GT-140281
7 May 2015

Effects of Narrow Band Gases on Materials used in Gas Distribution Networks

Final Report

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Colophon

Title	Effects of Narrow Band Gases on Materials used in Gas Distribution Networks. Final report
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Preface

This report is part of the results of the EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems within the Current Distribution Band for Natural Gas in the Netherlands". The working title of this project is "Effects of Narrow Band Gases on Materials". It is part of the EDGaR program subtheme 1.2 “Technical consequences of the diversity in the gas streams for pipeline integrity and gas treatment”

The following partners are involved in this project:

- Enexis
- Liander
- Stedin
- Gasunie
- Kiwa

Kiwa is project leader.

This project is closely related to the research projects with the working titles "Effects of Wide Band Gases on Materials" and "Impact of Sustainable Gases on Joints used in Gas Distribution Systems".

This final report gives the results of the experiments that were performed combined with the results of a literature review [1] and the description of the experimental setup [2,3].

Summary

The existing Dutch gas infrastructure has been designed for distribution of (pseudo) Groningen gas (G-gas). Network operators explore the possibilities to make the gas supply more sustainable and to extend the variety of gas sources. For this reason the effects of the change to narrow band gases were evaluated in this EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems within the Current Distribution Band for Natural Gas in the Netherlands". Narrow band gases are defined as upgraded or downgraded gas that has about the same physical properties (e.g. Wobbe index, Calorific value) as G-gas. The concentration limits of the different components present in narrow band gases are based on the additional terms and conditions applicable to Dutch biomethane producers of 2009. Differences in chemical composition between G-gas and narrow band gases are mainly found in the levels of CO_2 and H_2S. Differences also exist in the concentrations of trace components such as halogens.

This project answers the following main research question:

Are the most important materials used in the Dutch gas distribution network resistant to narrow band gases?

The project made use of relevant scientific and technological literature and involved experiments of 600 days in duration. The results are summarised in Table 1 below.

Table 1. The effect of components present in narrow band gases on the most important gas distribution materials based on literature review and experiments.

	Sulphur containing components	H_2S	Mercaptans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
PVC	none		probably none		none			probably none		unknown	none	none, unless liquid (impact resistance)		none	
PE	none		probably none		none			probably none		unknown	none	none, unless liquid		none	
NBR	none		probably none		none			probably none		none		none, unless liquid		none	
steel	water and CO_2			probably none					H_2S and water: possibly	unknown	water and H_2S	probably none		water, (H_2S) and CO_2	none
	water, CO_2 and O_2										water, (H_2S) and O_2				
Cu	none			probably none	none	probably none			unknown		none	probably none		none	none
Al	water and CO_2			probably none	none	probably none			unknown		none	probably none		none	none
	water and O_2													water and H_2S	

░	=	The effect is unknown, but is expected to be very small or non-existent.
🟩	=	This component within the concentrations of narrow band gases does not affect materials.
▒	=	The effect is unknown.
🟧	=	Deleterious effects are expected under some conditions.

The table shows that the answer to the main research question is:
Yes, the most important materials used in the Dutch gas distribution network are resistant to narrow band gases. However, this is only valid if water is absent in the gas distribution grid. Without water, corrosion of metallic materials (steel, copper and aluminium) cannot occur and only a few adjustments in restrictions on the maximum allowable concentrations of gas components in narrow band gases are necessary.

Possible solutions to reduce the risk of the presence of water in the gas distribution grid include:

- Increase the distribution pressure to 100 mbar(g). At 100 mbar(g) gas pressure the risk of ground water entering the gas grid (water ingress) is significantly lower than at 30 mbar(g) gas pressure.
- Decreasing the water dew temperature of the gas at gas entry points. In other words, the gas must be dried (the relative humidity must be lowered) before it enters the gas distribution grid. This solution deserves a prominent role in the processing of sustainable gases to upgrade it to narrow band gases.

In addition to drying the gas to remove water, it is also important to prevent the formation of liquid hydrocarbons. This may occur if the concentration of aromatic hydrocarbon vapours is too high. These liquids have a negative effect on the mechanical properties of polymeric materials. At present, the maximum allowable limit for aromatic hydrocarbons in narrow band gases is 10 000 ppm.
In G-gas the maximum measured concentration of aromatic hydrocarbon vapour in the last ten years in the Dutch gas distribution grid is 800 ppm. This concentration did not lead to obvious liquid formation and thus material degradation. It is therefore recommended that the concentration of aromatic hydrocarbon vapour in narrow band gases is limited to 800 ppm.

Furthermore, it is important to note that the effects of several gas components have not been tested (HCN and CO). This is due to the toxicity of these gases to humans, which makes experiments in the laboratory dangerous. The influence of these toxic gases on important polymeric and metallic materials therefore remains unknown. In some cases the literature indicates that a negative effect of these gas components may be possible. It is therefore recommended that HCN and CO should be prevented from entering the gas distribution grid or that their concentration should at least be kept as low as possible. It is recommended to limit the maximum concentration of H_2S to 160 ppm.

The above-mentioned recommendations are summarised in Table 2 where water is not present in the existing Dutch gas distribution grid. Adjustment of the limiting values for other gas components in narrow band gases in accordance with the additional terms and conditions applicable to Dutch biomethane producers is not required.
(Please note: this excludes joints, which are investigated in another project).

However, it is not always possible to prevent water from entering the gas distribution grid. Where this occurs, gas with a high humidity will be present and the combination of H_2S, CO_2 and O_2 may lead to severe corrosion in especially steel, but also in copper and aluminium. It is therefore needed to limit the O_2 concentration to 100 ppm (0.01 mol%) for humid narrow band gases.

This limiting value is also suitable for copper and aluminium. However, severe corrosion can still occur in aluminium without the presence of CO_2. More research using low CO_2 concentrations is therefore recommended.

Table 2. Recommended limiting values for several gas components in narrow band gases where water is not present in the gas distribution grid or in narrow band gases.

Limiting value	Reason
< 800 ppm aromatic hydrocarbons (vapour)	Liquid hydrocarbons, including mono- and polycyclic aromatic hydrocarbons and higher hydrocarbons (e.g. terpenes), have a negative effect on the mechanical properties of polymeric pipe materials. At present, the maximum allowable limit for aromatic hydrocarbons in narrow band gases is 10 000 ppm. It is recommended that the maximum concentration be limited to 800 ppm. 800 ppm is the maximum measured concentration of aromatic hydrocarbons in G-gas in the last ten years.
low concentrations of CO and HCN	The effects of CO and HCN were not determined due to their high toxicity to humans. Because of this health and safety risk and because only limited information could be obtained about the possible effects of these components on the most important materials used in the Dutch gas distribution grid, it is recommended that the maximum concentration of CO and HCN be limited as much as possible.

When water is present in the gas grid or in narrow band gases additional recommendations to the ones given in Table 2 are needed and given in Table 3. Adjustment of the limiting values for other components in narrow band gases in accordance with the additional terms and conditions applicable to Dutch biomethane producers are not required.
(Please note: this excludes joints, which are investigated in another project).

Table 3. Additional recommended limiting values for several gas components in narrow band gases where water is present in the gas distribution grid or in narrow band gases.

Limiting value	Reason
< 0.01 mol% O_2	The combination of H_2S, CO_2 and O_2 may lead to severe corrosion in steel, copper and aluminium. This limiting concentration, combined with the current limiting values for H_2S and CO_2, is found to limit the effect on metallic materials to an acceptable level.
possibly > 0 mol% CO_2	If both H_2S and O_2 come into contact with aluminium or copper, in the absence of CO_2, severe corrosion may occur. It is unknown if CO_2 must also be present for the above proposed limiting value. More research using low CO_2 concentrations is therefore recommended.

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List of Symbols and Abbreviations

General

DSO	distribution system operator

Gases

BTX	benzene, toluene and xylene
CO	carbon monoxide
CO_2	carbon dioxide
DCM	dichloromethane
G-gas	Groningen gas
H_2	hydrogen
H_2S	hydrogen sulfide
HCl	hydrochloric acid
HCN	hydrogen cyanide
N_2	nitrogen
NH_3	ammonia
O_2	oxygen

Materials

Al	aluminium	
Cu	copper	
CuO	copper(II) oxide	
CuS	copper monosulphide	
PVC	poly(vinyl chloride)	
	PVC-CPE	impact-modified PVC, using chlorinated polyethylene produced by Pipelife
	PVC-A	impact-modified PVC, using butylacrylate produced by Wavin
	PVC-HI	impact-modified PVC, (PVC-A or PVC-CPE)
	PVC-U	unplasticized (rigid) PVC, produced by Polva* or Wavin
	PVC-U type 1	unplasticized (rigid) PVC, produced by Polva*
	PVC-U type 2	unplasticized (rigid) PVC, produced by Wavin
	PVC-U type 3	unplasticized (rigid) PVC, water pipe produced in 2011 by Wavin
PE	polyethylene	
	HDPE 50	first generation high density PE
	HDPE 63	first generation high density PE
	HDPE 80	second generation high density PE
	MDPE 80	second or third generation medium density PE
	HDPE 100	third generation high density PE
POM	polyoxymethylene (polyacetal)	
	hPOM	homopolymer POM
NBR	nitrile butadiene rubber	
SBR	styrene-butadiene rubber	
St	steel	

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* Nowadays Pipelife

Test-related

ESC	environmental stress cracking
HAZ	heat-affected zone
MAC	maximum accepted concentration
T_{BD}	brittle-ductile transition temperature
σ	standard deviation
$\sigma_{100\%}$	stress at 100 % elongation (sometimes called “modulus”)
σ_y	upper yield stress
σ_{UTS}	ultimate tensile strength
$\varepsilon_{F\%}$	elongation at break
ε_{Fmm}	displacement at break
v_{corr}	corrosion rate
mm/y	millimetre per year, a unit of corrosion rate
MPa	megapascal, a unit of stress
bar(g)	bar gauge, a unit of gauge pressure, i.e. pressure in bars above ambient or atmospheric pressure
ppm	parts per million, a unit of very low concentrations
ppb	parts per billion, a unit of extremely low concentrations
mg/m^3(n)	milligram per cubic meter under standard conditions for temperature and pressure (0°C and 101,325 Pa), a unit of concentration
mol%	molar percentage, a unit of concentration
°C	degree Celsius, a unit of temperature

1 Introduction

1.1 Background

Network operators are currently exploring the possibility of making the supply of gas more sustainable and of extending the variety of gas sources that can be used. In this respect the use of the existing gas infrastructure, to which almost all customers in the Netherlands are connected, for the transport and distribution of gases originating from these alternative sources should be evaluated. This would allow the supply of sustainable gas to occur using the entire existing natural gas infrastructure (pipeline systems, appliances, industrial installations, etc.) in the most cost-effective manner.

The existing Dutch gas infrastructure has been designed for the transport and distribution of (pseudo) Groningen gas (G-gas). However, this situation will change in future. Natural gases from other sources, including biogas and SNG, must also be transported.
This rapidly expanding variety of gases should preferably be transported and distributed through the existing natural gas infrastructure, as (partial) replacement of this infrastructure would be extremely costly. This means that the network companies consider even partial degradation to be highly undesirable. Despite the fact that these gases generally have a composition that differs to that of the natural gas used to date, it is important that the distribution network does not suffer from increased problems with materials as a result of the transport of these gases.

Aside from the use of natural gases from other sources, the introduction of sustainable gases is likely to begin with upgraded biogases that have similar combustion characteristics to G-gas. For these gases, preliminary specifications have already been defined on the basis of the current distribution band for natural gas types in the Netherlands. Nevertheless, the effects of various components at different concentration levels in these gases (as compared to G-gas) on the integrity of the gas network are still not fully known.

In distinguishing between the various gases that may be injected into the gas network, a distinction can be made between the following three types of gas compositions (Table 4). See the literature review [1] and chapter 2.1 for the composition of G-gas and narrow band gas.

Table 4. Definition of G-gas, narrow band gas and wide band gas.

G-gas	Narrow band gas	Wide band gas
Groningen gas (used as reference gas)	Pseudo - Groningen gas, e.g. upgraded biogas to "green gas" quality	All other sustainable gases, e.g. raw biogases, partially upgraded sustainable gases, SNG and other natural gases (e.g. H-gas)

The present report focusses on the effects of the transport of narrow band gases on materials used in gas distribution systems. Two other reports consider the influence of wide band gases on materials [4] and the influence of sustainable gases on joints and connections [5], respectively. A literature review performed by Gasunie discusses the effects of the transport of wide band gases on materials used in gas transport systems [6,7].

1.2 Goal

The goal of this project is to answer the following principle research question:

Are the most important materials used in the Dutch gas distribution network resistant to narrow band gases?

The following sub-questions are relevant in this respect:

- a) What exactly are narrow band gases?
- b) What are the most important materials used in the Dutch gas distribution network?
- c) What are the critical (long-term) failure mechanisms for the most important materials in gaseous environments?
- d) Which of these long-term failure mechanisms are dependent on components present in narrow band gases?
- e) Will the use of certain narrow band gases result in unacceptable reductions in the lifespans of the various materials?

Sub questions a) to d) were answered in a literature review [1]. The experiments were aimed at providing an answer to sub-question e). This experimental work was intended to supply answers regarding the influence of certain components in narrow band gases, to give information about these effects under the practical circumstances of long-term exposure and to determine what the limiting concentrations should be.

It is important to note that the objective of these experiments was not to be exhaustive with respect to the components present in narrow band gases and the materials used in the Dutch gas distribution network. Therefore, the effects of various trace components are not investigated and it is emphasised that only the effects on most important materials are discussed.
The experimental work in this report focussed on gases with a possible negative effect. Gases that (are expected to) have no negative effect were not used (although there are some exceptions due to the experimental setup).
The effects of narrow band gases on the Dutch gas transport network have been investigated by Gasunie / DNV.GL and are part of the EDGaR project A5 [6,7].

1.3 Approach

The first phase of the project involved the study of relevant literature. This literature was evaluated with regard to sub-questions a) until e) listed in section 1.1. For some gas component/material combinations it was not possible to draw solid conclusions as to whether deleterious effects could be expected under certain conditions. In these cases it was proposed that additional experiments need to be performed [1].

Special test setups were designed to evaluate the influence of various gas components on the materials in question. The experimental setup is described in separate reports [2,3].

This final report presents the results of the experiments in combination with information from the literature, so as to give a complete picture of the influence of narrow band gases on the resistance of the most important materials used in the Dutch gas distribution network to narrow band gases.

1.4 Reading Guide

The above mentioned approach is further elaborated in chapter 2, in which a summary of the results of the literature review and a description of the experimental setup is given. Chapter 3 discusses the effects of narrow band gases on polymeric materials. Chapter 4 discusses the effects of narrow band gases on metallic materials.

In each section, the importance of a specific material in the Dutch gas distribution network is highlighted (more information can be found in [1]). Specific testing details are then given. Following this, the results of the experiments are discussed and compared with the information gathered from the literature. The section ends with a conclusion for the material in question, in which the results of the experiments are combined with the findings from the literature review to arrive at a final assessment of the expected resistance of the specific material to narrow band gases.

This report ends with overall conclusions in chapter 5 and recommendations for the distribution system operators (DSOs) in chapter 6.

2 Literature Review & Experimental Setup

This chapter explains the approach of the EDGaR research project "Effects of Narrow Band Gases on Materials", which was performed to evaluate the influence of narrow band gases on the Dutch gas distribution materials. The project consisted of three parts: a literature review [1], an experimental setup [2,3] and finally the overall conclusions resulting from the experiments.

2.1 Literature Review

The first step in the literature involved preparing an inventory of the materials used in Dutch gas distribution systems. This very long list was structured on the basis of importance and vulnerability by examining the quantities involved and the potential safety impact of the particular material. With respect to plastic piping systems, the most important pipe materials are PE and PVC. NBR is widely used in gas regulators, and is as such important. In metal piping systems, the principle materials are steel and copper. Aluminium is widely used as a shell material for regulators, and is as such important.

In the second step, the chemical gas compositions of the different types of sustainable and new gases were examined. The result was an extensive list of different components. These were subsequently categorised into groups based on their chemical composition. The first column in Table 5 shows the categorised chemical gas compositions.
A distinction can be made between G-gas and narrow band gas. G-gas, so-called Groningen gas, is natural gas from the large gas field near Slochteren in the Netherlands. This gas has a relatively high nitrogen content in comparison to other gas fields. Narrow band gases are defined as upgraded or downgraded gases that have the same physical properties (e.g. Wobbe index, Calorific value) as G-gas. The concentration limits for the composition of narrow band gases are based on the additional terms and conditions applicable to Dutch biomethane producers [8]. Differences in chemical composition between G-gas and narrow band gases are mainly found in the levels of CO_2 and H_2S. There are also differences in the concentrations of trace components such as halogens. Table 5 shows a comparison between the chemical composition of average G-gas and the limiting values of narrow band gases.

As the third step in the literature review, several scientific and technological literature sources were studied with regard to the differences between G-gas and narrow band gases in order to determine whether deteriorating influences could be expected at these concentration levels on the materials present in the gas distribution network. With regard to polymeric materials (PE, PVC and NBR), the survey focused primarily on the effect on environmental stress cracking (ESC). For metallic materials (steel, copper and aluminium), the survey focused on the occurrence of corrosion. ESC in polymeric materials and corrosion of metallic materials are considered to be the most important failure mechanisms where these materials are exposed to narrow band gases.
Table 6 shows the results of the literature study with regard to the influence of different gas components in narrow band gases on the most important gas distribution materials. The effect specified applies to the maximum concentrations found in narrow band gases in the literature examined. The colours indicate what is known about the effect of the gas components present in narrow band gases on the various materials.

Table 5. Concentration limitations of various components for narrow band gases and average concentration values of various components for G-gas.

Chemical compound/mix	**G-gas average [9]**	**Narrow band gases limiting values [8]**	**Unit**
Sulphur (total)	6.7	45	mg/m^3 (n)
Inorganically bound sulphur (H_2S)	0.4	5	ppm
Mercaptane	< 1.0	10	mg/m^3 (n)
Odorant value (*THT*)	17.7	> 10; nom 18; < 40	mg/m^3 (n)
Chlorine-containing compounds	< 0.1	50	mg/m^3 (n)
Fluorine-containing compounds	< 0.1	25	mg/m^3 (n)
Ammonia (NH_3)	< 0.1	4	ppm
Hydrogen chloride (*HCl*)	< 1.0	1	ppm
Hydrogen cyanide (*HCN*)	< 1.0	10	ppm
Carbon monoxide (*CO*)	< 100	10 000	ppm
Carbon dioxide (CO_2) in dry gas	0.9	10.3	mol%
Aromatic hydrocarbons	800 (max. value [10])	10 000	ppm
Benzene	-	500	ppm
Toluene	-	-	ppm
Oxygen (O_2) in dry gas	< 100	5 000	ppm
Hydrogen (H_2)	< 0.01	12	mol%
Methane (CH_4)	81.29	No limit	mol%
Nitrogen (N_2)	14.32	No limit	mol%
Ethane (C_2H_6)	2.87	-	mol%

Table 6. The effects of components present in narrow band gases on the most important gas distribution materials based on literature review.

	Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
PVC	probably none	none	probably none			unknown		probably none		unknown	possibly	none, unless liquid (impact resistance)		probably none	unknown
PE	probably none	none	probably none	none	probably none	unknown		probably none		unknown	none	none, unless liquid		none	
NBR	probably none				none	unknown		probably none		none		probably none, unless liquid		none	
Steel	with water: possibly		probably none						with H_2S and water: possibly	with water: possibly		probably none		with water: possibly	none
Cu	with water: possibly, depending on their mutual influence			probably none	with water: possibly	probably none			unknown		with water: possibly	probably none		with water: possibly	unknown
Al	unknown			probably none	none	probably none			unknown		with water: possibly	probably none		none	unknown

░	=	The effect is unknown, but is expected to be very small or non-existent.
🟩	=	This component within the concentrations of narrow band gases does not affect materials.
🟨	=	The effect is unknown.
🟧	=	Deleterious effects are expected under some conditions.

The literature survey was in some cases inconclusive. For the polymeric materials, these conditions are indicated with the light orange blocks. For the metallic materials, they can be found in the dark orange blocks. These orange blocks formed the starting point for further experimental research.

More detailed information about the literature review can be found in [1].

2.2 Experimental Setup

The literature survey demonstrated that the knowledge available at present is sometimes inconclusive. For polymeric materials in particular, little was known about the influence of gases containing fluorine or chlorine components, CO_2 or H_2. The effect of the combination of H_2S, O_2 and CO_2 at different concentration levels on metallic materials in an aqueous environment was also unknown. Lab experiments focussed on these so-called "white spots" were therefore initiated.

Two types of lab experiments were devised:

1. Experiment type 1: to determine whether a chemical component has any effect on a given material at the maximum occurring concentration level of this component in narrow band gases.
2. Experiment type 2: to determine the extent to which the material is affected by a given chemical component at different concentration levels of this component in narrow band gases.

Almost all experiments on the polymeric materials were of type 1, since nothing at all was known about the effect of the chemical components in question on these materials. In order to determine the effect on the polymeric materials, specially designed environmental stress cracking (ESC) experiments were set up. In these tests the material samples were exposed to the specified environmental and mechanical loading.
The experiments conducted on the metallic materials were mostly type 2 experiments. While it was known that the chemical components under consideration affect these metals, the extent to which they affect the corrosion rate at the concentration levels found in narrowband gases was not yet known. The concentration levels at which corrosion problems arise in an aqueous environment were therefore determined by means of specially designed corrosion experiments.

The gas pressures used in the Dutch gas distribution grid lie predominantly at 30 and 100 mbar(g) and 1, 4 and 8 bar(g). This fact, along with practical reasons, motivated the decision to perform the experiments at the gas pressures of around 30 mbar(g) and 8 bar(g). These two situations could lead to differences as a result of the fact that at higher pressures the same concentration leads to a higher partial pressure and thus a higher absolute concentration. This could increase the effect of the chemical component on the material.

2.2.1 Testing the Effect of Narrow Band Gases on Polymeric Materials

The effect of sustainable gases on polymeric materials was tested by means of environmental stress cracking (ESC) experiments. Many different ESC methods have been described in literature and have been standardised [11]. All such methods are based on the same principle: a stress is applied to the material well below its yield strength while the material is exposed to the chemical component under consideration. Specially designed environmental stress cracking methods, in which samples are taken from pipes and fittings, have been devised for this investigation: dumbbells under constant tensile stress (Figure 1), rings in a U-clamp under constant strain (Figure 2) and NBR rings over oversized pipes under constant strain (Figure 3). In designing the experimental setups, special attention was paid to obtaining reproducible and reliable results (e.g. maintaining gas concentrations at a constant level during exposure and correcting the constant load by the cross-sectional area of the tested samples).

Table 7 gives an overview of all the applicable types of polymeric materials and the applied ESC methods. The PE and PVC samples were taken directly from pipes. For old materials (e.g. HDPE 50 and PVC-U) this necessitated the excavation of such pipes from the Dutch gas distribution network. The exception to this was MDPE 80 which was sourced directly from the stock of materials at Kiwa. This can also be seen in the production year of these materials. For other PE, PVC and NBR materials, newly fabricated materials were used. These materials were fabricated in 2012. The NBR materials were taken from the sealing rings of new PVC couplers.

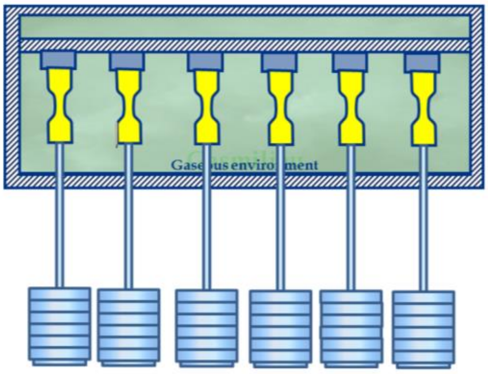

Figure 1. Schematic view of the constant load equipment for testing PE and PVC samples.

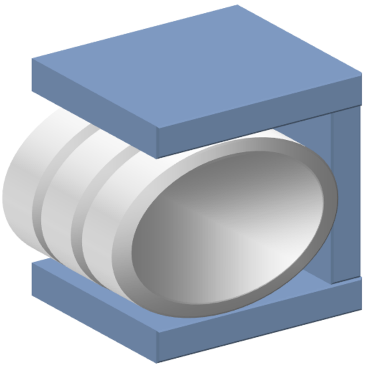

Figure 2. Principle of a U-clamp test on PE and POM rings.

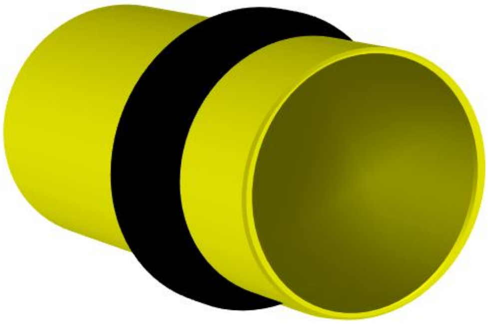

Figure 3. Setup used to expose stressed NBR rings to a particular gaseous environment using an oversized pipe.

Table 7. Used types of materials, their condition and the ESC methods employed.

Polymeric materials		**Condition of material**	**Internal Kiwa code**	**Production year**	**ESC methods**	**Applied stress / strain**
PE	HDPE50	Old and used	PE 2012-058	1973	Constant load	4 MPa
					U-clamp	1.9%
	MDPE80	Old and not used	PE 3	1990	Constant load	8 MPa
					U-clamp	1.9%
	HDPE100	New	PE 2012-122	2012	Constant load	10 MPa
					U-clamp	1.9%
PVC	PVC-U – type 1	Old and used	PVC 2004-001	1973	Constant load	20 MPa
	PVC-U – type 2	Old and used	PVC 2012-062	1960	Constant load	20 MPa
	PVC-HI – type 1	New	PVC 2012-083	2012	Constant load	20 MPa
	PVC-HI – type 2	New	PVC 2012-084	2012	Constant load	20 MPa
Rubber	NBR	New	OV 2012-071	2012	Ring over pipe	Undefined

Table 8. Overview of polymeric materials and the related investigated gaseous environments, including an explanation of these concentration levels of the gaseous environments.

Polymeric materials	**Gaseous environments**	**Test pressure (bar(g))**	**Explanation of the concentration levels (see also Table 5)**
PE, PVC, NBR	100 mol% N_2	0.03	Nitrogen was chosen as a matrix gas and 100 mol% N_2 is therefore used for reference purposes.
NBR	5 ppm H_2S	0.03	The maximum allowable concentration of H_2S in narrow band gases is 5 ppm.
PE, PVC, NBR	75 mg/m^3 DCM	0.03	The maximum allowable concentration of halogen-containing chemicals in narrow band gases is 75 mg/m^3.

Table 8 shows the polymeric materials and the gaseous environments used. The chemical compositions of the gaseous environments are based on the "white spots" identified in the literature survey. The concentration levels of these gaseous environments were based on the values given for the maximum concentrations found in narrow band gases. An explanation of the concentration levels is given below and also shown in Table 8.

