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## Abstract

In order to prepare for a future use of hydrogen as a fuel gas, it became evident that very little information existed regarding the compatibility between long-term exposure and transportation of hydrogen in natural gas pipelines. A program was therefore set to study the transportation in a small-scale pilot grid.

*The main focus was the long-term hydrogen compatibility of the pipe materials, but leakage and function of connections, valves and gas meters were also monitored.*

The test program included a selection of steel pipes from the Danish gas transmission grid and polymer pipes from the Danish and Swedish gas distribution grids.

The test of polymer pipes was devised so that part of the grid was to be dug up each year and analysis performed on the pipes; in this way any form of influence on the integrity of the polyethylene pipe would be detected.

The analytical program for the polymer pipes was devised in order to detect any influence on the additives in the polyethylene pipe material as this has an influence on oxidative resistance, as well as checking already encountered possible degradation caused by extrusion of the material. Further tools, such as rheology and melt flow rate, were used for detecting any structural changes on the material. On the mechanical property side, the tensile strength and modulus were followed as well as the most important property for the pipeline, namely slow crack growth.

*Main conclusions of the test and analysis work indicate that hydrogen will not increase the degradation of the tested polymer pipe materials. Slightly increased leakage compared to natural gas service was observed. Pipe connections, valves etc. must be checked periodically for hydrogen leak resistance.*

## 1. Introduction

It has become ever clearer that the resource of natural gas is an energy source that will be less important in the future due to limitations in natural reserves. In order to prepare for the future, the gas industry is looking at alternative gaseous fuels, one such fuel gas is hydrogen.

Large reserves of natural gas are still discovered, which can contribute to about 50% of the world energy mix for a longer time, but hydrogen gas is expected to become more and more available from converted wind energy via electrolysis. This gas can be fed to the natural gas network, and the whole gas network, including underground storage facilities, acts as a big buffer (Power to gas). Alternatively, existing gas networks are gradually converted to pure hydrogen transport systems.

During preparation for a future use of hydrogen, it became evident that very little information exists regarding the compatibility between long-term exposure and transportation of hydrogen in polyethylene gas distribution pipelines. A program was, therefore, set to study the transportation in a small-scale pilot grid at the field test facilities of Danish Gas Technology Centre situated at the Scion-DTU research centre in Hoersholm, Denmark.

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<sup>1</sup> B.SC., B.Com - Danish Gas Technology Centre

<sup>2</sup> M.SC. – Borealis Polymers OY.

The test program included polymer pipes from the Danish and Swedish gas distribution grids.

## 1.1 Organization

The project partners were Danish Gas Technology Centre and Borealis AB. Danish Gas Technology Centre was project manager and responsible for design, construction and operation of the field test facilities. Borealis - one of the biggest suppliers of raw material from polyethylene for the production of pipes for e.g. pressure pipes for gas distribution - provided analytical services for the determination of compatibility problems between polyethylene pipes and hydrogen during the 10 year exposure period 2006-2016.

## 2. Polymer pipe test and analysis

A dominant part of the natural gas distribution grid consists today of polyethylene pipes due to polyethylene's excellent track record as a reliable piping material with minimal maintenance. The reason for this is the inherent properties like its corrosion free nature, the possibility to create fully weldable systems, its high ductility and excellent low-temperature properties.

### 2.1. Test set-up

During the test phase, the polymer pipes were exposed to pure hydrogen continuously for 4 years. The pressure was around 4 barg and the temperature around 8 °C. The pipes were placed according to the regulations for normal gas distribution grids in Denmark around one meter below surface and placed in layers of sand. See figure 1.



Figure 1. Test site facilities during construction phase

The program was devised so that a part of the test grid was to be dug up each year and analyses were to be performed on the pipes. In this way, any form of influence on the integrity of the polyethylene pipe would be detected. The pipes were analysed before exposure to hydrogen, then the pipes were dug up after 1 year, 2 years, 3 years, 4 years and 10 years of exposure. The 10 years of exposure was only performed for PE 100 pipes.

