

GT-140282
7 May 2015

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

Final Report





GT-140282

7 May 2015

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

Final Report

© 2015 Kiwa N.V.
All rights reserved. No part of
this report may be
reproduced, stored in a
database or retrieval system,
or published, in any form or in
any way, electronically,
mechanically, by print,
photoprint, microfilm or any
other means without prior
written permission from the
publisher.

Kiwa Technology B.V.
Wilmersdorf 50
Postbus 137
7300 AC Apeldoorn
The Netherlands

Tel. +31 55 539 33 93
Fax +31 55 539 34 94
www.kiwatechnology.nl

Colophon

Title	Effects of Wide Band Gases on Materials used in Gas Distribution Networks. Final Report
Project Number	100201907
Project Manager	R.J.M. Hermkens B Eng
Contractor	EDGaR
Quality Assurance	prof. dr. M. Wolters MSc F.L. Scholten MSc
Project Members	W.B. Berends MSc dr. J. Breen J.H. Brugman J.H.A.M. Heerings MSc A. Hendriks BSc H.A. Ophoff MSc P.J. Postma BSc F.L. Scholten MSc M. Schrijver P.H.G.M. Stens H. Westerhuis
Authors	J. de Bruin MSc W.J. Rittel MSc E.J.W. van der Stok MSc J. Weller MSc



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 Expanding the Distribution Band of the Gas Quality in the Netherlands". The working title of this project is "Effects of Wide Band Gases on Materials". It is part of the EDGaR program subtheme 1.2 "Technical consequences of the diversity in 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 Narrow 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 a 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. Because the process of upgrading sustainable “raw” gases to narrow band gases is expensive, the next step will likely be to look for possibilities to extend the range of allowable gas compositions. This will save costs for upgrading. These gases are called wide band gases and the effects of these gases were researched in this EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems Expanding the Distribution Band of the Gas Quality in the Netherlands".

This project answers the following main research question:

What are the maximum allowable concentrations of gas components in wide band gases when using the existing Dutch gas infrastructure for the transport of these gases?

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

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

	Sulphur containing components	H ₂ S	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 (up to 160 ppm)		probably none			none		probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
PE	none (up to 160 ppm)		probably none			none		probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
NBR	none (up to 160 ppm)		probably none			none		probably none		none	none	none, unless liquid		none	
steel	water and CO ₂		probably none						with H ₂ S and water: possibly	unknown	water and H ₂ S		probably none	water, (H ₂ S) and CO ₂	none
	water, CO ₂ and O ₂										water, (H ₂ S) and O ₂				
Cu	water and CO ₂		probably none		none (with water up to 50 ppm)		probably none		unknown		water and O ₂		probably none	water and CO ₂	none (up to 20 mol%)
	water, CO ₂ and O ₂										water, H ₂ S and O ₂			water, H ₂ S and CO ₂	
Al	water and CO ₂		probably none		none		probably none		unknown		none		probably none	none	none (up to 20 mol%)
	water and O ₂													water and H ₂ S	

	=	The effect is unknown, but is expected to be very small or non-existent.
	=	This component in wide 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 depends on whether water is present in the gas distribution grid or not. Without water, corrosion of metallic materials (steel, copper and aluminium) cannot occur and only a few restrictions on



the maximum allowable concentrations of gas components in wide band gases are necessary.

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 wide 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, only traces of aromatic hydrocarbon vapour are found in wide band gases.

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 wide 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) or have not been tested at high concentrations (> 160 ppm H₂S). 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 H₂S to 160 ppm.

Finally, the literature was inconclusive about the effects of H₂ on some materials. The effects of H₂ were tested up to 20 mol%, while the concentration H₂ in wide band gases could be as high as 62 mol%. Therefore, the effect of H₂ at higher concentrations remains unknown for PVC, PE, copper and aluminium. It is therefore recommended that the maximum concentration of H₂ be limited to 20 mol%.

The above-mentioned recommendations are summarised in Table 2 where water is not present in the existing Dutch gas distribution grid. Limiting values for other gas components in wide band gases are 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 H₂S, CO₂ and O₂ may lead to severe corrosion in steel, copper and aluminium.

For steel the following acceptable maximum concentrations were determined in the experiments:

- H₂S should be limited to 34 ppm,
- CO₂ should be limited to 10.3 mol%, and
- O₂ should be limited to 100 ppm (0.01 mol%).

These limiting values are also suitable for copper and aluminium. However, severe corrosion can still occur in aluminium without the presence of CO₂. More research using low CO₂ concentrations is therefore recommended.



Table 2. Recommended limiting values for several gas components in wide band gases where water is not present in the gas distribution grid or in wide 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. Although only traces of these substances are currently found in wide band gases, 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.
< 160 ppm H ₂ S	The effect of H ₂ S at a higher concentration than 160 ppm was not tested due to its high toxicity to humans. Because of this health and safety risk and because no information could be obtained about the possible effect of this component on the most important materials used in the Dutch gas distribution grid, it is recommended that the maximum concentration of H ₂ S be limited to 160 ppm.
< 20 mol% H ₂	The effect of H ₂ with a higher concentration than 20 mol% was not determined for the investigated materials. The effect at higher concentrations is therefore unknown.

Finally, the effects of NH₃ on copper were tested at concentrations of up to 50 ppm in humid gas. The literature was inconclusive about the effects of 100 ppm NH₃ (which may occur in wide band gases) on copper. The effects of NH₃ at concentrations of up to 100 ppm is therefore currently unknown for copper materials. More research using higher NH₃ concentrations is recommended.

When water is present in the gas grid or in wide band gases additional recommendations to the ones given in Table 2 are needed and given in Table 3. Limiting values for other components in wide band gases 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 wide band gases where water is present in the gas distribution grid or in wide band gases.

Limiting value	Reason
< 34 ppm H ₂ S	The combination of H ₂ S, CO ₂ and O ₂ may lead to severe corrosion in steel, copper and aluminium. These limiting concentrations are found to limit the effect on metallic materials to an acceptable level.
< 10.3 mol% CO ₂	
< 0.01 mol% O ₂	
< 50 ppm NH ₃	The effects of NH ₃ with a higher concentration than 50 ppm was not tested for the investigated materials. The influence at higher concentrations is therefore unknown.
possibly > 0 mol% CO ₂	If both H ₂ S 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 values. More research using low CO ₂ concentrations is therefore recommended.

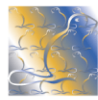


Contents

	List of Symbols and Abbreviations	7
	General	7
	Gases	7
	Materials	7
	Test-related	8
1	Introduction	9
1.1	Background	9
1.2	Goal	9
1.3	Approach	10
1.4	Reading Guide	10
2	Literature Review & Experimental Setup	12
2.1	Literature Review	12
2.2	Experimental Setup	14
2.3	Implementation of the Lab Experiments	18
2.4	Results	21
3	Effects on polymeric materials	22
3.1	Polyvinyl Chloride (PVC)	22
3.2	Polyethylene (PE)	30
3.3	Elastomeric Materials (NBR)	35
4	Effects on Metallic Materials	44
4.1	Steel	44
4.2	Copper	51
4.3	Aluminium	55
5	Conclusions	59
6	Recommendations	61



I	Initial Craze Formation in ESC Tests on PVC	64
II	Ductility and the Brittle-Ductile Transition Temperature (T_{BD})	66
III	Determination of the Standard Deviation of T_{BD}	68
IV	Results of all tests	72
IV.1	Polyvinyl Chloride (PVC)	72
IV.2	Polyethylene (PE)	82
IV.3	Elastomeric Materials (NBR)	87
IV.4	Steel	92
IV.5	Copper	93
IV.6	Aluminium	94
V	References	95



List of Symbols and Abbreviations

General

DSO distribution system operator

Gases

BTX benzene, toluene and xylene
CO carbon monoxide
CO₂ carbon dioxide
DCM dichloromethane
G-gas Groningen gas
H₂ hydrogen
H₂S hydrogen sulfide
HCl hydrochloric acid
HCN hydrogen cyanide
N₂ nitrogen
NH₃ ammonia
O₂ 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
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)
NBR nitrile-butadiene rubber
SBR styrene-butadiene rubber
St steel

* 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
$\epsilon_{F\%}$	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

In order to make the supply of gas more sustainable and to extend the variety of gas sources that may be used, the network operators are currently exploring the possibility of using the existing gas infrastructure, to which almost all households in the Netherlands are connected, for the transport and distribution of gases originating from alternative sources. This will allow the supply of sustainable gas to take place using the entire existing natural gas infrastructure (pipeline systems, appliances, industrial installations, etc.), in the most cost-effective manner.

Due to the tendency towards the replacement of fossil fuels with sustainable gases such as biomethane, SNG etc., it is desirable that a rapidly expanding variety of gases should be transported and distributed through the gas infrastructure described above. The introduction of these sustainable gases is likely to begin with upgraded (narrow band) gases, which are cleaned before they are fed into the natural gas grid. In several countries, including the Netherlands, national specifications for these narrow band gases are now in place [4]. These upgraded and cleaned gases have compositions and properties comparable to those of the natural gas used to date (Groningen gas or G-gas), although the concentrations of some components may deviate from those in G-gas. The limits as determined for narrow band gases are however arbitrary and lack a solid foundation. Research that may lead to alterations to these narrow band limits took place in another project [5].

Because the process of upgrading sustainable raw gases to narrow band gases is expensive, the next step in replacing fossil fuels with sustainable gases will probably be to minimise upgrading raw gases. This will save costs but will also lead to new gas compositions. These gases are referred to as wide band gases and do not fulfil the requirements for narrow band gases as stated in report GT-140281 [5].

The following three types of gas compositions can therefore be distinguished:

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 [5]	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 wide band gases on materials used in gas distribution systems. Two other reports will consider the influence of narrow band gases on the Dutch gas distribution network [5] and the influence of sustainable gases on joints and connections [6], respectively. A literature review performed by Gasunie discusses the effects of the transport of wide band gases on materials used in gas transport systems [7,8].

1.2 Goal

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

What are the maximum allowable concentrations of gas components in wide band gases when using the existing Dutch gas distribution network for the transport of these gases?



The following sub-questions are relevant in this respect:

- a) What exactly are wide band gases?
- b) What are the gas component/material combinations that are most likely to lead to premature failure within the desired lifespan?

In order to study these gas component/material combinations, the following sub-questions must be answered:

- c) What are the critical failure mechanisms for the pipeline materials under consideration?
- d) Can these failure mechanisms be modelled to establish maximum allowable gas component concentrations?

The main goals of this project are therefore:

- A. To determine which gas components at which concentrations in wide band gases may be harmful to the materials used in the existing Dutch gas infrastructure.
- B. To provide a sound technical understanding of the long-term behaviour of the affected pipeline materials when transporting wide band gases.

Sub-questions a) to d) were answered in the literature review [1]. The aim of the experiments was to answer the questions arising from the main goals A and B. This experimental work was intended to supply answers regarding the influence of certain components in wide 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 wide 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 that may lead to negative effects. 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 wide band gases on the Dutch gas transport network have been investigated by Gasunie / DNV.GL and are part of the EDGaR project A5 [7,8].

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) to d) listed in section 1.2. For some gas/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 wide band gases on the resistance of the most important materials used in the Dutch gas distribution network.

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 wide band gases on polymeric materials. Chapter 4 discusses the effects of wide 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 wide 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 Wide Band Gases on Materials", which was performed to evaluate the influence of wide 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 review 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 wide 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. Wide band gases are defined as all sustainable gases including raw gases and partially upgraded sustainable gases. This means that the physical properties and the chemical composition of wide band gases may be completely different to those of G-gas and that the concentrations of chemical compositions may lie anywhere within a very broad range. Table 5 shows a comparison between the chemical composition of average G-gas and the maximum concentration values found in wide 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 wide 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 of 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 wide band gases.

Table 6 shows the results of the literature study with regard to the influence of different gas components in wide band gases on the most important gas distribution materials. The effect specified applies to the maximum concentrations found for wide band gases in the literature examined. The colours indicate what is known about the effect of the gas components present in wide band gases on the various materials.

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.



Table 5. Maximum chemical concentrations found in wide band gases and average values for G-gas.

Chemical compound/mix	G-gas average [9]	Wide band gases max. found concentration [1]	Unit
Sulphur (total)	6.7	-	mg/m ³ (n)
Inorganically bound sulphur (H ₂ S)	0.4 ppm	4 300 mg/m ³ (n)	
Mercaptane	< 1.0	-	mg/m ³ (n)
Odorant value (THT)	17.7	-	mg/m ³ (n)
Chlorine-containing compounds	< 0.1	735	mg/m ³ (n)
Fluorine-containing compounds	< 0.1	256	mg/m ³ (n)
Ammonia	< 0.1	100	ppm
Hydrogen chloride (HCl)	< 1.0	Traces (ppb)	ppm
Hydrogen cyanide (HCN)	< 1.0	Traces (ppb)	ppm
Carbon monoxide (CO)	< 100	700 000	ppm
Carbon dioxide (CO ₂) in dry gas	0.9	59.0	mol%
Aromatic hydrocarbons	800 (max. value [10])	Traces (ppm)	ppm
Benzene	-	11.4	ppm
Toluene	-	76.2	ppm
Oxygen (O ₂) in dry gas	< 100	26 000	ppm
Hydrogen (H ₂)	< 0.01	62	mol%
Methane (CH ₄)	81.29	99.8	mol%
Nitrogen (N ₂)	14.32	50.9	mol%
Ethane (C ₂ H ₆)	2.87	2	mol%

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

	Sulphur containing components	H ₂ S	Mer-captans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO ₂	Hydro-carbons	Aromatic hydro-carbons	O ₂	H ₂
PVC	unknown		probably none		unknown			probably none	unknown	possibly	none, unless liquid (impact resistance)		probably none	unknown	
PE	unknown		probably none		unknown			probably none	unknown	none	none, unless liquid		none	probably none	
NBR	unknown	possibly	probably none		none	possibly		probably none	none		possibly, if unsaturated	probably none, unless liquid	none		
Steel	with water: possibly		probably none					with H ₂ S 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 in wide band gases does not affect materials.
	=	The effect is unknown.
	=	Deleterious effects are expected under some conditions.



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 sulphur, fluorine or chlorine components, CO₂, ammonia or H₂. The effect of the combination of H₂S, O₂ and CO₂ 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 wide 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 wide 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 environment 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 wide band 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 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 Wide 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).

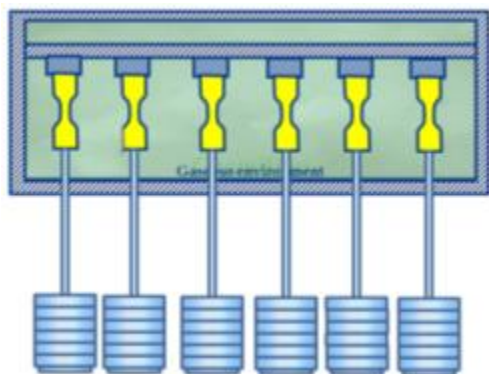


Figure 1. Schematic view of the constant load equipment for testing PE and PVC samples.

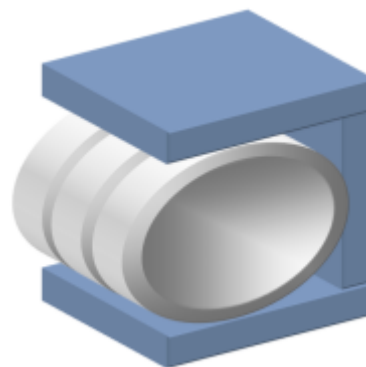


Figure 2. Principle of a U-clamp test on PE and POM rings.

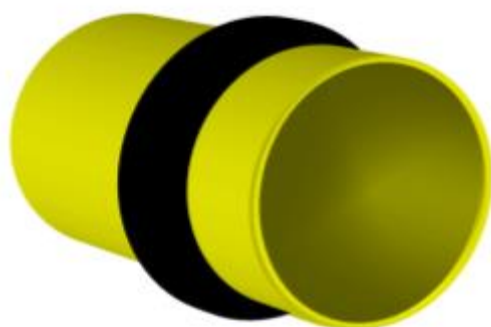


Figure 3. Setup used to expose stressed NBR rings to a particular gaseous environment using an oversized pipe.

Table 7 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.

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	PE3	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-CPE	New	PVC 2012-083	2012	Constant load	20 MPa
	PVC-A	New	PVC 2012-084	2012	Constant load	20 MPa
Rubber	NBR	New	OV 2012-071	2012	Ring over pipe	Undefined



Table 8 shows the polymeric materials and the gaseous environments used. The chemical compositions of the gaseous environments were 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 wide 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 model gas for all halogen-containing materials. The highest concentration of chlorine-containing components found is 735 mg/m³ in wide band gases. For fluorine-containing components, this figure is 256 mg/m³. It was therefore decided to use dichloromethane (DCM) as a model gas for halogen-containing gas at a concentration of 1000 mg/m³.

Sulphur-containing components may also be present in a wide variety of gases. H₂S is considered to be the most aggressive of these components and has the highest risk of adverse effects on polymeric materials. It was therefore decided to use H₂S as a model gas for sulphur-containing components and to investigate the effects of this gas only.