Of all the chlorine-containing and fluorine containing components that may occur in the gases under consideration, it is known that dichloromethane (DCM) is one of the most aggressive halogenated organics as regards its effect on PVC. It was therefore decided to use DCM as a model gas for all halogen-containing materials. The highest concentration of chlorine-containing components found is 50 mg/m^3 in narrow band gases. For fluorine containing components, this figure is 25 mg/m^3. It was therefore decided to use dichloromethane (DCM) as a model gas for halogen-containing gas at a concentration of 75 mg/m^3.

The effects of CO and HCN were not tested due to their high toxicity to humans. It is therefore questionable whether the maximum concentration permitted will be determined by their effect on the various materials rather than by their risk to human health. Similar to H_2S, 100 times the MAC value could be considered. This would mean for HCN, which has a MAC value of 10 ppm, a maximum concentration of 1000 ppm is ‘safe’. For CO, with a MAC value of 25 ppm, this would lead to a maximum concentration of 2500 ppm. Nevertheless, it was not considered safe to evaluate the influence of these gases on the (polymeric) materials in the laboratory.

After the period of exposure the environmental stress cracking samples were subjected to non-destructive (visual changes) and destructive testing. This will be discussed in the separate sections covering the individual materials.
Some samples were not exposed to stress and were used to determine mass or dimensional changes of the polymeric polymeric materials.

More detailed information about the experimental setup for testing the influence of narrow band gases on polymer piping systems can be found in [2] and [3].

2.2.2 Testing the Effect of Narrow Band Gases on Metallic Materials

Testing the effect of narrow band gases on metallic materials was mainly aimed at determining the influence on corrosion. The effect on the corrosion rate was determined for different concentration levels of the tested components (Type 2 test).
The steel and copper samples used in the experiments were obtained from strips taken from plates that have the same metallic structure as pipes. The aluminium samples were taken from pressure regulators.
For the occurrence of corrosion in metallic materials, the presence of water is required. The samples were therefore partially submerged in water while gas was flushed through an autoclave. The temperature around the autoclave was kept constant at 25 °C by means of a surrounding water bath. Figure 4 shows an illustration of the experimental setup.

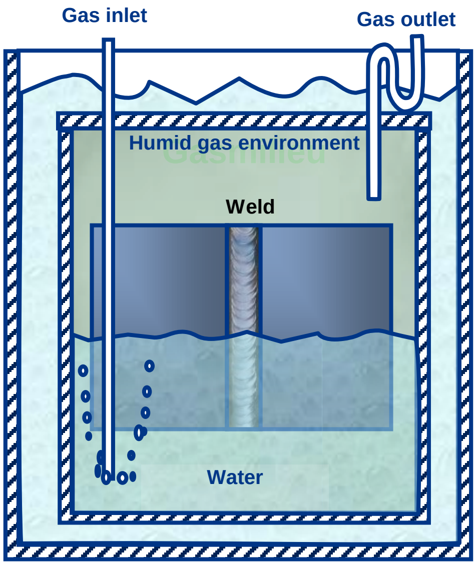

Figure 4. Experimental setup (autoclave) for corrosion testing of metals.

Table 9 gives an overview of the metallic materials tested, the used gaseous environments and the test pressures. The concentration levels were based on the "white spots" and the limits derived from the literature survey [1]. Due to the large overlap/interaction with the investigation of the influence of wide band gases [4] on metals the concentration levels of these gases are also given. The matrix gas was N_2 in all cases.

Table 9. Metallic materials tested, used gaseous environments and test pressures.

Material	**Gas number**	**Gas conditions**				**Pressure (bar(g))**	**Explanation of the concentration levels (see also Table 5 and [4])**
		Relative Humidity (%)	**CO_2 (mol%)**	**O_2 (mol%)**	**H_2S (ppm)**		
steel, copper & aluminium	1	100	50	0.01	160	0.03	Worst case wide band gas with low O_2 level, low pressure
		100	50	0.01	160	8.0	Worst case wide band gas with low O_2 level, high pressure
		50	50	0.01	160	0.03	Worst case wide band gas with low O_2 level and 50% R.H.
	2	100	50	0	160	0.03	Worst case biogas with without O_2
	3	100	0	3	160	0.03	H_2S worst case wide band gas without CO_2
	4	100	50	3	160	0.03	Worst case biogas with normal O_2 level
	5	100	50	3	0	0.03	CO_2 worst case wide band gas without H_2S
	6	100	0	0.5	34	0.03	O_2 en H_2S inside narrow band gas limits
	7	100	10	0.5	34	0.03	CO_2, O_2 en H_2S inside narrow band gas limits
	8	100	10	0.1	34	0.03	Effects of low O_2 levels are unknown, therefore this concentration was chosen
	9	100	10	0.01	34	0.03	Effects of low O_2 levels are unknown, therefore this extremely low concentration was chosen

It was known that most of the chemical components listed may have an effect on the metallic materials (see Table 6). However, the concentration levels that must be present before negative effects arise and in particular the interactions between the various gas components (especially the effect of O_2) that may increase or decrease the corrosion rate were still unknown. The gas conditions and quantities were determined using the methodology of Design of Experiments (DoE) [12]. Table 9 also includes an explanation of the specified concentration levels.

During the period of exposure the corrosion rate was followed by measuring the material thickness and mass at set intervals. The effect of each gaseous concentration on the corrosion rate was calculated and trend lines were constructed to determine if failure before 50 years of usage is expected.
Possible negative effects due to transport of corrosion products to filters or valves were not considered in this research.

More detailed information about the experimental setup for testing the influence of narrow band gases on metal piping systems can be found in [2] and [3].

2.3 Implementation of the Lab Experiments

The tests described in section 2.2 required specially designed test rigs, for both the plastic and metal piping systems. Due to differences in the test environments, the test rigs for determining the effects of narrow band gases on plastic and metal piping systems differed. In both cases the test rigs needed to be able to hold a large number of samples and required special safety measures due to the severe toxicity of some of the gases (specially H_2S) and the elevated pressures of up to 8 bar(g). The concentration levels of the chemical components were maintained at very constant levels throughout the test period.

Figure 5 shows some PE and PVC dumbbell samples clamped in their holders before the constant load experiments were started. Figure 6 shows PE ring samples in U-clamps. Figure 7 and Figure 8 show details of the test rig for the polymeric samples under constant load (PE and PVC) and constant strain (NBR). Figure 9 and Figure 10 show the complete 30 mbar(g) and 8 bar(g) test rigs.

Figure 5. PE and PVC dumbbell samples clamped for ESC experiments.

Figure 6. PE ring samples in U-clamps.

Figure 7. Constant load experiments on PVC dumbbell samples.

Figure 8. Constant load experiments on PE dumbbell samples and constant strain experiments on NBR samples that have been placed over oversized pipes.

Figure 9. Full-scale test rig for 30 mbar(g). Inside the test rigs, the materials are exposed to various gases.

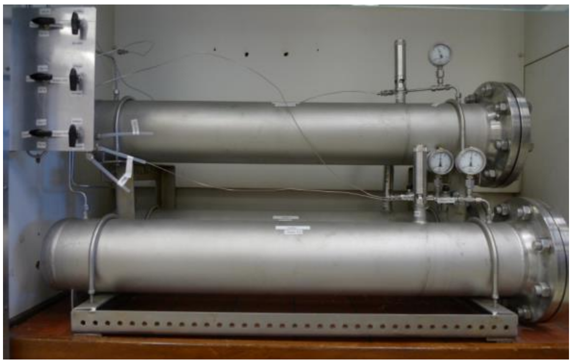

Figure 10. Full-scale test rig for 8 bar(g). Inside the test rigs, the materials are exposed to various gases.

To prevent desorption of the various gases from the polymeric materials, they were tested immediately after they had been released from exposure. The polymeric samples were therefore exposed to the gases for different periods of time, because it was not possible to test all samples simultaneously. Table 10 gives an overview of the exposure times of the materials for the various gases. It can be seen that the materials were exposed to the gases for an average duration of about 600 days.

Table 10. Exposure times and pressures of the samples for various gases.

Polymeric materials	**Gaseous environments**	**Pressure bar(g)**	**Exposure time**		
			Start date	**End date**	**Total (days)**
PE, PVC, NBR	100 mol% N_2	0.03	18-1-2013	22-9-2014	612
NBR	5 ppm H_2S	0.03	7-2-2013	9-10-2014	609
PE, PVC, NBR	75 mg/m^3 DCM	0.03	22-1-2013	8-9-2014	594

Figure 11 shows the metallic materials in a special PTFE holder used to place them in the test rig, while Figure 12 shows the entire test rig for the corrosion experiments. Figure 13 shows an impression of the experimental setup used during the exposure period of 600 days.

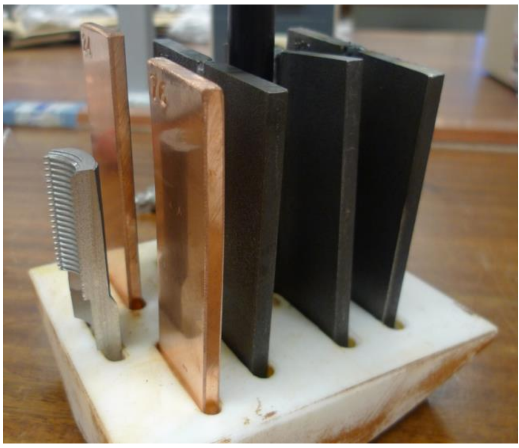

Figure 11. Metallic samples in a special PTFE holder for the corrosion test.

Figure 12. Complete setup for the corrosion tests.

Figure 13. Impression of the experimental setup (right photo: EDGaR/Jan Buwalda).

For each gas composition, several exposure durations (1, 3, 6, 9 and 19 months) were used to determine the development of corrosion damage to the exposed materials with time. For all gas compositions, the experiments were conducted at a slight overpressure of approx. 30 mbar at a temperature of 25ºC. Gas was continuously bubbled through the water in the test rig at a gas flow rate of 1 l/h continuously. The effects of the gas components were thus tested as well in a liquid environment as in a humid gas environment (100% relative humidity). For gas number 1 (see Table 9), the materials were additionally exposed to a relative humidity of 50% and at an overpressure of 8 bar(g). During the experiments gas flow rate, test temperature, water level, water acidity (pH) and gas composition at the outlet were tested on a regular basis in order to monitor the experiments.

The only noteworthy deviation from the setup is the actual composition of the test gas as measured at the gas outlet of the corrosion cells. Gas number 2 was intended to contain <5 ppm oxygen, a figure that was also certified by the gas supplier. However, the actual O_2 concentration at the outlet was ~30 ppm. It is unknown whether the oxygen was introduced at the gas sampling point or elsewhere in the setup.

2.4 Implementation of Field Experiments

In addition to the laboratory tests, field experiments were also performed. The purpose of these tests was to determine whether narrow band gases have any adverse effects that had not previously been foreseen from tests at various gaseous environments in the laboratory. For the field experiments, two rigs were inserted into the Dutch distribution grid; one was installed directly after a biomethane feed (meaning narrow band quality, see Figure 14), whereas the other was installed in a pipeline carrying G-gas quality only (Figure 15). The G-gas test rig was installed for reference purposes.

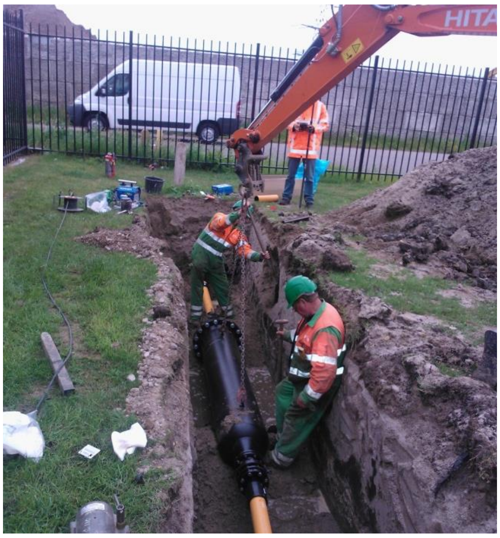

Figure 14. Test rig under biomethane conditions (narrow band gases).

Figure 15. Test rig under G-gas conditions.

The test rigs were filled with the same material types as used in the laboratory experiments. However, the grades of these material types were different from that used in the laboratory experiments. This means that comparison between laboratory and field experiments was not straightforward. Figure 16 gives an overview of the different materials used in the test rigs for exposure to G-gas and narrow band gas for a period of two years. In the test rigs several materials were under tension.

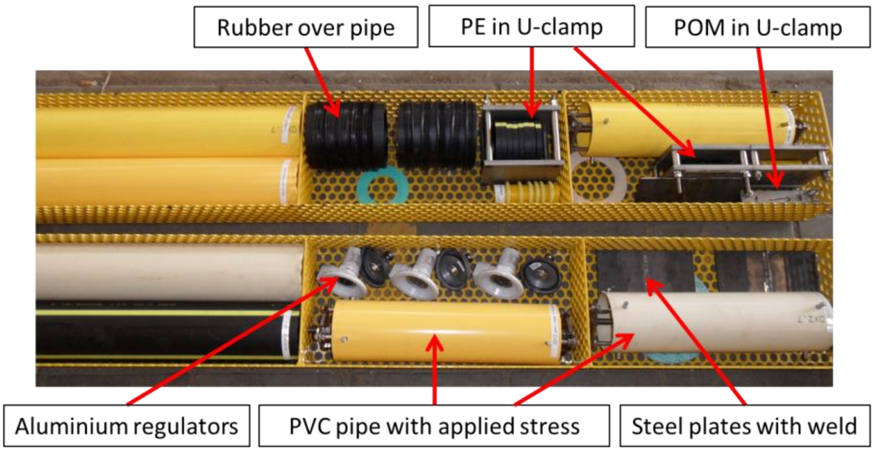

Figure 16. An overview of the materials placed in the test rigs for field exposure to G-gas and narrow band gas for a period of two years.

Where applicable, the materials were exposed to G-gas and narrow band gases under the same applied stresses as mentioned in the lab conditions. Table 11 gives an overview of the sample design at the applied stress or strain, where applicable.

After an exposure period of two years (25 months: narrow band gases; 26 months: G-gas) the materials were non-destructively and destructively evaluated in a similar manner to the lab samples to detect any degradation in quality.

Table 11. Overview of materials and their applied stress/strain in the test rigs for field exposure.

Materials	Sample design	Applied stress/strain
HDPE50 MDPE80 HDPE100	Pipe	None
	Ring in U-clamp	Strain at 1.9%
PVC-U – type 3 PVC-CPE PVC-A	Pipe	None
	Pipe under constant strain	Starting stress at 20 MPa
hPOM	Ring in U-clamp	Strain at 3.1%
SBR NBR	Ring over pipe	Stress (undefined)
Steel	Plate	No
Steel with weld	Plate with GMAW weld	Yes, due to welding, stress is present at the Heat Affected Zone
Copper	Pipe	No
Copper & brass	Pipe and brass fitting	Yes, with different torques
Aluminium	Regulator	No

2.5 Results

The overall results of the literature review and the experiments (lab and field) for each material are given after every section of the material in question.

3 Effects on Polymeric Materials

3.1 Polyvinyl Chloride (PVC)

3.1.1 *The Importance of PVC in the Dutch Gas Distribution Network*

In the Netherlands, the distribution of G-gas takes place through a grid containing approximately 77 600 km of PVC pipes, These which make up over 60% of the Dutch distribution grid. PVC-U pipes account for 20 800 km of this total, while PVC-HI pipes account for 56 800 km [13]. Most of the PVC-U pipes were installed in the 1960s when the G-gas field at Slochteren in the north of the Netherlands began production. In the 1970s, a transition towards the installation of more PVC-HI began. In 1974 the Dutch test specification for PVC-U pipes in gas distribution networks were withdrawn [14]. PVC-HI is still installed today for the distribution of gas.

3.1.2 *Test Method*

The experimental setup as described in chapter 2 was used to expose PVC materials to various components in narrow band gases over a period of 600 days.

The following four tests were also performed on PVC directly after exposure:

- Mass change. The mass of PVC specimens not subject to stress was compared before and after exposure to the various components in wide band gases.
- Dimensional change. The dimensions of PVC specimens not subject to stress were compared before and after exposure to the various components in wide band gases.
- Visual and microscopic investigation. PVC dumbbell specimens subject to a tension stress under constant load were examined for crazes caused by environmental stress cracking (ESC).
- Tensile impact experiments. PVC dumbbell specimens subject to a tension stress under constant load were tested using tensile impact experiments to determine the brittle-ductile transition temperature (T_{BD}) as a measure for embrittlement.

3.1.3 *The Influence of Narrow Band Gases on PVC*

3.1.3.1 *General*

To get an idea about the scatter in the results of the experiments the results of all specimens (including the ones exposed to wide band gases) are considered in this section.

Of all the test specimens (288) exposed to a constant load of 20MPa and exposed at the same time to various gaseous environments, none of the specimens exposed to narrow band concentrations broke. Only two broke during the 600 days of testing, which were exposed to wide band concentrations.
After 600 days of exposure, crazes were found in all PVC-U - gas combinations, including the reference samples that had been exposed to nitrogen. It is likely that the crazes occurred due to the high stress and did not arise as a result of exposure to the various gases. See appendix I for extra information about this initial craze formation. For PVC-U, the craze-forming threshold was reached within the experiment period of 600 days with 20 MPa, whereas the threshold for PVC-HI was apparently not reached. Although, this is in contradiction with earlier found literature [1] where a threshold value of 20 MPa for both PVC-U and PVC-HI was found [15,16], other literature sources indicate that a stress of 20 MPa is high enough for craze formation in PVC-U [17,18].

For the tensile impact experiments carried out after exposure, the same test specimens were used as for the constant load experiments. If a significant deterioration of the materials occurs after applying a constant load of 20 MPa for a period of 600 days in combination with the various gases, then this should become visible as a shift in the brittle-ductile transition temperature (T_{BD}) to higher temperatures (see also appendix II). This T_{BD} is the temperature at which the material behaviour under impact loading changes from brittle to ductile. PVC is an inhomogeneous material by nature and T_{BD} is more a temperature range than one single transition temperature. Therefore, 30 specimens would be preferred to obtain an accurate value for the T_{BD}. However, due to cost considerations 12 specimens per PVC type were used in the experiments. This introduces an extra uncertainty and thus an increase in the standard deviation in the determination of T_{BD}. To address this for PVC-U and PVC-HI an estimation of the standard deviation (σ) in the determination of T_{BD} was made for both 12 and 30 specimens not subject to stress (see Table 12 and appendix III).

Table 12. Estimated standard deviation in T_{BD} for 12 or 30 specimens for both PVC-U and PVC-HI.

	Estimated standard deviation (σ) for 12 specimens	**Estimated standard deviation (σ) for 30 specimens**
PVC-U	±6.6 °C	±3.5°C
PVC-HI	±5.4 °C	±2.6°C

This relative large standard deviation in T_{BD} is applicable for each gas component/material combination, including exposure to N_2. For example an effect of a certain gas may seem to be present when the T_{BD} of samples exposed to that gas is compared to the T_{BD} of samples exposed to N_2, while it is only a consequence of the uncertainty in T_{BD} of the samples exposed to N_2.

To determine the effect of the various gases on PVC more accurately, the average value of all samples for all gases was determined. This average is a better reference, since more samples are used. The T_{BD} of the samples exposed to a certain gas were then compared to the average value instead of the T_{BD} of N_2.
For the four different PVC materials (see Table 7), T_{BD} for each gas mixture is plotted in Figure 17 to Figure 20. The average obtained for all the gases is indicated in these graphs with a dashed line.
For PVC-U type 2 and PVC-A, T_{BD} was also determined separately using 76 specimens without applying stress or exposure to a gaseous environment (see appendix III). From the graphs it can be concluded that T_{BD} for the 76 specimens is similar to the average T_{BD} determined for the samples exposed to the various gases. This validates the assumption that the average T_{BD} of all samples for all gases is a better reference than the T_{BD} of N_2 alone. It is assumed that this is also valid for PVC-U type 1 and PVC-CPE, although no experiments with 76 specimens were performed for these materials. The average value was used for further analysis.

From the graphs it can be seen that PVC-U type 2 shows the largest scatter. This is an old pipe from the 1960s. It was specifically chosen for this research as no “old recipe” PVC-U pipe is produced today. Extrusion of PVC-U types was not controlled so well at that time, which may explain the rather high inhomogeneity of the pipe materials, and thus the rather high scatter in the T_{BD} values.

A detailed explanation of the effects of the various gases on PVC is given in the next sections.

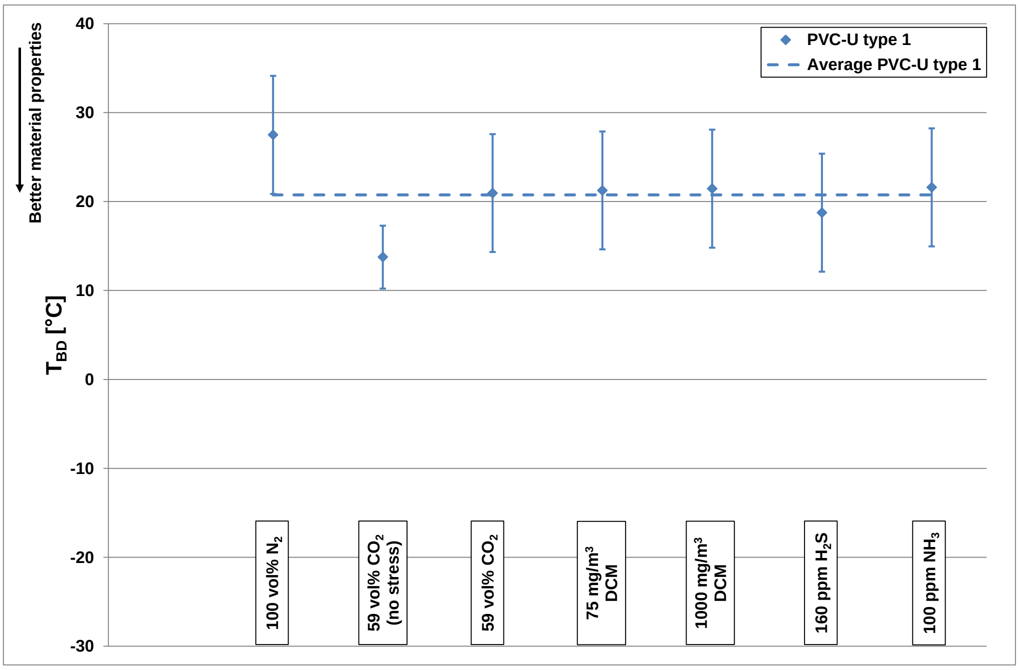

Figure 17. T_{BD} of PVC-U type 1 for the different gaseous environments.

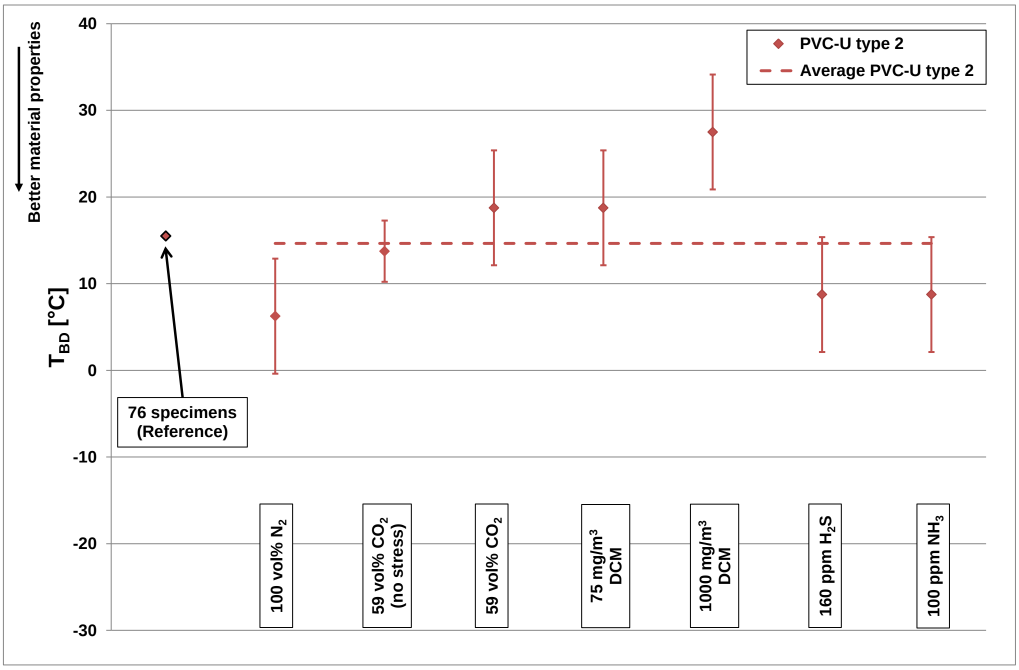

Figure 18. T_{BD} of PVC-U type 2 for the different gaseous environments.

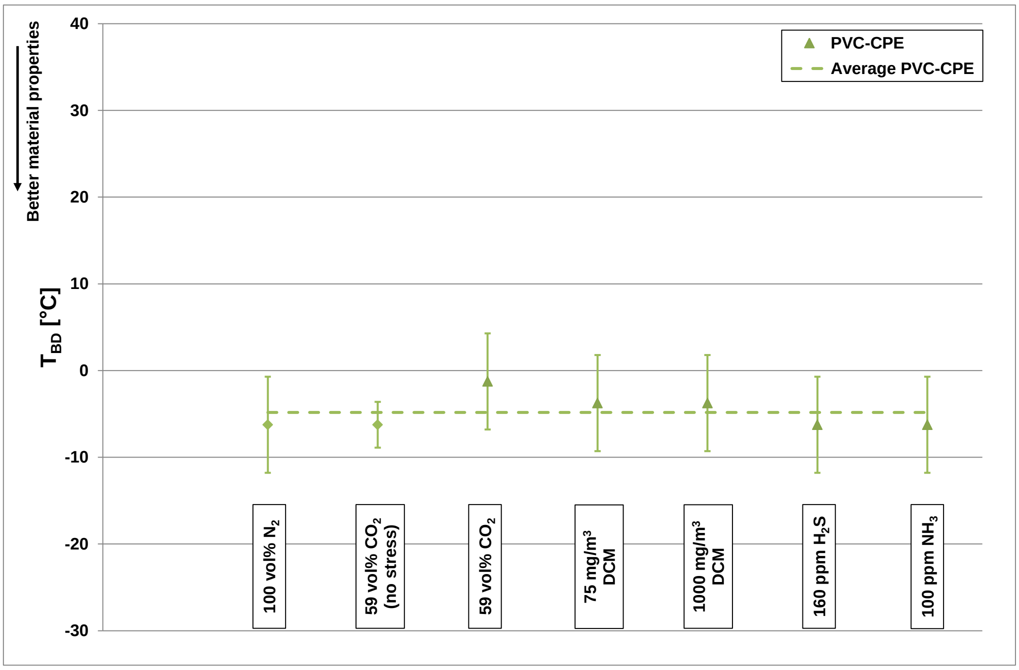

Figure 19. T_{BD} of PVC-CPE for the different gaseous environments.