### 2.2 Samples used in the analysis

The samples consisted of three distinctly different materials:

1. A yellow solid-wall PE 80 medium-density polyethylene (PE 80 MDPE).
2. An orange solid-wall PE 100 high-density polyethylene (PE 100 HDPE), referred to as "PE 100 type I".
3. A natural coloured pipe with an orange outer protective layer. The natural coloured material is PE 100 high-density polyethylene (PE 100 HDPE), referred to as "PE 100 type II".

For each material, samples of various production years were included. Some of the pipes were also previously used in the Danish natural gas grid. The oldest pipes were subjected to natural gas for 20 years before exposure to H<sub>2</sub> in the pilot grid.

*General note: CH<sub>4</sub> in text and figures should be read as Danish natural gas!*

### 2.3 The analytical program

The annual analyzing program consisted of:

1. Structural changes in the polymer.
2. Consumption of antioxidants.
3. Change of tensile properties.
4. Change of slow crack growth properties of the material.
5. Surface oxidation.

The reason for this choice was that if no influence is detected in these properties then one can assume that polymer pipes are compatible with hydrogen and can safely be used, seen from a polymer structure property and pipe property point of view.

## 3 Results

### General findings

During the investigations we found that there are basic quality level differences between pipes of different manufacturing years (see figure 2 and fig. 9). These production-batch related changes in the material properties increase the scatter of results of the analysis to a higher level than normally expected.

### 3.1 Determination of structural changes

Pressure pipe PE polymers are high molecular weight materials with a broad molecular weight distribution and the physical properties of the polymer are determined to a large extent by the high molecular weight portion of the material. We have determined to use rheology since this is more sensitive to changes in the high molecular portion and these changes are coupled to physical properties of the material. See also ASTM 4440-95a and EP1137707-rheological description).

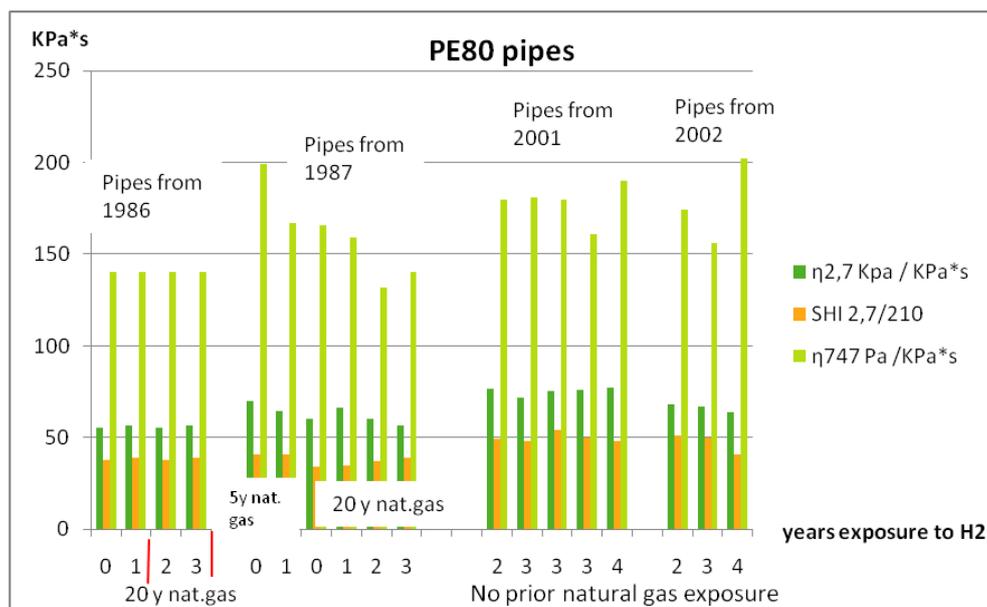


Figure 2. Rheological results of PE 80 pipes of different manufacturing years

Depending on manufacturing year there are differences in molecular weight, Mw, molecular weight distribution, MWD, and high molecular weight portion. The rheological result clearly indicates that different values rely on the basic quality level difference of the polymer manufactured in different years. Other changes within each group can be considered normal variations considering differences in polymer manufacturing and pipe manufacturing. There is no indication of changes caused by hydrogen exposure.