According to the literature, the highest concentration of H₂S is 3085 ppm. However, this level of H₂S in wide band gases is too toxic to allow its presence in the Dutch gas distribution network. The Dutch DSOs consider a concentration level of 100 times the maximum MAC value of H₂S over an exposure period of eight hours to be acceptable. The MAC value of H₂S is 1.6 ppm. It was therefore decided to use H₂S at a concentration of 160 ppm as a model gas.

Table 8. Overview of polymeric materials and the related investigated gaseous environments, including an explanation of the 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 so 100 mol% N ₂ was therefore used for reference purposes.
NBR*	5 ppm H ₂ S	0.03	The maximum allowable concentration of H ₂ S in narrow band gases is 5 ppm [5].
NBR*	80 ppm H ₂ S	0.03	This concentration is between that of the wide and narrow band gases
PE, PVC, NBR	160 ppm H ₂ S	0.03	The concentration of 160 ppm H ₂ S for wide band gases was chosen by the Dutch DSOs as acceptable (= 100 times the MAC value for eight hours).
		8.0	
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 [5].
NBR*	550 mg/m ³ DCM	0.03	This concentration is between that of wide and narrow band gases.
PE, PVC, NBR	1000 mg/m ³ DCM	0.03	The maximum concentration of halogen-containing chemicals found in wide band gases is 1000 mg/m ³ .
		8.0	
PE, PVC, NBR	100 ppm NH ₃	0.03	The maximum concentration of NH ₃ found in wide band gases is 100 ppm.
		8.0	
PVC, NBR	59 mol% CO ₂	0.03	The maximum concentration of CO ₂ found in wide band gases is 59 mol%.
NBR	G-gas	0.03	G-gas was used for reference purposes with SBR for joints [6].
NBR	2 mol% propene	0.03	The maximum concentration of propene found in wide band gases is 2 mol%.

* A type 2 test is used in order to determine the effect of H₂S and DCM on NBR.



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 H₂S, 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 materials.

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

2.2.2 Testing the Effect of Wide Band Gases on Metallic Materials

Testing the effect of wide 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.

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 narrow band gases on metals [5] the concentration levels of these gases are also given. The matrix gas was N₂ in all cases.

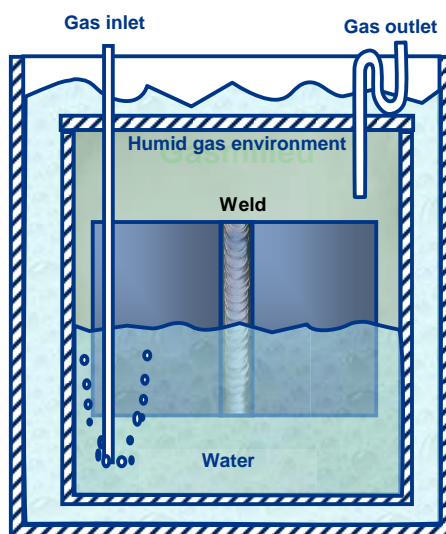


Figure 4. Experimental setup (autoclave) for corrosion testing of metals.



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 [5])
		Relative Humidity (%)	CO ₂ (mol%)	O ₂ (mol%)	H ₂ S (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 without O ₂
	3	100	0	3	160	0.03	H ₂ S 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 ₂ S
	6	100	0	0.5	34	0.03	O ₂ en H ₂ S inside narrow band gas limits
	7	100	10	0.5	34	0.03	CO ₂ , O ₂ en H ₂ S 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 O₂) 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 a short 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 wide 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 wide 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 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.

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.

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 ₂ S	0.03	7-2-2013	9-10-2014	609
NBR	80 ppm H ₂ S	0.03	7-2-2013	9-10-2014	609
PE, PVC, NBR	160 ppm H ₂ S	0.03	30-1-2013	29-9-2014	607
		8.0	8-2-2013	16-10-2014	615
NBR	75 mg/m ³ DCM	0.03	22-1-2013	8-9-2014	594
NBR	550 mg/m ³ DCM	0.03	7-2-2013	9-10-2015	609
PE, PVC, NBR	1000 mg/m ³ DCM	0.03	25-1-2013	1-9-2014	584
		8.0	8-2-2013	29-10-2014	628
PE, PVC, NBR	100 ppm NH ₃	0.03	29-1-2013	13-10-2014	622
		8.0	8-2-2013	25-9-2014	594
PVC, NBR	59 mol% CO ₂	0.03	23-1-2013	20-10-2014	635
NBR	G-gas	0.03	7-2-2013	9-10-2014	609
NBR	2 mol% propene	0.03	7-2-2013	9-10-2014	609



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 approximately 30 mbar at a temperature of 25°C. Gas was continuously bubbled through the water in the test rig at a gas flow rate of 1 l/h. The effects of the gas components were thus tested in a liquid environment as well 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 O₂ 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 Results

The overall results of the literature review and the lab experiments 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 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 wide 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 Wide Band Gases on PVC*

3.1.3.1 *General*

Of all the test specimens (288) exposed to a constant load of 20 MPa and exposed at the same time to gaseous environments, only two broke during the 600 days of testing. The first specimen that broke had been in contact with 1000 mg/m³ DCM (see section 3.1.3.6). The second specimen had been in contact with 100 ppm NH₃ (see section 3.1.3.7).

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 of 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 11 and appendix III).

Table 11. 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 14 to Figure 17. 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.

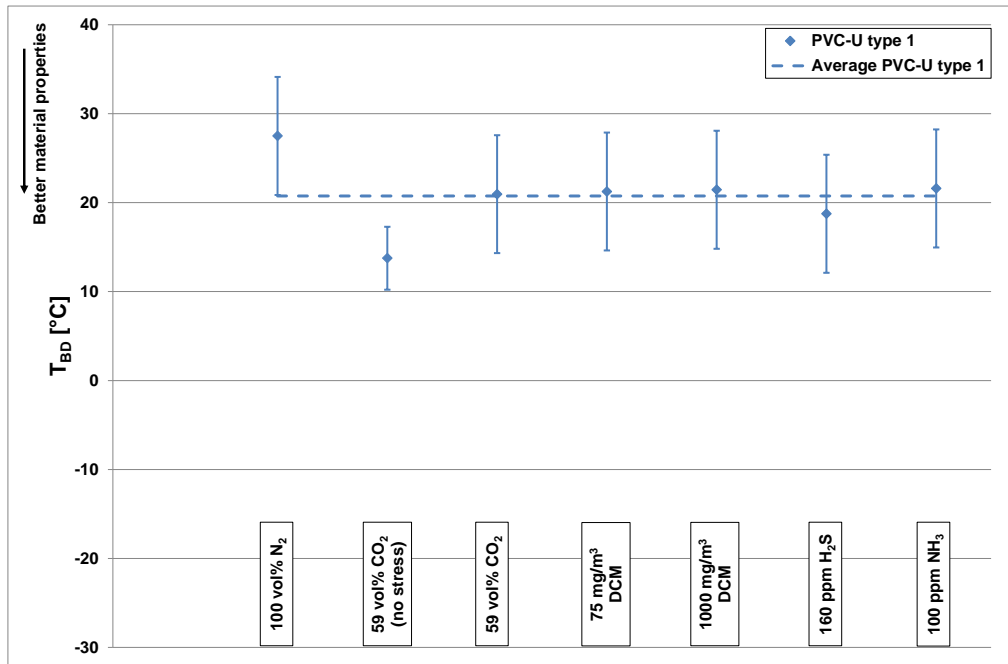


Figure 14. T_{BD} of PVC-U type 1 for the different gaseous environments.

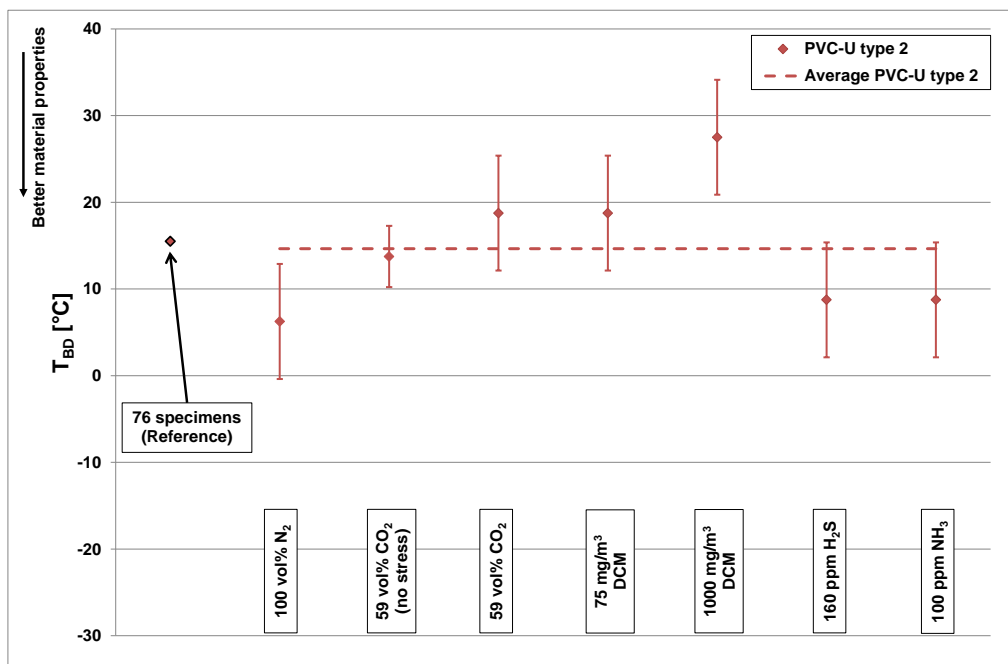


Figure 15. T_{BD} of PVC-U type 2 for the different gaseous environments.

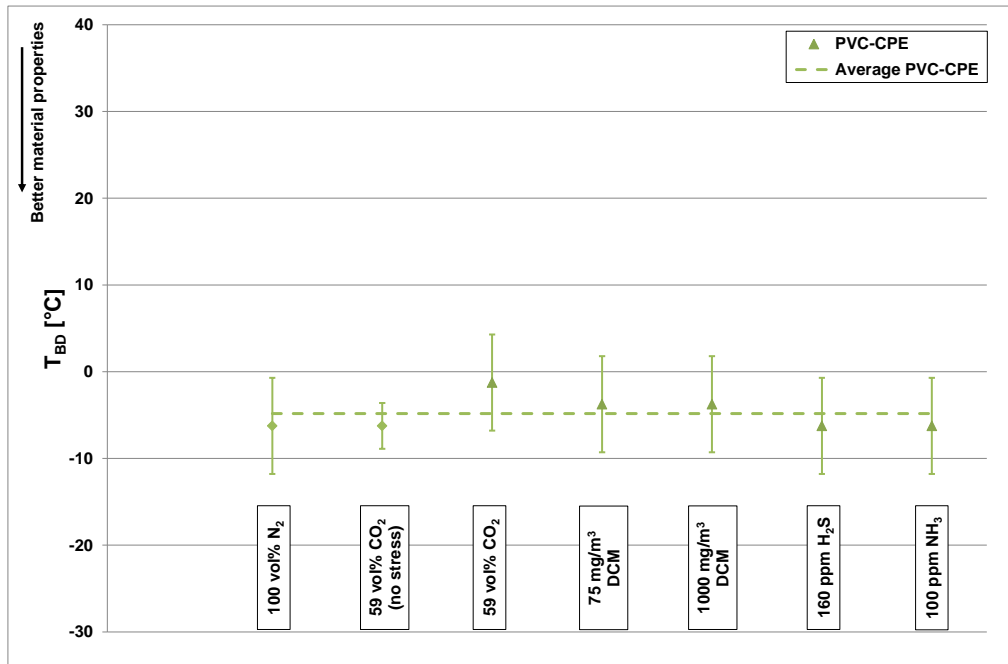


Figure 16. T_{BD} of PVC-CPE for the different gaseous environments.

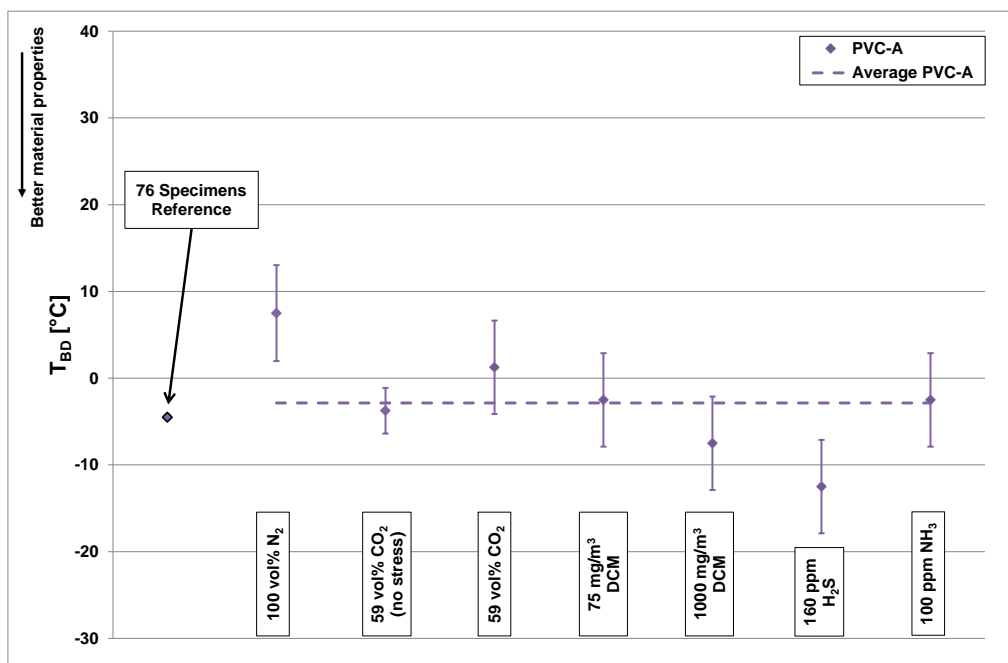


Figure 17. T_{BD} of PVC-A for the different gaseous environments.

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 CO₂ 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% CO₂ 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 of craze growth under the influence of 59 mol%CO₂ 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 14 to Figure 17. All results are well within 1 standard deviation. From this it can be concluded that exposure to a gaseous mixture having 59 mol% CO₂ in combination with significant stress does not lead to the deterioration of PVC-U and PVC-HI 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% H₂ [20]. No effect for H₂ at up to this concentration level was measured in PVC materials. The effect of higher concentrations of H₂ is unknown.

3.1.3.5 Effects of Hydrogen Sulphide

H₂S causes a change in colour (dark brown to black) at the surface of lead-stabilised PVC pipes. This layer is very thin. The literature [1] was not conclusive about the effects of the proposed concentration of 160 ppm H₂S. Therefore additional experiments have been carried out.

After exposure to 160 ppm H₂S for a period of 600 days, discoloration was clearly visible in the PVC-U material (see Figure 18). Only PVC-U had this dark layer, since the modern PVC-HI material used for these tests contain no lead as a stabiliser.



Figure 18. The dark layer after H₂S exposure is only visible on PVC-U (top row) and not on PVC-HI (bottom row).



From the experiments it follows that no dimensional change took place. No measurable change in mass occurred either. This indicates that no significant absorption or depletion occurred in any of the four PVC materials.

During the exposure period of 600 days under tensile stress, none of the specimens broke.

Microscopic research revealed some crazing. This research showed that these crazes had formed early in the exposure process under the relatively large stress of 20 MPa (at 15 MPa crazes start to form (see appendix I)). The exposure to H₂S after the initial formation of the crazes made these crazes visible in PVC-U (both types) through the discoloration caused by the reaction of the H₂S with the lead stabiliser (see Figure 19 and Figure 20).

From the tensile impact tests (see Figure 14 to Figure 17) it follows that exposing samples to H₂S has no effect on the T_{BD} of the four different PVC materials. Both PVC-U materials as well as PVC-CPE the determined transition temperatures are not significantly different (within one standard deviation). PVC-A is slightly different from the average, but still well within two standard deviations of the average (95% confidence limit).

From this it can be concluded that applying 160 ppm H₂S in combination with significant stress does not lead to the deterioration of PVC-U and PVC-HI materials.

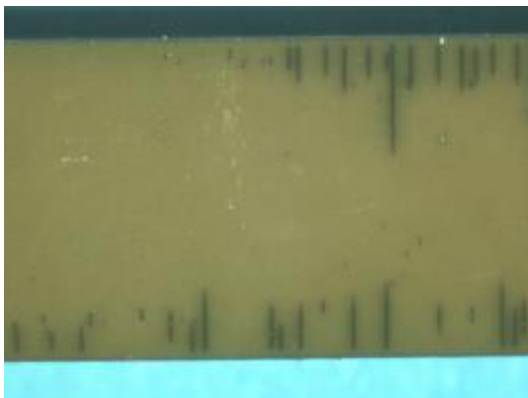


Figure 19. Crazes visible in PVC-U (type 1) exposed to H₂S. These crazes were caused by the relatively large stress and not by the exposure to H₂S.