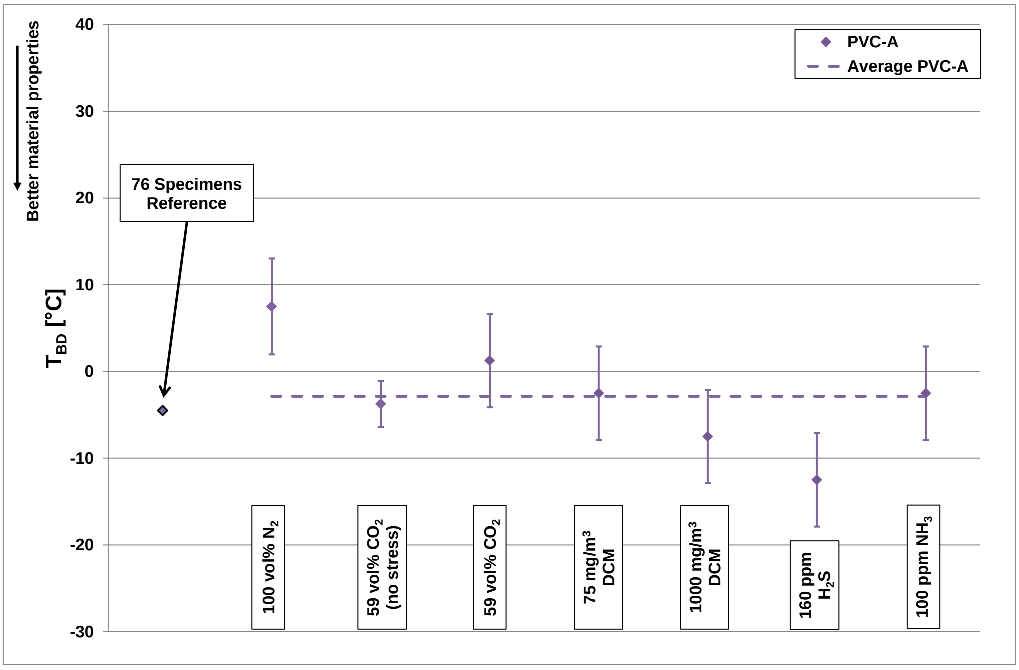

Figure 20. T_{BD} of PVC-A for the different gaseous environments.

3.1.3.2 Effects of Hydrocarbons

On the basis of the studied literature [1] it was concluded that ESC will only occur if a condensate (hydrocarbons in liquid form) is present in the PVC gas pipe for a longer period of time in combination with a very high stress (point load or line load). The impact resistance would also decrease slightly (embrittlement) under these conditions. The presence of liquid hydrocarbons should therefore be avoided. No additional experiments were performed to confirm this.

3.1.3.3 Effects of Carbon Dioxide

The studied literature [1,19] confirmed that effects for carbon dioxide could not be ruled out. The literature indicated that CO_2 may have a plasticizing effect, which could lead to more rapid craze formation. The impact strength may also be affected.

However, no indication of ESC was registered in any of the four PVC materials during the experiment. None of the specimens broke after applying 20 MPa and 59 mol% CO_2 for a period of 600 days. Microscopic research revealed crazes, but it was confirmed that these had formed at the beginning of the ESC test under the influence of the 20 MPa stress only. There were no indications for craze growth under the influence of CO_2 present. See appendix I for extra information about this initial craze formation.

Furthermore, no dimensional or mass change was measured for any of the four PVC materials during the entire test period. This indicates that no significant absorption or depletion occurred (see appendix IV.1).

The T_{BD} for the four materials also showed no significant change, as can be seen in Figure 17 to Figure 20. All results are well within 1 standard deviation. From this it can be concluded that exposure to a gaseous mixture having 59 mol% CO_2 in combination with significant stress does not lead to the deterioration of PVC-U and PVC-HI materials.

Narrow band gases can contain up to 10.3 mol% CO_2. It can therefore be concluded that CO_2, within the range of narrow band gases does not deteriorate PVC materials.

3.1.3.4 Effects of Hydrogen

The studied literature [1] confirmed that the effect of hydrogen is unknown. PVC materials were tested in the field at concentrations of up to 20 mol% H_2 [20]. No effect for H_2 at up to this concentration level was measured in PVC materials.
Narrow band gases can contain up to 12 mol% H_2. It can therefore be concluded that H_2, within the range of narrow band gases does not deteriorate PVC materials.

3.1.3.5 Effects of Hydrogen Sulphide

On the basis of the studied literature [1] it was concluded that PVC pipes are relatively resistant to H_2S at low concentrations (≤ 5 ppm).
The experiments also tested the impact on PVC pipes of exposure to 160 ppm H_2S. This was part of the research on the effects of wide band gases [4]. From these experiments it was concluded that negative effects are not expected in exposure up to a concentration of 160 ppm H_2S.

3.1.3.6 Effects of Chlorine-Containing and Fluorine-Containing Components

It is known from the literature [1] that some organic chlorides can attack PVC. For example, dichloromethane is specifically used for attacking poorly gelled PVC in the so-called dichloromethane test (used to determine the degree of gelation of PVC). Organic fluorides may have the same effect on PVC as organic chlorides. For the wide band experiments it was decided to use dichloromethane (DCM) as a model gas for halogen-containing gases at a maximum concentration of 75 mg/m^3, which is within the limits of narrow band gases (see chapter 2).

The T_{BD} for the four materials showed no significant change, as can be seen in Figure 17 to Figure 20. All results are well within 1 standard deviation. From this it can be concluded that exposure to a gaseous mixture having 75 mg/m^3 DCM in combination with significant stress does not lead to the deterioration of PVC-U and PVC-HI materials.

3.1.3.7 *Effects of Other Components*

Practically no literature about the effects of other components present in wide band gases was found [1]. Extra information about the influence of O_2 was however found. This revealed that neither PVC-U nor PVC-HI are degraded by O_2 at room temperature [21].

Next to laboratory tests also field tests were performed. In these field tests the influence of air, G-gas and narrow band gases on PVC-U type 3, PVC-CPE and PVC-A* was tested. The T_{BD} of the different materials under the various gaseous environments are given in Figure 21 to Figure 23. It can be concluded from the figures that not any significant influence of any of the gases on any of the tested PVC materials is present.

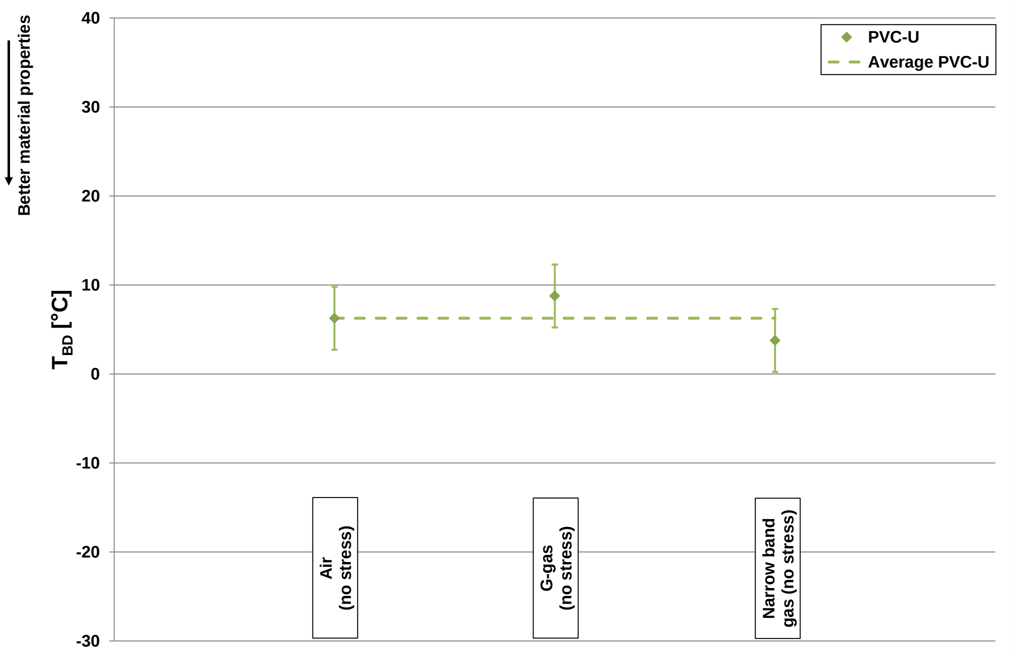

Figure 21. T_{BD} of PVC-U type 3 for the different gaseous environments in the field test.

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* The PVC-U, PVC-CPE and PVC-A pipes used in the field test were of another production batch than the PVC-U, PVC-CPE and PVC-A pipes used in the laboratory tests. The T_{BD} is therefore not the same for both batches.
The T_{BD} of PVC-U type 3 is lower than the T_{BD} of PVC-U type 1 and 2. This is probably a consequence of improved production methods (type 3 was produced in 2011, while type 1 and 2 were produced in 1973 and 1960 respectively).

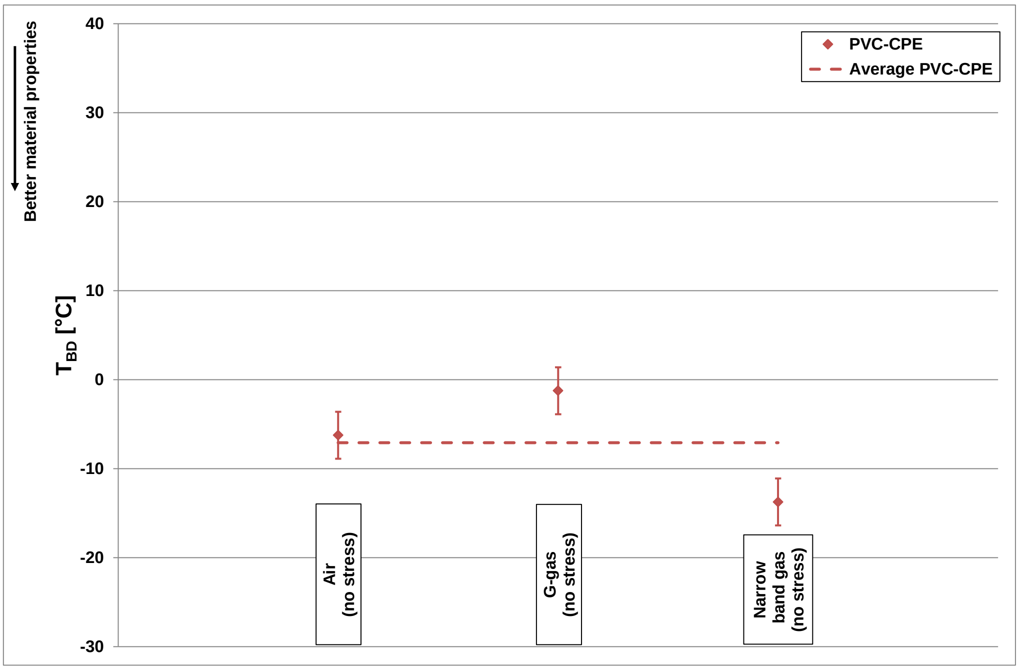


Figure 22. T_{BD} of PVC-CPE for the different gaseous environments in the field test.

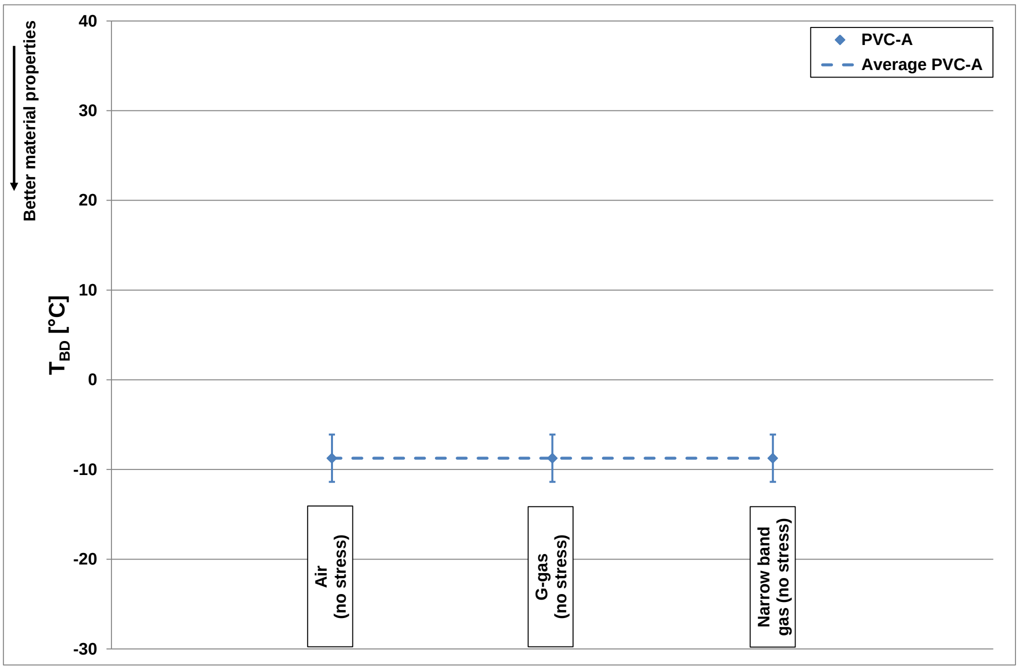


Figure 23. T_{BD} of PVC-A for the different gaseous environments in the field test.

3.1.4 Conclusions

The laboratory experiments and literature led to the conclusion that no deleterious effects on PVC-U and PVC-HI materials in narrow band concentrations were found for H_2S and sulphur-containing components, ammonia, halogen-containing organic components, CO_2 and O_2. Field tests furthermore revealed that H_2 has no effect on PVC materials. No negative effects on material properties of PVC were found for (aromatic) hydrocarbons in gaseous form either. However, liquid aromatic hydrocarbons (e.g. BTX and terpenes) will have a negative effect on the mechanical properties of PVC.

Since the concentrations of HCl and HCN in wide band gases are low, a negative effect is unlikely. The effect of mercaptans and odorant is probably non-existent as can be seen from the fact that the current concentrations of these components in the distribution grid does not cause any problems. Finally, the effect of CO has not been investigated (for safety reasons) and remains unknown.

These conclusions are summarised in Table 13 below:

Table 13. The effect of various components present in narrow band gases on PVC. Most components will have no deleterious effect (green), while for others or little or no deleterious effect is expected (light green). The effect of CO is unknown (light orange).

Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid (impact resistance)		none	

3.2 Polyethylene (PE)

3.2.1 The Importance of PE in the Dutch Gas Distribution Network

Polyethylene (PE) is one the most commonly used plastic pipe materials. The Dutch distribution network contains more than 20 000 km of PE mains [13] (see also Table 14). In addition, PE is one of the most important pipe materials in use in service lines. There are several different types of PE. These are distinguished from one another on the basis of their generation. First generation PE, also referred to as HDPE 50 or HDPE 63, was installed between 1968 and 1978. Second generation PE, also referred to as MDPE 80 or HDPE 80, has been produced since 1975 and it is still in production. The third generation (MDPE 80 or HDPE 100) has been available since 1990 and is currently the most commonly installed PE material.

Table 14. The importance of PE in the Dutch gas distribution network.

Material	**Length (km)**	**Period of installation (year)**	**MOP* (bar)**	**Material-standard**
1st generation PE (HDPE 50 or HDPE 63)	*5 107*	1968 - 1978	4 §	-
2nd generation PE (MDPE 80 or HDPE 80)	*14 422*	1975 to present	4 §	[22]
3rd generation PE (MDPE 80 or HDPE 100)		1990 to present	8 §	
Total	19 529			

* MOP = maximum operating pressure

§ *Value may be lower. This is dependent upon the SDR (Standard Dimensional Ratio), the type of PE (PE80 or PE100) and the part of the distribution system in question.*

3.2.1 *Test methods*

The experimental setup as described in chapter 2 was used to expose PE materials to various components in wide band gases for a period of 600 days.

The following five tests were also performed on PE directly after exposure:

- Mass change. The mass of PE dumbbell specimens not subject to stress was compared before and after exposure to the various components in wide band gases.
- Dimensional changes. The dimensions of PE dumbbell specimens and rings not subject to stress were compared before and after exposure to the various components in wide band gases.
- Upper yield stress σ_y. PE dumbbell specimens and rings subject to a stress were tested using tensile experiments in order to determine the upper yield stress.
- Elongation at break $\varepsilon_{F\%}$. PE dumbbell specimens subject to a stress were tested using tensile experiments in order to determine the elongation at break.
- Displacement at break ε_{Fmm}. PE rings subject to a stress were tested using tensile experiments in order to determine the displacement at break.

Tensile testing on dumbbells was carried out in accordance with ISO 527-4 [23]. Tensile testing on rings was carried out in accordance with ISO 8496 [24].

For each test, five dumbbells and six rings were tested under each condition. For the statistical analysis, the average value of the quintuple or sextuple was used. When two groups were compared, a student t-test (95% confidence level) was used [25].

3.2.2 *The Influence of Narrow Band Gases on PE*

3.2.2.1 *Effects of Hydrocarbons*

The studied literature [1] led to the conclusion that no deleterious effect could be expected for hydrocarbons unless these hydrocarbons were in the liquid phase (e.g. terpenes). The upper yield stress of PE materials will be lowered if the PE materials remain in contact with liquid hydrocarbons (e.g. terpenes) for several months. Research performed at Kiwa Technology has proven that the displacement at break will not change. The formation of liquid hydrocarbons should nevertheless be avoided in narrow band gases. No additional experiments were performed to confirm this.

3.2.2.2 *Effects of Oxygen, Carbon Dioxide and Nitrogen*

The studied literature [1] revealed that no deleterious effects were expected for O_2, CO_2 or N_2. No additional experiments were therefore performed with these components in the range of concentrations present in narrow band gases.

3.2.2.3 *Effects of Hydrogen*

It was concluded on the basis of the studied literature [1] that no deleterious effect were expected H_2. No additional experiments were therefore performed with these components in the range of concentrations present in narrow band gases.

3.2.2.4 *Effects of Hydrogen Sulphide*

It was concluded on the basis of the studied literature [1] that PE pipes are relatively resistant to H_2S at low concentrations (≤ 5 ppm). The impact of 160 ppm H_2S of PE pipes was also tested. This was part of the research on the effects of wide band gases [4]. In these experiments it was found that no negative effect were observed for PE materials exposed to 160 ppm H_2S.

3.2.2.5 *Effects of Chlorine-Containing and Fluorine-Containing Components*

The studied literature [1] indicated that deleterious effects on PE for halogen-containing components in wide band gases could not be ruled out. Therefore additional experiments were performed.

After 600 days of exposure, no noteworthy mass or dimensional changes in the PE materials were observed (see appendix IV.2). This indicates that no significant absorption or depletion occurred.

Furthermore, there was no statistically significant difference between the mechanical characteristics (upper yield stress (σ_y) and elongation at break ($\varepsilon_{F\%}$)) of the samples exposed to 75 mg/m^3 DCM and the reference samples exposed to nitrogen at 30 mbar(g). This was the case for all the investigated PE materials (HDPE 50, MDPE 80 and HDPE 100).
The results of the comparison is given in Figure 24 (upper yield stress) and Figure 25 (elongation at break). It is therefore concluded that the maximum concentration of halogen-containing components present in narrow band gases (= 75 mg/m^3) combined with a significant stress does not deteriorate PE materials.

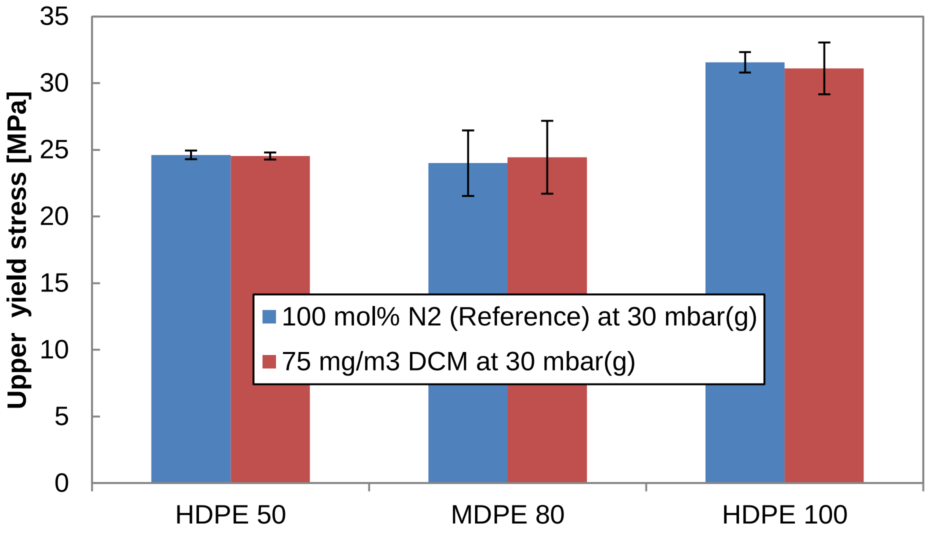


Figure 24. Upper yield stress of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N_2 (reference).

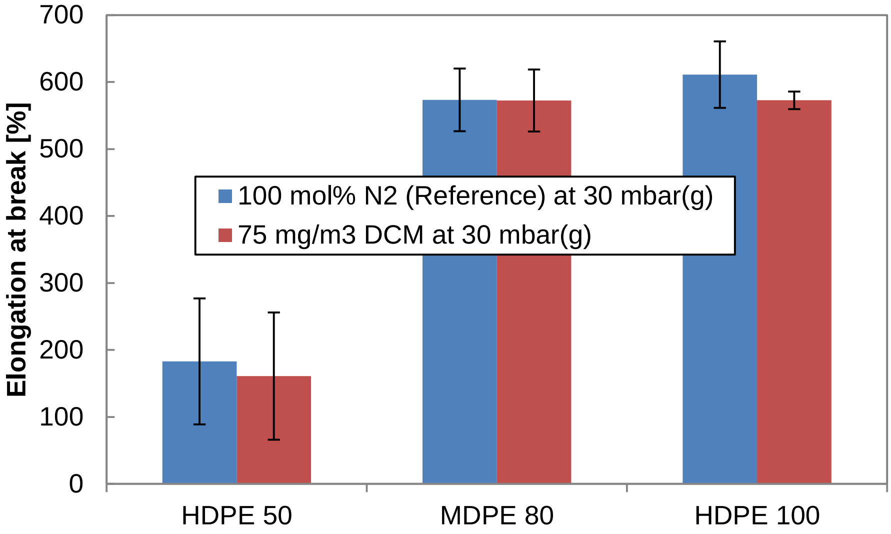


Figure 25. Elongation at break of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N_2 (reference).

3.2.2.6 Effects of Other Components

PE rings were also tested in a field test [2,3]. After two years of exposure, no noteworthy mass change of various PE materials was observed. This is shown in Figure 26 in which the mass increase of the PE samples exposed to biomethane is compared to that of the reference samples exposed to G-gas over a period of two years.

The differences in mass change of the samples exposed to narrow band gases are for all materials (HDPE 50, MDPE 80 and HDPE 100) overall lower compared to the differences in swelling of the PE materials exposed to G-gas. Although these differences are significantly different the effects are small and in favour for biomethane. Next to that, total amount of swelling of the PE samples exposed to G-gas was relatively low and therefore the effect of biomethane on PE is negligible.

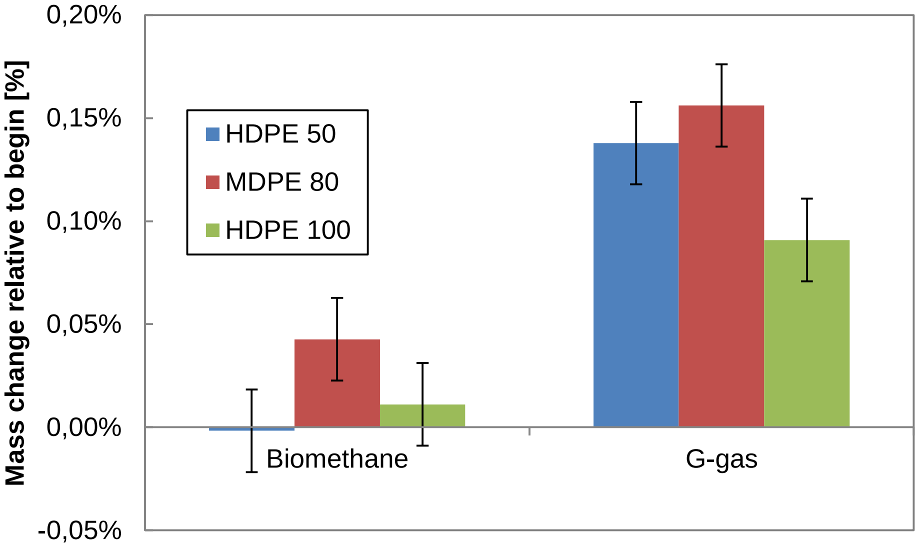


Figure 26. Mass change of PE materials (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of two years to biomethane and G-gas.

The results of the mechanical characteristics (upper yield stress (σ_y) and displacement at break (ε_{Fmm})) for the various PE materials (HDPE 50, MDPE 80, HDPE 100) after exposure to respectively biomethane and G-gas, are given in Figure 27 and Figure 28. There was no statistically significant difference between the mechanical characteristics of the HDPE 50 and MDPE 80 materials. For the HDPE 100 materials there was a statistically significant difference in the upper yield stress. The upper yield stress of the samples exposed to biomethane is significantely higher than the samples exposed to G-gas. This means that HDPE 100 materials in biomethane can withstand a higher mechanical stress compared to PE materials exposed to G-gas. This could be seen as beneficial for PE materials although the mechanism for this phenomenon is still unknown and this conclusion is based on a limited number of experiments. From the experiments on PE materials exposed to biomethane in a field test it is concluded that these materials are likely to be resistant to this environment.

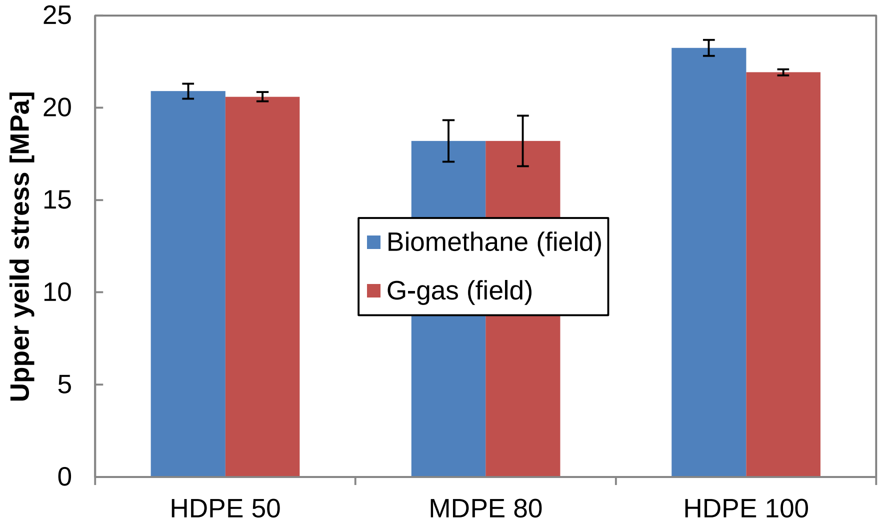


Figure 27. Upper yield stress of PE material rings (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of two years to biomethane and G-gas.