In the case of PE100 type II pipes, figure 3 clearly indicates that there is no effect on the PE100 type II pipe from the use of the pipes in the pilot hydrogen grid in Denmark for up to 10 years. The variation seen is a combination of manufacturing year, sample and test variations.

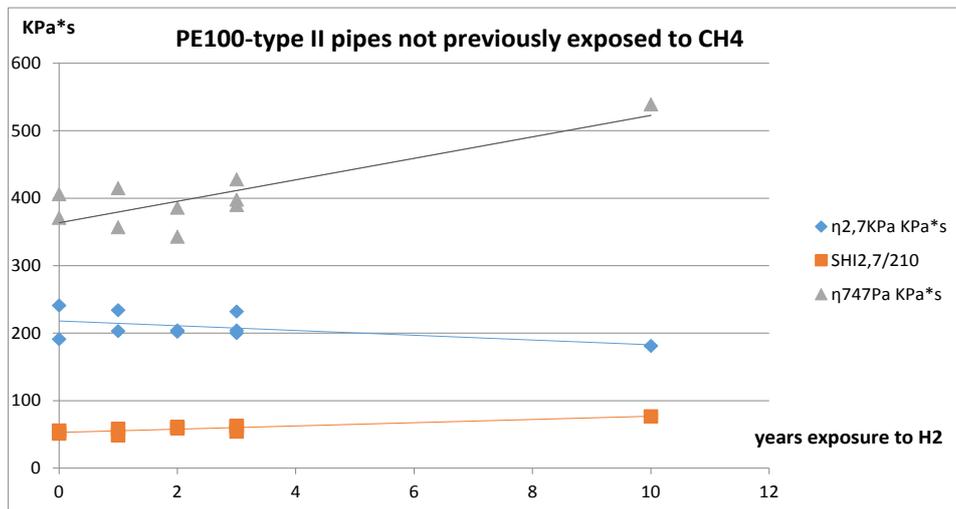


Figure 3. Rheology of PE 100 type II pipes, used for transportation of H<sub>2</sub> in the pilot grid, not previously exposed to CH<sub>4</sub>

**PE100 type II pipes previously used for 4 and 10 years in the natural gas transportation grid in Denmark**

In the case of the PE100 type II pipes, a pipe that has previously been used for 4 years in the Danish natural gas pipe grid has also been evaluated for 2 years in the hydrogen transportation grid in Denmark.

As can be seen in the diagram in figure 4 there is no difference between a non-used pipe or a pipe that has been subjected to 1 or 2 years of hydrogen transport without previous use and the pipe that has first been used for 4 years of natural gas transportation and then subjected to 2 years of hydrogen transport.