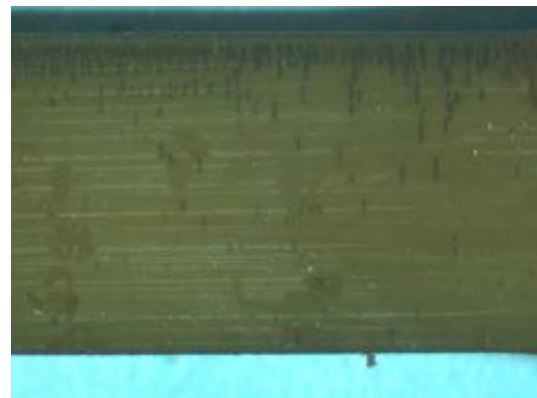


Figure 20. Crazes visible in PVC-U (type 2) exposed to H₂S. These crazes were caused by the relatively large stress and not by the exposure to H₂S.

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 1000 mg/m³ (see chapter 2).

In the ESC test, 1 out of 12 PVC-U type 1 specimens broke during the testing period of 600 days (see Figure 21). Another specimen (PVC-U type 2) showed a craze over the whole width of the specimen. This was even visible without using a microscope (see Figure 22).

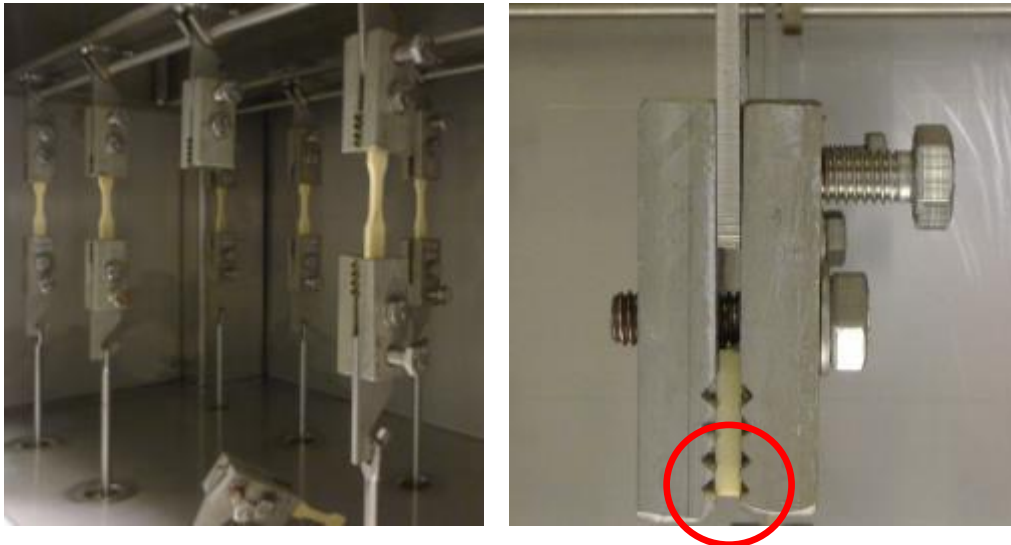


Figure 21. One specimen of PVC-U type 1 broke, but this was probably due to excessive stress caused by the sharp edges of the clamp.

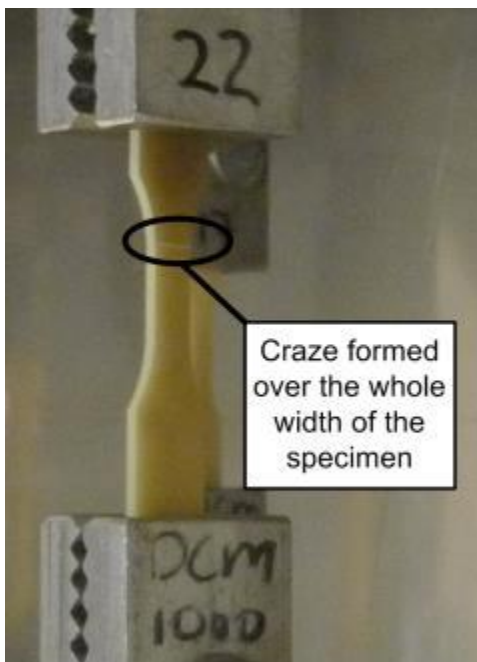


Figure 22. In PVC-U type 2 a craze was formed over the whole width of the specimen.

The samples of the two PVC-HI types showed no crazing. Further microscopic research showed no increased number of crazes for the two PVC-U materials when compared to the reference specimens, which had been exposed to nitrogen.

Furthermore, no dimensional or mass change was noted for any of the four PVC materials during the entire test period. This indicates that no significant absorption or depletion occurred.

The results for the tensile impact tests can be seen in Figure 14 to Figure 17. This leads to the following conclusions:

- 1000 mg/m³ DCM vapour has no deleterious effect on PVC-U type 1.



- The test specimens of PVC-U type 2 showed some embrittlement after exposure to 1000 mg/m³ DCM vapour, but the results were still close to the average values. As PVC-U type 2 has proven to be a very inhomogeneous pipe, the difference can be attributed to scatter in the results.
- The results of tests of PVC-CPE showed a minor improvement in impact strength, but this is not statistically significant. This can therefore be considered as scatter.
- The test specimens of PVC-A showed a minor decline in material properties, but this is not statistically significant. This can therefore also be considered as scatter.

From this it can be concluded that even the relatively high concentration of 1000 mg/m³ DCM vapour has no deleterious effect on the material properties of the tested PVC 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 O₂ was however found. This revealed that neither PVC-U nor PVC-HI are degraded by O₂ at room temperature [21].

The studied literature [1] revealed that the effect of ammonia vapour (up to 100 ppm) is unknown. The effect of 100 ppm ammonia (NH₃) on the four different PVC materials was therefore tested.

In the ESC test in an environment of 100 ppm ammonia, 1 specimen out of the 12 broke (PVC-U type 1). This was probably due to the high stress around the sharp edge of the clamp, which was similar to that shown in Figure 21. Microscopic research revealed crazes in the PVC-U materials, but these were of the same size and were equally numerous as those in the reference materials (exposed to N₂). This indicates that these crazes were formed by the relatively high stress of 20 MPa and not by ESC caused by the presence of ammonia.

Furthermore, no dimensional or mass change was noted in 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 results for the impact tests can be seen in Figure 14 to Figure 17. All measurements are well within a spread of 1 standard deviation. So it can be concluded that applying 100 ppm NH₃ vapour in combination with significant stress does not lead to the deterioration of PVC-U and PVC-HI materials.

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 wide band concentrations were found for H₂S and sulphur-containing components (up to 160 ppm), ammonia, halogen-containing organic components, CO₂ or O₂ at wide band concentrations. Field tests furthermore revealed that H₂ at up to 20 mol% 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 12 below:

Table 12. The effect of various components present in wide band gases on PVC. 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 ₂ S	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	none (up to 20 mol%)

3.2 Polyethylene (PE)

3.2.1 The Importance of PE in the Dutch Gas Distribution Network

Polyethylene (PE) is one of the most commonly used plastic pipe materials. The Dutch distribution network contains more than 20 000 km of PE mains [13] (see also Table 13). 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 13. The importance of PE in the Dutch gas distribution network.

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

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 $\epsilon_{F\%}$. 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 Wide 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 [26] has proven that the displacement at break will not change. The formation of liquid hydrocarbons should nevertheless be avoided in wide 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 wide band gases.

3.2.2.3 Effects of Hydrogen

It was concluded on the basis of the studied literature [1] that hydrogen probably has no effect. PE 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 on PE materials was measured. The effect for higher concentrations of H_2 is unknown but is expected to be non-existent.

3.2.2.4 Effects of Hydrogen Sulphide

The literature [1] indicated that deleterious effects on PE materials for hydrogen sulphide (H_2S) or sulphur-containing components in wide band gases could not be ruled out. Therefore additional experiments have been carried out.

After 600 days of exposure, no noteworthy mass or dimensional changes in the PE materials (see appendix IV.2) were observed. 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 ($\epsilon_{F\%}$)) of the dumbbell samples exposed to 160 ppm H_2S 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 detailed results of the comparison are given in Figure 23 and Figure 24. It is therefore concluded that applying 160 ppm H_2S at 30 mbar(g) in combination with significant stress does not lead to the deterioration of PE materials.

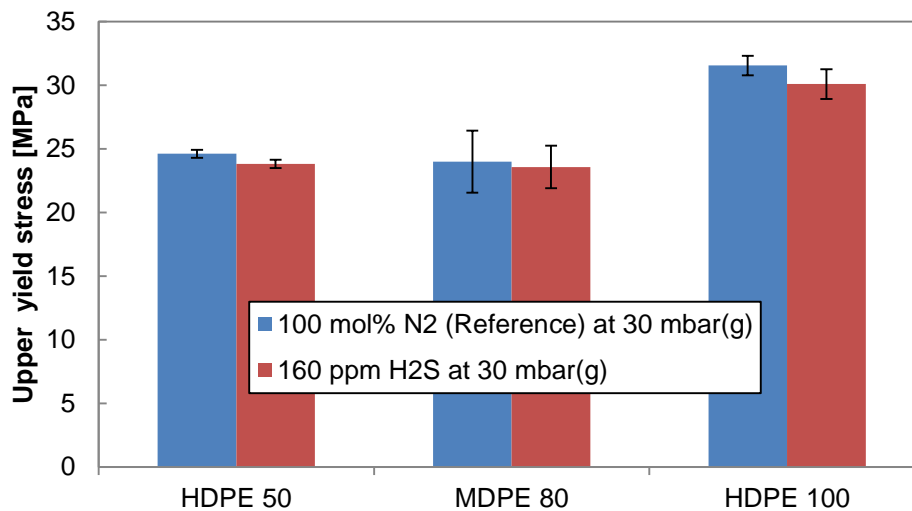


Figure 23. Upper yield stress of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 160 ppm H₂S and N₂ (reference).

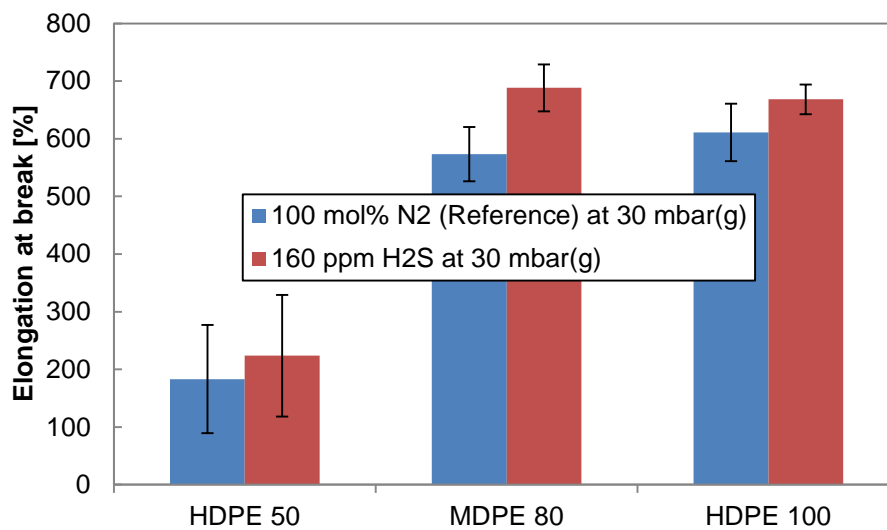


Figure 24. Elongation at break of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 160 ppm H₂S and N₂ (reference).

In addition, there was no statistically significant difference between the mechanical characteristics (upper yield stress (σ_y) and displacement at break (ϵ_{Fmm})) of the rings exposed to 160 ppm H₂S at the two pressures (30 mbar(g) and 8 bar(g)). This was the case for all three investigated PE materials (HDPE 50, MDPE 80 and HDPE 100). The results of the comparison are given in Figure 25 and Figure 26. It can be concluded from these results that pressure of the gaseous H₂S environment has no effect on the mechanical characteristics of the exposed PE samples.

It is therefore concluded that 160 ppm of H₂S in wide band gases does not cause harm to PE materials.

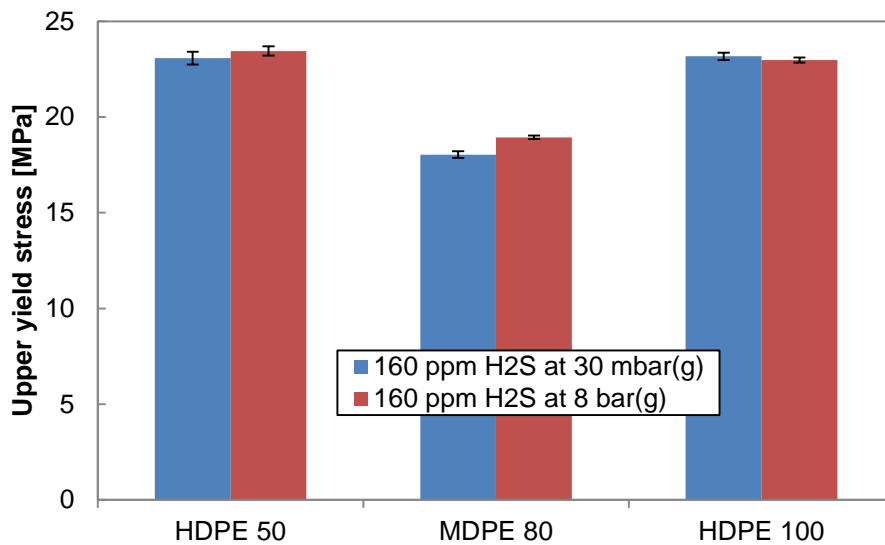


Figure 25. Upper yield stress of PE rings (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 160 ppm H₂S at 30 mbar(g) and 8 bar(g).

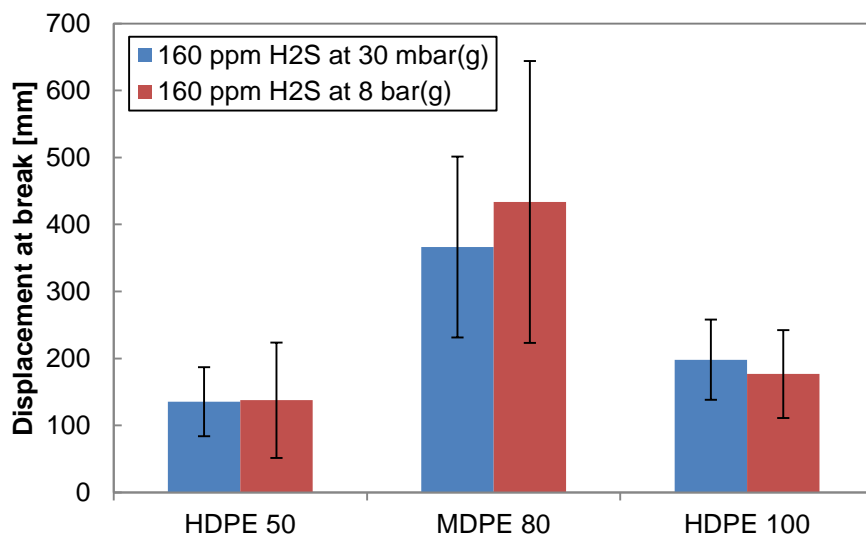


Figure 26. Displacement at break of PE rings (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 160 ppm H₂S at 30 mbar(g) and 8 bar(g).

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. 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 ($\epsilon_{F\%}$)) of the dumbbell samples exposed to 1000 mg/m³ 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).

In addition, there was no statistically significant difference between the mechanical characteristics (upper yield stress (σ_y) and displacement at break (ϵ_{Fmm})) of the rings exposed to 1000 mg/m³ DCM at the two pressures (30 mbar(g) and 8 bar(g)). This was the case for all the investigated PE materials (HDPE50, MDPE80 and HDPE100). It can be concluded from these results that the pressure of the gaseous halogen environment has no effect on the mechanical characteristics of the exposed PE samples. It is therefore concluded that 1000 mg/m³ DCM in wide band gases does not deteriorate PE materials.

The detailed results of all tests can be found in appendix IV.2.

3.2.2.6 *Effects of Ammonia*

The studied literature [1] indicated that deleterious effects on PE for ammonia in wide band gases could not be ruled out. Therefore additional experiments have been carried out in an environment containing 100ppm of ammonia.

After 600 days of exposure, negligible mass or dimensional changes in the PE materials were observed. 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 ($\epsilon_{F\%}$)) of the dumbbell samples exposed to 100 ppm NH₃ 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).

In addition, there was no statistically significant difference between the mechanical characteristics (upper yield stress (σ_y) and displacement at break (ϵ_{Fmm})) of the rings exposed to 100 ppm NH₃ at the two pressures (30 mbar(g) and 8 bar(g)). This was the case for all the investigated PE materials (HDPE50, MDPE80 and HDPE100). It can be concluded from these results that the pressure of an gaseous NH₃ environment has no effect on the mechanical characteristics of the exposed PE samples.

It is therefore concluded that 100 ppm NH₃ in wide band gases does not deteriorate PE materials.