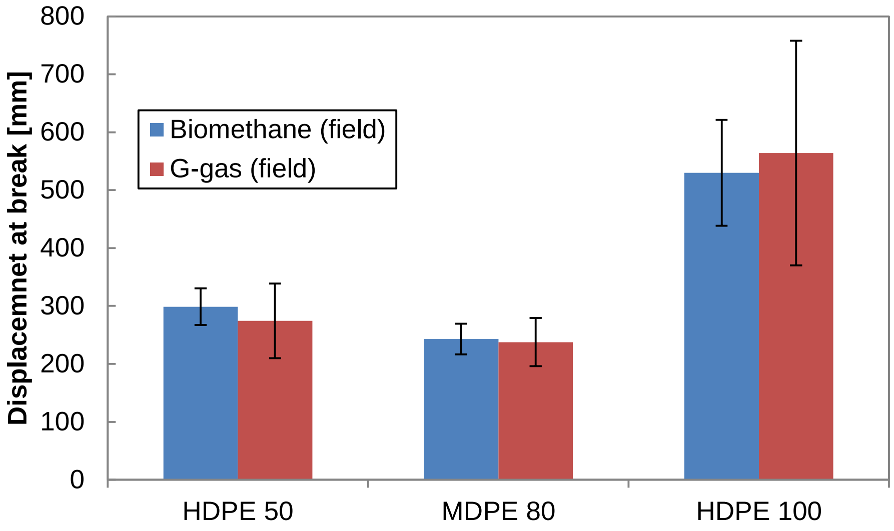


Figure 28. Displacement at break of PE material rings (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of two years to biomethane and G-gas.

3.2.3 *Conclusions*

The laboratory experiments and literature led to the conclusion that no deleterious effects on PE materials in narrow band concentrations were found for H_2S and sulphur containing components, ammonia, halogen containing organic components, CO_2 or O_2. Field tests furthermore revealed that H_2 has no effect on PE materials. No negative effects on material properties were found in literature for (aromatic) hydrocarbons in gaseous form either. However, liquid aromatic hydrocarbons (e.g. BTX and terpenes) will have a negative effect on the mechanical properties of PE.

Since the concentrations of HCl and HCN in wide band gases are low, a negative effect is unlikely. The effect of mercaptans and odorant is probably non-existent as can be seen from the fact that the current usage of these components in the distribution grid does not cause any problems. Finally, the effect of CO has not been investigated (for safety reasons) and remains unknown.

These conclusions are summarised in Table 15 below.

Table 15. The effect of components present in narrow band gases on PE. Most components will have no deleterious effect (green), while for others little or no deleterious effect is expected (light green). The effect of CO is unknown (light orange).

Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
none		probably none	none					probably none		unknown	none	none, unless liquid		none	

3.3 Elastomeric Materials (NBR)

3.3.1 *The Importance of Rubber in the Dutch Gas Distribution Network*

Elastomeric materials, especially rubber and in particular NBR, are used in gas pressure regulators as diaphragms [1]. The effects on these materials will be discussed here. The effects on rubbers used in other components of the Dutch gas network, such as sealing rings in PVC joints, will be discussed in "Impact of Sustainable Gases on Joints used in Gas Distribution Systems" [5].

3.3.2 *Test Method*

The experimental setup as described in chapter 2 was used to expose of NBR to various components in narrow band gases for a period of 600 days.

The following six tests were also performed on NBR directly after exposure:

- Mass change.
- Hardness (IRHD). The hardness was measured in accordance with ISO 48 [26].
- Tensile tests. The stress at 100 % elongation, elongation at break and tensile strength were measured in accordance with ISO 37 using type 2 samples [27].
    - Stress at 100% elongation (sometimes called “modulus”) ($\sigma_{100\%}$)
    - Elongation at break ($\varepsilon_{F\%}$)
    - Ultimate Tensile Strength (σ_{UTS})
- Dimensional change, measured before exposure, directly after exposure and one hour after exposure.
    - Inner diameter
    - Outer diameter
    - Thickness

For each test, two rings were tested for each condition. The exception was the mass change, for which all rings were measured. Three samples were made from each ring. The median value of the three samples for each ring was used for the statistical analysis in accordance with the relevant test standard [26,27].
When two groups of test results were compared a student t-test (95% confidence level) was used. When multiple groups of test results were compared an Anova comparison (95% confidence level) was made [25].

3.3.3 The Influence of Narrow Band Gases on Rubber

3.3.3.1 Effects of Hydrocarbons

The literature [1] revealed that, due to the low concentrations of aromatic hydrocarbons found in wide band gases, it is not expected that these components will affect elastomeric diaphragms in e.g. pressure regulators. However, the presence of any liquid aromatic hydrocarbons will negatively affect the mechanical properties of these materials.

The experiments also tested the effects of G-gas, which contains relatively high concentrations of hydrocarbons. After a period of 600 days these experiments resulted in negligible mass change (a maximum difference of 0.25% was found, which can be regarded as experimental scatter). This indicates that no significant absorption or depletion occurred.

Furthermore, there was no statistically significant difference between the samples exposed to G-gas and the reference samples exposed to nitrogen as regards hardness, stress at 100% elongation, elongation at break or tensile strength (see Figure 29 for a visual comparison of the average values).

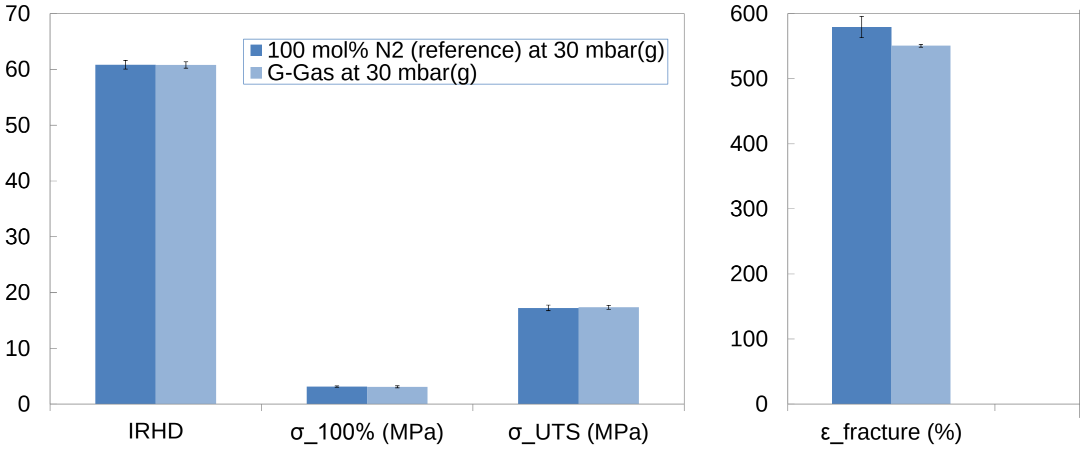


Figure 29. Comparison of the average values of hardness (IRHD), stress at 100 % elongation ($\sigma_{100\%}$) and tensile strength (σ_{UTS}) (left) and strain at fracture ($\varepsilon_{F\%}$) (right) for two NBR rings exposed to N_2 (reference) and two NBR rings exposed to G-gas (natural gas).

No profound dimensional change was observed either. All rings, whether exposed to nitrogen or to G-gas, immediately returned to almost their original dimensions when removed from the oversized pipe. They all remained slightly deformed. The extent of this plastic deformation was in the same range for all rings. Because no noteworthy difference in dimensional change between nitrogen and G-gas was found, no effect on the functioning of elastomeric diaphragms is expected.

Research on NBR rings submerged in liquid limonene showed a high degree of absorption of the fluid and severe mechanical degradation [28]. It was shown that cymene has an even stronger deleterious effect on NBR than limonene. Liquid terpenes will therefore negatively affect the mechanical properties of NBR.

The detailed results of all tests can be found in appendix IV.3.

3.3.3.2 Effects of Carbon Monoxide, Carbon Dioxide and Hydrogen

The studied literature [1] led to the conclusion that no deleterious effect was expected for CO, CO_2 or H_2. Additional experiments were therefore not performed using CO and H_2 gaseous environments. Nevertheless, due to the setup of the experiments, the effects of CO_2 were also tested at much higher concentrations than 10.3 mol% which are possible in narrow band gases. At these high concentrations, not any deleterious effect of CO_2 was observed. Therefore, not any deleterious effect of CO_2 up to a concentration of 10.3 mol% is expected. The results of the experiments using the high concentrations are discussed in the wide band report [4].

3.3.3.3 Effects of Oxygen

As long as there are no large deformations of thin rubbers, no negative effects by O_2 were expected [1]. Therefore, additional experiments have not been performed with this component.

3.3.3.4 Effects of Hydrogen Sulphide

The studied literature [1] revealed that NBR diaphragms are relatively resistant to H_2S due to the low concentrations (≤ 5 ppm) in the gases considered.

Nevertheless, due to the setup of the experiments the effects of exposure to 5 ppm H_2S was also tested. After 600 days of exposure, the experiments resulted in no significant mass change. So no significant absorption of depletion has occurred. Furthermore, there is no statistically significant difference between the results of samples exposed to 5 ppm H_2S and the results of reference samples exposed to N_2 as regards hardness, stress at 100 % elongation, strain at fracture or tensile strength. The same results were found when compared to reference samples in G-gas.

No profound dimensional change was observed either. The results for rings exposed to H_2S were similar to those for rings exposed to N_2 and G-gas. No effect on the functioning of elastomeric diaphragms is therefore expected.

The detailed results of all tests can be found in appendix IV.3.

3.3.3.5 Effects of Chlorine-Containing and Fluorine-Containing Components

The literature [1] indicated that deleterious effects on NBR by halogen-containing components in narrow band gases could not be ruled out. For the experiments it is decided to use dichloromethane (DCM) as a model gas for all halogen containing gas at a concentration of 75 mg/m^3, see Chapter 2.

After 600 days, the experiments resulted in no mass change. This indicates that no significant absorption or depletion occurred. Furthermore, there was no statistically significant difference between the results of samples exposed to DCM and the results of reference samples exposed to N_2 as regards hardness, stress at 100 % elongation, strain at fracture and tensile strength. The same results were found when compared to reference samples in G-gas.

No profound dimensional change was observed either. The results for rings exposed to various concentrations of DCM were similar to those for rings exposed to N_2 and G-gas. No effect on the functioning of elastomeric diaphragms is therefore expected.

The detailed results of all tests can be found in appendix IV.3.

3.3.3.6 Effects of Other Components

It was concluded on the basis of the studied literature [1] that no deleterious effect was expected for ammonia. Nevertheless, NH_3 was also tested in the experiments at much higher concentrations than 4 ppm which is possible in narrow band gases [1]. At these high concentrations, not any deleterious effect of NH_3 was observed. It can therefore be concluded that ammonia, in concentrations within the range of narrow band gases, does not deteriorate NBR materials. The results of the experiments using the high concentrations are discussed in the wide band report [4].

It was concluded on the basis of the studied literature [1] that no deleterious effect was expected for HCl and HCN. Additional experiments with these components were therefore not carried out.

NBR rings were also tested in a field test [2,3]. These experiments resulted in no mass change for the samples in either the biomethane feed (narrow band gases quality) or in G-gas after two years. No significant absorption or depletion therefore occurred.
Furthermore, there was no statistically significant difference (ANOVA) between the results of samples exposed to biomethane and the results of samples exposed to G-gas as regards hardness, stress at 100 % elongation, strain at fracture and tensile strength.

Because the dimensions of the rings were not measured before the field test started, the absolute effects of exposure could not be addressed. Therefore the relative effects in various environments were evaluated using the average values of all other rings (before the experiments started) was used as a reference. It was found that all the dimensions of the rings exposed to the biomethane and G-gas feed were about the same as the dimensions of the rings exposed to N_2 and G-gas under laboratory conditions. No profound change in dimensions was therefore found.

The detailed results of all tests can be found in appendix IV.3.

3.3.4 Conclusions

The literature and experiments led to the conclusion that no deleterious effect for H_2S, halogen-containing organic components, ammonia, CO, CO_2, O_2 or H_2 within the specifications of narrow band gases is expected [29]. As the concentration limits of HCl and HCN in narrow band gases are low, a deleterious effect is unlikely. (Aromatic) hydrocarbons are not expected to have a negative effect on the mechanical and physical properties either. However, liquid aromatic hydrocarbons (e.g. BTX or terpenes) will negatively affect the mechanical properties of elastomeric diaphragms made of NBR.

These conclusions are summarised in Table 16 below.

Table 16. The effect of components present in narrow band gases on NBR. Most components will have no deleterious effect (green). For some components little or no deleterious effect is expected (light green).

Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
none		probably none		none			probably none		none		none, unless liquid		none	

4 Effects on Metallic Materials

4.1 Steel

4.1.1 The Importance of Steel in the Dutch Gas Distribution Network

The Dutch distribution network contains almost 27 500 km of steel mains (see also Table 17). Steel pipelines are mostly in use as high pressure gas distribution materials in the 8 bar(g) network. Grey cast iron pipes are used in rather old, 1 bar(g) pipelines and will be replaced in the coming years. Steel is also frequently employed in domestic gas piping and in service lines.

Table 17. The importance of steel in the Dutch gas distribution network.

Material	**Length (km)**	**MOP* (bar)**	**Material-standard**
Carbon steel	*19 228*	16	[30,31]
Grey cast iron[§]	*6 241*	1	[32]
Nodular cast iron	*2 015*	8	[33]
Total	27 484		

* MOP = maximum operating pressure

[§] Not permitted for new pipelines

4.1.2 Test Method

The experimental setup as described in chapter 2 was used to expose steel materials to various components in narrow and wide band gases (see also Table 18) for a period up to 19 months. Cast iron materials were not tested, but these materials are expected to corrode in a similar manner as steel.

Table 18. Gas compositions to which steel was exposed.

Gas number	**CO_2 (mol%)**	**O_2 (mol%)**	**H_2S (ppm)**
1	50	0.01	160
2	50	0	160
3	0	3	160
4	50	3	160
5	50	3	0
6	0	0.5	34
7	10	0.5	34
8	10	0.1	34
9	10	0.01	34

After the experiments, the corrosion samples were cleaned using cleaning methods as described in ASTM G1 [34] and were weighed to determine the total mass loss of the samples. After cleaning, the decrease in wall thickness was also determined using either optical microscopy (pitting depth) or a micrometre (general attack). Samples of the corrosion products were taken and examined for the 1 and 19-month experiments in order to determine the chemical composition of the corrosion products.

4.1.3 The Influence of Narrow Band Gases on Steel

4.1.3.1 Effects of Interactions between CO_2, O_2 and H_2S

The literature [1] revealed that, where water is present, the severity of material degradation by corrosion is mainly affected by the concentrations of CO_2, O_2 and H_2S. The effect of these constituents individually has been examined extensively for CO_2. The effect of the presence of H_2S is also well understood. In general, the corrosion rate increases with increasing concentration of CO_2 and with temperature, as is described in well-known corrosion models such as the *de Waard and Milliams nomogram*. In general, the corrosion rate for O_2 also increases with concentration. From sour service applications in the oil & gas industry it is well known that H_2S can cause stress corrosion cracking. H_2S may also cause corrosion problems through a mechanism where elemental sulphur is formed. The maximum allowable concentration of H_2S in narrow band gases is limited (= 5 ppm) and, given the current chemical specification for narrow band gases, no detrimental corrosion of steel gas pipes is expected due to the presence of H_2S alone. There are indications that traces of O_2 may have a large effect on the corrosion rate compared to higher concentrations.

Visual examination of the exposed and cleaned corrosion samples showed large differences in the corrosion products and in the severity of the attack between the different gas compositions. A summary of the results of the visual examination of the cleaned corrosion samples exposed to narrow band gases is given in Table 19.

Table 19. Results of the visual examination after cleaning of the corrosion samples exposed to various narrow band gases.

Gas no	Corrosion in water phase	Corrosion in gas phase
6	Uniform, preferential at waterline	Uniform
7	Uniform, preferential at weld and waterline	Uniform
8	Uniform, preferential at waterline	Negligible
9	Uniform, preferential at waterline	Negligible

The results of the mass loss measurements of the samples exposed to narrow band gases are shown in Figure 30. The exposure resulted in a linear mass loss with time. The mass loss indicated is the summarised mass loss of the mass loss in water phase, at waterline and in the gaseous phase. In the case of pitting, a linear fit may underestimate the level of attack.

For narrow band gases, the largest mass loss was observed for the 19 month exposition to gas number 7 (10 mol% CO_2, 0.5 mol% O_2, 34 ppm H_2S). The lowest mass loss was observed for gas number 9, with the lowest oxygen concentration tested in the range of narrow band gas concentrations.

The penetration depth of the corrosion attack was determined for the areas with the strongest corrosion damage using optical microscopy. This method gives a more accurate representation of the degree of attack, especially for pitting and localised corrosion (observed at the waterline for many test conditions). The penetration depth was converted to corrosion rate using the exposure time in order to visualise the effect on the integrity of steel components in the gas distribution system.

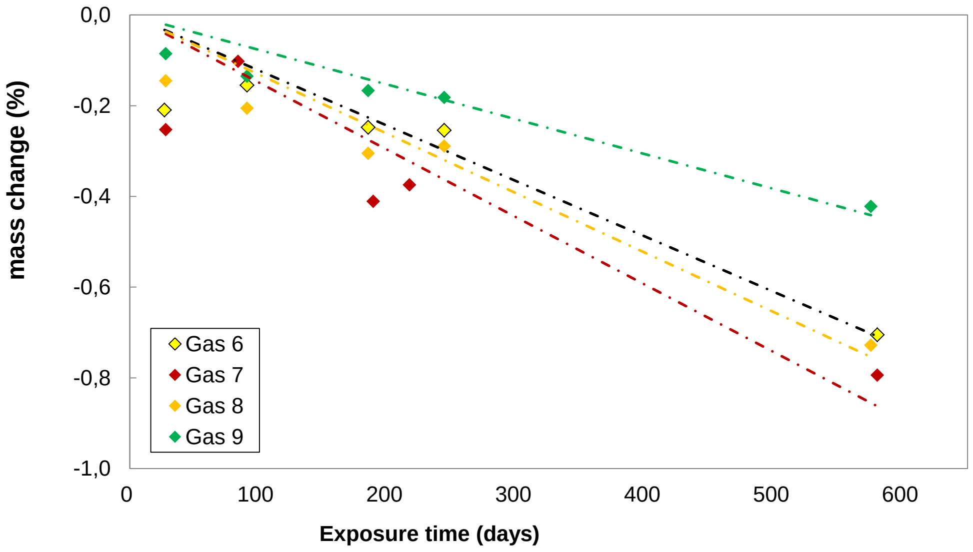


Figure 30. Mass loss of the cleaned steel specimens after exposure to various narrow band test gases. Gas number 9 (green) is the only narrow band gas with a corrosion rate not limiting the service life of steel to <50 years (see Table 20)

The corrosion rates summarised in Table 20 are shown in Figure 31 as a function of the gas composition. In Figure 31, the narrow band gases compositions can be found in the bottom left corner of the cube. The remainder of the data are part of the investigation to the effect of wide band gases [4]. Table 20 presents the results for the water phase, waterline and gas phase for the exposition to various narrow band gases. For the tested gas compositions a maximum penetration depth is observed at low O_2 concentration (gas number 8; 0.1 mol% O_2, 10 mol% CO_2 and 34 ppm H_2S). Because the largest penetration depth is measured at the waterline, the attacked surface area is limited. Therefore, the mass loss is limited as well.

For more details about the remainder of the test results it is referred to the wide band report [4].

Table 20. Results for corrosion rate determined by corrosion depth analysis of the cleaned corrosion samples exposed to various narrow band gases; red: <50 years, green: >50 years (lifespan assuming an original wall thickness of 4 mm).

Gas number	**In water phase (mm/year)**	**On waterline (mm/year)**	**In gas phase (mm/year)**
6	0.01	0.13	0.01
7	0.19	0.07	0.01
8	Negligible	0.32	Negligible
9	0.01	0.06	Negligible

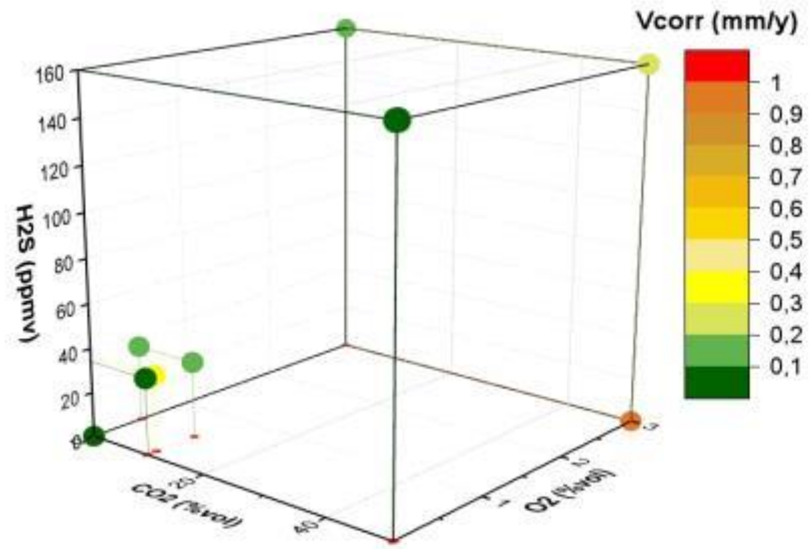


Figure 31. Corrosion rate (v_{corr}) of the steel specimens after exposure to the test gas as a function of the gas composition (CO_2, O_2 and H_2S concentration).

At the maximum CO_2 concentration in narrow band gases (= 10.3 mol% CO_2), it can be observed that the corrosion rate does not increase linearly with the O_2 concentration, because at 3 mol% O_2 the corrosion rate decreases. Instead, it appears that a maximum corrosion rate at low O_2 concentration was observed, as was also expected from the literature study [1]. The O_2 concentration at which the maximum corrosion rate is observed was not determined, because only a limited number of O_2 concentrations were studied. Different possible scenarios are sketched in Figure 32 using the maximum corrosion rate as observed in the experiments (see Table 20).

In the experiments, gas numbers 6, 7 and 8 all resulted in a corrosion rate limiting the lifetime of steel pipelines to less than 50 years. The effect however is limited compared to the effect of wide band gases where an expected lifespan of several years was observed for gas numbers 4 and 5. Only for gas number 9, with the lowest O_2 concentration the corrosion rate did not limit the lifetime of steel pipes.

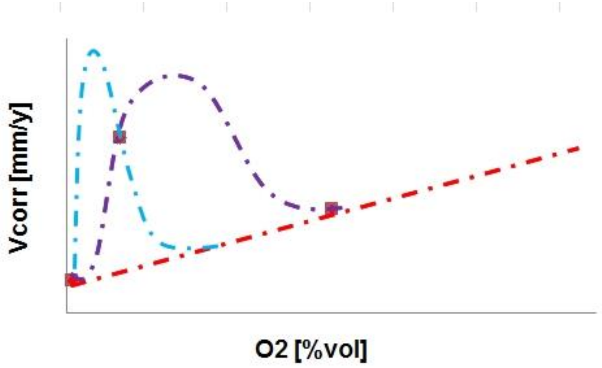


Figure 32. Sketch of the possible effect of low O_2 concentrations on the corrosion rate (Blue - maximum between 0.01 and 0.1 mol% O_2, Purple - maximum between 0.1 and 0.5 mol% O_2, Red - linear increase with corrosion rate as observed at higher O_2 concentrations).

In Figure 31 it can be seen that the highest corrosion rate is observed for gas number 5 (wide band gases, bottom right corner in Figure 31, high CO_2 and O_2 concentration). The presence of H_2S decreases the corrosion rate significantly, as was observed for gas number 4 (wide band gases, top right corner in Figure 31, high CO_2, O_2 and H_2S concentration). This effect related to the presence of H_2S might also occur for narrow band gases, but in the present work this was not investigated.

4.1.3.2 Suggestions for Further Research

There are indications that traces of oxygen may have a large effect on the corrosion rate in comparison to higher concentrations. It is therefore recommended that corrosion experiments be performed in order to further quantify the risk of corrosion, focusing on the interactions between CO_2, O_2 and H_2S and thereby also including ppm level O_2 concentrations.

4.1.3.3 Effects of Interactions between O_2, CO and CO_2

On the basis of the studied literature [1], it was concluded that the presence of CO_2 and CO may cause stress corrosion cracking. This is however a greater risk for high pressure gas transport than for low pressure gas distribution networks. Because this research project focusses mainly on gas distribution materials, the effects of interactions between O_2, CO and CO_2 were not studied further in the current work.

4.1.3.4 Field test with exposition to Narrow Band Gases

Steel specimens were also tested in field experiments [2,3]. The exposed samples showed a similar degree of superficial corrosion as the reference samples which were stored in a conditioned laboratory during the field test. Dry narrow band gases therefore do not deteriorate steel materials.

4.1.4 Conclusions

The presence of water is obviously of great influence on the corrosion of steel due to interactions involving O_2, CO_2 and H_2S. For narrow band gases, the most severe attack was observed either in the water phase or at the gas-water interface.

For all test conditions, the mass loss of the corrosion samples showed a linear trend with time, therefore justifying the extrapolation of the test results for longer exposure times.

The experiments were conducted at a constant test temperature of 25ºC. The corrosion rate was therefore higher than in gas distribution systems, which are operated at a temperature of approximately 7ºC. So the test approach can be considered conservative.

The corrosion tests were conducted using a maximum H_2S concentration of 34 ppm, which was chosen as the equivalent of the maximum admissible concentration of sulphur-containing compounds in narrow band gases (= 45 mg/m^3(n)). In the water phase a corrosion rate was observed, which is limiting the lifespan of steel pipes to less than 50 years. In the gas phase however no significant corrosion was observed. It can therefore be concluded that the existing steel gas infrastructure cannot be used for the transport of moist narrow band gases, but that in sufficiently dry gas corrosion problems are not expected.

Low oxygen levels (e.g. gas number 9; 100 ppm O_2 with 10 mol% CO_2 and 34 ppm H_2S) did not result in a corrosion rate limiting the lifespan for steel pipes less than 50 years. However the corrosion rate showed a local maximum between 0.01 and 0.5 mol% O_2. It is therefore recommended that the effect of low oxygen concentrations on the integrity of steel in the gas distribution network be further investigated.

No tests were performed to assess the effects of exposure to HCN and CO. The conclusions for these components therefore remain unchanged to those made in the literature review [1].

All conclusions are summarised in Table 21 below.

Table 21. The effect of components present in narrow band gases on steel. Some components will have no deleterious effect (green), while for others little or no deleterious effect is expected (light green). The effect of other components is unknown (light orange) or a deleterious effect may be present (orange). Components between brackets do not necessarily need to be present.