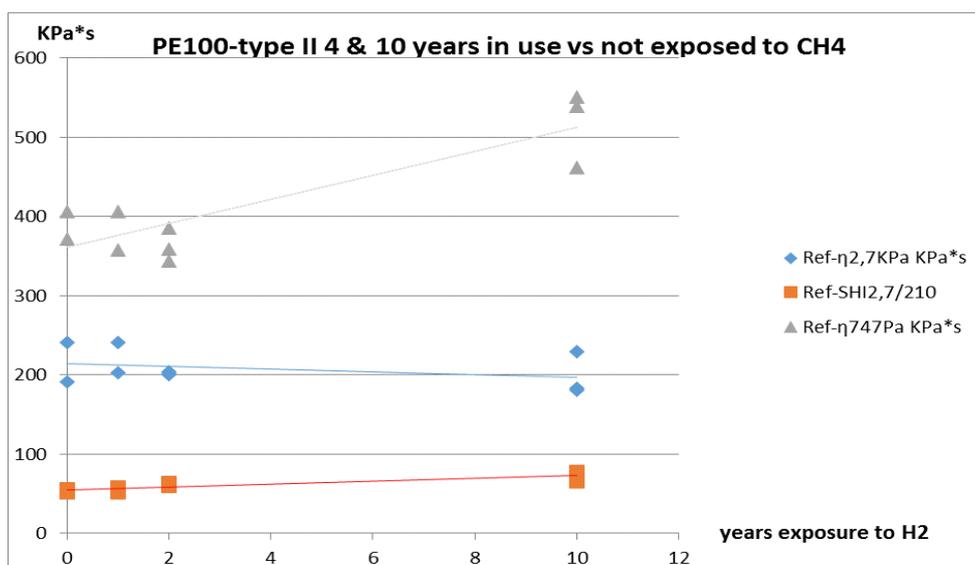


Figure 4. Rheology of PE100 type II pipes, used for transportation of H<sub>2</sub> in the pilot grid compared to the combined effect of 4 years of natural gas transportation followed by 2 years of H<sub>2</sub> transportation.

In conclusion, there was no adverse effect from the transportation of hydrogen on PE100 type I or PE100 type II for up to 4 years and 10 years. Nor was any effect seen on PE100 type II from the combined effect of use of 4 years for transportation of natural gas followed by 2 years of hydrogen transport. No effect was seen when comparing to pipe samples stored in DGC's dark cellar (exposed 10 years to air). The data for the air-only exposed pipe samples were measured after 10 years (figure 4).

### 3.2 Determination of oxidative power - consumption of antioxidants

In order to detect interaction between the transported medium and antioxidant (the pipe grades contain mainly phenolic antioxidants), the so-called Oxygen Induction Time (OIT, according to EN728) was chosen as it gives a quick and reliable measurement of the oxidation power of the additivation in the polymer. This has been determined at two temperatures to increase the accuracy of the determination.

#### PE80 pipes not previously used

As can be seen from figure 5, there is no effect from hydrogen transport on the antioxidative power of the additivation of the polymer pipes, measured as Oxygen Induction Time (OIT). This means that no interaction is found on the additivation of the polymer pipes from the hydrogen transport, and the long-term integrity of the pipe is assured. Similar results have been found for PE 100 and pipes previously exposed to natural gas for up to 20 years prior to the hydrogen exposure. In the Gas pipe standard (EN 1555), an OIT of 20 minutes at 200 °C is deemed sufficient for a 50-year lifetime at 20 °C.

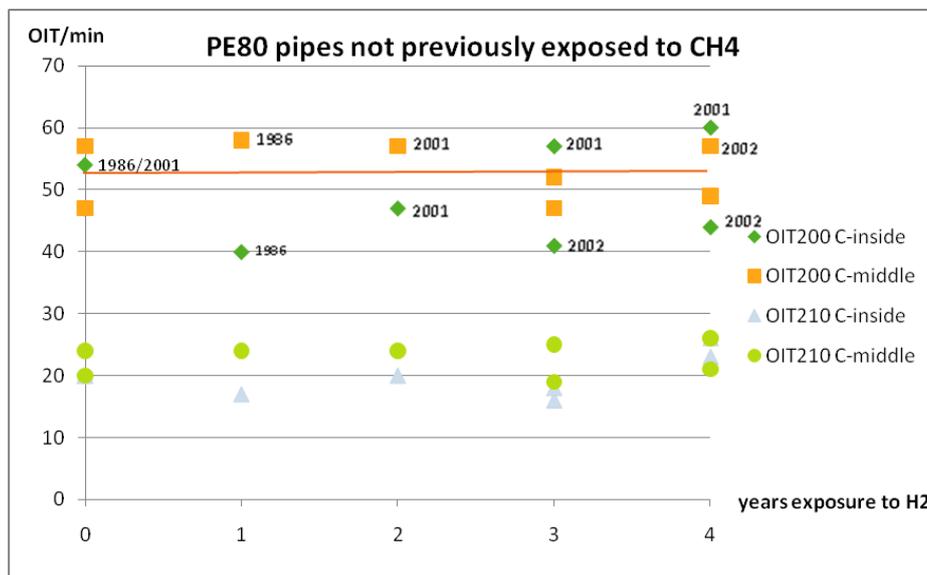


Figure 5. Oxygen Induction Time (OIT) versus years of hydrogen transport in the pilot hydrogen grid. Previously non-used pipes.