The detailed results of all tests can be found in appendix IV.2.

3.2.3 **Conclusions**

The experiments and literature led to the conclusion that no deleterious effects on PE materials in wide band concentrations were found for H₂S and sulphur-containing components (up to 160 ppm), ammonia, halogen-containing organic components, CO₂ or O₂. Field tests furthermore revealed that H₂ at up to 20 mol% 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 14 below.

Table 14. The effect of components present in wide 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 ₂ S	Mer-captans	Odorant	Ammonia	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		none	none (up to 20 mol%)

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" [6].

3.3.2 Test Method

The experimental setup as described in chapter 2 was used to expose NBR to various components in wide 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 [27].
- Tensile tests. The stress at 100% elongation, elongation at break and tensile strength were measured in accordance with ISO 37 using type 2 samples [28].
 - Stress at 100% elongation (sometimes called "modulus") ($\sigma_{100\%}$)
 - Elongation at break ($\epsilon_{F\%}$)
 - 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 test 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 [27,28].

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 Wide 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 27 for a visual comparison of the average values).

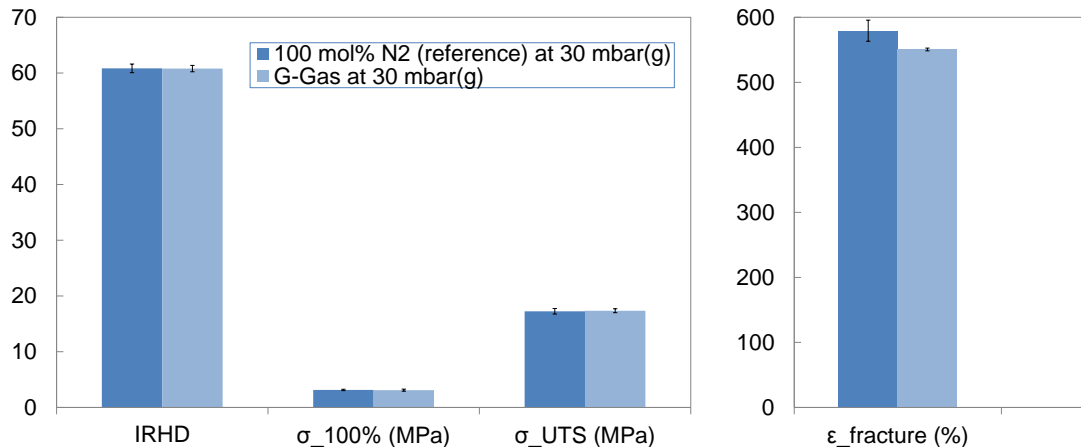


Figure 27. Comparison of the average values of hardness (IRHD), stress at 100 % elongation ($\sigma_{100\%}$) and tensile strength (σ_{UTS}) (left) and strain at fracture ($\epsilon_{F\%}$) (right) for two NBR rings exposed to N₂ (reference) and two NBR rings exposed to G-gas (natural gas).

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.

The literature also revealed that NBR can experience negative effects once in contact with unsaturated chemical compounds (e.g. propene, C₃H₆, and butadiene, C₄H₆) [1]. Experiments with 2 mol% propene (at 8 bar(g)) resulted in no mass change after a period of 600 days. Furthermore, there was no statistically significant difference (t-test) between the results of samples exposed to propene and the results of the reference samples exposed to nitrogen as regards hardness, stress at 100% elongation, elongation at break or tensile strength. The same results were found when compared to the results of the reference samples exposed to G-gas.



No profound dimensional change was observed either. The results for the rubber rings exposed to 2 mol% propene (at 8 bar(g)) were similar those for the rings exposed to nitrogen and G-gas. No effect on the functioning of elastomeric diaphragms is therefore expected.

Research on NBR rings submerged in liquid limonene showed a high degree of absorption of the fluid and severe mechanical degradation [29]. 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, CO₂ or H₂. 59 mol% The effects of CO₂ were also tested in the experiments (see chapter 2).

After 600 days of exposure, the experiments resulted in no noteworthy mass changes in the rubber materials. This indicates that no significant absorption or depletion occurred.

Furthermore, there was no statistically significant difference (t-test) between the samples in CO₂ and the reference samples in nitrogen as regards hardness, stress at 100% elongation, elongation at break 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 the rings exposed to 59 mol% CO₂ were similar to those for the rings exposed to nitrogen 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.

3.3.3.3 *Effects of Oxygen*

It was concluded on the basis of the studied literature [1] that no deleterious effects were expected for oxygen. Therefore, additional experiments have not been performed with this component in the range of concentrations present in wide band gases.

3.3.3.4 *Effects of Hydrogen Sulphide*

The studied literature [1] revealed that the effect of high concentrations of sulphur-containing components (up to 4 300 mg/m³) was unknown. Even the effects of the currently proposed lower concentration of 160 ppm H₂S were unclear. Therefore additional experiments have been carried out.

After 600 days of exposure, the experiments resulted in no noteworthy mass changes in NBR. This indicates that no significant absorption or depletion occurred.

Statistically, (ANOVA) a difference between results of samples exposed to 160 ppm H₂S at 8 bar(g) and results of samples exposed to G-gas in hardness could be determined with 95% confidence level. However, the difference was small and there was no clear trend (a lower hardness with increasing concentration from 5 ppm to 160 ppm at 30 mbar(g)), but rather one differing result. This is shown graphically in Figure 28.

There was no statistical significant difference (ANOVA) between the results of samples exposed to H₂S and the results of samples exposed to G-gas as regards stress at 100% elongation, elongation at break or tensile strength.



There was also no statistical significant difference (ANOVA) between the results of samples exposed to H₂S and the results of reference samples exposed to nitrogen as regards hardness, stress at 100% elongation, elongation at break or tensile strength.

No profound dimensional change was observed either. There seemed to be a trend for the inner diameter, which remained deformed to a larger extent with increasing concentration of H₂S (see Figure 29), although the 160 ppm H₂S at 8 bar(g) deviates from the trend. However, this trend disappeared entirely after one hour. The same effect was present for the outer diameter (see Figure 30).

The dimensional changes were more or less within the range of the dimensional changes after exposure to the reference gases (nitrogen 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.

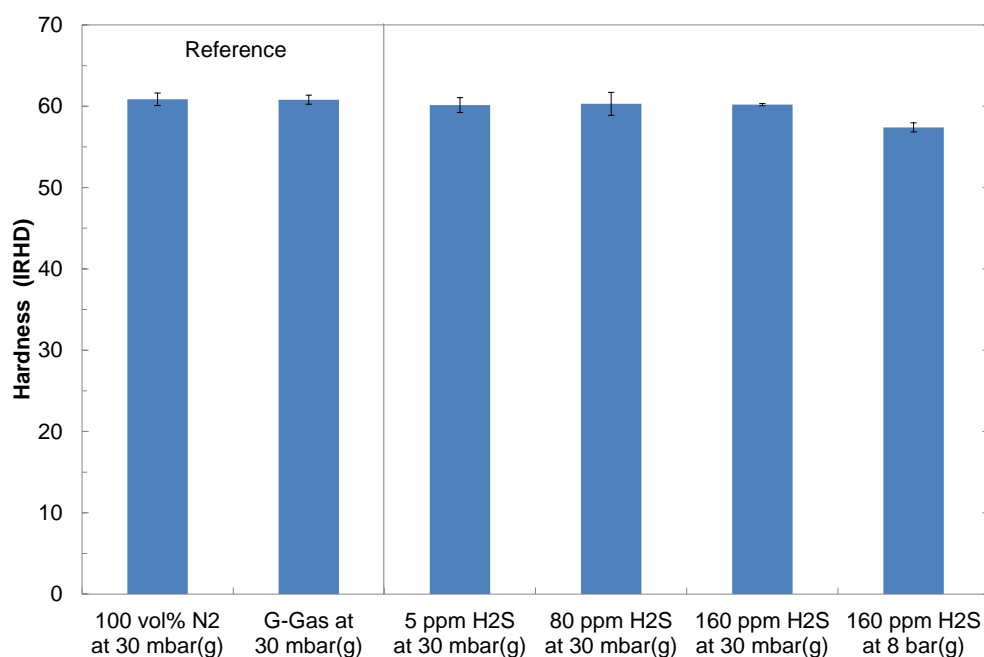


Figure 28. Hardness (IRHD) of NBR exposed for a period of 600 days to the reference gases (N₂ and G-gas) and H₂S at various concentrations. The result for 160 ppm H₂S at 8 bar(g) deviates statistically significant from the other components at 30 mbar(g). However, this difference is small.

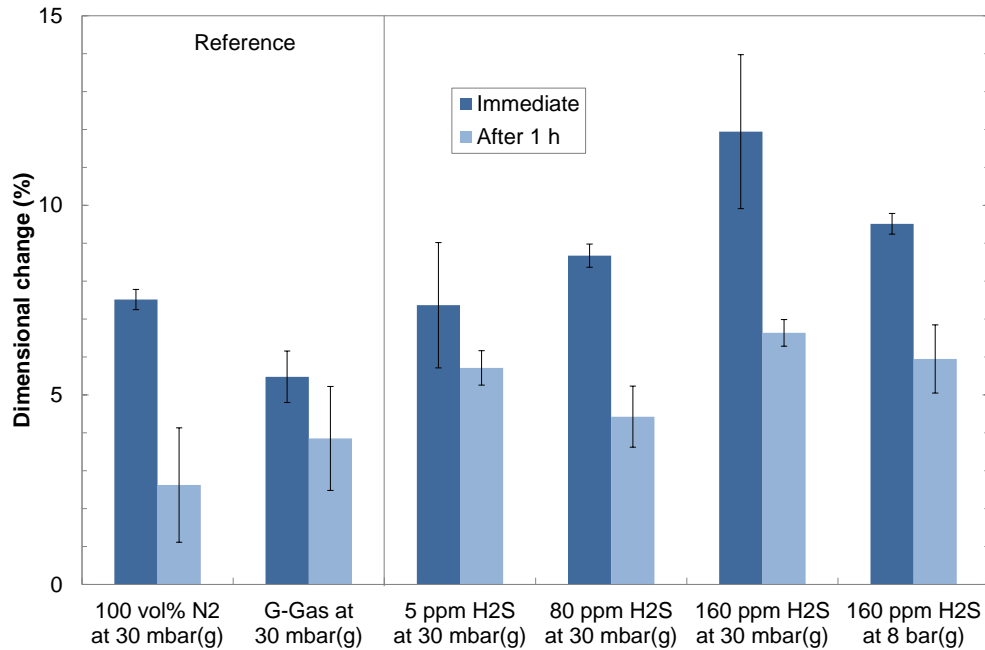


Figure 29. The difference in inner diameter of NBR rings after being exposed for a period of 600 days to the reference gases (nitrogen (N₂) and G-gas) and H₂S at various concentrations. The dimensions were measured immediately after removing the rings (110 mm) from the oversized pipe (125 mm) and after one hour and were subsequently compared to their original dimensions before exposure.

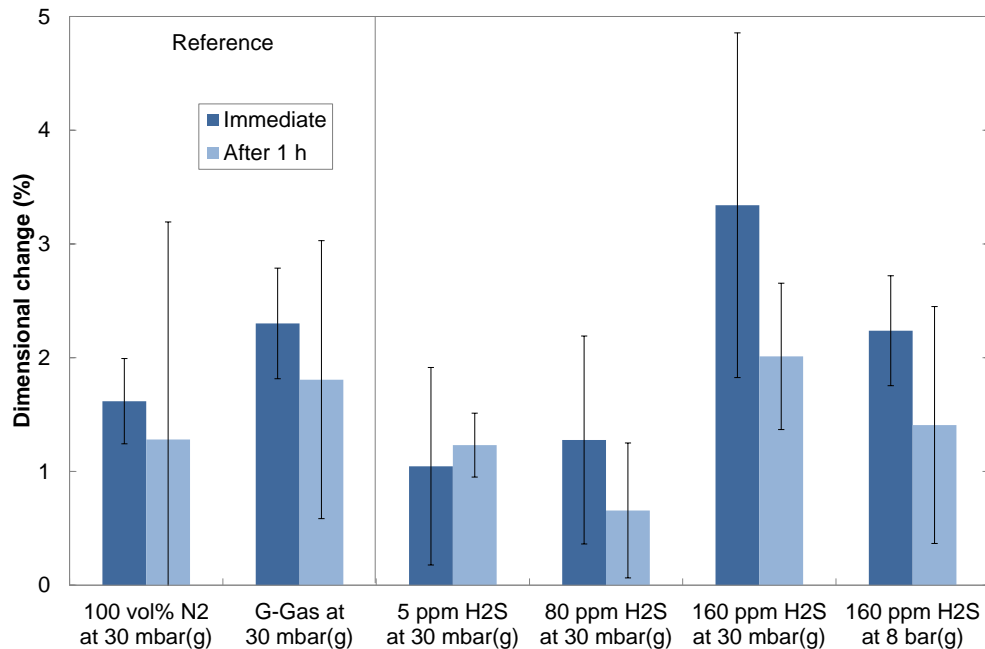


Figure 30. The difference in outer diameter of NBR rings after being exposed for a period of 600 days to the reference gases (nitrogen (N₂) and G-gas) and H₂S at various concentrations. The dimensions were measured immediately after removing the rings (110 mm) from the oversized pipe (125 mm) and after one hour and were subsequently compared to their original dimensions before exposure.



3.3.3.5 Effects of Chlorine-Containing and Fluorine-Containing Components

The literature [1] indicated that deleterious effects on NBR for halogen-containing components in wide band gases could not be ruled out. Therefore additional experiments have been carried out.

After 600 days, the experiments resulted in no noteworthy mass change (although there was a relatively high level of scatter at the concentration 1000 mg/m^3 at 8 bar(g)). This indicates that no significant absorption or depletion occurred.

Furthermore, there was no statistically significant difference (ANOVA) between the results of the samples exposed to DCM and the results of reference samples exposed to nitrogen as regards hardness, stress at 100% elongation, elongation at break or tensile strength. The same results were found when compared to reference samples exposed to G-gas.

Graphically, there seemed to be small trends indicating a deterioration in mechanical properties with increasing concentration (see Figure 31 to Figure 33). The differences were however very small, thus indicating that there is no statistically significant difference. This means that the concentrations used are (much) too low to have a negative effect.

No profound dimensional change was observed either. The results for rings exposed to various concentrations of DCM were similar to those for the rings exposed to nitrogen 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.

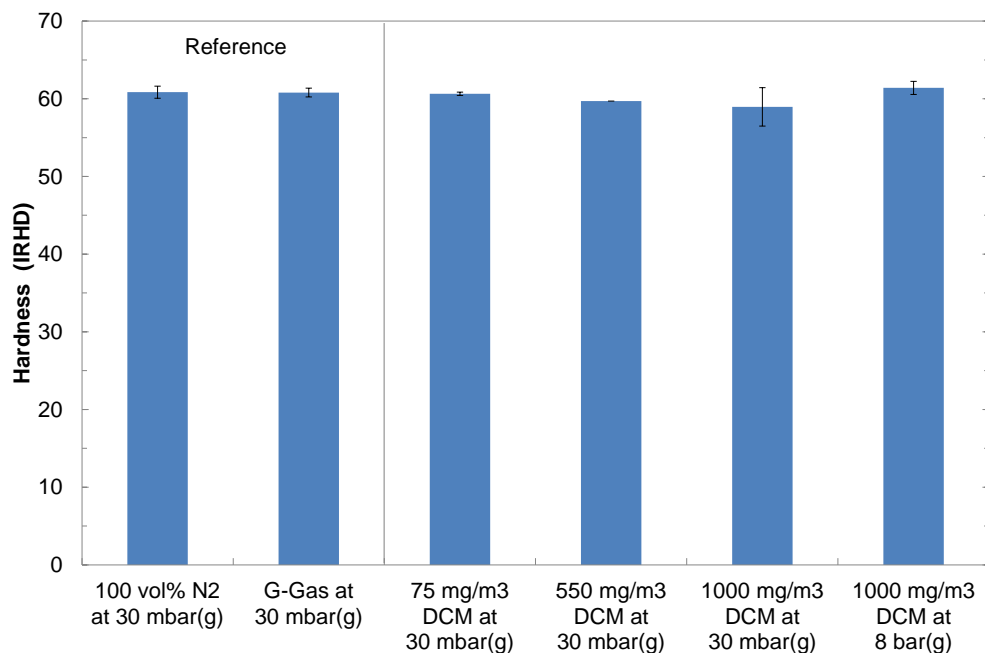


Figure 31. Hardness (IRHD) of NBR exposed for a period of 600 days to the reference gases (N₂ and G-gas) and DCM at various concentrations. There is no statistically significant difference between the different results.