<table>
<tr><th>Sulphur containing components</th><th>H_2S</th><th>Mer-captans</th><th>Odorant</th><th>Ammo-nia</th><th>Chlorine containing components</th><th>Fluorine containing components</th><th>HCl</th><th>HCN</th><th>CO</th><th>CO_2</th><th>Hydro-carbons</th><th>Aromatic hydro-carbons</th><th>O_2</th><th>H_2</th></tr>
<tr><td colspan="3">water and CO_2</td><td colspan="5" rowspan="2">probably none</td><td rowspan="2">H_2S and water: possibly</td><td rowspan="2">unknown</td><td>water and H_2S</td><td colspan="2" rowspan="2">probably none</td><td rowspan="2">water, (H_2S) and CO_2</td><td rowspan="2">none</td></tr>
<tr><td colspan="3">water,CO_2 and O_2</td><td>water, (H_2S) and O_2</td></tr>
</table>

4.1.5 *Recommendations*

The presence of water is of vital importance for the corrosion of steel. Reducing the risk of corrosion must therefore focus initially on preventing water from entering the steel pipe system. It is therefore recommended that the distribution pressure be increased to 100 mbar(g) for all connections; at 100 mbar(g) gas pressure the risk of water entering the low pressure grid is significantly lower. Drying also deserves a prominent role in the processing of raw biogas prior to introduction into the gas distribution system.
In the current work, the interactions between O_2, CO_2 and CO have not been studied. The conclusion therefore remains unchanged: stress corrosion cracking in a gaseous environment containing these components is possible in the presence of water.

4.2 Copper

4.2.1 *The Importance of Copper in the Dutch Gas Distribution Network*

Copper is used in service lines and also in domestic applications (which are not part of the gas distribution network but which represent a high risk in the case of severe attack).

4.2.2 *Test Method*

The experimental setup as described in chapter 2 was used to expose copper materials to various components in narrow and wide band gases (see also Table 22) for a period of 19 months.

Table 22. Gas compositions to which copper was exposed.

Gas number	CO_2 (mol%)	O_2 (mol%)	H_2S (ppm)
1	50	0.01	160
2	50	0	160
3	0	3	160
4	50	3	160
5	50	3	0
6	0	0.5	34
7	10	0.5	34
8	10	0.1	34
9	10	0.01	34

After the experiments, the corrosion samples were cleaned using cleaning methods as described in ASTM G1 [34] and weighed in order to determine the total mass loss of the samples. After cleaning, the decrease in wall thickness was also determined using either optical microscopy (pitting depth) or a micrometre (general attack). Samples of the corrosion products were taken and examined for the 1 and 19-month experiments in order to determine the chemical composition of the corrosion products.

4.2.3 The Influence of Narrow Band Gases on Copper

4.2.3.1 Effects of Interactions between CO_2, O_2 and H_2S

It was concluded on the basis of the studied literature [1] that the most important factor in the corrosion of copper is the presence of water. Where water is present, corrosion is mainly affected by the concentrations of CO_2, O_2 and H_2S.

Figure 33 shows the mass change of the cleaned corrosion samples. It can be observed that the mass change shows a linear trend with exposure time. This is in line with the visual examination, in which uniform attack was observed for all test conditions. It is shown in Figure 33 that for gas number 6 (0 mol% CO_2, 0.5 mol% O_2, 34 ppm H_2S) the attack was most severe.

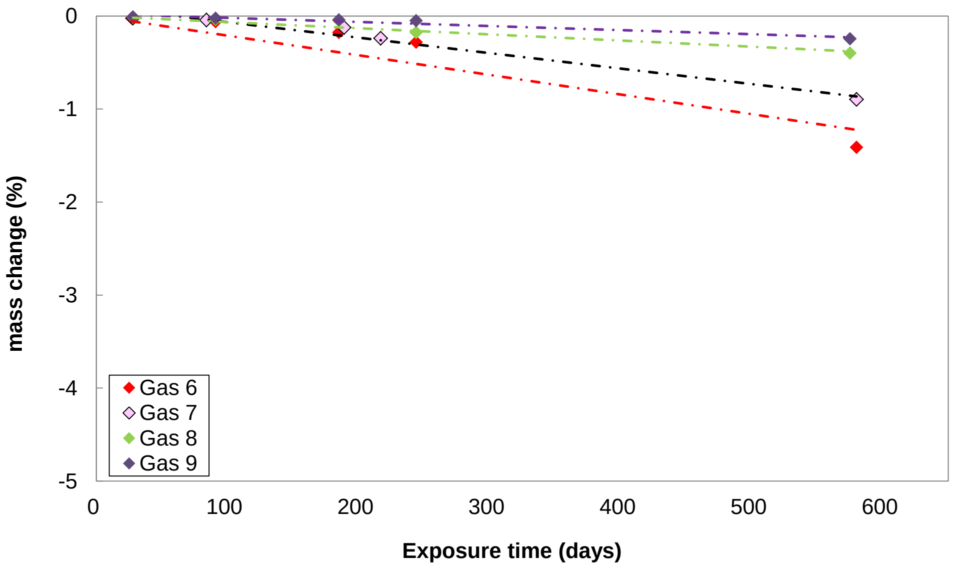


Figure 33. Mass loss of the cleaned copper samples for various narrow band gases after exposure to the test gas.

The decrease in wall thickness was converted to corrosion rate using the exposure time in order to visualise the effect on the integrity of copper components in the gas distribution system. The corrosion rates for the various narrow band gases are given in Table 23. This table presents the results for the water and gaseous phases.

From the results of the corrosion rate determination the same trend can be seen as from the mass loss experiments, with the strongest attack for the samples exposed to gas number 6 (0 mol% CO_2, 0.5 mol% O_2, 34 ppm H_2S).The attack by the narrow band gases was in most cases equal for the gaseous phase and the water phase. At the surface of the test specimens, the corrosion product started to crack and peel off after a longer period of attack. The composition of the corrosion products was comparable for all H_2S-containing gases, and appeared to be a mixture of CuS and CuO. These tended towards a 1:2 ratio for the test gases with 34 ppm H_2S (gas number 6 to gas number 9).

Table 23. Results for corrosion rate determined by decrease of wall thickness analysis of the cleaned corrosion samples; orange: ~ 50 years, green: >50 years (lifespan assuming an original wall thickness of 1 mm).

Gas number	**In water phase (mm/year)**	**In gaseous phase (mm/year)**
6	0.03	0.03
7	Negligible	0.00
8	0.01	0.01
9	0.01	0.01

The results of the corrosion rate determination summarised in Table 23 are shown in Figure 34 as a function of the gas composition. The bottom left corner in the cube shows the corrosion rate at the narrow band gas compositions. For more details about the remainder of the test results it is referred to the wide band report [4].

Given the similarity in the corrosion products at different H_2S concentrations, it appears that for narrow band gases, the interactions between H_2S, CO_2 and O_2 determine the corrosion rate.
Figure 34 shows that, in the presence of 34 ppm H_2S at low CO_2 and O_2 concentrations, the corrosion rate decreases with increasing O_2 concentration.

For none of the narrow band gases the corrosion rate was limiting the lifespan to less than 50 years. Only for gas number 6 a limitation of the lifetime to approximately 50 years was observed. It can therefore be concluded that there are no problems to be expected for copper exposed to narrow band gases containing 34 ppm H_2S, 10 mol% CO_2 and 0.5 mol% O_2.

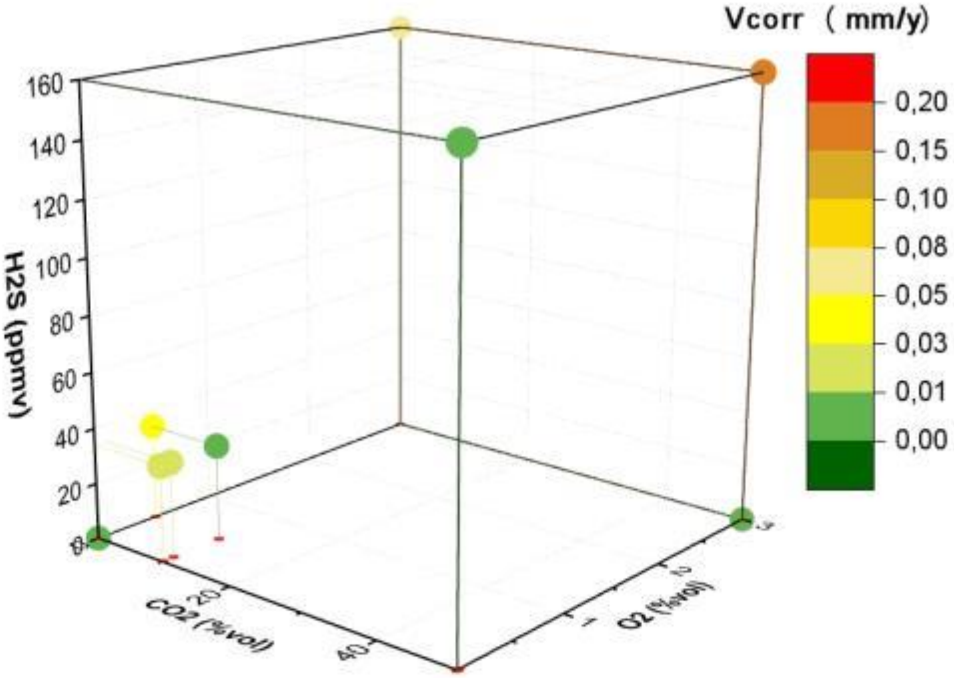


Figure 34. Corrosion rate (v_{corr}) of the copper specimens after exposure to the test gas as a function of the gas composition (CO_2, O_2 and H_2S concentration).

4.2.3.2 Effects of Ammonia

The influence of 50 ppm ammonia at a relative humidity of 50% was also tested. After 19 months, the experiments resulted in virtually no noteworthy stress corrosion cracking of the copper samples. No effect for the limiting value of ammonia (= 4 ppm) in narrow band gases on the integrity of copper pipes is therefore expected. For more information it is referred to the joints report [5].

4.2.3.3 Effects of Hydrogen

The studied literature [1] revealed that the effect of hydrogen is unknown. Copper materials were tested in the field at concentrations of up to 20 mol% H_2 [20]. No effect for H_2 on copper materials at up to this concentration level was measured.
Narrow band gases can contain up to 12 mol% H_2. It can therefore be concluded that H_2, within the range of narrow band gases, does not deteriorate copper materials.

4.2.4 Conclusions

The experiments with narrow band gases, led to the conclusion that gas with a high humidity is more aggressive to copper than water with dissolved gas. It is also concluded that the presence of CO_2 decreases the corrosion rate as a result of the combined presence of H_2S and O_2. It is therefore recommended that in case H_2S is present in narrow band gases, CO_2 shall also be present to lower the corrosion rate.

Nevertheless, the corrosion rate of copper materials exposed to narrow band gases is low and the lifespan of copper materials is not reduced to less than 50 years.

It can therefore be concluded that there are no problems to be expected for copper materials exposed to narrow band gases containing H_2, NH_3, H_2S, CO_2 and O_2.

No tests were performed to assess the effects of exposure to HCN and CO. The conclusions for these components therefore remain unchanged to those made in the literature review [1].

All conclusions are summarised in Table 24 below.

Table 24. The effect of various components present in narrow band gases on copper. Some components will have no deleterious effect (green), while for others little or no deleterious effect is expected (light green). The effect of other components is unknown (light orange).

Sulphur containing components	H_2S	Mercaptans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
none			probably none	none	probably none			unknown		none	probably none		none	none

4.3 Aluminium

4.3.1 The Importance of Aluminium in the Dutch Gas Distribution Network

The Dutch G-gas transport and distribution network contains aluminium. It is mostly used in gas pressure regulators and gas meters. As these regulators and meters are used for domestic applications, failure of these components due to corrosion would immediately lead to unacceptable risks.

4.3.2 Test Method

The experimental setup as described in chapter 2 was used to expose aluminium materials to various components in narrow and wide band gases (see also Table 25) for a period of 19 months.

Table 25. Gas compositions to which aluminium was exposed.

Gas number	CO_2 (mol%)	O_2 (mol%)	H_2S (ppm)
1	50	0.01	160
2	50	0	160
3	0	3	160
4	50	3	160
5	50	3	0
6	0	0.5	34
7	10	0.5	34
8	10	0.1	34
9	10	0.01	34

After the experiments, the corrosion samples were cleaned using cleaning methods as described in ASTM G1 [34] and weighed in order to determine the total mass loss of the samples. After cleaning, the decrease in wall thickness was also determined using either optical microscopy (pitting depth) or a micrometre (general attack). Samples of the corrosion products were taken and examined for the 1 and 19-month experiments in order to determine the chemical composition of the corrosion products.

4.3.3 The Influence of Narrow Band Gases on Aluminium

4.3.3.1 Effects of Interactions between CO_2, O_2 and H_2S

The studied literature [1] confirmed that aluminium has excellent corrosion resistance. The most important factor in the corrosion of aluminium is the presence of water. Where water is present, corrosion is mainly affected by the concentration of CO_2 or the presence of chloride ions. On the basis of the literature the corrosion effects on aluminium caused by the constituents in narrow band gases cannot be predicted. Therefore additional experiments were carried out.

Figure 35 shows the mass change of the cleaned corrosion samples. From the mass loss data, none of the test results show a clear correlation of the mass change with the exposure time. The mass loss of the samples is negligible, although discoloration of the samples was observed as well as some pitting corrosion for exposure to gas number 6 (0 mol% CO_2, 0.5 mol% O_2, 34 ppm H_2S). The mass loss was in the same order of magnitude as the mass loss caused by cleaning of the samples (pickling error). For none of the test gases attack of the aluminium materials was observed in the gaseous phase.

For samples exposed to gas number 6, pitting corrosion was observed at the machined surfaces (sides of the samples as well as the thread) as illustrated in Figure 36.

From the chemical analyses of the corrosion products on the surface of the aluminium test samples it became apparent that the corrosion products contained high concentrations of iron, sulphur and oxygen, together with some aluminium. It is therefore likely that these products were not corrosion products of aluminium but were rather deposits of steel corrosion products arising as a result of the combined exposure of the different test materials in the test rig (see chapter 2).

The decrease in wall thickness was converted to a corrosion rate using the exposure time in order to visualise the effect on the integrity of aluminium components in the gas distribution system. The corrosion rates of the various narrow band gases are given in Table 26. This table presents the results for the water and gaseous phases.

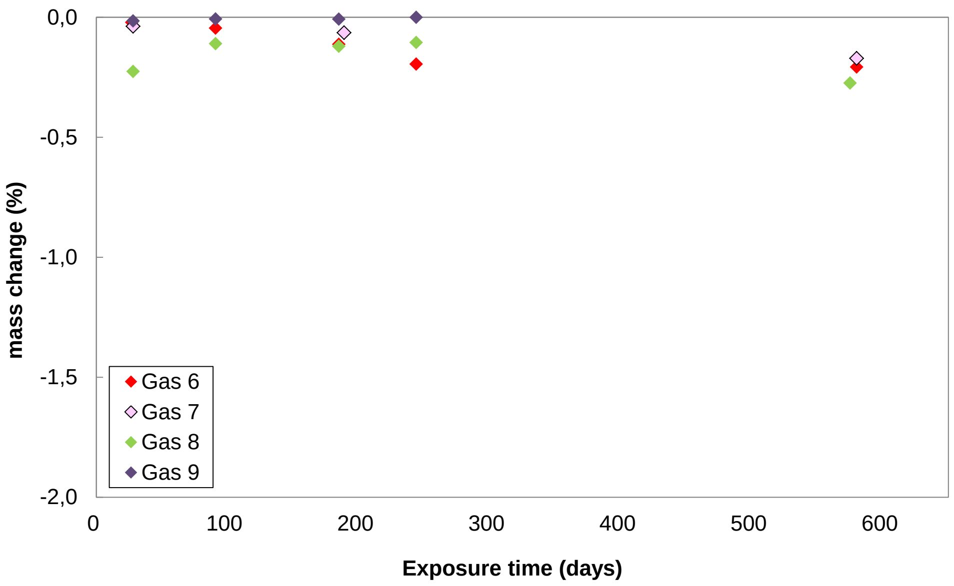


Figure 35. Mass loss of the cleaned aluminium samples after exposure to various narrow band test gases.

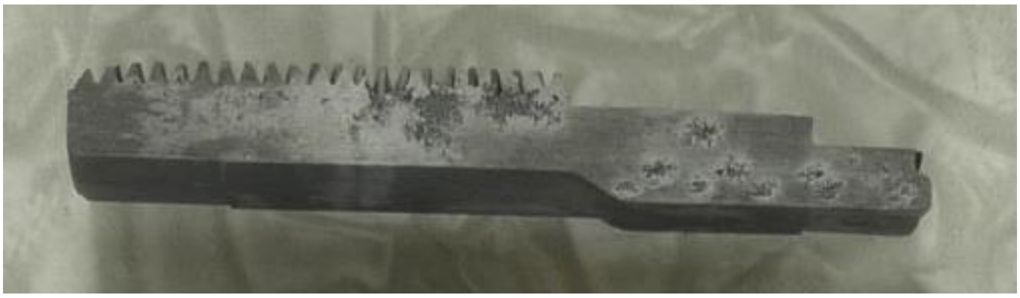


Figure 36. Pitting corrosion on machined surfaces of the corrosion sample after 19 month exposure to gas number 3. Similar corrosion was observed at samples exposed to gas number 6.

For narrow band gases, only a substantial corrosion rate was observed with gas number 6 (0 vol CO_2, 0.5 mol% O_2, 34 ppm H_2S) while for the other narrow band gases no decrease in wall thickness could be observed. The attack mainly occurred at machined surfaces (both cutting planes and thread) in the water phase and was rather localised.

Table 26. Results for corrosion rate determined by corrosion depth analysis of the cleaned corrosion samples exposed to various narrow band gases; red: < 50 years, green: >50 years (lifespan assuming an original wall thickness of 2 mm).

Gas number	In water phase (mm/year)	In gaseous phase (mm/year)
6	0.19	Negligible
7	Negligible	Negligible
8	Negligible	Negligible
9	Negligible	Negligible

The results of the corrosion rates determination summarised in Table 26 are shown in Figure 37 as a function of the gas composition. The bottom left corner in the cube shows the corrosion rate at the narrow band gas compositions. For more details about the remainder of the test results it is referred to the wide band report [4].

In the absence of CO_2, the corrosion rate increases with increasing H_2S and O_2 concentration, as can be seen in Figure 37. As O_2 alone does not cause corrosion problems for aluminium, it is assumed that the observed increase in corrosion rate was caused by the increased concentration of H_2S.
Condensation of water in gases containing H_2S but no CO_2 can therefore cause corrosion problems in aluminium. Failure of aluminium components may occur as a result of penetration of the wall thickness and loss of function of the thread of the components.

CO_2 concentrations in the narrow band gases range (< 10.3 mol% CO_2), of which the literature study indicated they may lead to the corrosion of aluminium, did not lead to a noticeable effect in the experiments performed in this research. This can be seen from the low corrosion rate at the high CO_2 concentration (= 50 mol% CO_2) side of Figure 37. The reason for this is unknown.

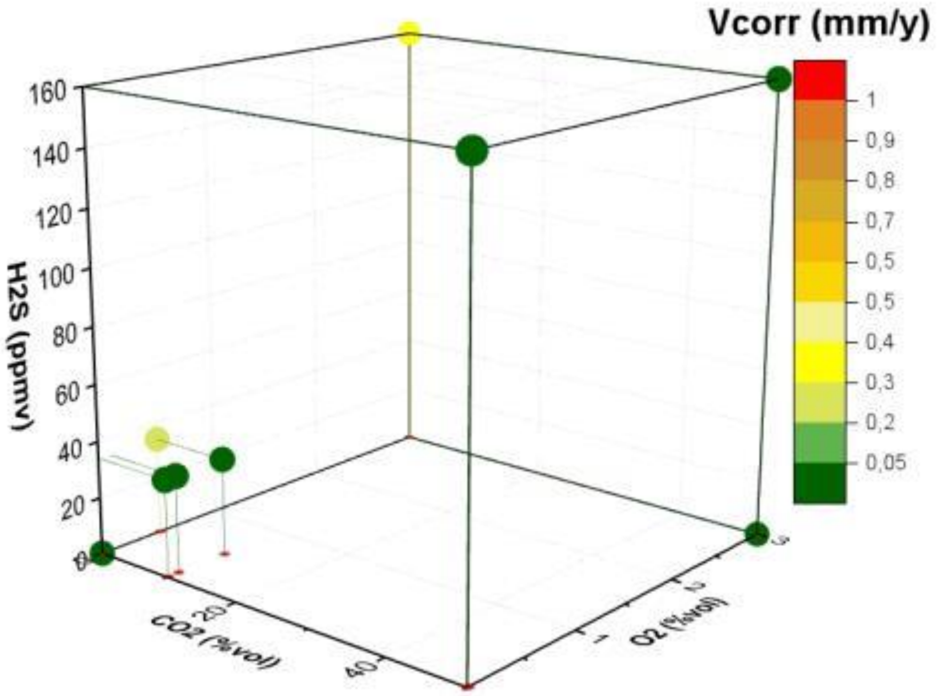


Figure 37. Corrosion rate (v_{corr}) of the aluminium specimens after exposure to the test gas as a function of the gas composition (CO_2, O_2 and H_2S concentrations).

4.3.3.2 *Effects of Hydrogen*

The studied literature [1] indicated that the effect of hydrogen on aluminium is unknown. Aluminium materials were tested in the field at concentrations up to 20 mol% H_2 [20]. No effect for H_2 on aluminium materials at up to this concentration level was observed.
Narrow band gases can contain up to 12 mol% H_2. It can therefore be concluded that H_2, within the range of narrow band gases does not deteriorate aluminium materials.

4.3.4 *Conclusions*

The literature indicates that corrosion due to CO_2 alone is also possible. However, this was not investigated experimentally. In combination with H_2S and O_2, CO_2 appears to inhibit corrosion. For the effects of CO_2, the conclusion in the summarising table has therefore changed from orange (based on the literature review [1]) to green (based on the experiments carried out).

In the presence of O_2 and absence of CO_2, significant corrosion of aluminium due to the presence of H_2S was observed. The experiments led to the conclusion that, in the presence of CO_2, no corrosion will take place due to the presence of H_2S. The use of aluminium with gases containing H_2S and not containing CO_2 should therefore be avoided. For H_2S, the conclusion in the summarising table has therefore changed from orange to green in the presence of CO_2 and remains orange in the absence of CO_2.

O_2 alone is not expected to cause corrosion problems with aluminium; the conclusion in the summarising table has therefore changed from orange to green. As corrosion was observed in the presence of H_2S and water, the conclusion under these circumstances remains orange.

Corrosion was observed in the water phase and was localised on machined surfaces (e.g. threads) only. For aluminium, the importance of drying the gas and preventing water ingress into the low pressure distribution network must therefore be emphasised once again.

No tests were performed to assess the effects of exposure to HCN and CO. The conclusions for these components therefore remain unchanged to those made in the literature review [1].

Table 27. The effect of various components present in narrow band gases on aluminium. Some components will have no deleterious effect (green), while for others little or no deleterious effect is expected (light green). The effect of other components is unknown (light orange) or a deleterious effect may be present (orange).

Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
water and CO_2			probably none	none	probably none			unknown		none	probably none		none	none
water and O_2													water and H_2S	

5 Conclusions

All the results of the project "Effects of Narrow Band Gases on Materials" are summarised in Table 28 below.

Table 28. The effect of components present in narrow band gases on the most important gas distribution materials based on literature review and experiments.

	Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
PVC	none		probably none		none			probably none		unknown	none	none, unless liquid (impact resistance)		none	
PE	none		probably none		none			probably none		unknown	none	none, unless liquid		none	
NBR	none		probably none		none			probably none		none		none, unless liquid		none	
steel	water and CO_2			probably none					H_2S and water: possibly	unknown	water and H_2S	probably none		water, (H_2S) and CO_2	none
	water,CO_2 and O_2										water, (H_2S) and O_2				
Cu	none			probably none	none	probably none			unknown		none	probably none		none	none
Al	water and CO_2			probably none	none	probably none			unknown		none	probably none		none	none
	water and O_2													water and H_2S	

▢	=	The effect is unknown, but is expected to be very small or non-existent.
🟩	=	This component within the concentrations of narrow band gases does not affect materials.
🟧	=	The effect is unknown.
🟥	=	Deleterious effects are expected under some conditions.

The following main conclusions can be drawn from this research project.

For the most important polymeric materials (PVC, PE and NBR) used in the Dutch gas distribution grid no negative effects are expected for any component up to the maximum concentration allowed in narrow band gases. This is valid with the following two exceptions:

- Due to health and safety reasons the effect of CO in narrow band gases on PVC and PE was not tested. The effect of this gas component is therefore still unknown.
- The presence of any liquid aromatic hydrocarbons will negatively affect the mechanical properties of the most important polymeric materials.

For the most important metallic materials (steel, copper and aluminium) used in the Dutch gas distribution grid, the occurrence of water or moisture is of great influence on the corrosion process. Without water, no corrosion can occur.
For copper, gas with a high humidity is even more aggressive than water with dissolved gas.

If gas with a high humidity occurs, the combination of H_2S, CO_2 and O_2 within narrow band limits can lead to severe corrosion in steel.

The experiments show that lowering the O_2 level below 100 ppm (0.01 mol%) is needed to reduce the corrosion rate to an acceptable level. Only decreasing the CO_2 concentration is not enough to reduce the corrosion rate. More research is needed to determine the effect of low H_2S concentrations. In these experiments H_2S is also used as model gas for other sulphur containing components.

The combination of H_2S CO_2 and O_2 in humid gas can lead to severe corrosion in steel, copper and aluminium. Limiting O_2 to 100 ppm (0.01 mol%) leads to an acceptable corrosion rate. For copper and especially aluminium it is very important that CO_2 is present in the gaseous environment. Severe corrosion can occur if humid gas containing H_2S and O_2, but without CO_2, comes into contact with these materials. The minimum concentration level of CO_2 to prevent this severe corrosion is unknown

Based on literature, corrosion due to CO_2 alone is also possible for both copper and aluminium. However, this was not investigated further in the experiments carried out.

The effect of HCN and CO in narrow band on metals was not tested because of health and safety reasons. From literature it was found that HCN can also have a negative effect on the corrosion rate of steel. The effect of HCN on copper and aluminium remain unknown. Also the effect of CO on all three metals is still unknown.

6 Recommendations

The most significant recommendation that would enable the existing Dutch gas distribution grid to transport narrow band gases, is that water be prevented from entering the gas distribution grid. Without the presence of water, corrosion of metallic materials (steel, copper and aluminium) cannot occur. Only a few adjustments on the maximum allowable concentrations of gas components in narrow band gases are recommended.

Possible solutions to reduce the risk of the presence of water in the gas distribution grid include:

- Increasing the distribution pressure to 100 mbar(g). At 100 mbar(g) gas pressure the risk of ground water entering the gas grid (water ingress) is significantly lower than at 30 mbar(g) gas pressure.
- Decreasing the water dew temperature of the gas at gas entry points. In other words, the gas must be dried (the relative humidity must be lowered) before it enters the gas distribution grid. This solution deserves a prominent role in the processing of sustainable gases to upgrade it to narrow band gases.

In addition to drying the gas to remove water, it is also important to prevent the formation of liquid hydrocarbons. This may occur if the concentration of aromatic hydrocarbon vapours is too high. These liquids have a negative effect on the mechanical properties of polymeric materials. At present, the maximum allowable limit for aromatic hydrocarbons in narrow band gases is 10 000 ppm.
In G-gas the maximum measured concentration of aromatic hydrocarbon vapour in the last ten years in the Dutch gas distribution grid is 800 ppm. This concentration did not lead to obvious liquid formation and thus material degradation. It is therefore recommended that the concentration of aromatic hydrocarbon vapour in narrow band gases is limited to 800 ppm.

