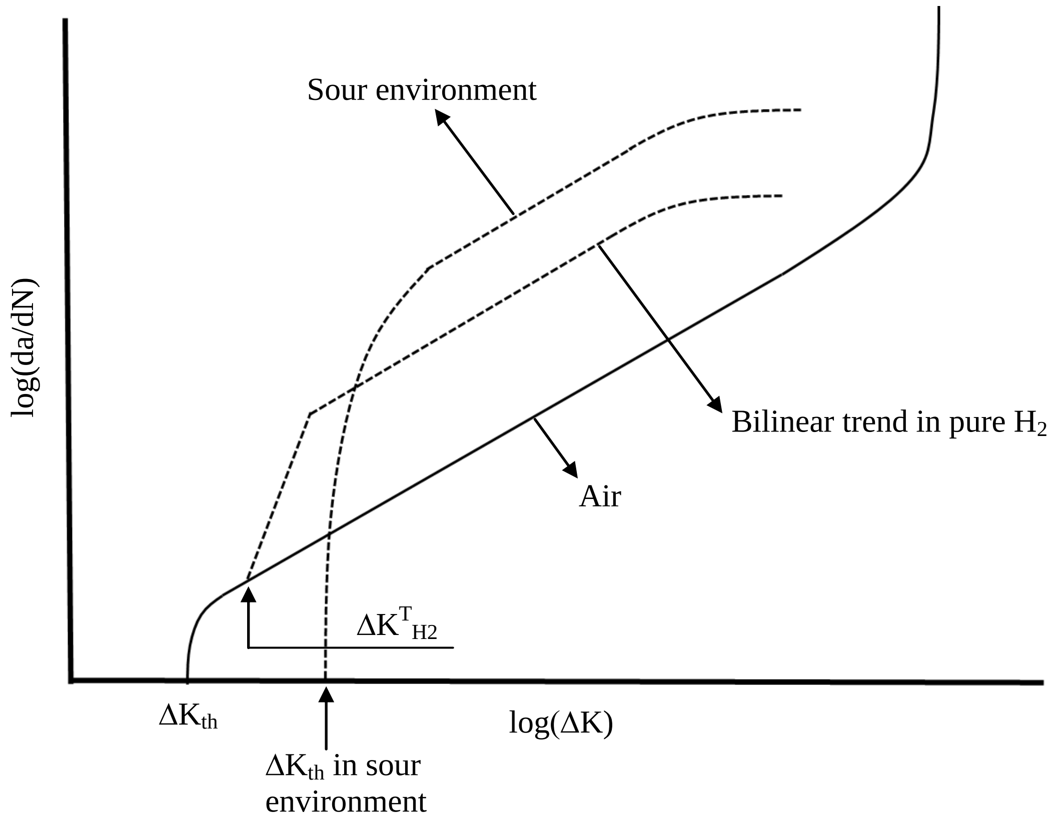

Figure 5: Schematic behavior of fatigue crack propagation rate curves in different hydrogenating environments

In the present work the three samples tested in autoclave environment showed fatigue crack growth with an initial applied $\Delta K < 8$ MPa*m$^{1/2}$.
For the interpretation of these tests results the following hypothesis can be done:

- Samples were not immersed in an aqueous solution, therefore it is possible that less corrosion products were formed at the crack tip so that the aforementioned crack closure mechanism is less pronounced;
- Presence of moisture at the crack tip, without having the samples immersed in the aqueous solution, could have determined local environmental conditions at the crack tip with water supersaturated with H_2S at a higher concentration than the target value reported in Table 1. Such conditions could have enhanced the hydrogen penetration into the steel.

Authors of the present work consider that the experimental points obtained in autoclave environment could represent the first part of a bilinear crack propagation rate diagram, where, in the second part, the slope becomes parallel to air with a mechanism similar to what is reported in case of pure H_2.
Such hypothesis is being verified through further tests carried out at ΔK levels higher than the ones reported in the present work.

8 Conclusions

In this paper a methodology developed to estimate fatigue crack growth rate data from small cracks under wet H_2S conditions is presented.

Even though the methodology was successfully verified in air it is still under validation in case of H_2S conditions through other tests repetitions.

The test methodology consists in: i) precracking at R=-2 for $N=10^7$ cycles of specimens containing small EDM notches; ii) interrupted axial fatigue tests under wet H_2S atmosphere; iii) SEM observation of fracture surfaces.

The data of interrupted fatigue tests will be useful to obtain a prospective da/dN diagram which can be used for crack growth assessment of pressure vessels in contaminated CNG environment. Further tests are presently on going to explore regions with initial applied ΔK values higher than the ones employed in the present work.

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