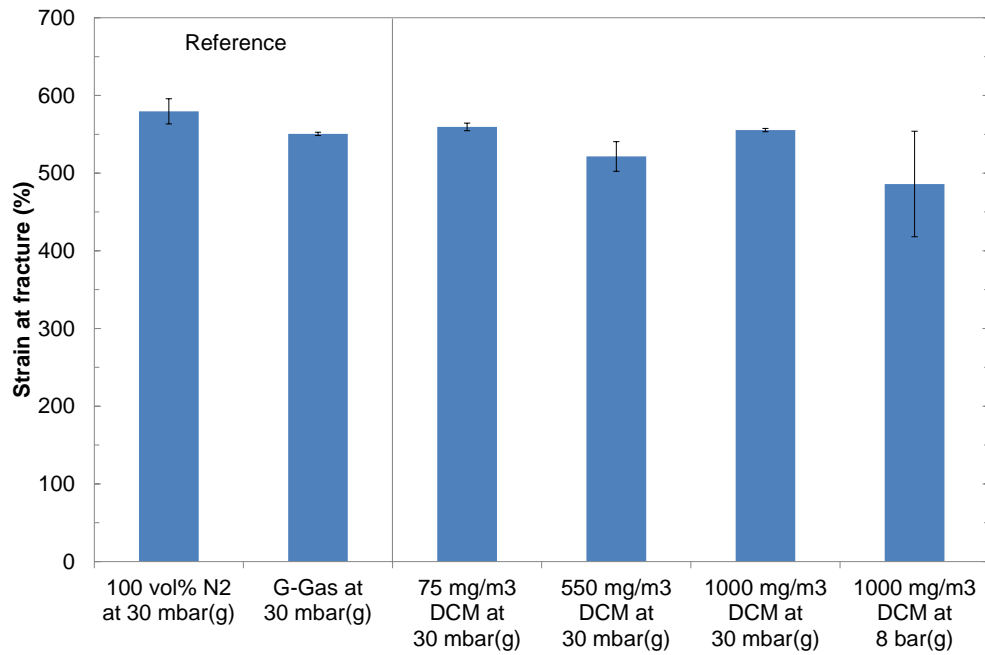


Figure 32. The elongation at break of NBR exposed for a period of 600 days to the reference gases (N_2 and G-gas) and DCM at various concentrations. There is no statistically significant difference between the different results.

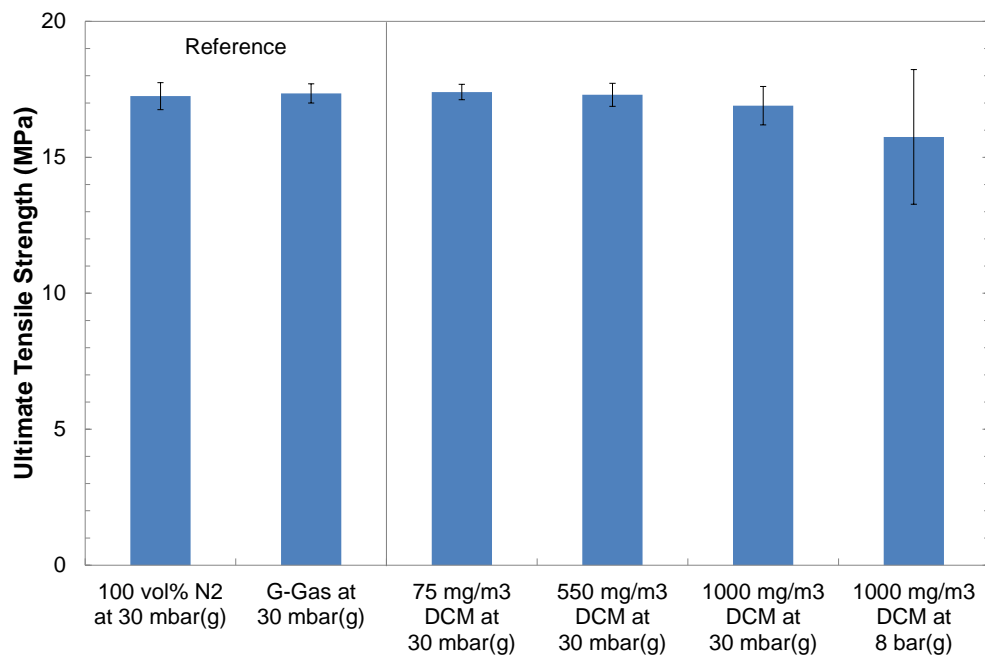


Figure 33. The ultimate tensile strength of NBR exposed for a period of 600 days to the reference gases (N_2 and G-gas) and DCM at various concentrations. There is no statistically significant difference between the different results.



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, the effects of 100 ppm NH_3 were also tested in the experiments (see chapter 2).

After 600 days, the experiments resulted in no noteworthy mass change (although there was a relatively high level of scatter for 100 ppm NH_3 at 30 mbar(g)). This indicates that no significant absorption or depletion occurred.

Furthermore, there was no statistically significant difference (ANOVA) between the results of samples exposed to NH_3 and the results of reference samples exposed to nitrogen as regards stress at 100% elongation, elongation at break or tensile strength (see Figure 34).

However, a difference between the results of hardness was observed: the samples exposed to 100 ppm NH_3 at 30 mbar(g) had a slightly lower hardness than those exposed to the reference gases (see Figure 35). However, the samples exposed to 100 ppm NH_3 at 8 bar(g) had a similar hardness. This means that there is no (clear) trend and that it is probably just an individual deviation. The same results were found when compared to reference samples in G-gas.

No profound dimensional change was observed either. The results for the rings exposed to the two concentrations of NH_3 were similar to those for the rings exposed to N_2 and G-gas. No effect on the functioning of elastomeric diaphragms is therefore expected.

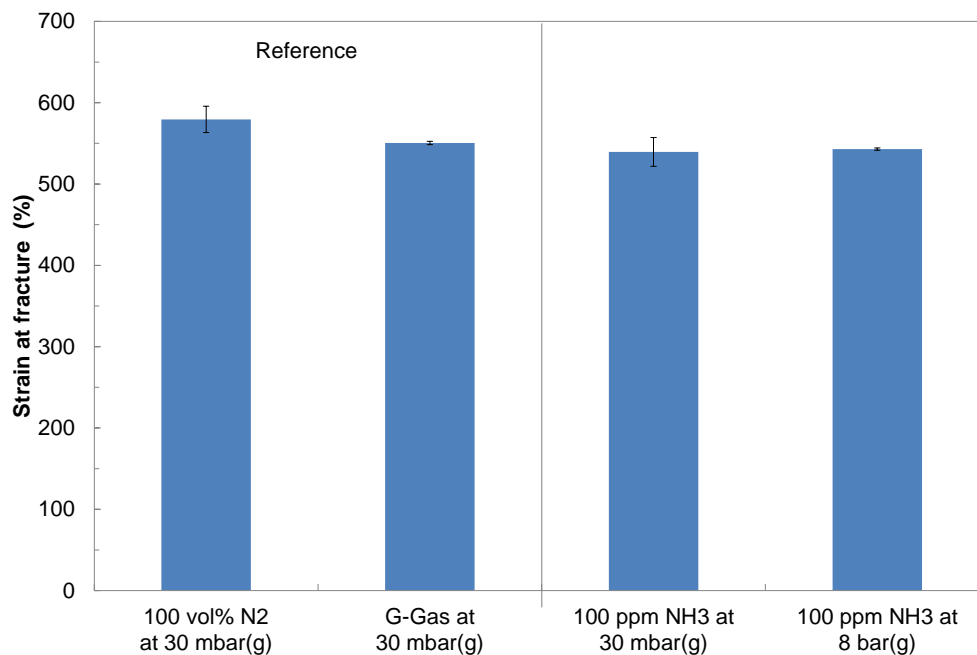


Figure 34. The elongation at break of NBR exposed for a period of 600 days to the reference gases (N_2 and G-gas) and NH_3 at two concentrations. There is no statistically significant difference between the different groups.

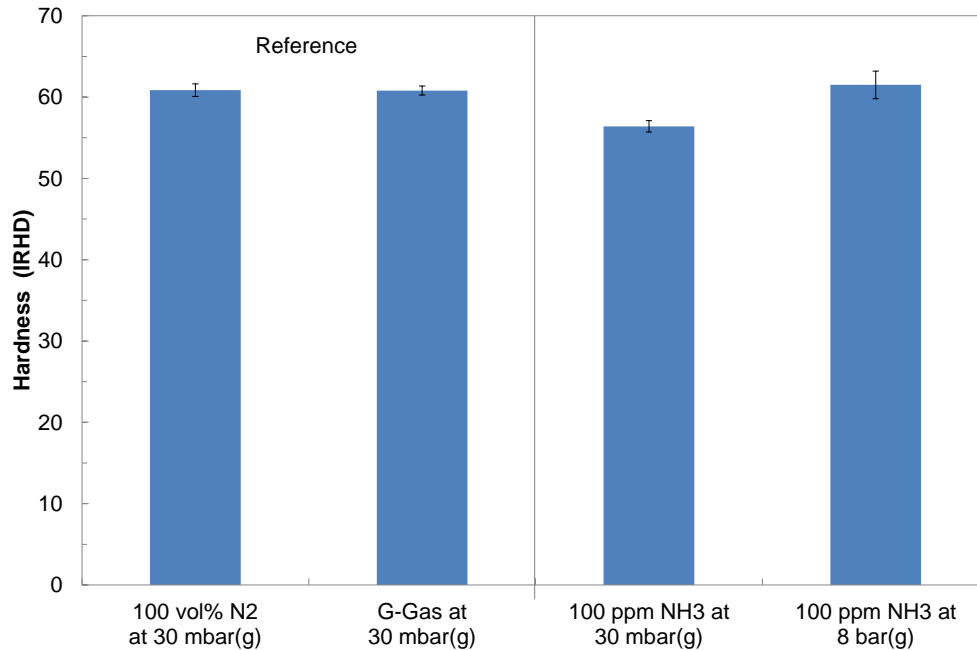


Figure 35. Hardness (IRHD) of NBR exposed for a period of 600 days to the reference gases (N₂ and G-gas) and NH₃ at two concentrations. Statistically, there is a difference between 100 ppm NH₃ at 30 mbar(g) and the other results.

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.

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 H₂S (up to 160 ppm), halogen-containing organic components, ammonia, CO, CO₂, O₂ or H₂ in wide band gases is expected. As the concentrations of HCl and HCN in wide 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 15 below.

Table 15. The effect of components present in wide 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 ₂ S	Mer-captans	Odorant	Ammono-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		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 16). 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 16. 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 wide band gases (see also Table 17) 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 17. Gas compositions to which steel was exposed.

Gas number	CO ₂ (mol%)	O ₂ (mol%)	H ₂ S (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 Wide Band Gases on Steel

4.1.3.1 Effects of Interactions between CO₂, O₂ and H₂S

The literature [1] revealed that, where water is present, the severity of material degradation by corrosion is mainly affected by the concentrations of CO₂, O₂ and H₂S. The effect of these constituents individually has been examined extensively for CO₂. The effect of the presence of H₂S is also well understood. In general, the corrosion rate increases with increasing concentration of CO₂ 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 O₂ also increases with concentration. From sour service applications in the oil & gas industry it is well known that H₂S can cause stress corrosion cracking. H₂S may also cause corrosion problems through a mechanism where elemental sulphur is formed. The maximum allowable concentration of H₂S in wide band gases is limited and, given the current chemical specification for wide band gases, no detrimental corrosion of steel gas pipes is expected due to the presence of H₂S alone. There are indications that traces of O₂ 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 product 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 is given in Table 18.

Table 18. Results of the visual examination after cleaning of the corrosion samples.

Gas number	Corrosion in water phase	Corrosion in gas phase
1 HD	Uniform	Uniform, preferential HAZ
1 LD	Uniform	Uniform
1 LD 50% RH	n.a.	Negligible
2	Uniform, preferential at waterline	Uniform
3	Uniform, preferential at waterline	Uniform
4	Superficial pitting, preferential at waterline	Uniform
5	Severe pitting	Uniform
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

HAZ means heat-affected zone, for more information see joints report [6].

For most test gases the exposure resulted in a tendency towards linear mass loss with time. Examples of mild (gas number 9) and moderate (gas number 3) uniform attack show a good linear fit, as can be seen in Figure 36. The mass loss indicated is the summarised average mass loss of the mass loss in the water phase, at the waterline and in the gaseous phase.

In the case of pitting, a linear fit may underestimate the level of attack. The onset of pitting attack affects the corrosion rate as shown with the linear fit for gas number 5 in Figure 36. All results of the mass loss measurements are given in appendix IV.4.

The largest mass loss was observed for the 9-month (270 days) exposure to gas number 5 (high CO₂, high O₂, no H₂S). With the longest exposure time, the mass loss was lower than for the experiment with the second longest exposure time. This deviation from the general tendency towards a linear trend in mass loss with time can be explained by the onset of localised attack in this gaseous environment. Some of the corrosion samples for gas number 5 are shown in Figure 37.

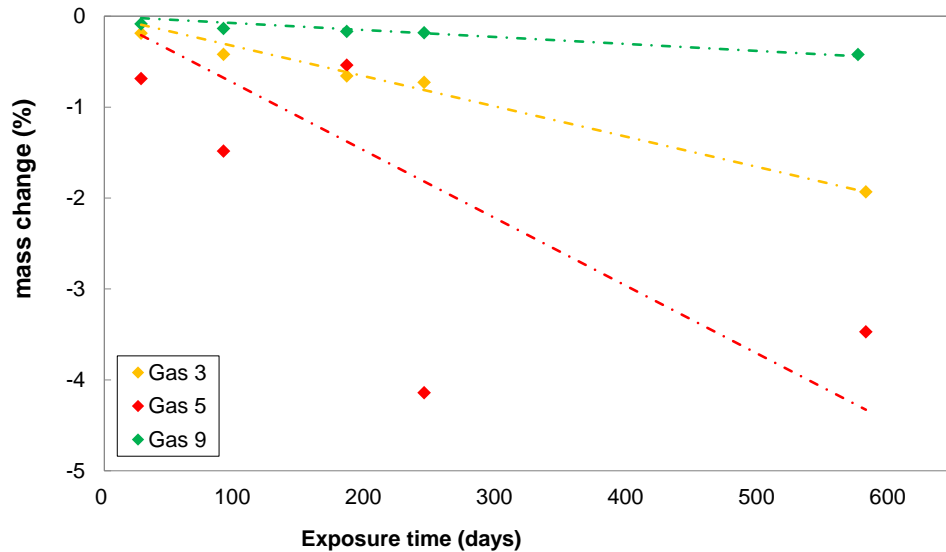


Figure 36. Mass loss of the cleaned steel specimens after exposure to the various test gasses.

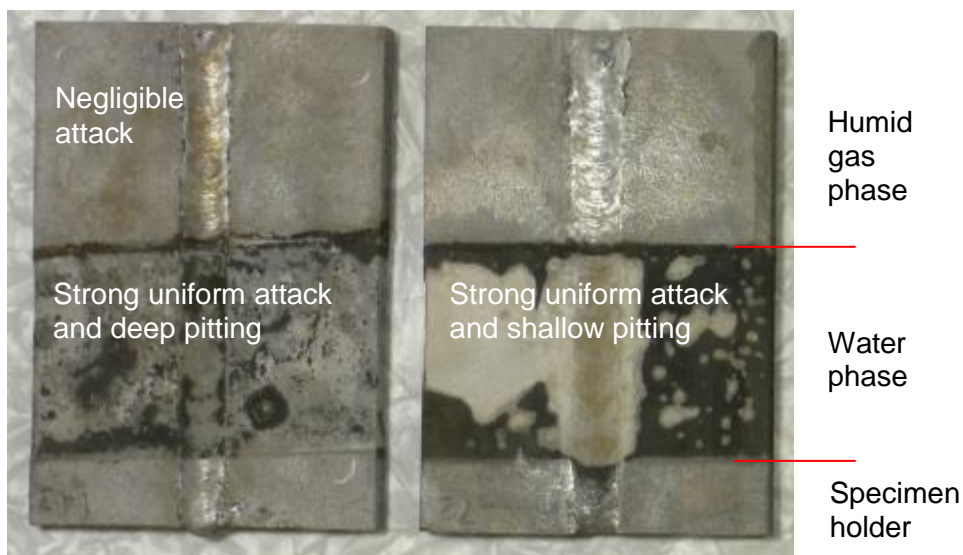


Figure 37. Cleaned corrosion samples after exposure to gas number 5 for 9 months (right) and 19 months (left).

With gas number 4 (high CO₂, high O₂, high H₂S), localised corrosion was also observed. However, the attack was much less aggressive than that of gas number 5. With gas number 5, wide craters penetrating deep into the wall thickness were formed, while with gas number 4 the attack was in the form of superficial pinholes. The occurrence of localised attack was observed for longer periods of exposure (9 and 19 months) but not for the shorter exposure times.

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.



The corrosion rates summarised in Table 19 are shown in Figure 38 as a function of the gas composition. Table 19 presents the results for the water phase, waterline and gas phase.