Furthermore, it is important to note that the effects of several gas components have not been tested (HCN and CO). This is due to the toxicity of these gases to humans, which makes experiments in the laboratory dangerous. The influence of these toxic gases on important polymeric and metallic materials therefore remains unknown. In some cases the literature indicates that a negative effect of these gas components may be possible. It is therefore recommended that HCN and CO should be prevented from entering the gas distribution grid or that their concentration should at least be kept as low as possible. It is recommended to limit the maximum concentration of H_2S to 160 ppm.

The above-mentioned recommendations are summarised in Table 29 where water is not present in the existing Dutch gas distribution grid. Adjustment of the limiting values for other gas components in narrow band gases in accordance with the additional terms and conditions applicable to Dutch biomethane producers is not required.
(Please note: this excludes joints, which are investigated in another project).

However, it is not always possible to prevent water from entering the gas distribution grid. Where this occurs, gas with a high humidity will be present and the combination of H_2S, CO_2 and O_2 may lead to severe corrosion in especially steel, but also in copper and aluminium. It is therefore needed to limit the O_2 concentration to 100 ppm (0.01 mol%) for humid narrow band gases.

Table 29. Recommended limiting values for several gas components in narrow band gases where water is not present in the gas distribution grid or in narrow band gases.

Limiting value	Reason
< 800 ppm aromatic hydrocarbons (vapour)	Liquid hydrocarbons, including mono- and polycyclic aromatic hydrocarbons and higher hydrocarbons (e.g. terpenes), may have a negative effect on the mechanical properties of polymeric pipe materials. At present, the maximum allowable limit for aromatic hydrocarbons in narrow band gases is 10 000 ppm. It is recommended that the maximum concentration be limited to 800 ppm. 800 ppm is the maximum measured concentration of aromatic hydrocarbons in G-gas in the last ten years.
low concentrations of CO and HCN	The effects of CO and HCN were not determined due to their high toxicity to humans. Because of this health and safety risk and because only limited information could be obtained about the possible effects of these components on the most important materials used in the Dutch gas distribution grid, it is recommended that the maximum concentration of CO and HCN be limited as much as possible.

This limiting value is also suitable for copper and aluminium. However, severe corrosion can still occur in aluminium without the presence of CO_2. More research using low CO_2 concentrations is therefore recommended.

When water is present in the gas grid or in narrow band gases additional recommendations to the ones given in Table 29 are needed and given in Table 30. Adjustment of the limiting values for other components in narrow band gases in accordance with the additional terms and conditions applicable to Dutch biomethane producers are not required.
(Please note: this excludes joints, which are investigated in another project).

Table 30. Additional recommended limiting values for several gas components in narrow band gases where water is present in the gas distribution grid or in narrow band gases.

Limiting value	Reason
< 0.01 mol% O_2	The combination of H_2S, CO_2 and O_2 may lead to severe corrosion in steel, copper and aluminium. This limiting concentration, combined with the current limiting values for H_2S and CO_2, is found to limit the effect on metallic materials to an acceptable level.
possibly > 0 mol% CO_2	If both H_2S and O_2 come into contact with aluminium or copper, in the absence of CO_2, severe corrosion may occur. It is unknown if CO_2 must also be present for the above proposed limiting value. More research using low CO_2 concentrations is therefore recommended.

I Initial Craze Formation in ESC Tests on PVC

The applied stress in the ESC (environmental stress cracking) tests for the PVC materials was 20 MPa. Additional tests were performed to determine if the used PVC samples from crazes when exposed to a stress of 20 MPa. This additional testing revealed that PVC-U starts forming crazes at approximately 15 MPa and higher. Craze formation in PVC-HI starts at higher stresses. The stress at which the crazes start to form is dependent on the time of testing but also on the material properties (which are in turn is dependent on composition and extrusion conditions).

The 20 MPa stress level in this research project was therefore high enough for ESC to take place within 600 days of exposure. Examples of these crazes are shown in Figure 38 and Figure 39.

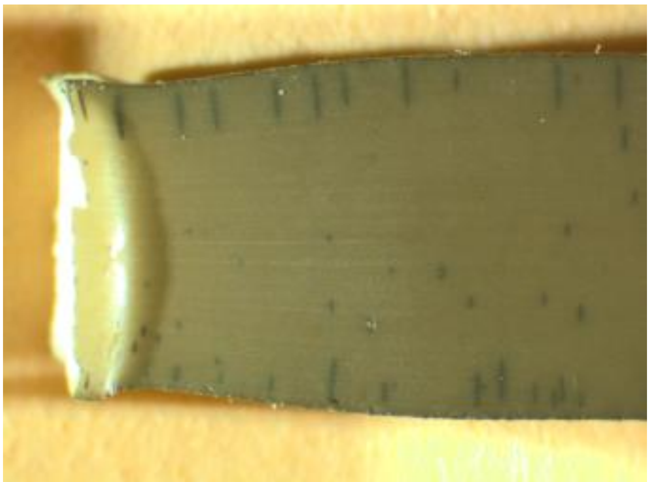


Figure 38. Crazes that have formed in PVC-U type 2 at 20 MPa. These have become discoloured as a result of exposure to H_2S for a period of 600 days.

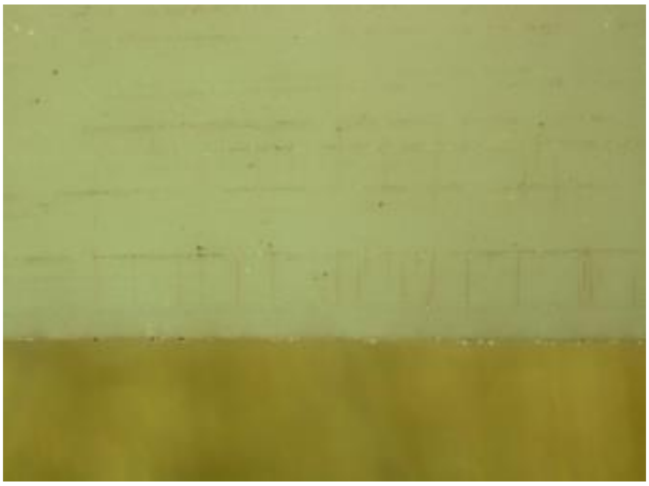


Figure 39. Crazes that have formed in PVC-U type 2 at 20 MPa that was exposed to 100% N_2. The crazes were deliberately coloured afterwards through exposure to H_2S without an applied stress to make them better visible.

As can be seen from Figure 39 crazes also formed under the influence of 100% N_2. The N_2 is considered to be a reference gas that does not accelerate the ESC process. Craze initiation in PVC therefore already occurs in an inert environment (N_2) provided that the stress is sufficiently high. The additional tests indicated that it is likely that these crazes formed early (within the first few days) after applying the 20 MPa stress. Finally, it must also be noted that only the PVC-U materials (both types) showed craze formation. No craze formation was observed in the PVC-HI materials. Further research is needed to determine the reason for this difference, but it may be due to a blunting process occurring in PVC-HI.

II Ductility and the Brittle-Ductile Transition Temperature (T_{BD})

The ductility of the PVC material was characterised using a tensile impact test. This newly-improved test method has been developed at Kiwa Technology [35]. Dumbbell-shaped test samples taken in the length direction of the pipe were first machined from each individual pipe as shown in Figure 40. These dumbbells were subsequently broken at a high impact velocity at temperatures ranging from -25 °C to +50 °C as shown in Figure 41 and Figure 42.

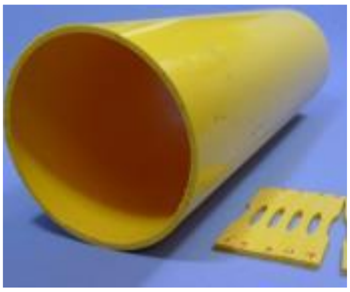


Figure 40. PVC-HI pipe with dumbbell-shaped specimens.

Figure 41. Cooling of a PVC specimen.

Figure 42. Impacting the specimen.

When testing the specimens, the difference between brittle and ductile fractures can easily be distinguished visually (see Figure 43). Specimens that break with ductile fractures show stress whitening and a distorted fracture area, while specimens that break with brittle fractures do not show any distortion at the macroscopic level. This differing behaviour can also be seen in the force-displacement graphs resulting from measurements made during testing (see Figure 44). It can clearly be seen that ductile fractures consume more energy than brittle ones (surface area under graphs).

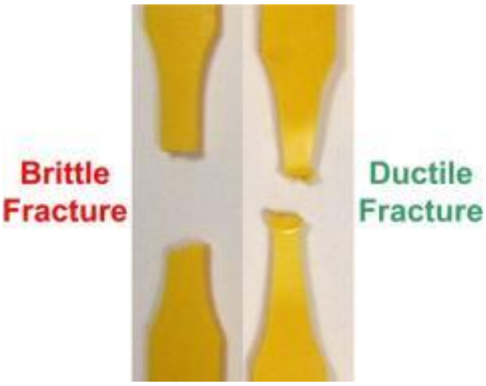


Figure 43. Brittle and ductile fractures can be distinguished visually.

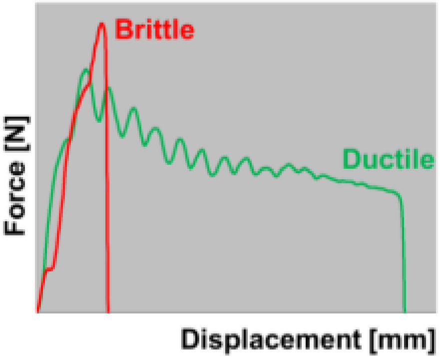


Figure 44. Force-displacement graphs for brittle and ductile fractures.

The fracture behaviour of PVC during impact is dependent not only on the material quality but is also strongly influenced by temperature. This is where the brittle-ductile transition temperature (T_{BD}) plays an important role. This is the temperature at which the material behaviour under impact changes from brittle to ductile. A low transition temperature represents a good PVC material and a high transition temperature points to a poor PVC material. A schematic graph of the transition temperature of a good and a poor PVC pipe is given in Figure 45. In Figure 46 some results of experiments on a good and a poor PVC pipe are given. Aside from some scatter, the transition temperature is clearly visible. This scatter is normal and intrinsic to PVC, since PVC is by nature an inhomogeneous material.

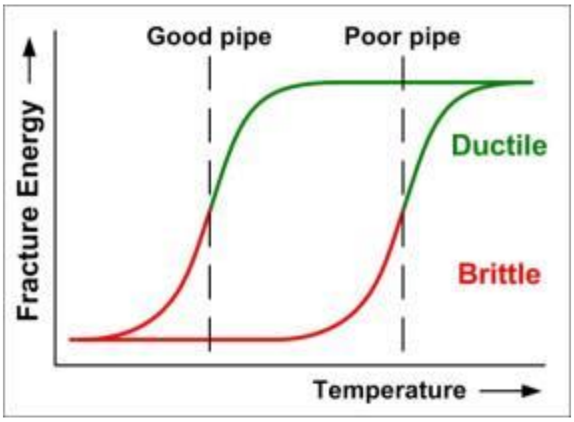


Figure 45. Schematical graph of the brittle-ductile-transition-temperature for a good and a poor PVC pipe.

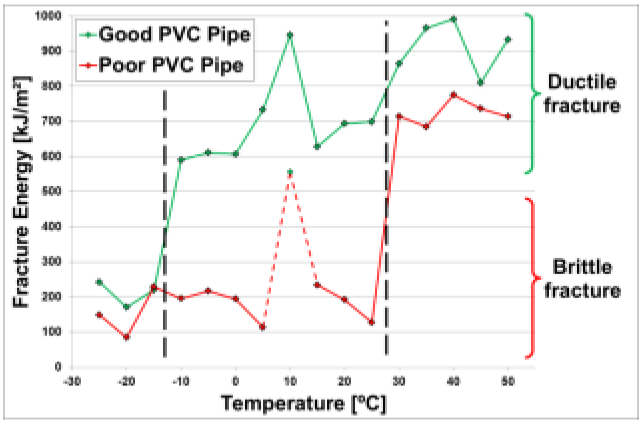


Figure 46. Graph of the brittle-ductile-transition-temperature for a good and a poor PVC pipe in practise.

In theory, PVC pipes of poorer material quality will have a higher brittle-ductile transition temperature and consequently a lower fracture resistance on average than pipes with better material qualities. In practice this means that work on PVC pipes, such as construction or repairs, should preferably take place above this transition temperature.

III Determination of the Standard Deviation of T_{BD}

PVC is by nature an inhomogeneous material (see also appendix II). This introduces scatter in experimental results, which in turn means that the T_{BD} (brittle-ductile transition temperature, see appendix II) is more of a transition range than a single point. Normally, this T_{BD} can be measured more accurately by testing more specimens. However, due to cost limitations and the existing need for large numbers of PVC test specimens, a limit of 12 specimens per gas/PVC type combination was chosen. This introduced a higher scatter than would normally be present for this Kiwa impact test. To get an impression of the size of the standard deviation, two types of PVC were thoroughly tested:

1. PVC-U type 2
2. PVC-A

Firstly, 76 test specimens of PVC-U type 2 were machined and tested using the tensile impact test. A different test temperature was used for each specimen across a range of -25 °C to +50 °C in incremental steps of 1 °C (see Figure 47).

This was also carried out using PVC-A (see Figure 48).

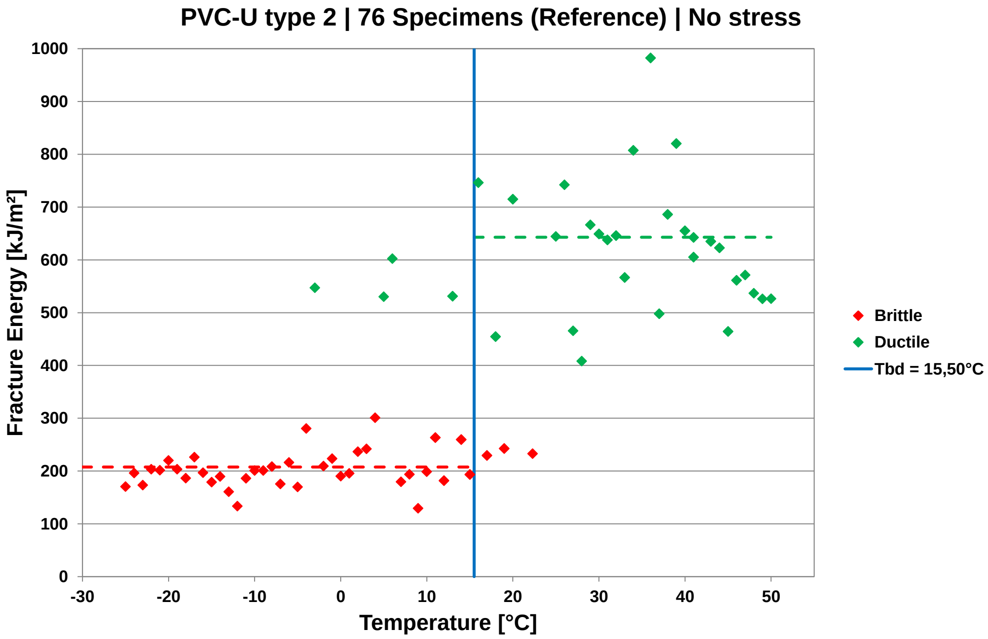


Figure 47. PVC-U type 2 tested from -25°C to +50°C in steps of 1°C.

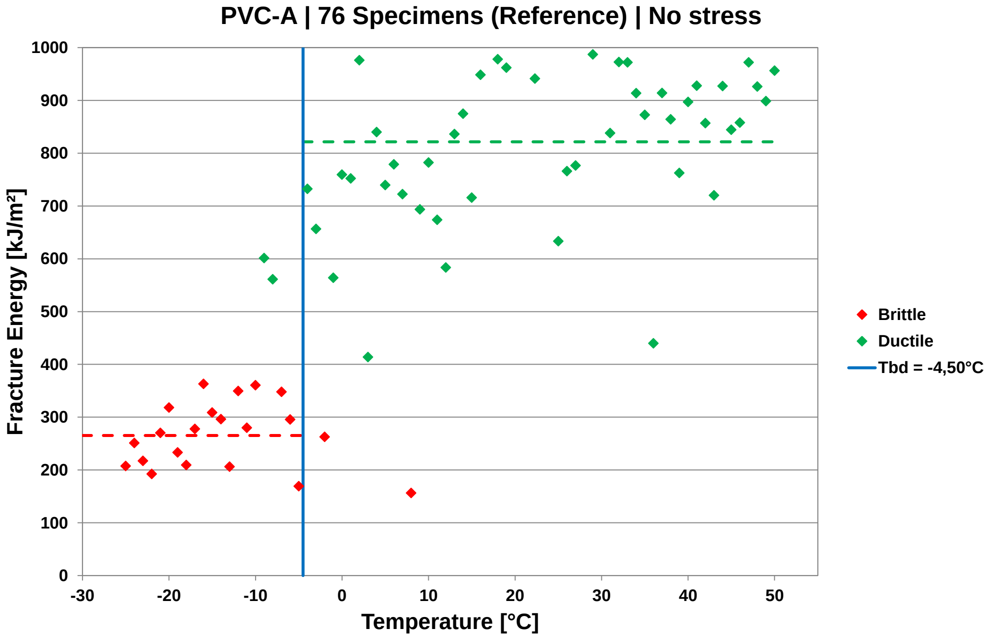


Figure 48. PVC-A tested from -25 C to +50 C in steps of 1°C.

Secondly, a Monte Carlo Simulation was performed in order to determine the standard deviation of T_{BD}. A limited number of specimens were randomly selected from the 76 measurement points for this simulation. T_{BD} was then calculated for these specimens in accordance with the Kiwa test standard. The random selection was performed 1000 times in order to arrive at an estimation of the standard deviation of T_{BD}, for both PVC-U and PVC-HI, with either 12 or 30 randomly selected test specimens (see Figure 49 to Figure 52).

The results are summarised in Table 31.

Table 31. Estimated standard deviation for 12 or 30 randomly selected specimens for both PVC-U and PVC-HI.

	Estimated σ for 12 specimens	**Estimated σ for 30 specimens**
PVC-U	6.6 °C	3.5 °C
PVC-HI	5.4 °C	2.6 °C

As can be seen, the standard deviation for a test with 30 randomly selected specimens is significantly lower than that for a test with 12 randomly selected specimens as can be expected. It can also be seen that PVC-HI has a lower scatter than PVC-U. The standard deviations in Table 31 are used for estimations of the standard deviation in this report.

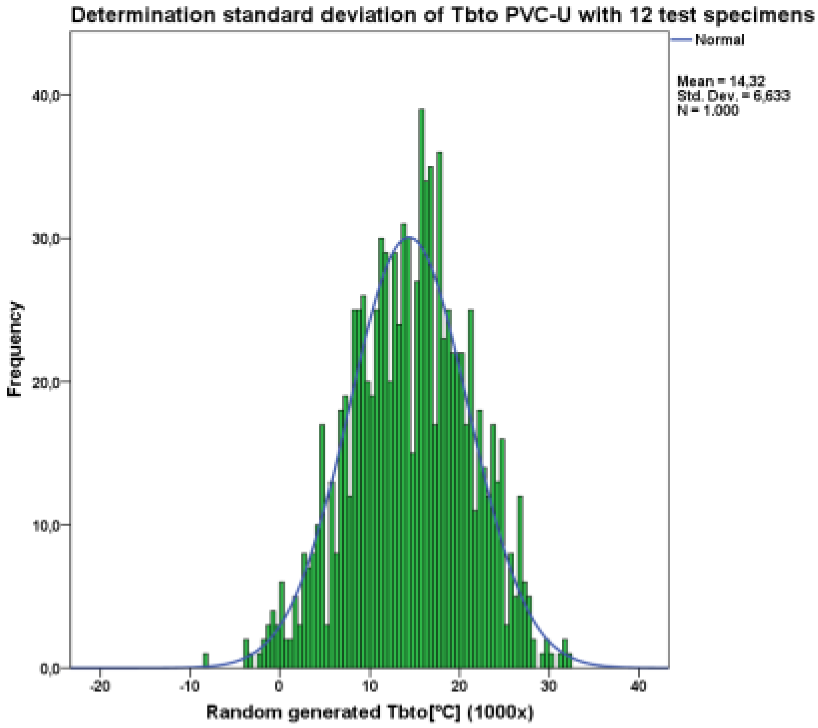


Figure 49. Determination of standard deviation of T_{BD} PVC-U type 2 with 12 randomly selected test specimens.

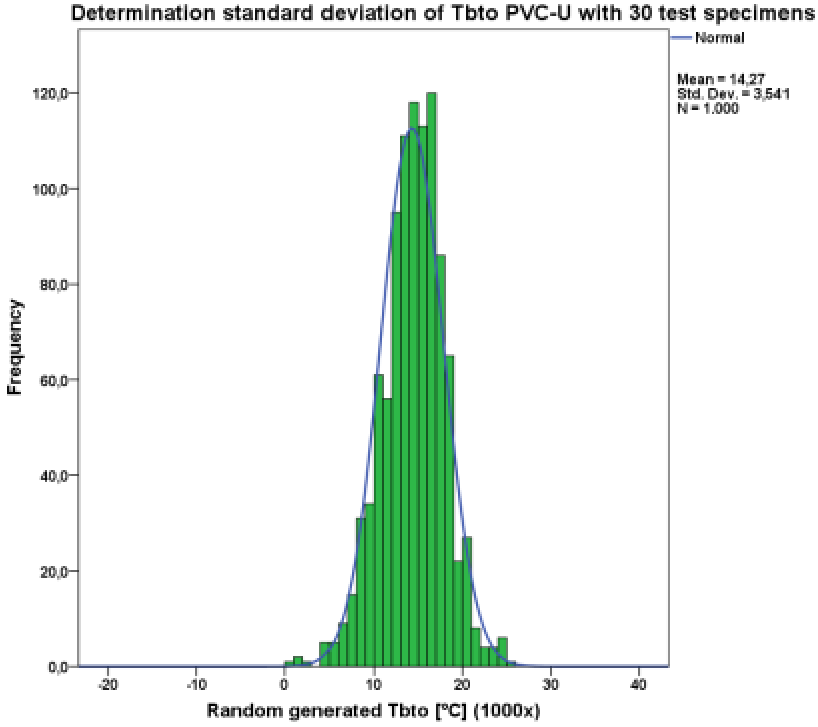


Figure 50. Determination of standard deviation of TBD PVC-U type 2 with 30 randomly selected test specimens.

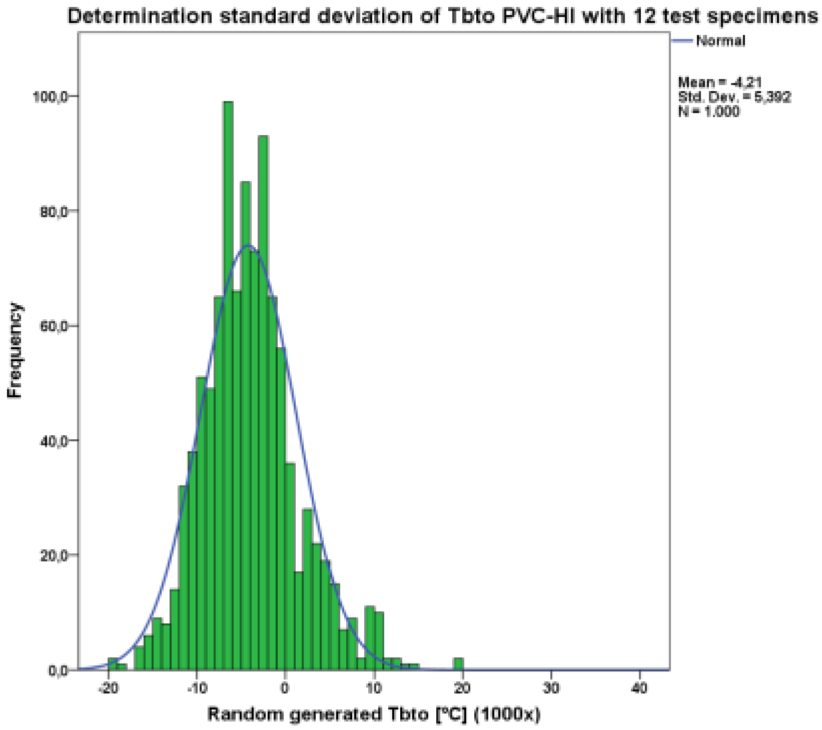


Figure 51. Determination of standard deviation of T_{BD} PVC-A with 12 randomly selected test specimens.

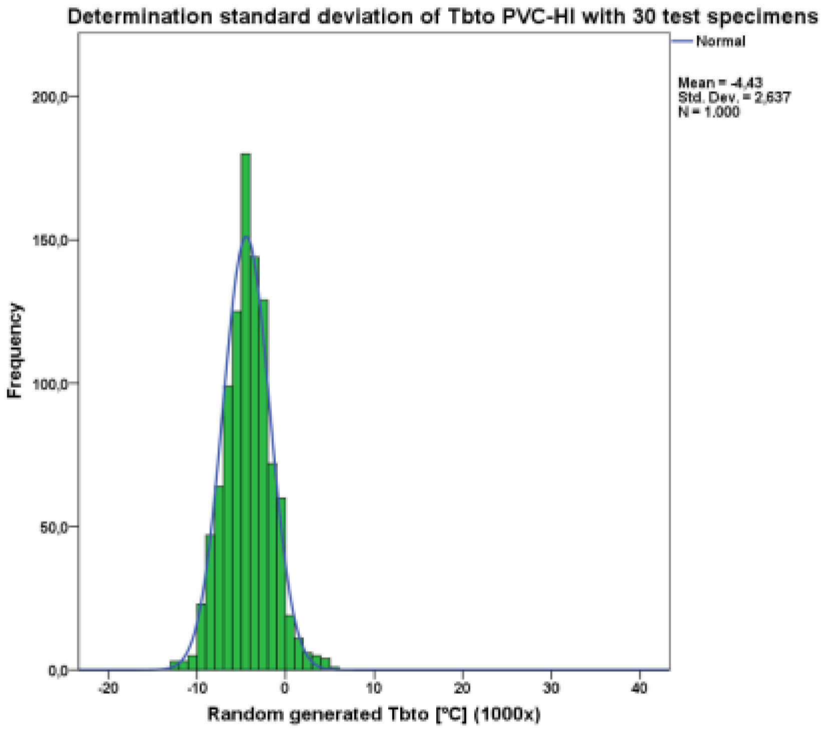


Figure 52. Determination of standard deviation of T_{BD} PVC-A with 30 randomly selected test specimens.

IV Results of all tests

In this appendix the results of all individual experiments are given. These are only added for reference purposes. The most important conclusions drawn from this data are given in the text of the report.

IV.1 Polyvinyl Chloride (PVC)

In this appendix the results of the experiments on PVC are given. The results of the experiments of the samples exposed to wide band concentrations are left out and can be found in [4].