The scatter in the diagram is caused by samples of different years of manufacture, additive variation, sampling and measurement.

#### PE100 type II previously used for 0, 4 and 10 years in the natural gas grid

Among the PE100 type II samples were also pipes that were first used for 4 years in the natural gas grid, then used in the pilot grid for 0, 1 and 2 years of hydrogen transport. The results show that there is no significant difference between samples first used for 4 years in the natural gas grid followed by two years in the hydrogen grid and samples that were not previously in the natural gas grid before two years of exposure to hydrogen or for that matter samples that has not been used at all. As expected, the OIT have slightly decreased after exposure to natural gas and hydrogen in 10 years' time. No big deviation can be seen between 10 years' exposure (CH<sub>4</sub> and H<sub>2</sub>) when comparing with the sample that was stored in the dark cellar (exposed to air) for 10 years. The results are partly shown in figure 6, where the four different measurements are placed in relatively small clusters.

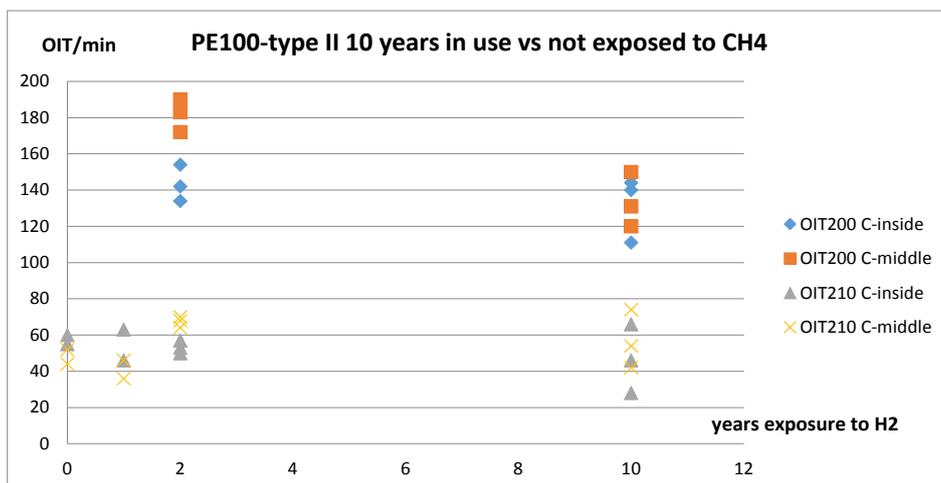


Figure 6. Oxygen induction time (OIT) versus years of hydrogen transport in the pilot hydrogen grid. A sample previously used in comparison to pipes previously not used.

### 3.3 Determination of changes in tensile properties

It is investigated if hydrogen exposure causes changes in tensile modulus and elongation at break . Measurements have been done for pipe samples not previously used and pipes used 5 or 20 years in the natural gas grid. In both cases no significant changes in tensile properties are found. Examples are shown in figure 7 and figure 8. It is neither possible to detect any negative influence on tensile modulus nor on elongation at break. There could be a possible increase of modulus with time, however, the change in comparison to the scatter in the test and the fact that samples of different manufacturing year were used, made the observation clearly uncertain.