From Table 19 and Figure 38 it can be seen that the highest corrosion rate was observed for gas number 5 (bottom right corner in Figure 38, high CO₂ and O₂ concentration). The presence of H₂S decreases the corrosion rate significantly, as is observed for gas number 4 (top right corner, high CO₂, O₂ and H₂S concentration). From this observation and the observed aggressive pitting for gas number 5 and mild superficial pitting for gas number 4, it can be concluded that in the interaction between H₂S, CO₂ and O₂, H₂S prevents the occurrence of aggressive pitting. A high concentration of both CO₂ and O₂ results in the highest corrosion rates observed, while at a high CO₂ concentration alone the corrosion rate is low, even in the presence of H₂S. High O₂ concentrations must therefore be avoided in gas distribution systems if the presence of water cannot be ruled out.

Table 19. Results for corrosion rate determined by corrosion depth analysis of the cleaned corrosion samples; red: < 50 years, orange: ~ 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)
1 HD	Negligible	Negligible	0.18
1 LD	Negligible	Negligible	0.09
1 LD 50% RH	--	--	Negligible
2	Negligible	Negligible	0.07
3	0.03	0.13	0.06
4	0.31	0.31	Negligible
5	1.13	Negligible	Negligible
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

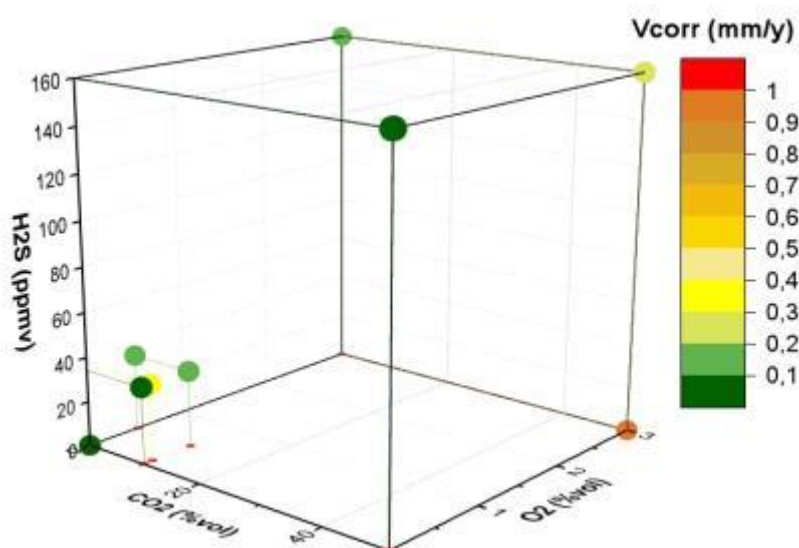


Figure 38. Corrosion rate (v_{corr}) of the steel specimens after exposure to the test gas as a function of the gas composition (CO₂, O₂ and H₂S concentration).



From the series of experiments with moderate CO₂ and H₂S concentrations and various oxygen concentrations (0.01, 0.1 and 0.5 mol%, gases 7, 8 and 9) it can be observed that at low O₂ concentrations there is a peak in the corrosion rate expected from the literature survey [1]. Very low O₂ concentrations (the measured oxygen concentration of the test gas from the gas outlet of the test rig was approximately 30 ppm) did not result in a very high corrosion rate, as shown in the experiment with gas number 2. From the test results it is expected that the maximum corrosion rate at low O₂ concentrations in wide band gas will occur between 100 ppm (0.01 mol%) and 0.5 mol% O₂, as illustrated in Figure 39.

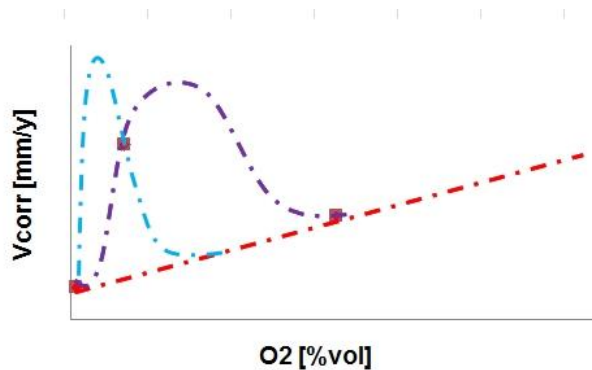


Figure 39. Sketch of the possible effect of low O₂ concentrations on the corrosion rate (Blue - maximum between 0.01 and 0.1 mol% O₂, Purple - maximum between 0.1 and 0.5 mol% O₂, Red - linear increase with corrosion rate as observed at higher O₂ concentrations).

Another notable result is that, for many of the employed test gases, the most severe attack took place at the waterline or below water level. For gas number 1 however, both in the 8 bar(g) experiment and in the atmospheric pressure experiment, the strongest attack was observed above the waterline, i.e. in the moist gas environment. The attack was strongest in the heat-affected zone surrounding the weld. This is remarkable as the most severe attack was expected either in the water phase or at the waterline. A possible explanation is the formation of a thick grey/white moist layer in the gaseous phase as illustrated in Figure 40.

Chemical analysis indicated that this was likely to be ferrous hydroxide with a varying amount of sulphur/sulphides. Although this layer was found in all experiments, the formation of this product was not observed in the experiment with gas number 1 with a relative humidity of approximately 50%. For most other gas compositions above the waterline a similar composition of the corrosion product was observed. However, in none of the other test circumstances was a pronounced attack and/or formation of a thick layer of corrosion product observed above the waterline. The attack in the gaseous phase for gas number 1 is therefore likely due to a combination of high CO₂ concentration (50 mol%), low O₂ concentration (100 ppm) and high humidity.



Figure 40. Corrosion sample from the experiment with gas number 1 at 8 bar(g). The exposed sample (left) shows a thick grey/white layer of ferrous hydroxides in the gas phase and the cleaned sample (right) shows preferential attack in the heat-affected zone (HAZ).

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 CO₂, O₂ and H₂S and thereby also including ppm level O₂ concentrations.

It is also recommended to investigate the effects of high CO₂ concentrations, with low O₂ in the absence of H₂S more extensively, in order to determine whether this increases the corrosion rate as observed with high O₂ and high CO₂ concentration. Furthermore, it is recommended that moderate CO₂ concentrations be tested, with low O₂ in the absence of H₂S, in order to determine whether this also increases the corrosion rate.

Finally, further testing with gas number 1 at 100% humidity in exclusively gaseous circumstances (samples not partially submerged) is also recommended.

4.1.3.3 Effects of Interactions between O₂, CO and CO₂

On the basis of the studied literature [1], it was concluded that the presence of CO₂ 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 O₂, CO and CO₂ were not studied further in the current work.

4.1.4 Conclusions

The presence of water is obviously of great influence on the corrosion of steel due to interactions involving O₂, CO₂ and H₂S. For most test conditions, the most severe attack was observed in the water phase. The exception to this was test gas number 1 (50 mol% CO₂, 100 ppm O₂ and 160 ppm H₂S), where the strongest attack was observed in the moist gas phase. The corrosion tests were conducted with a



maximum H₂S concentration of 160 ppm, which is the maximum admissible concentration of H₂S in gas distribution networks. It can therefore be concluded that the existing steel gas infrastructure cannot be used for the transport of raw biogas. Raw biogas is often moist, and has H₂S concentrations exceeding the tested H₂S concentrations. In order to be able to transport raw biogas, a minimum treatment of removing H₂S and drying the gas is required.

For all test conditions (except for gas number 5), 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 25 °C. The corrosion rate was therefore higher than in gas distribution systems, which are operated at a temperature of approximately 7 °C. The test approach can be considered conservative.

At high concentrations of CO₂ (50 mol%) and H₂S (160 ppm) with low O₂ concentrations (100 ppm), high corrosion rates are possible in the gaseous phase at high humidity (100% RH), possibly limiting the lifespan of steel pipelines to less than 50 years. In the experiments, it was observed that the corrosion rate is not a linear function of O₂ concentration. The literature study led to the conclusion that, at ppm level oxygen, there is a peak in the corrosion rate. This was also observed in the experiments.

Low oxygen levels (gas number 2: <30 ppm O₂ with 50 mol% CO₂ and 160 ppm H₂S / gas number 9: 100 ppm O₂ with 10 mol% CO₂ and 34 ppm H₂S) did not result in a corrosion rate limiting the lifespan of steel to less than 50 years. However, the corrosion rate showed a local maximum between 0.01 and 0.5 mol% O₂. It is therefore recommended that the effect of low oxygen concentrations on the integrity of steel in the gas distribution network be further investigated.

At high concentrations of CO₂ (50 mol%) and O₂ (3 mol%), the presence of H₂S seems to lead to superficial pitting (0.31 mm/y), while the absence of H₂S leads to severe pitting (1.1 mm/y) at longer exposure times in the water phase. From the experiments at high pressures it can be estimated that the corrosion rate would be even higher at a gas pressure of 8 bar(g) than at the 30 mbar(g) used in the experiment with gas number 5. Both experiments with high CO₂ and O₂ concentration show unacceptable corrosion in the presence of water.

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 20 below.

Table 20. The effect of components present in wide 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.

Sulphur-containing components	H ₂ S	Mer-captans	Odorant	Ammono-nia	Chlorine-containing components	Fluorine-containing components	HCl	HCN	CO	CO ₂	Hydro-carbons	Aromatic hydro-carbons	O ₂	H ₂
water, CO ₂	probably none						with H ₂ S and water: possibly	unknown	Water, H ₂ S	probably none	water, (H ₂ S), CO ₂	none		
water, CO ₂ and O ₂									water, (H ₂ S) and O ₂					



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.

Furthermore, the use of steel should be avoided in gas applications with high CO₂ and O₂ concentrations in the absence of H₂S (for example in biogas generation directly after the H₂S scrubber, as the gas stream may still have a high humidity and risk of condensation). In unfavourable situations this can lead to perforation of the piping within a few years.

In the current work, the interactions between O₂, CO₂ 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 wide band gases (see also Table 21) for a period of 19 months.

Table 21. Gas compositions to which copper was exposed.

Gas number	CO ₂ (mol%)	O ₂ (mol%)	H ₂ S (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 Wide Band Gases on Copper

4.2.3.1 Effects of Interactions between CO₂, O₂ and H₂S

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 CO₂, O₂ and H₂S.

Figure 41 shows some examples of 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. All test results can be found in appendix IV.5.

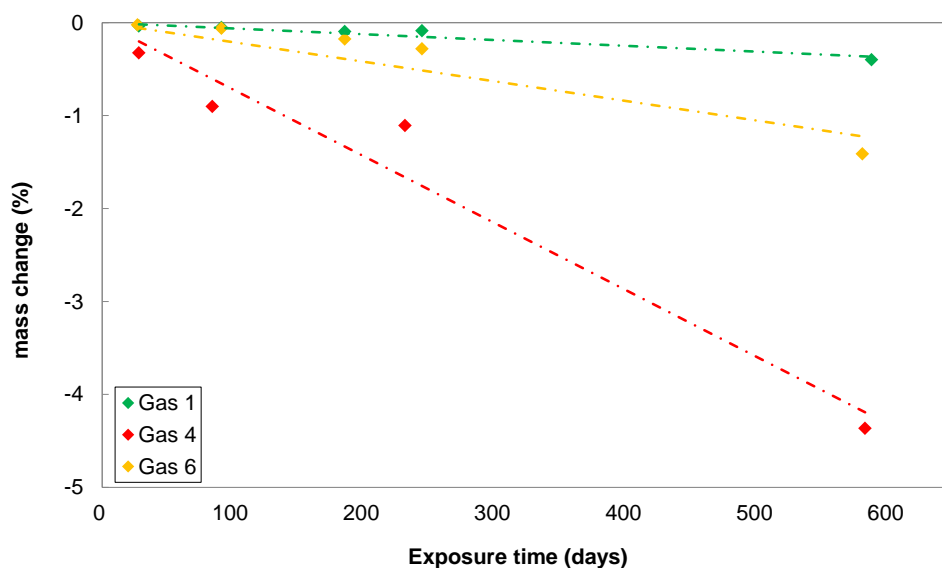


Figure 41. Mass loss of the cleaned copper samples for gas numbers 1, 4 and 6 after exposure to the various test gasses.

It can be observed from the test results that gas number 4 (50 mol% CO₂, 3 mol% O₂ and 160 ppm H₂S, see Figure 41) caused the largest attack, followed by gas number 3 and gas number 6 (see appendix IV.5). This also follows from the wall thickness determination as given in Table 22. The most severe attack was observed for gas number 3 and gas number 4 in the gaseous phase, although the most severe attack was expected in the water phase.

For most specimens, the corrosion products started to crack and peel off after a longer period of attack. For gas number 4 however, the corrosion product formed a thick layer that could slide off of the sample like a shell. This meant that the corrosion product did not adhere tightly to the surface. The composition of the corrosion products was comparable for all H₂S-containing gases, and appeared to be a mixture of CuS and CuO. These occurred in a ratio of approximately 1:1 for the test gases with 160 ppm H₂S (gas number 1 to gas number 4) and tended towards a 1:2 ratio for the test gases with 34 ppm H₂S (gas number 6 to gas number 9).

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 are given in Table 22. This table presents the results for the water and gaseous phases.

The corrosion rates summarised in Table 22 are shown in Figure 42 as a function of the gas composition.



Table 22. Results of the corrosion rate determination by corrosion depth analysis of the cleaned corrosion samples; red: < 50 years, orange: ~ 50 years, green: > 50 years (lifespan assuming an original wall thickness of 1 mm).

Gas number	in water phase (mm/year)	in gas phase (mm/year)
1 HD	0.01	0.01
1 LD	0.01	0.01
1 LD 50% RH	--	0.01
2	0.01	0.01
3	Negligible	0.08
4	Negligible	0.19
5	0.01	0.01
6	0.03	0.03
7	Negligible	0.00
8	0.01	0.01
9	0.01	0.01

Given the similarity in the corrosion products at different H₂S concentrations, it appears that the interactions between H₂S, CO₂ and O₂ determine the corrosion rate. Figure 42 shows that, in the presence of 34 ppm H₂S at low CO₂ and O₂ concentrations, the corrosion rate decreases with increasing O₂ concentration. It can also be seen that increasing the O₂ concentration from 0 mol% to 3 mol% at 50 mol% CO₂ and 160 ppm H₂S increases the corrosion rate. Similarly, increasing the CO₂ concentration from 0 mol% to 50 mol% at 3 mol% O₂ and 160 ppm H₂S increases the corrosion rate. Without H₂S (gas number 5), there is no significant corrosion due to high CO₂ and O₂ concentration (50 mol% and 3 mol% respectively).

It can therefore be concluded that, at narrow band concentrations, the presence of both O₂ and CO₂ decreases the corrosion rate arising as a result of the presence of H₂S (see also [5]). For wide band concentrations, high CO₂ and H₂S concentrations as well as high CO₂ and O₂ concentrations do not lead to corrosion problems. High concentrations of H₂S, CO₂ and O₂ however increase the corrosion rate.

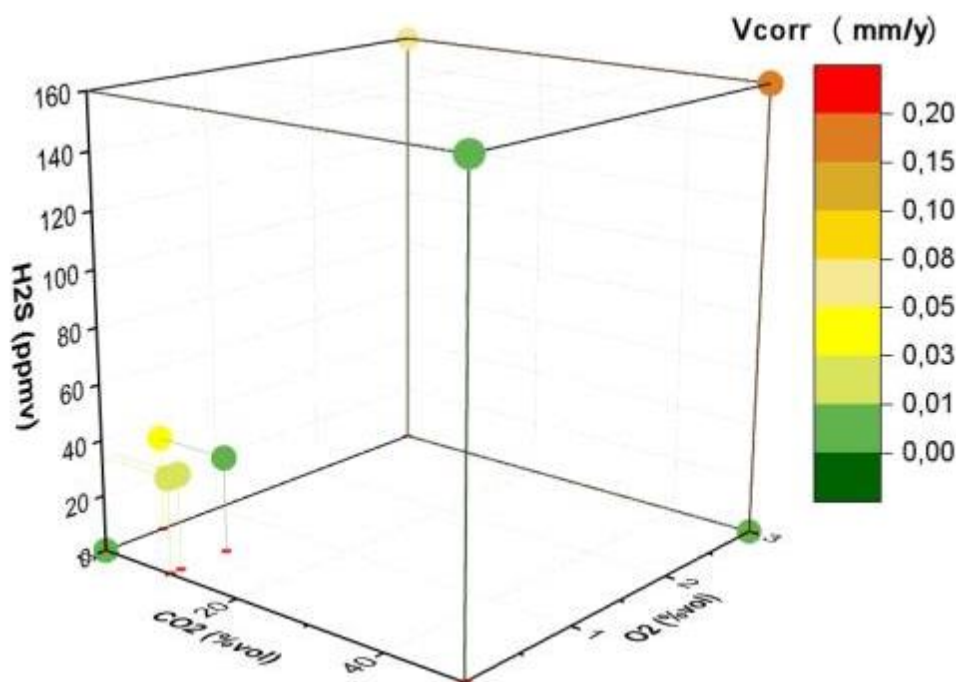


Figure 42. Corrosion rate (v_{corr}) of the copper specimens after exposure to the test gas as a function of the gas composition (CO₂, O₂ and H₂S concentration).



4.2.3.2 Effects of Ammonia

Stress corrosion cracking was not observed after 19 months of exposure to a test gas with 50 ppm NH₃ and a relative humidity of 50%. No effect for NH₃ (up to 50 ppm) on the functioning of copper pipes is therefore expected. For more information it is referred to the joints report [6].