IV.1.1 Mass Change

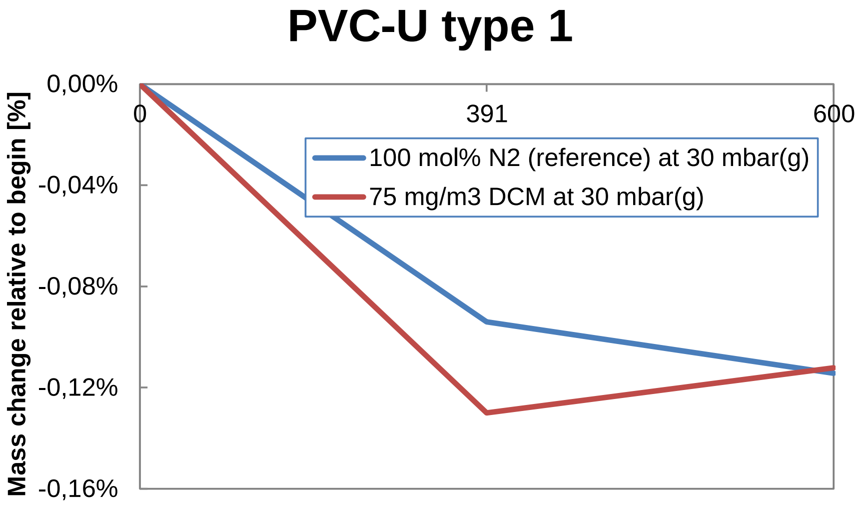


Figure 53. Mass change of PVC-U type 1 materials which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N$_2$ (reference).

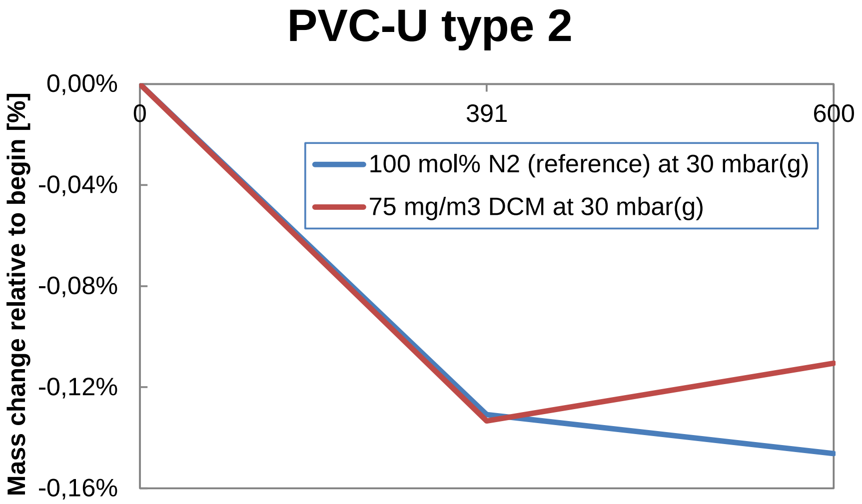


Figure 54. Mass change of PVC-U type 2 materials which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N$_2$ (reference).

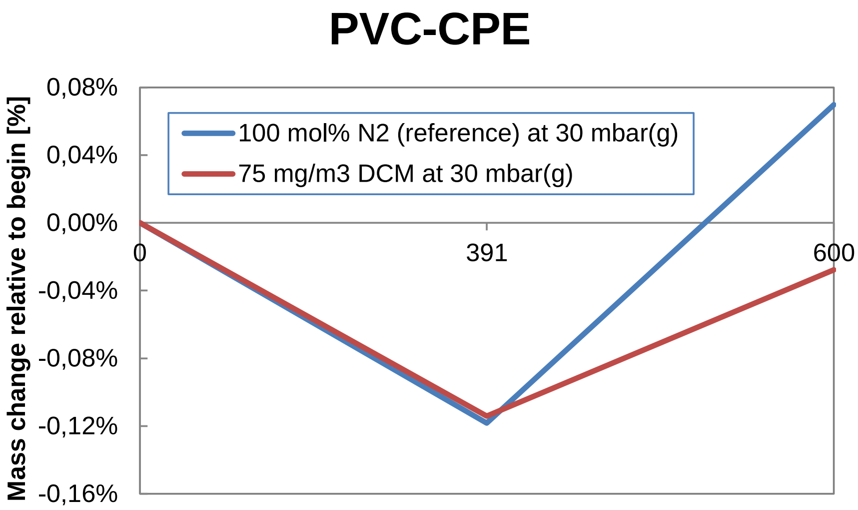


Figure 55. Mass change of PVC-CPE materials which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N_2 (reference).

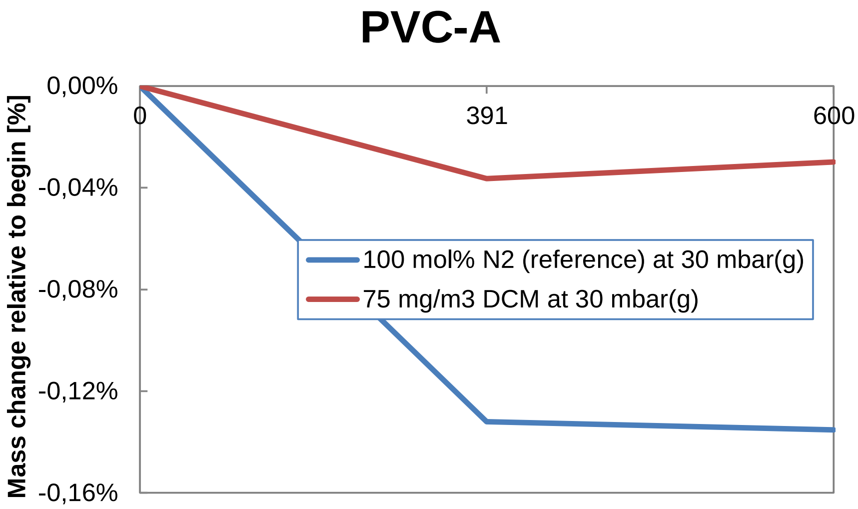
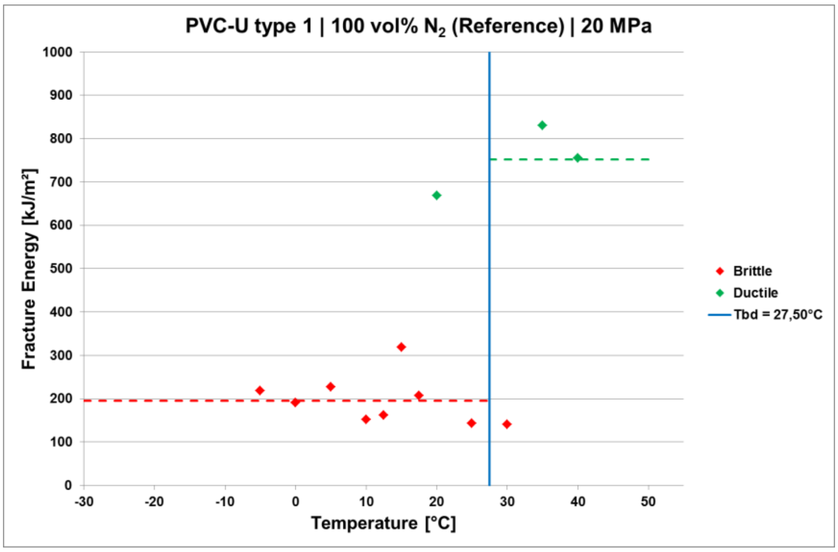
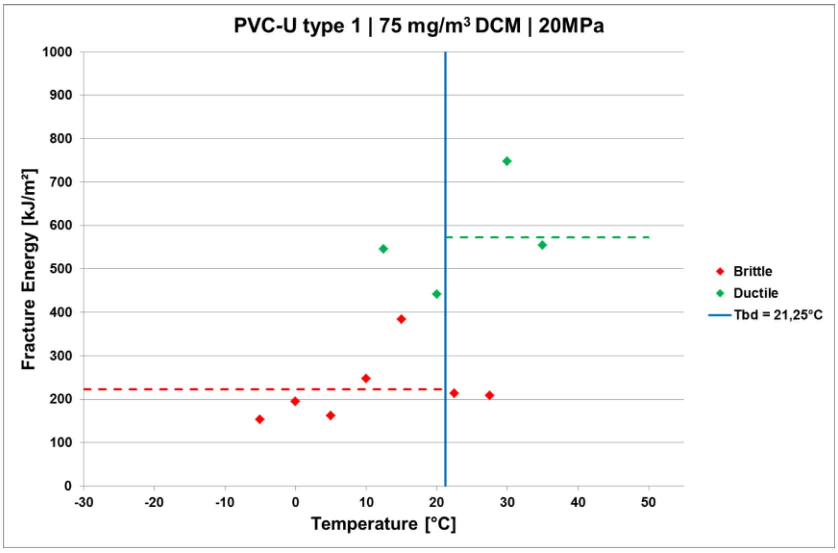
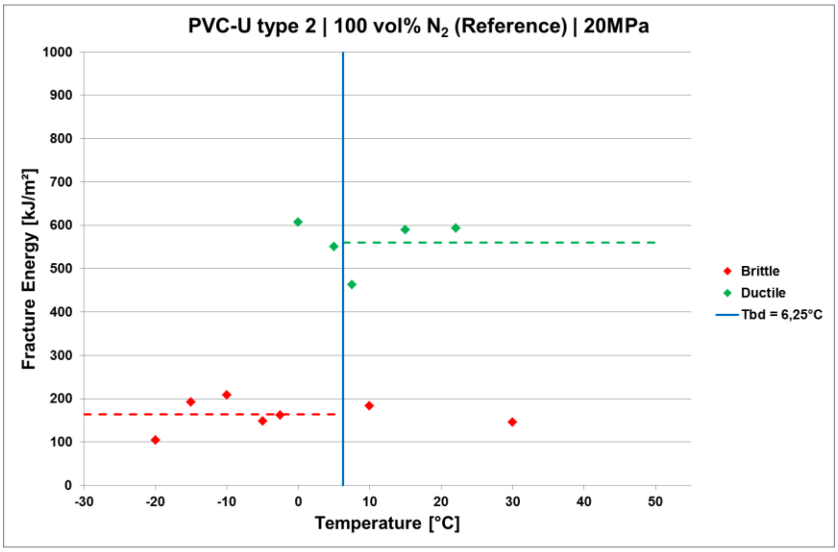


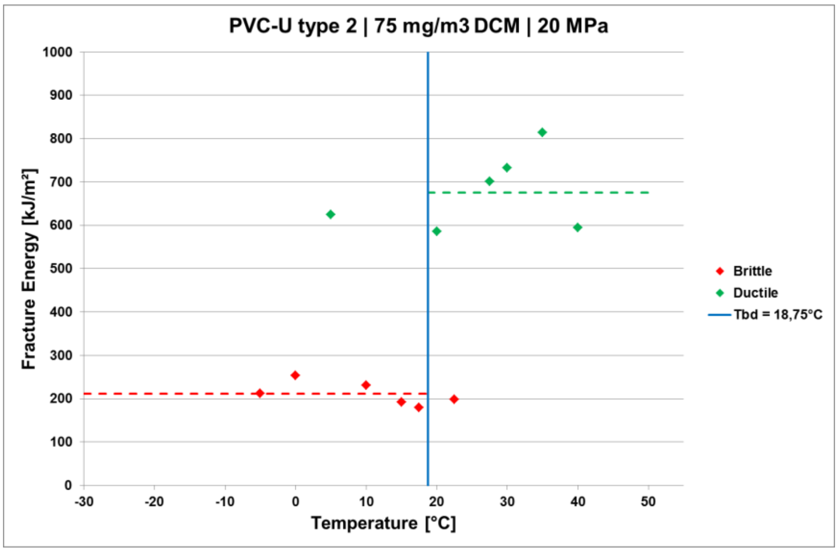
Figure 56. Mass change of PVC-A materials which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N_2 (reference).

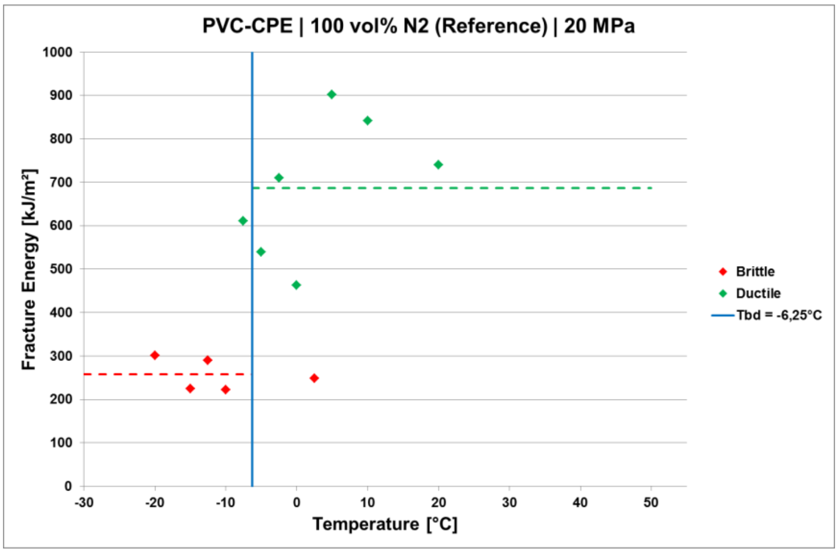
IV.1.2 Brittle-Ductile Transition Temperature

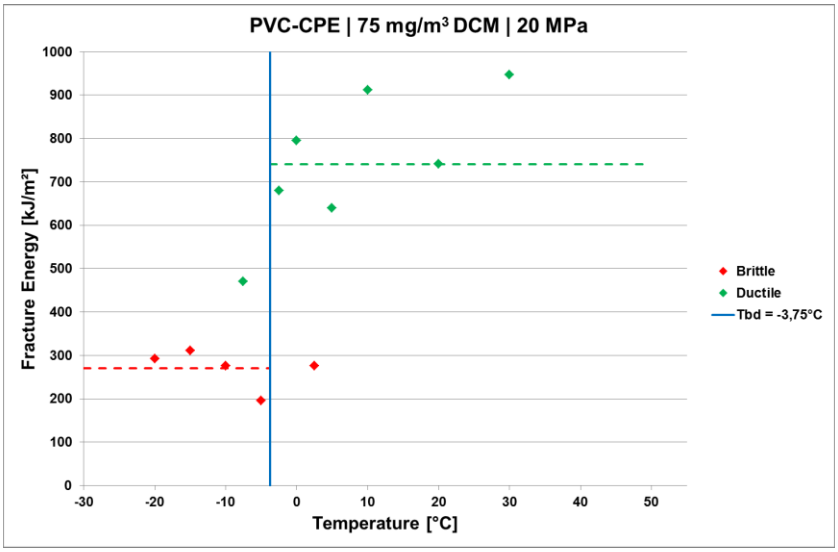


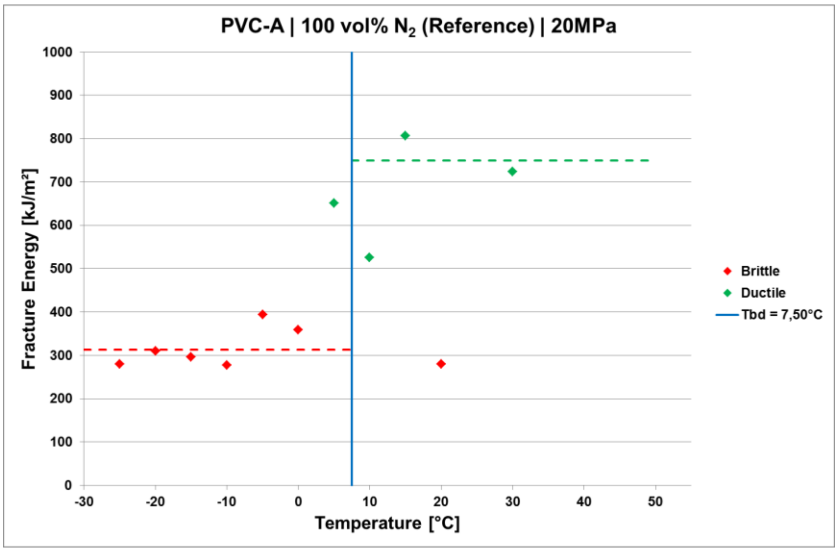


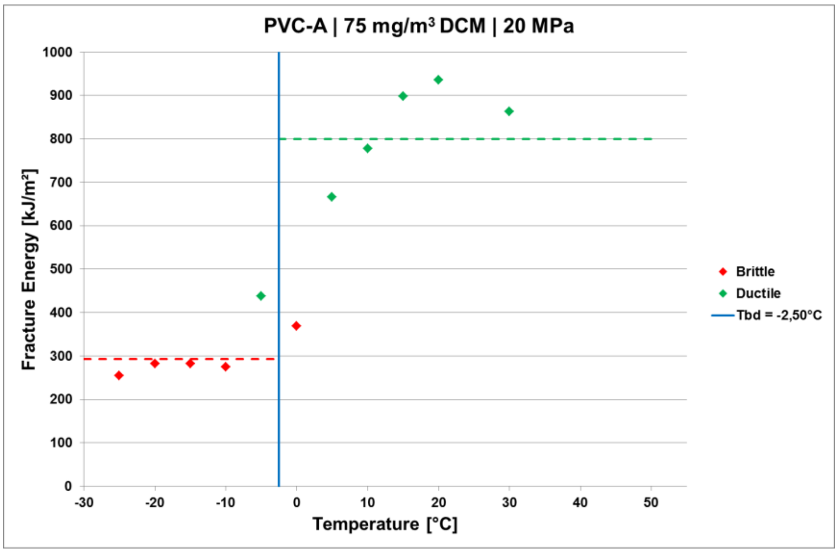


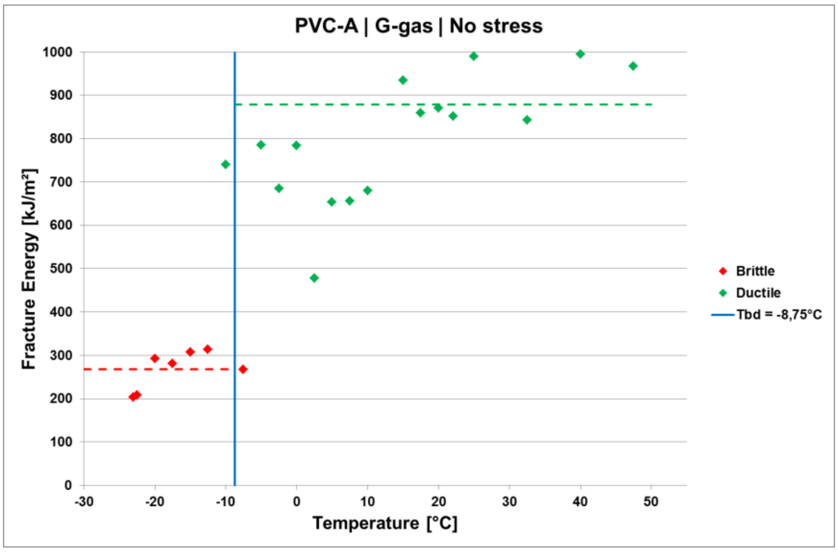

PVC-U type 2 | 75 mg/m3 DCM | 20 MPa
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = 18,75°C

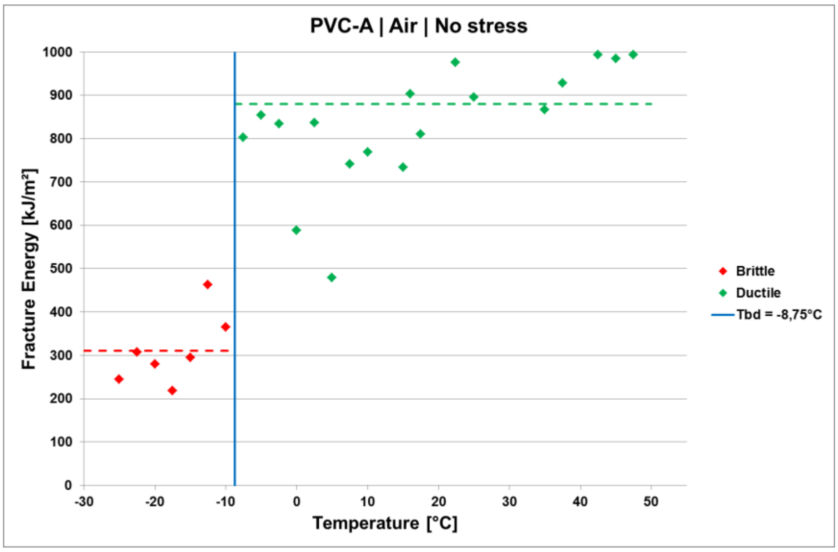

PVC-CPE | 100 vol% N2 (Reference) | 20 MPa
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -6,25°C

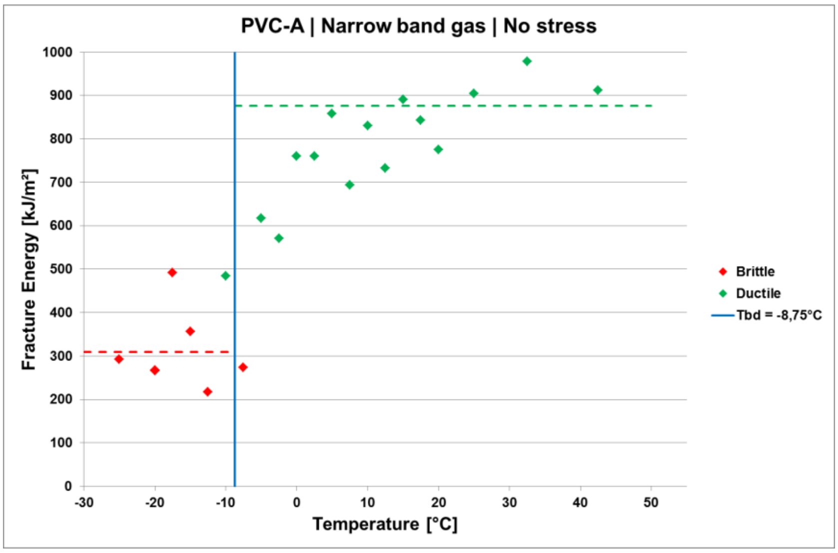

PVC-CPE | 75 mg/m³ DCM | 20 MPa
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -3,75°C

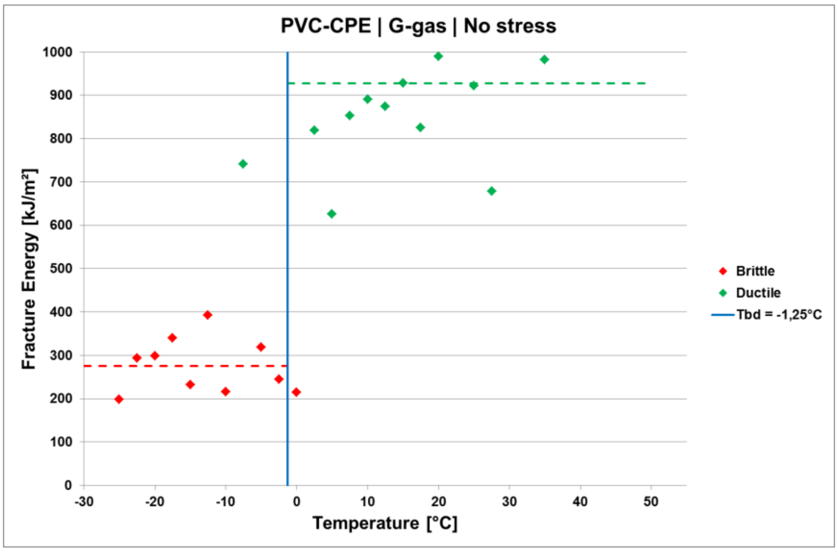

PVC-A | 100 vol% N_2 (Reference) | 20MPa
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = 7,50°C

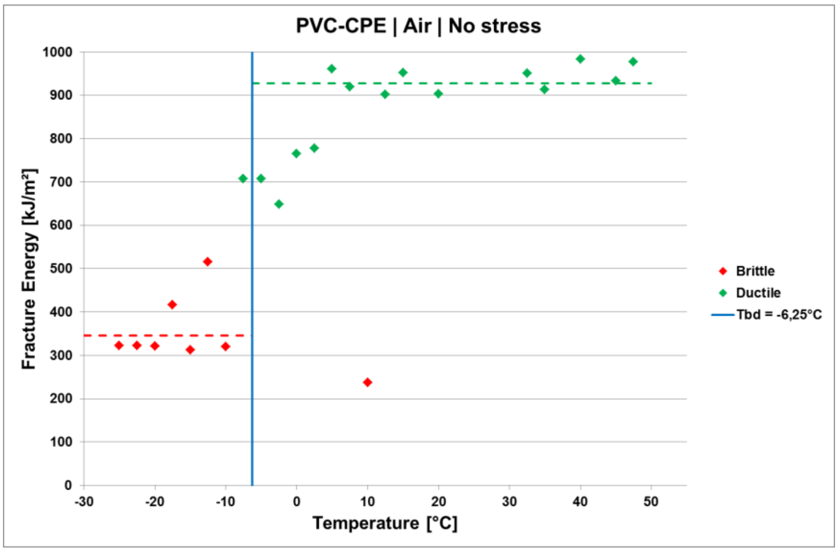

PVC-A | 75 mg/m³ DCM | 20 MPa
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -2,50°C