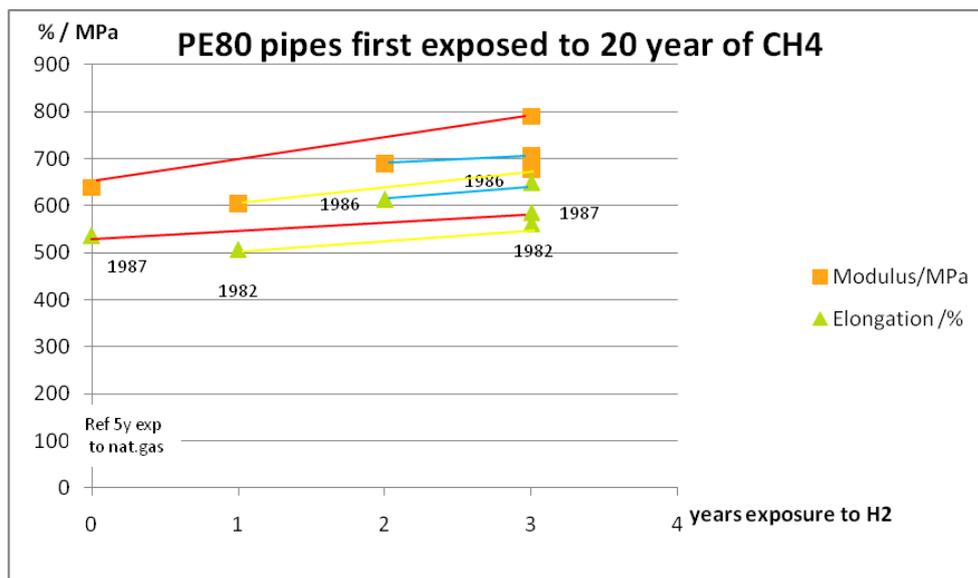


Figure 7. Elongation at break and tensile modulus versus years of exposure to hydrogen of pipes previously used for 20 years in the natural gas grid