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% H₂ [20]. No effect for H₂ on copper materials at up to this concentration level was measured. The effect for higher concentrations of H₂ is unknown but is not expected to be detrimental.

4.2.4 Conclusions

The literature and experiments led to the conclusion that gas with a high humidity is more aggressive to copper than water with dissolved gas.

H₂S and O₂ in combination with a high humidity in a gaseous environment result in a high corrosion rate. The corrosion rate as a result of the combined presence of H₂S and O₂, is increased by CO₂. Similarly, O₂ increases the corrosion rate due to the combined presence of H₂S and CO₂. The combination of high O₂, CO₂ and H₂S concentration is typical for raw biogas. As such, the use of copper should be avoided in raw biogas applications with high concentrations of these three gases, since the maximum expected lifespan would then be limited to less than 50 years.

No effect for NH₃ (only up to 50 ppm) on the functioning of copper pipes is expected.

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 23 below.

Table 23. The effect of various components present in wide 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) or a deleterious effect may be present (orange).

Sulphur-containing components	H ₂ S	Mer-captans	Odorant	Ammonia	Chlorine-containing components	Fluorine-containing components	HCl	HCN	CO	CO ₂	Hydro-carbons	Aromatic hydro-carbons	O ₂	H ₂
Water, CO ₂			probably none	none (with water up to 50 ppm)	probably none				unknown	Water, O ₂	probably none		Water, CO ₂	none (up to 20 mol%)
Water, CO ₂ and O ₂										Water, H ₂ S and O ₂			Water, H ₂ S and CO ₂	

4.2.5 Recommendations

The use of copper materials should be avoided in gas applications with high CO₂ and O₂ concentrations in the presence of H₂S and moisture (for example in biogas generation before the drier and H₂S scrubber).



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 wide band gases (see also Table 24) for a period of 19 months.

Table 24. Gas compositions to which aluminium was exposed.

Gas number	CO ₂ (mol%)	O ₂ (mol%)	H ₂ S (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 Wide Band Gases on Aluminium

4.3.3.1 Effects of Interactions between CO₂, O₂ and H₂S

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 CO₂ or the presence of chloride ions. On the basis of the literature, the corrosion effects on aluminium caused by the constituents in wide band gases cannot be predicted. However, the possible existence of high concentrations of CO₂ makes corrosion likely if water is present. Therefore additional experiments were carried out.

Figure 43 shows the mass change of the cleaned corrosion samples. From the mass loss data, only the mass loss for the exposure to gas number 3 (0 mol% CO₂, 3 mol% O₂ and 160 ppm H₂S) shows a clear correlation with time. The mass loss of the other samples is negligible, although discoloration of the samples was observed. All test results can be found in appendix IV.5.

For the samples exposed to gases containing CO₂ (all except gas numbers 3 and 6), only discoloration of the exposed surface below the water line was observed, together with a mild mass loss in the same order of magnitude as the mass loss caused by the cleaning of the samples (pickling error). For samples exposed to gas numbers 3 and



6, pitting corrosion was observed at the machined surfaces (sides of the samples as well as the thread) as illustrated in Figure 44.

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 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 are given in Table 22. This table presents the results for the water and gaseous phases.

The highest corrosion rate was observed with gas number 3 (0 mol% CO₂, 3 mol% O₂ and 160 ppm H₂S). However, with gas number 6 (0 mol% CO₂, 0.5 mol% O₂ and 34 ppm H₂S), the corrosion rate was also substantial. This can be seen in Table 25. The attack mainly occurred at machined surfaces (both cutting planes and thread) in the water phase and was rather localised. The number of corrosion pits formed for gas number 3 was higher than that for gas number 6.

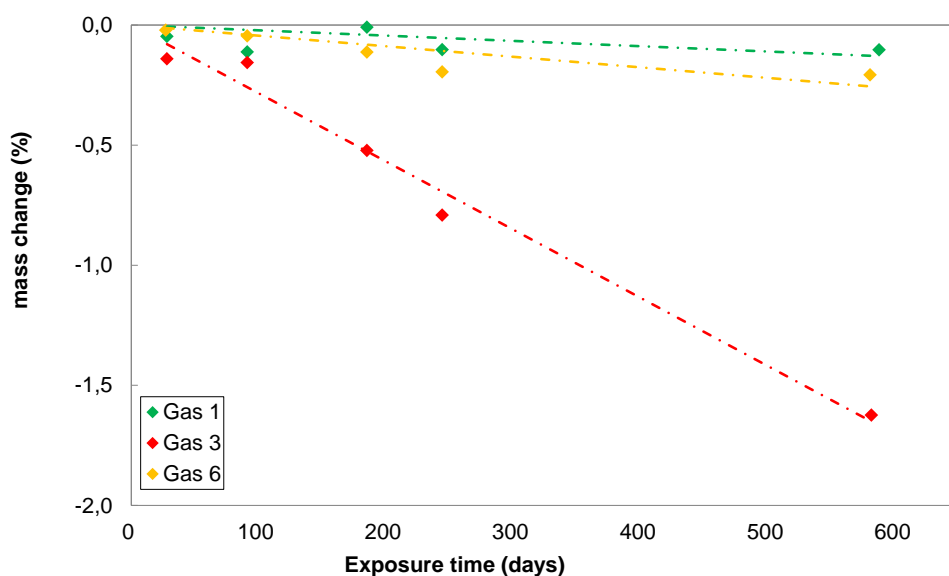


Figure 43. Mass loss of the cleaned aluminium samples for gas number 1, 3 and 6 after exposure to the various test gases.



Figure 44. Pitting corrosion on machined surfaces of the corrosion sample after 19-month exposure to gas number 3.



The corrosion rates summarised in Table 25 are shown in Figure 45 as a function of the gas composition.

In the absence of CO₂, the corrosion rate increases with increasing H₂S and O₂ concentration, as can be seen in Figure 45. As O₂ 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 H₂S.

Condensation of water in gases containing H₂S but no CO₂ 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.

High CO₂ concentrations, 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 CO₂ concentration (= 50 mol% CO₂) side of Figure 45. The reason for this is unknown.

Table 25. Results for corrosion rate determination by corrosion depth analysis of the cleaned corrosion samples; red: <50 years, green: >50 years (lifespan based on assuming an original wall thickness of 2 mm).

Gas number	in water phase (mm/year)	in gas phase (mm/year)
1 HD	Negligible	Negligible
1 LD	Negligible	Negligible
1 LD 50% RH	--	Negligible
2	Negligible	Negligible
3	0.31	Negligible
4	Negligible	Negligible
5	Negligible	Negligible
6	0.19	Negligible
7	Negligible	Negligible
8	Negligible	Negligible
9	Negligible	Negligible

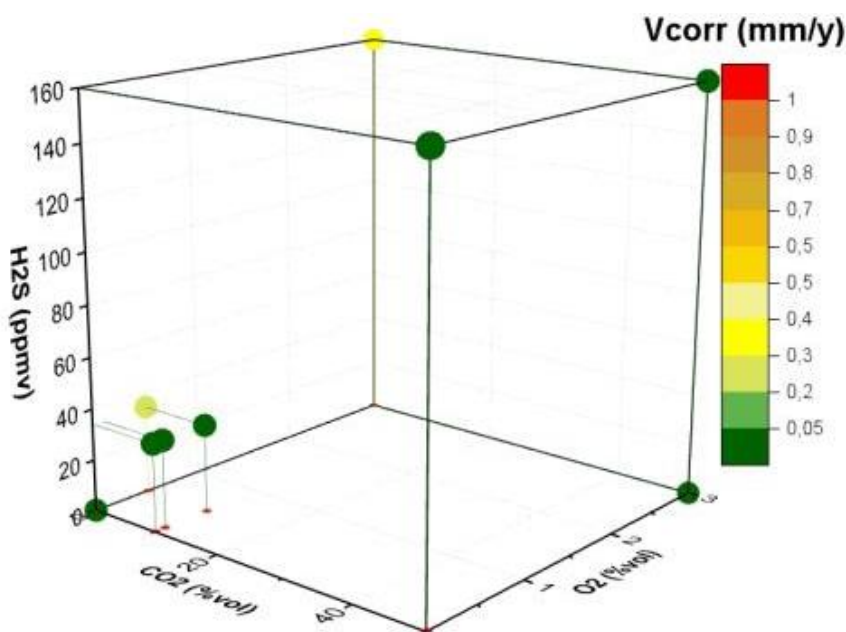


Figure 45. Corrosion rate (v_{corr}) of the aluminium specimens after exposure to the test gas as a function of the gas composition (CO₂, O₂ and H₂S concentrations).



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 of up to 20 mol% H₂ [20]. No effect for H₂ on aluminium materials at up to this concentration level was observed. The effect of higher concentrations of H₂ is unknown, but is not expected to be detrimental.

4.3.4 Conclusions

The literature indicates that corrosion due to CO₂ alone is also possible. However, this was not investigated experimentally. In combination with H₂S and O₂, CO₂ appears to inhibit corrosion. For the effects of CO₂, 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 O₂ and absence of CO₂, significant corrosion of aluminium due to the presence of H₂S was observed. The experiments led to the conclusion that, in the presence of CO₂, no corrosion will take place due to the presence of H₂S. The use of aluminium with gases containing H₂S and not containing CO₂ should therefore be avoided. For H₂S, the conclusion in the summarising table has therefore changed from orange to green in the presence of CO₂ and remains orange in the absence of CO₂.

O₂ 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 H₂S 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].

All conclusions are summarised in Table 26 below.

Table 26. The effect of various components present in wide 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 ₂ S	Mer-captans	Odorant	Ammonia	Chlorine-containing components	Fluorine-containing components	HCl	HCN	CO	CO ₂	Hydrocarbons	Aromatic hydrocarbons	O ₂	H ₂
water and CO ₂			probably none	none	probably none			unknown		none	probably none		none	none (up to 20 mol%)
water and O ₂													water and H ₂ S	



5 Conclusions

All the results of the project "Effects of Wide Band Gases on Materials" are summarised in Table 27 below.

Table 27. The effect of components present in wide band gases on the most important gas distribution materials based on literature review and experiments.

	Sulphur containing components	H ₂ S	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 (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
PE	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
NBR	none (up to 160 ppm)		probably none		none			probably none		none	none	none, unless liquid		none	
steel	water and CO ₂		probably none						with H ₂ S and water: possibly	unknown	water and H ₂ S	probably none	water, (H ₂ S) and CO ₂	none	
	water, CO ₂ and O ₂										water, (H ₂ S) and O ₂				
Cu	water and CO ₂		probably none		none (with water up to 50 ppm)				unknown		water and O ₂	probably none	water and CO ₂	none (up to 20 mol%)	
	water, CO ₂ and O ₂										water, H ₂ S and O ₂		water, H ₂ S and CO ₂		
Al	water and CO ₂		probably none		none				unknown		none	probably none	none	none (up to 20 mol%)	
	water and O ₂												water and H ₂ S		

	=	The effect is unknown, but is expected to be very small or non-existent.
	=	This component in wide 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 at levels up to the maximum concentrations found in wide band gases. This is valid with the following exceptions:

- Due to health and safety reasons the effect of H₂S at higher concentrations than 160 ppm in wide band gases on the most important polymeric materials was not tested. Although no deleterious effect on PVC, PE and NBR was measured at this concentration level, the effect of this gas component at higher concentrations is still unknown.
- Due to health and safety reasons the effect of CO in wide 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.
- The effect of H₂ at higher concentrations than 20 mol% in wide band gases on PVC and PE was not tested. Although no deleterious effect on these materials was measured at this concentration level, the effect of this gas component at higher concentrations is still unknown.



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, corrosion cannot occur.

For copper, gas with a high humidity is even more aggressive than water with dissolved gas.

The combination of H_2S , CO_2 and O_2 in humid gas can lead to severe corrosion in steel, copper and aluminium. When this combination of gas components occurs an acceptable corrosion rate for steel can be achieved by completely removing O_2 . It is not sufficient to completely remove H_2S or CO_2 . When O_2 cannot completely be removed from the humid gaseous environment, the following maximum concentrations were determined in the experiments:

- 34 ppm H_2S
- 10.3 mol% CO_2
- 100 ppm (0.01 mol%) O_2

However, more research could lead to adjustments in these values.

These limiting values are also suitable for copper and aluminium. Completely removing O_2 from the humid gaseous environment is also a good solution for these materials. However, a wider composition range is permissible for copper and aluminium. For both copper and aluminium it is also effective to completely remove H_2S . 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 wide band gases 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 wide 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 restrictions on the maximum allowable concentrations of gas components in wide 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 wide 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, only traces of aromatic hydrocarbon vapour are found in wide band gases.

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 wide 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) or have not been tested at high concentrations (> 160 ppm H₂S). 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 H₂S to 160 ppm.

Finally, the literature was inconclusive about the effects of H₂ on some materials. The effects of H₂ were tested up to 20 mol%, while the concentration H₂ in wide band gases could be as high as 62 mol%. Therefore, the effect of H₂ at higher concentrations remains unknown for PVC, PE, copper and aluminium. It is therefore recommended that the maximum concentration of H₂ be limited to 20 mol%.

The above-mentioned recommendations are summarised in Table 28 where water is not present in the existing Dutch gas distribution grid. Limiting values for other gas components in wide band gases are not required.
(Please note: this excludes joints, which are investigated in another project).



Table 28. Recommended limiting values for several gas components in wide band gases where water is not present in the gas distribution grid or in wide 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. Although only traces of these substances are currently found in wide band gases, 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.
< 160 ppm H ₂ S	The effect of H ₂ S at a higher concentration than 160 ppm was not tested due to its high toxicity to humans. Because of this health and safety risk and because no information could be obtained about the possible effect of this component on the most important materials used in the Dutch gas distribution grid, it is recommended that the maximum concentration of H ₂ S be limited to 160 ppm.
< 20 mol% H ₂	The effect of H ₂ with a higher concentration than 20 mol% was not determined for the investigated materials. The effect at higher concentrations is therefore unknown.

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 H₂S, CO₂ and O₂ may lead to severe corrosion in steel, copper and aluminium.

For steel the following acceptable maximum concentrations were determined in the experiments:

- H₂S should be limited to 34 ppm,
- CO₂ should be limited to 10.3 mol%, and
- O₂ should be limited to 100 ppm (0.01 mol%).

These limiting values are also suitable for copper and aluminium. However, severe corrosion can still occur in aluminium without the presence of CO₂. More research using low CO₂ concentrations is therefore recommended.

Finally, the effects of NH₃ on copper were tested at concentrations of up to 50 ppm in humid gas. The literature was inconclusive about the effects of 100 ppm NH₃ (which may occur in wide band gases) on copper. The effects of NH₃ at concentrations of up to 100 ppm is therefore currently unknown for copper materials. More research using higher NH₃ concentrations is recommended.

When water is present in the gas grid or in wide band gases additional recommendations to the ones given in Table 28 are needed and given in Table 29. Limiting values for other components in wide band gases are not required. (Please note: this excludes joints, which are investigated in another project).



Table 29. Additional recommended limiting values for several gas components in wide band gases where water is present in the gas distribution grid or in wide band gases.

Limiting value	Reason
< 34 ppm H ₂ S	The combination of H ₂ S, CO ₂ and O ₂ may lead to severe corrosion in steel, copper and aluminium. These limiting concentrations are found to limit the effect on metallic materials to an acceptable level.
< 10.3 mol% CO ₂	
< 0.01 mol% O ₂	
< 50 ppm NH ₃	The effects of NH ₃ with a higher concentration than 50 ppm was not tested for the investigated materials. The influence at higher concentrations is therefore unknown.
possibly > 0 mol% CO ₂	If both H ₂ S 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 values. 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 46 and Figure 47.

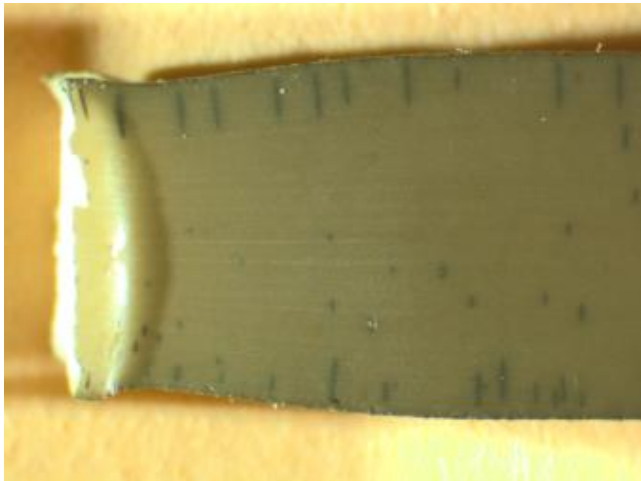


Figure 46. Crazes that have formed in PVC-U type 2 at 20 MPa. These have become discoloured as a result of exposure to H₂S for a period of 600 days.



Figure 47. Crazes that have formed in PVC-U type 2 at 20 MPa that was exposed to 100% N₂. The crazes were deliberately coloured afterwards through exposure to H₂S without an applied stress to make them better visible.