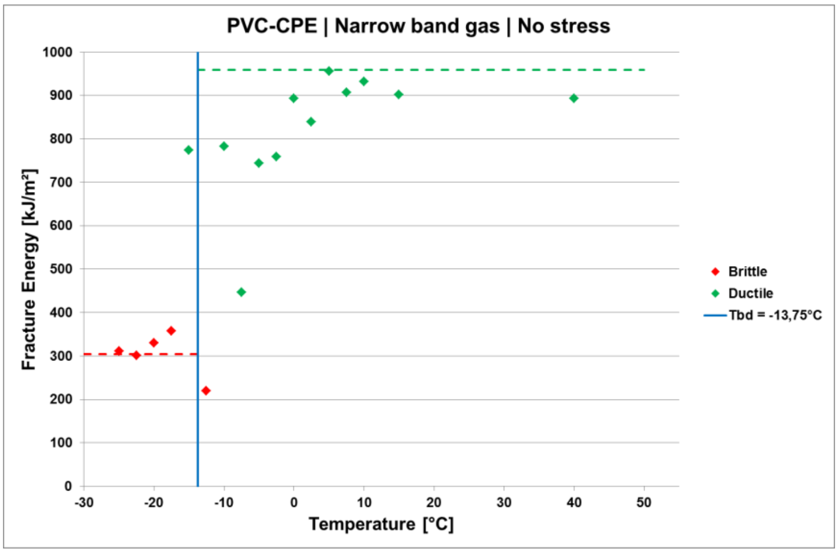

PVC-A | G-gas | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -8,75°C

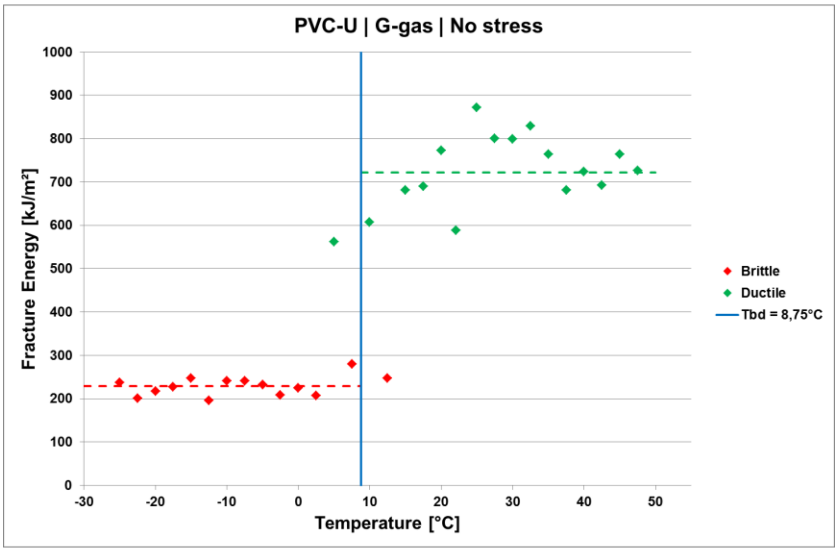

PVC-A | Air | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -8,75°C

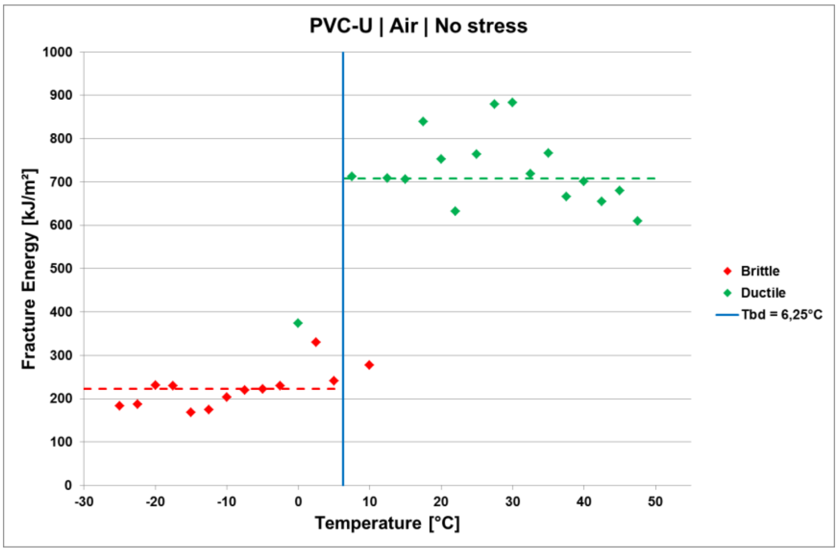

PVC-A | Narrow band gas | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -8,75°C

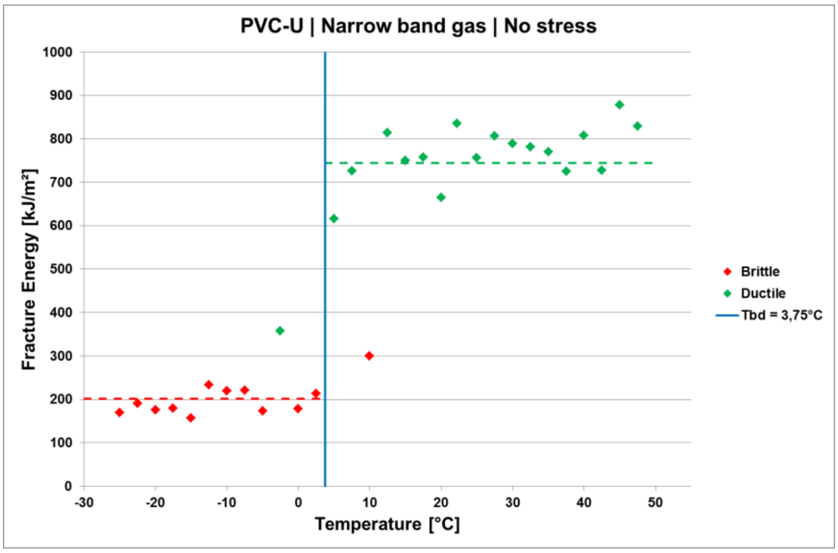

PVC-CPE | G-gas | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -1,25°C


PVC-CPE | Air | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -6,25°C


PVC-CPE | Narrow band gas | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = -13,75°C


PVC-U | G-gas | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = 8,75°C


PVC-U | Air | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = 6,25°C


PVC-U | Narrow band gas | No stress
Fracture Energy [kJ/m²]
1000
900
800
700
600
500
400
300
200
100
0
-30
-20
-10
0
10
20
30
40
50
Temperature [°C]
Brittle
Ductile
Tbd = 3,75°C

IV.2 Polyethylene (PE)

In this appendix the results of the experiments on PE are given. The results of the experiments of the samples exposed to wide band concentrations are left out and can be found in [4].

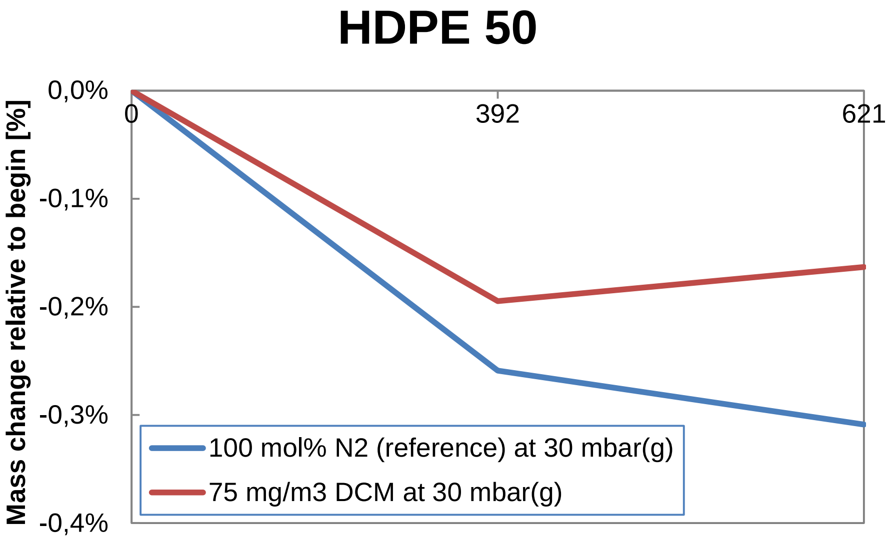


Figure 57. Mass change of HDPE 50 materials which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N_2 (reference).

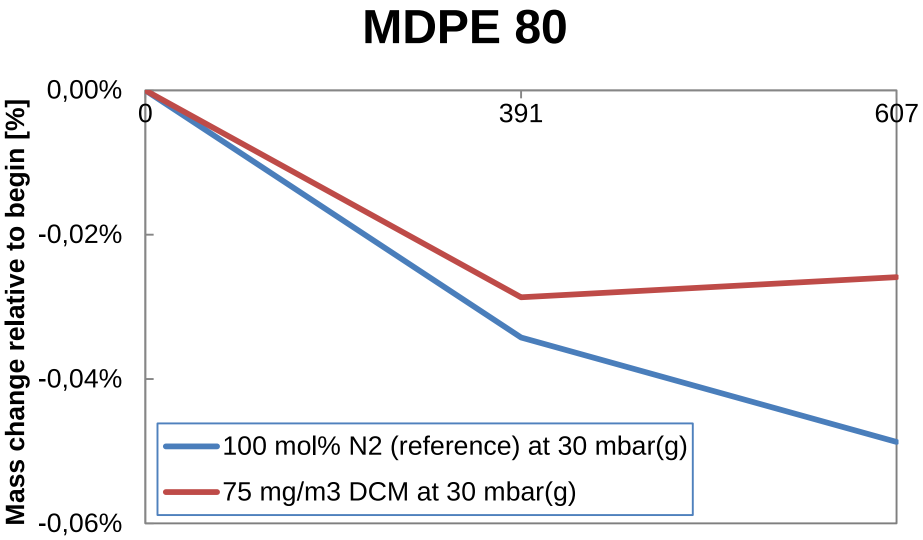


Figure 58. Mass change of MDPE 80 materials which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N_2 (reference).

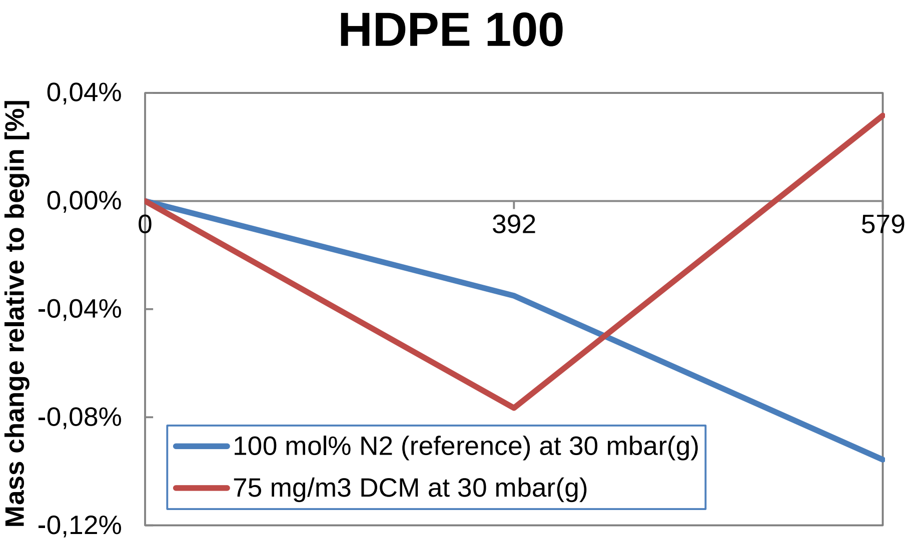


Figure 59. Mass change of HDPE 100 materials which had been exposed for a period of 600 days to 75 mg/m^3 DCM and N_2 (reference).

IV.3 Elastomeric Materials (NBR)

In this appendix the results of the experiments on NBR are given. The results of the experiments of the samples exposed to wide band concentrations are left out and can be found in [4] and [5].

IV.3.1 Mass Change

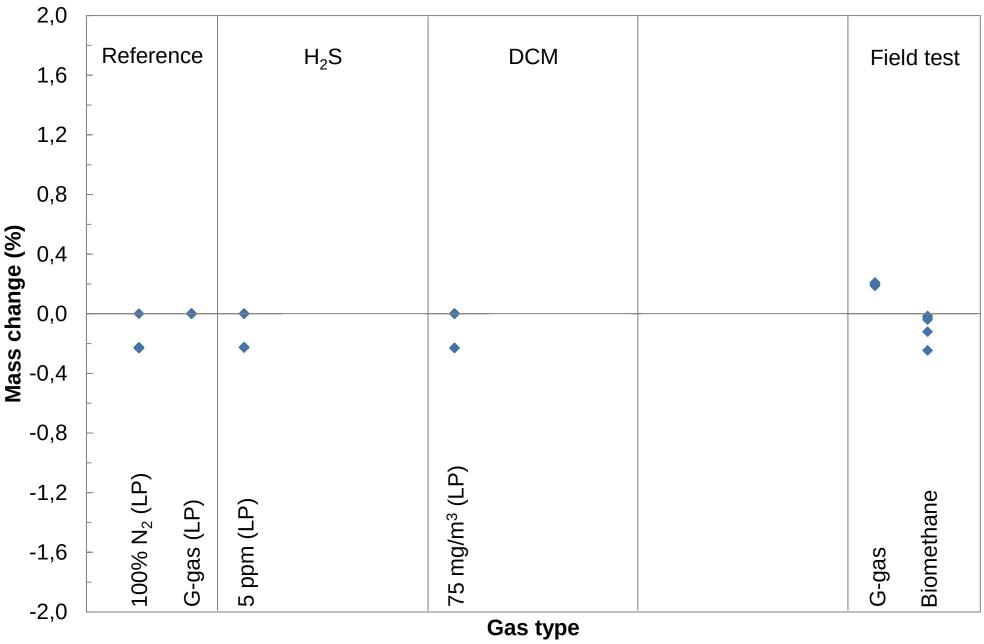


Figure 60. Mass change of NBR samples which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

IV.3.2 Mechanical Properties

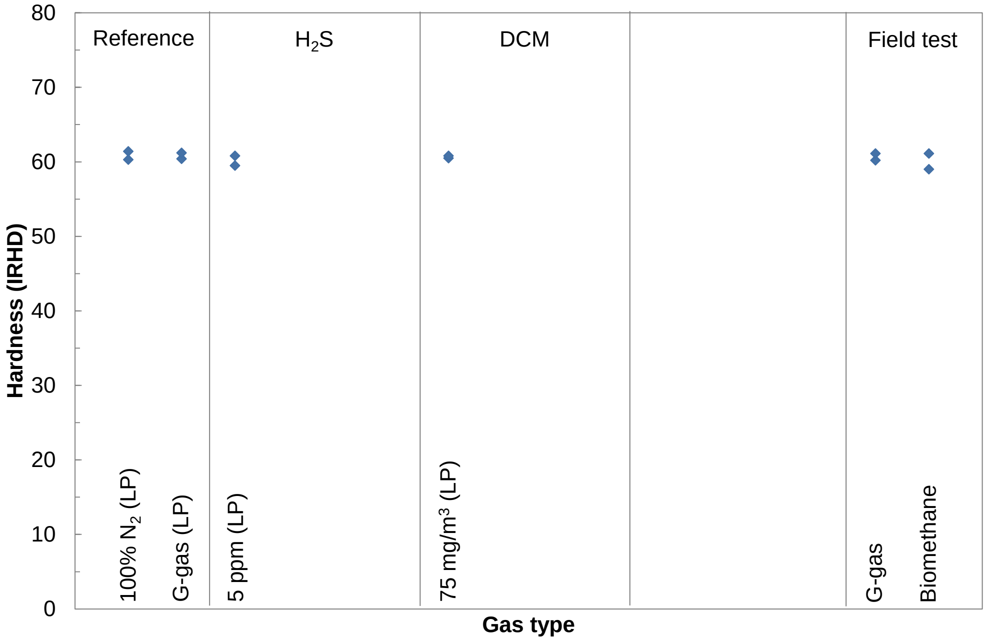


Figure 61. Hardness of NBR samples which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

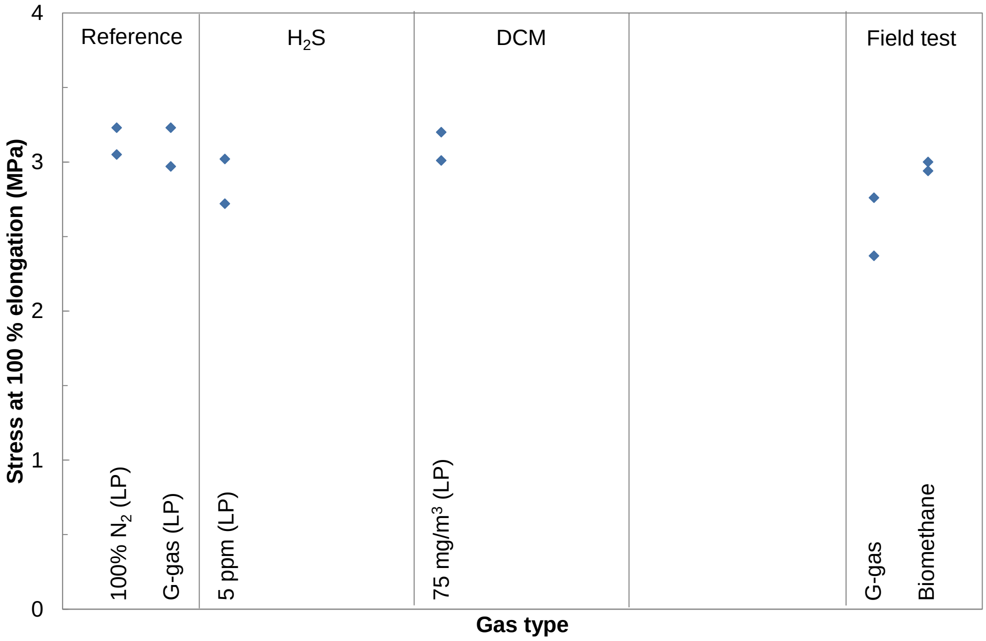


Figure 62. Stress at 100 % elongation of NBR samples which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

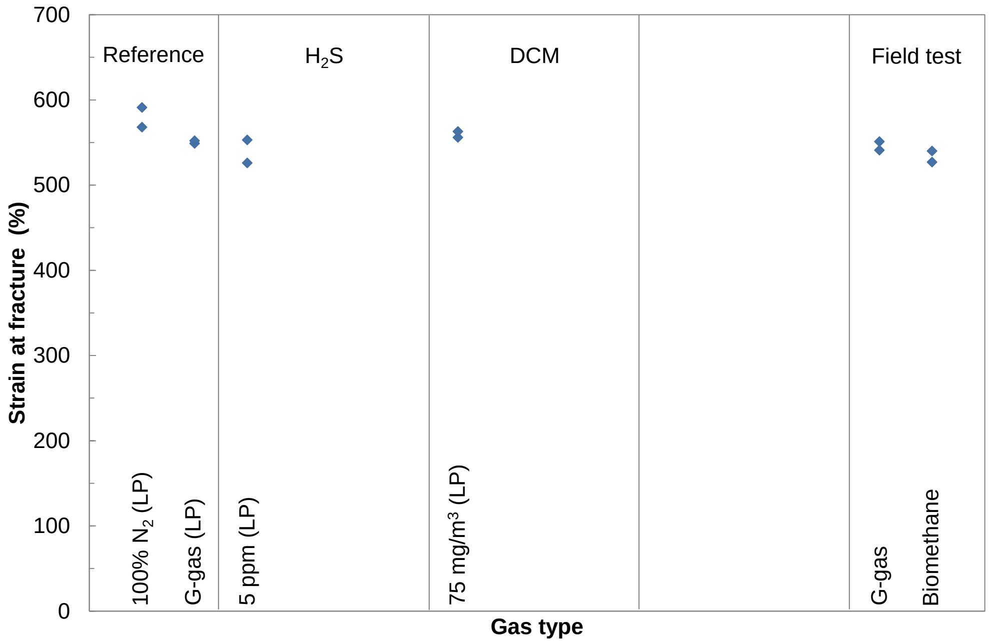


Figure 63. Strain at fracture of NBR samples which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

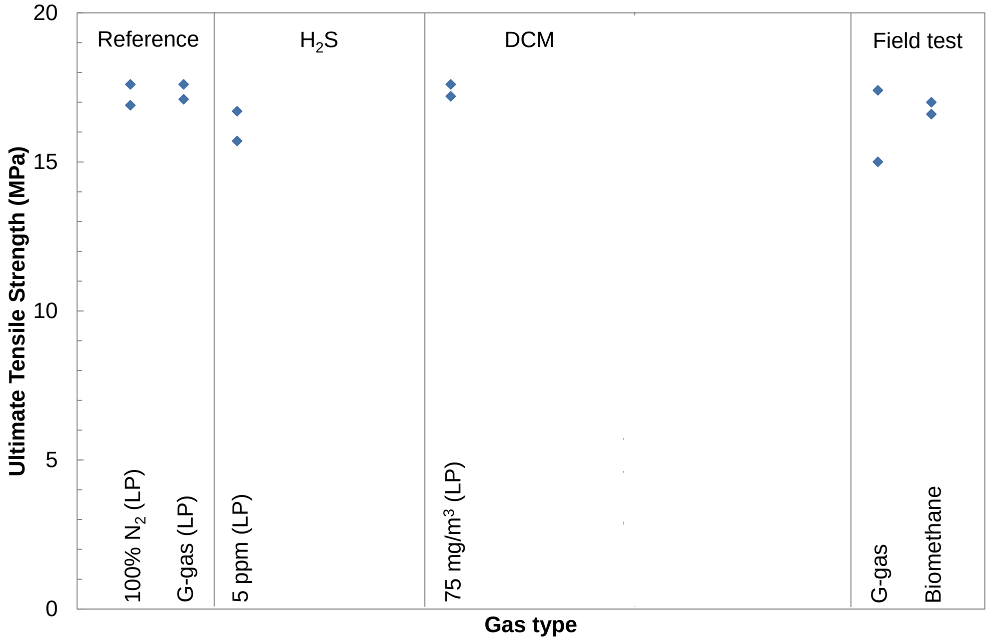


Figure 64. Ultimate tensile strength of NBR samples which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

IV.3.3 Dimensional Change

The dimensions were measured immediately after removing the rings from the oversized pipe (125 mm) and after 1 hour. They were subsequently compared to their original dimensions before exposure. The original dimensions for the field test were estimated.

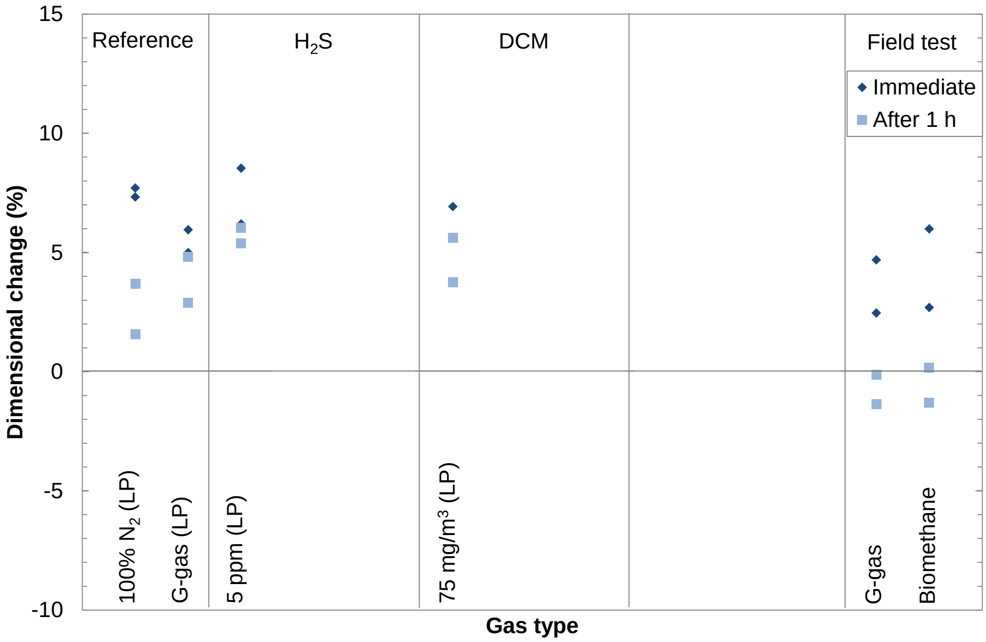


Figure 65. The difference in inner diameter of NBR rings which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

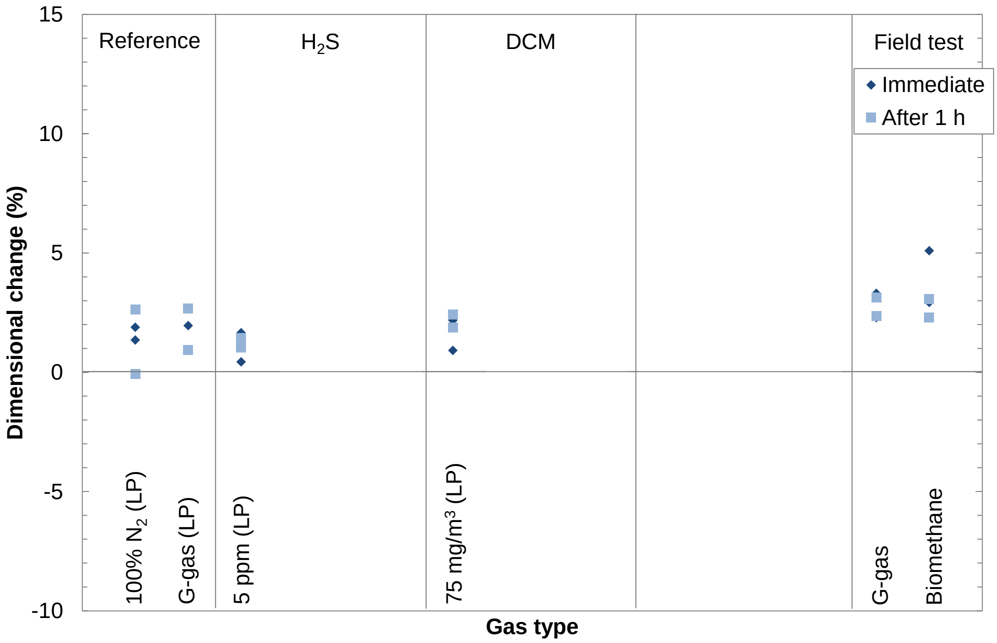


Figure 66. The difference in outer diameter of NBR rings which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

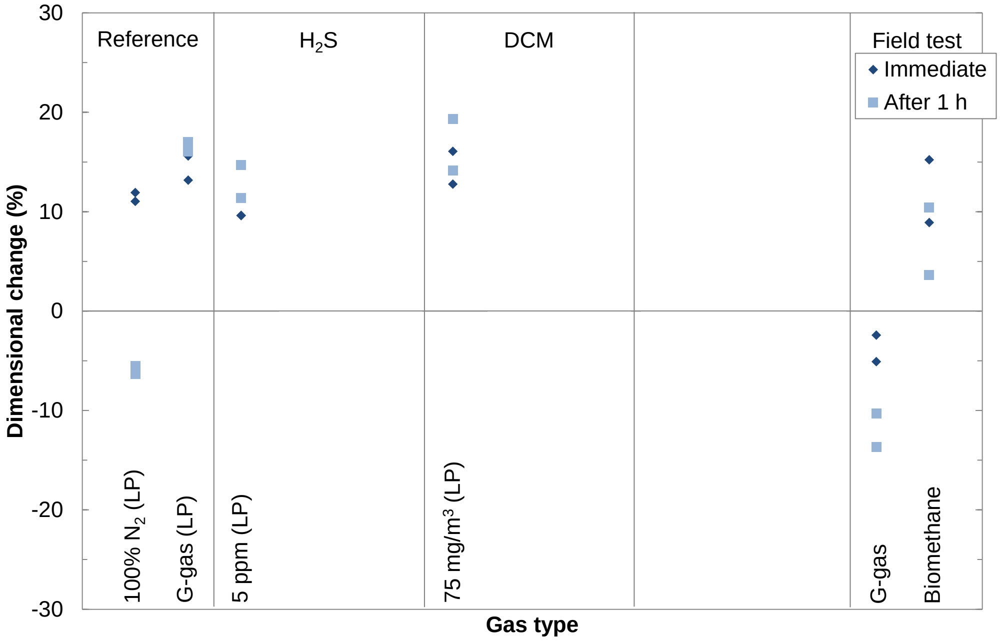


Figure 67. The difference in thickness of NBR rings which had been exposed for a period of 600 days to various narrow band gases. LP is low pressure.

IV.4 Steel

For the results of all steel experiments, see [4].

IV.5 Copper

For the results of all copper experiments, see [4].

IV.6 Aluminium

For the results of all aluminium experiments, see [4].

V References

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