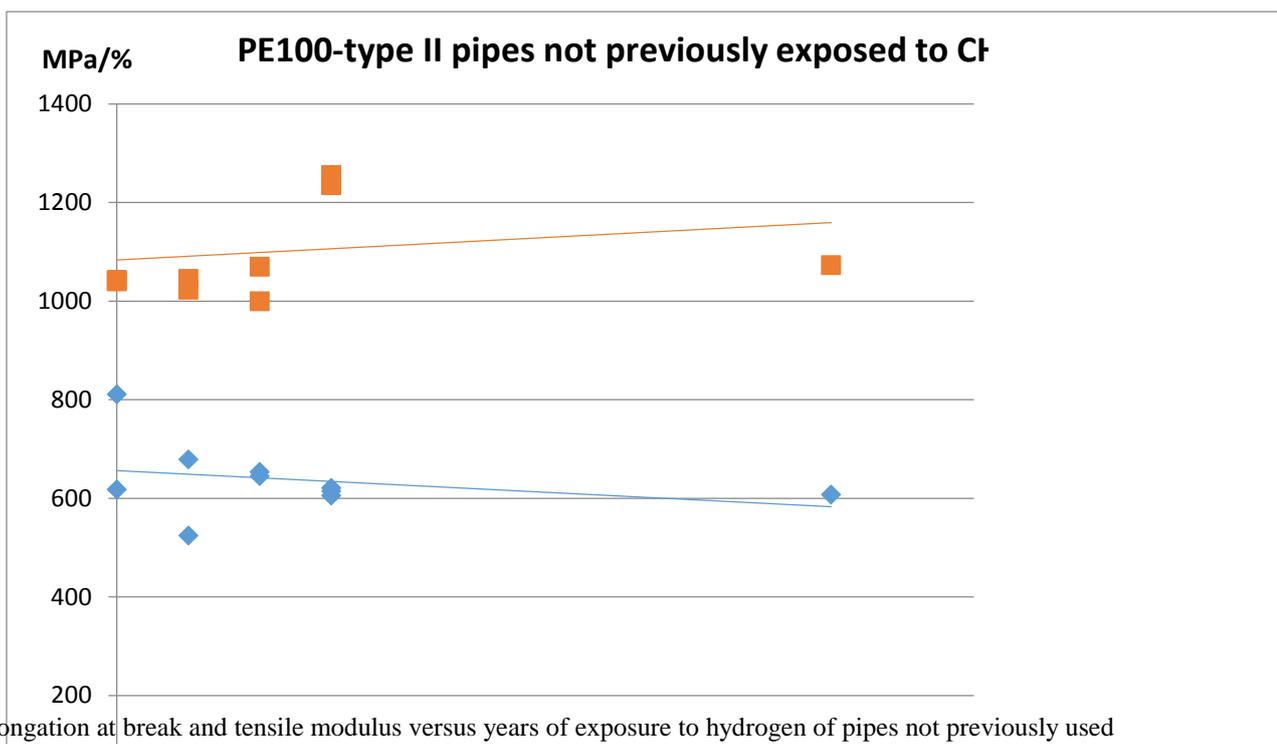


Figure 8. Elongation at break and tensile modulus versus years of exposure to hydrogen of pipes not previously used

### 3.4 Determinations of changes of slow crack growth

#### PE80 pipes

In the ESCR we have the same situation as in the other properties; there are no indications of changes in this property compared with the time in the pilot hydrogen grid (see figure 9). In this diagram no exposure and 1 year exposure of pipes with a prehistory of 5 years natural gas transportation have been used, as true references are missing. However, as can be seen in figure 9, there are quality level differences between pipes from different manufacturing years.

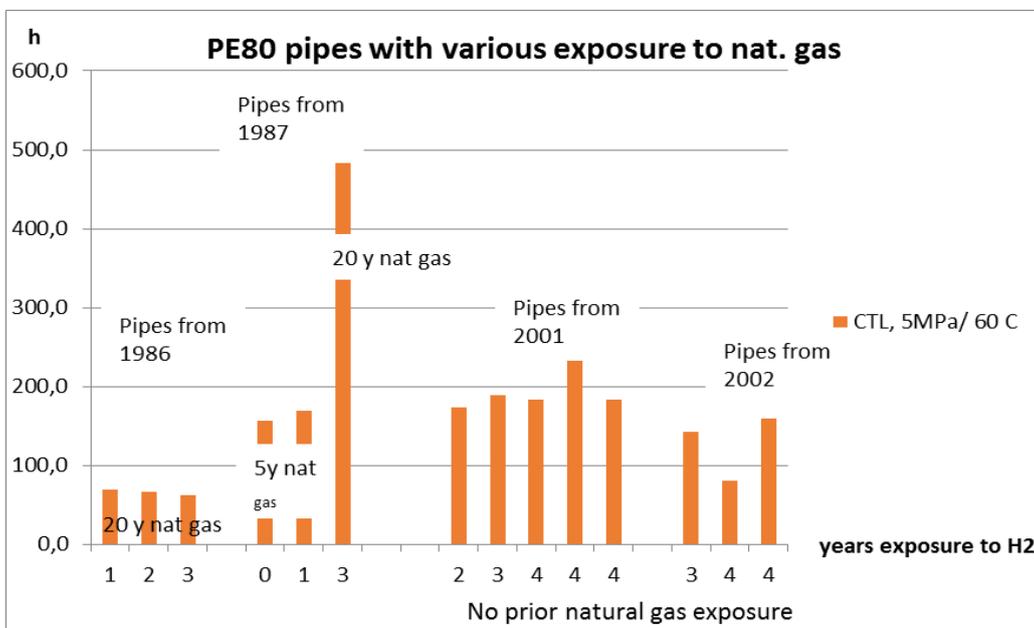


Figure 9. CTL resistance to slow crack growth of PE80 pipes of different manufacturing years

## PE100 – type II pipes

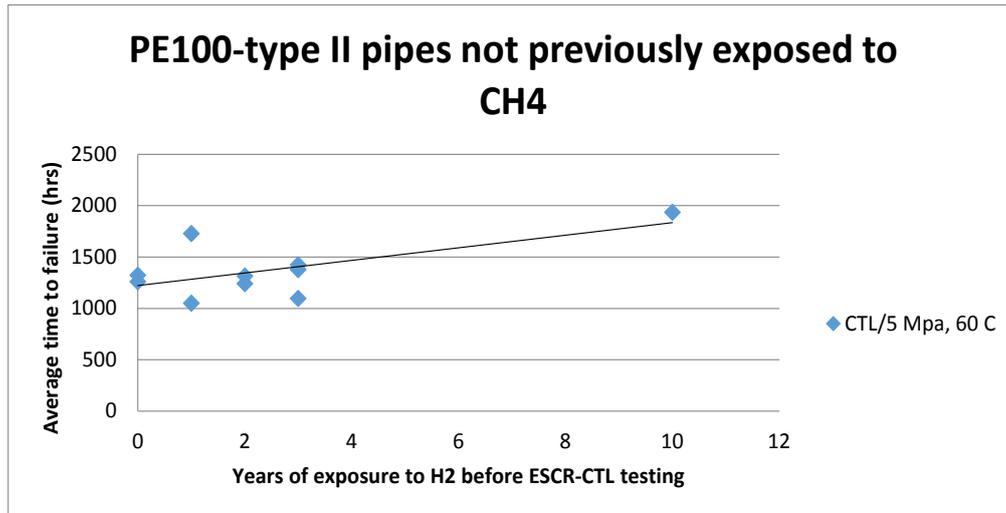


Figure 10. CTL resistance to slow crack growth of new PE100 pipes as a function of hydrogen exposure time

Figure 10 shows that the CTL resistance for the PE100 pipe material was not reduced by the hydrogen exposure. The same picture was seen in the case of PE100 pipe that before 2 years of use in the pilot hydrogen gas grid had been used for 4 years in the natural gas grid. This pipe is depicted in comparison to pipes not previously used in the natural gas grid with different exposure time in the pilot hydrogen grid. No difference can be detected between a pipe that has not been used, a pipe not used in the natural gas grid but different number of years in the pilot grid and the pipe that was used 4 years in the natural gas grid and then exposed to hydrogen for 2 years in the pilot grid,.

#### 4. Conclusion

##### In short

4 years (PE80) and 10 years (PE100) of continuous hydrogen exposure and subsequent laboratory tests based on international standards indicate no influence on PE80 or PE100 natural gas pipes' durability.

##### In detail

1. No influence on the basic structure on the pipes measured with rheology according to ASTM 4440-95a.
2. No influence on additivation/oxidative strength on the pipes measured with oxygen induction time (OIT) according to EN 728.
3. No influence on the pipes measured as elongation at break and tensile modulus according to ISO 527.
4. No influence on the slow crack growth properties measured as CTL at 5 MPa/60 C according to ISO6252-1992 / ASTM1473 F.

#### 5. Acknowledgements

We wish to express our sincere gratitude to our former project partner, the late Mats Bäckman from Borealis who has been of great importance to the comprehensive laboratory work and subsequent analysis.

#### 6. References

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3. EN1555 Plastic piping systems for the supply of gaseous fuels-Polyethylene(PE) - Part 1 General, December 2002
4. ASTM 4440-95a

**Abbreviations used**

SCG = Slow crack growth  
OIT = Oxygen Induction Time  
ESCR = Environmental Stress Cracking  
CTL = Constant Tensile Load, name of test method.  
PE100 = Polyethylene pipe material classified MRS 10,0 MPa  
MRS = Minimum required strength at 50 years  
DGC = Danish Gas Technology Centre  
FTIR = Fourier Transform Infra Red analysis  
MFR = Melt Flow Rate  
FRR = Flow Rate Ratio  
ISO = International Organisation for Standardisation  
MPI = Magnetic Particle inspection  
CH<sub>4</sub> = Danish natural gas  
Mw = Molecular weight  
MWD = Molecular weight distribution