As can be seen from Figure 47 crazes also formed under the influence of 100% N₂. The N₂ 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 (N₂) 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 48. These dumbbells were subsequently broken at a high impact velocity at temperatures ranging from $-25\text{ }^{\circ}\text{C}$ to $+50\text{ }^{\circ}\text{C}$ as shown in Figure 49 and Figure 50.



Figure 48. PVC-HI pipe with dumbbell-shaped specimens.

Figure 49. Cooling of a PVC specimen.

Figure 50. Impacting the specimen.

When testing the specimens, the difference between brittle and ductile fractures can easily be distinguished visually (see Figure 51). 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 52). It can clearly be seen that ductile fractures consume more energy than brittle ones (surface area under graphs).

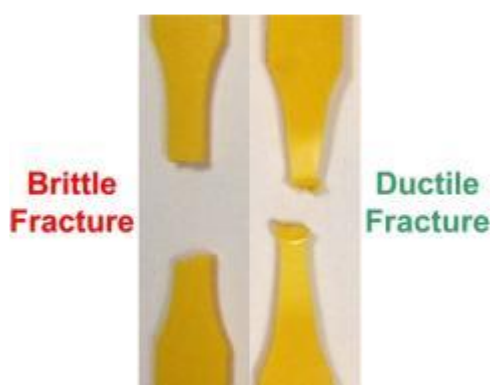


Figure 51. Brittle and ductile fractures can be distinguished visually.

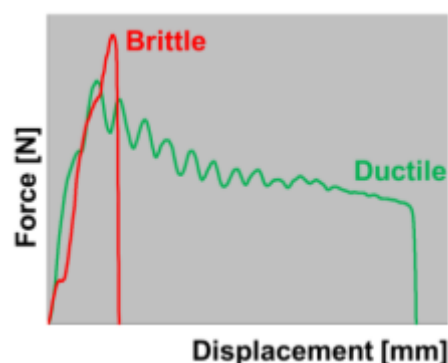


Figure 52. Force-displacement graphs for brittle and ductile fractures.

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 53. In Figure 54 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.

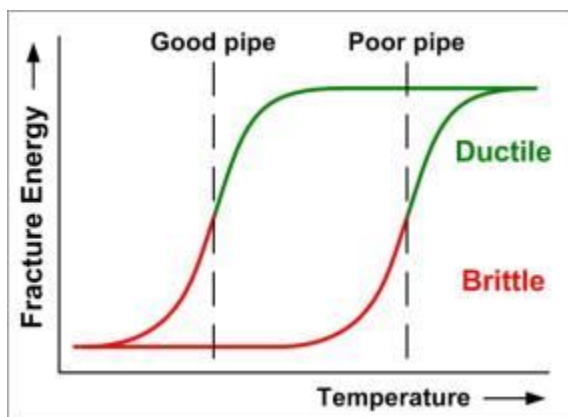


Figure 53. Schematic graph of the brittle-ductile-transition-temperature for a *good* and a *poor* PVC pipe.

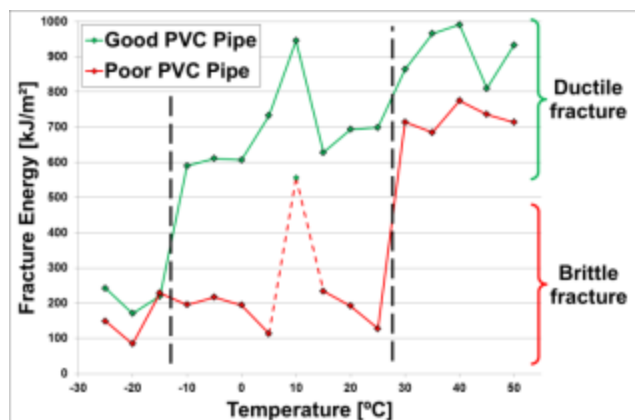


Figure 54. Graph of the brittle-ductile-transition-temperature for a *good* and a *poor* PVC pipe in practise.

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 $-25\text{ }^{\circ}\text{C}$ to $+50\text{ }^{\circ}\text{C}$ in incremental steps of $1\text{ }^{\circ}\text{C}$ (see Figure 55).

This was also carried out using PVC-A (see Figure 56).

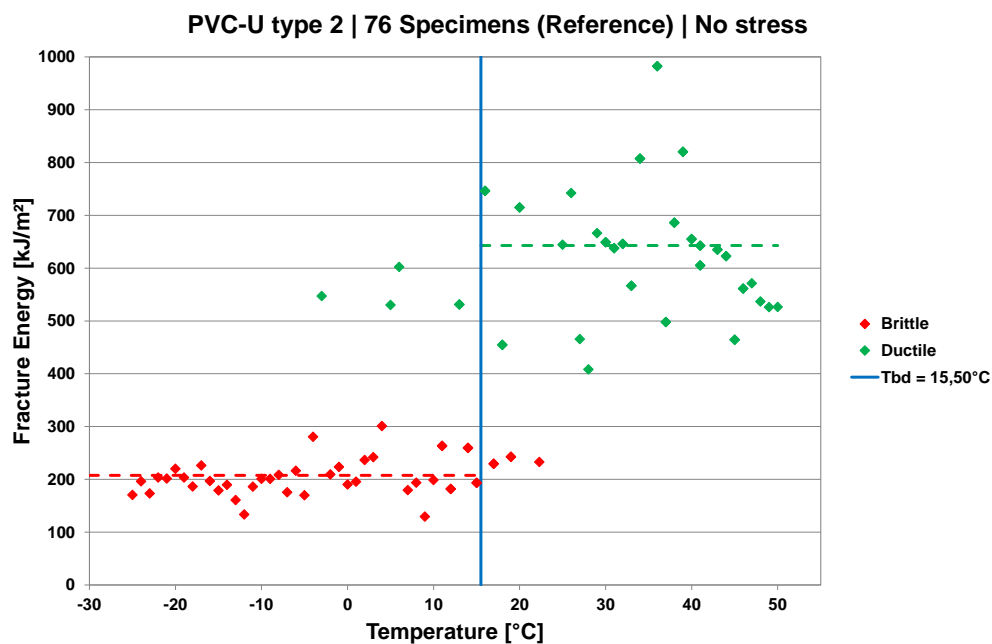


Figure 55. PVC-U type 2 tested from $-25\text{ }^{\circ}\text{C}$ to $+50\text{ }^{\circ}\text{C}$ in steps of $1\text{ }^{\circ}\text{C}$.

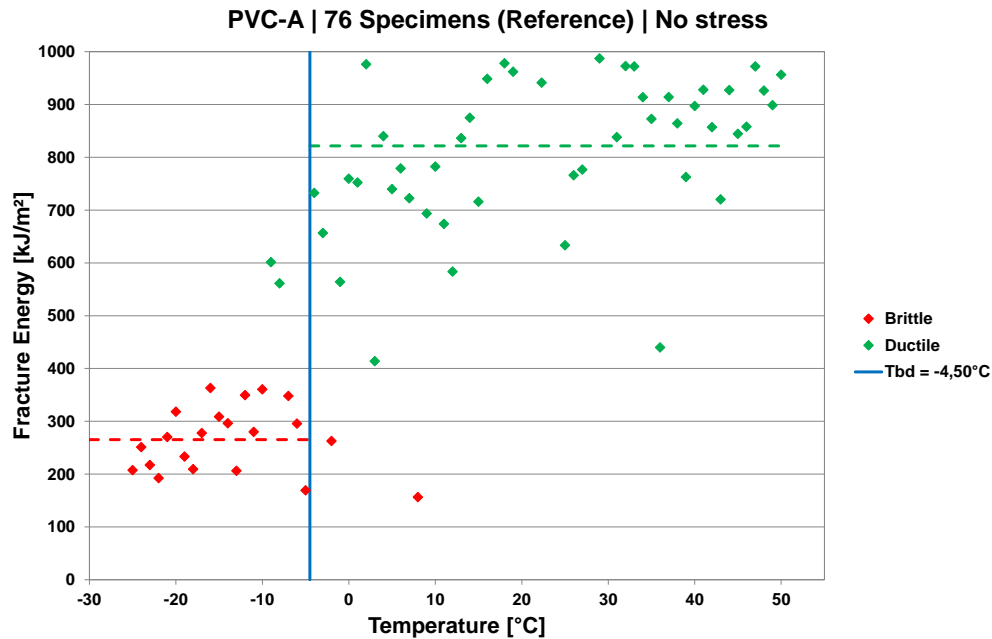


Figure 56. PVC-A tested from -25 C to +50 C in steps of 1°C.

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 57 to Figure 60).

The results are summarised in Table 30.

Table 30. 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 30 are used for estimations of the standard deviation in this report.

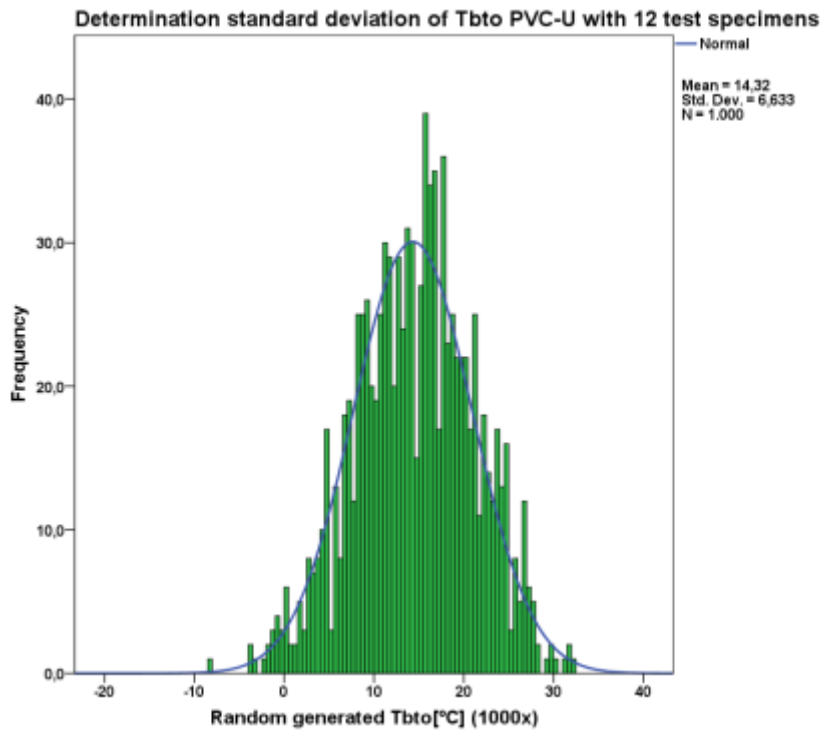


Figure 57. Determination of standard deviation of T_{BD} PVC-U type 2 with 12 randomly selected test specimens.

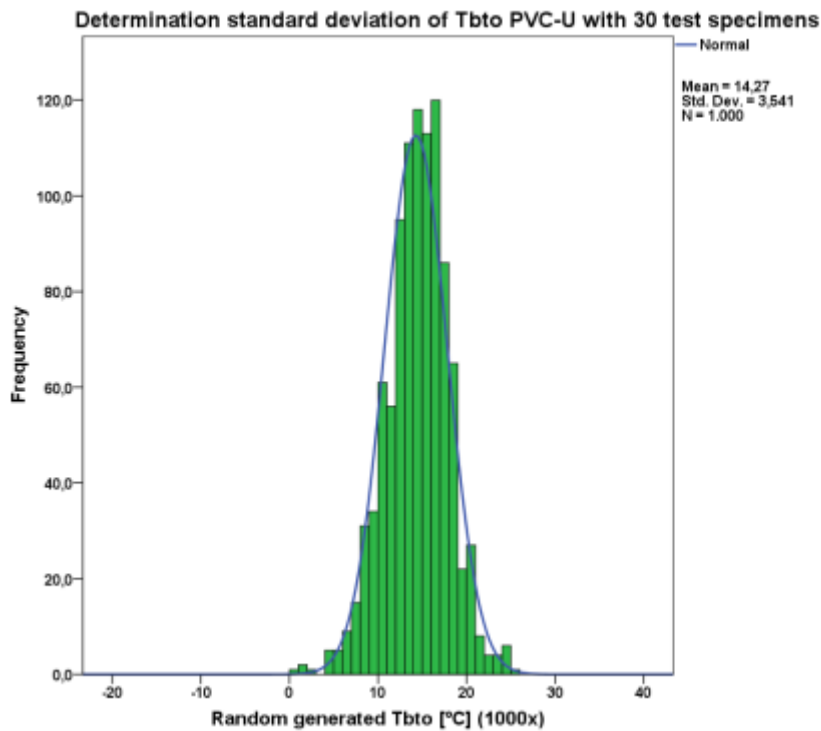


Figure 58. Determination of standard deviation of T_{BD} PVC-U type 2 with 30 randomly selected test specimens.

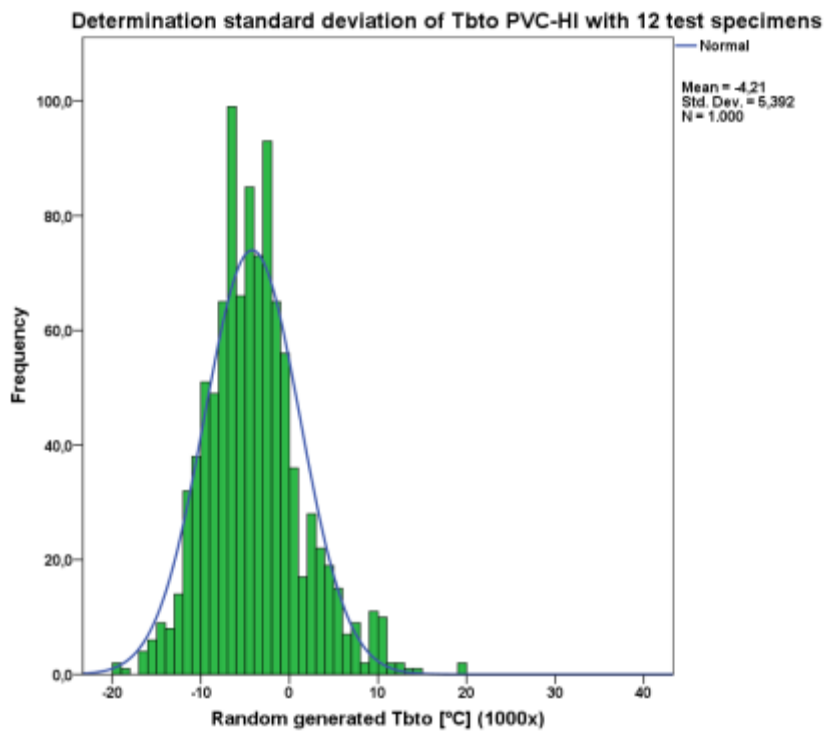


Figure 59. Determination of standard deviation of T_{BD} PVC-A with 12 randomly selected test specimens.

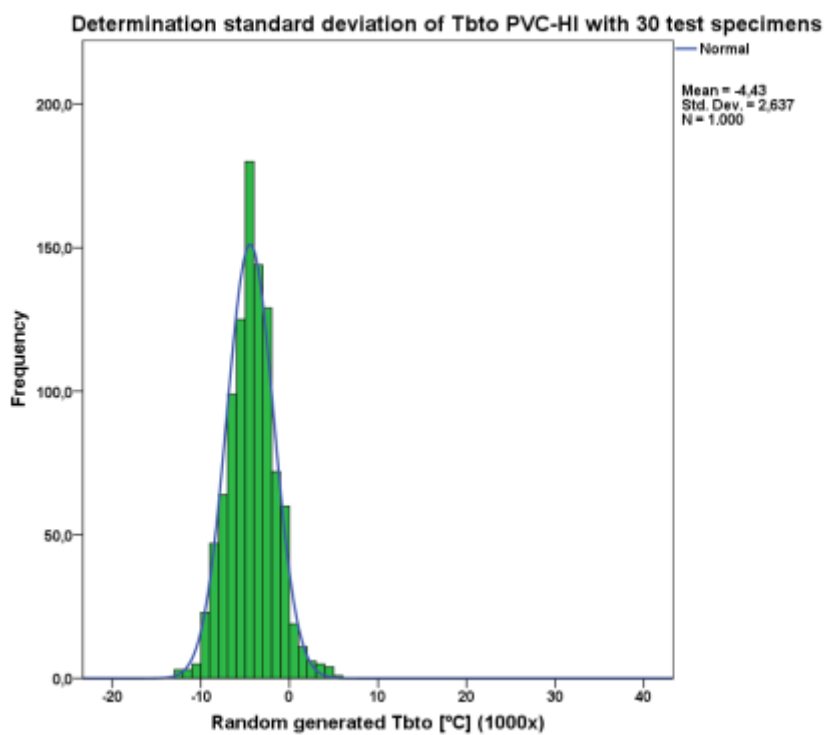


Figure 60. Determination of standard deviation of T_{BD} PVC-A with 30 randomly selected test specimens.



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 narrow band concentrations are left out and can be found in [5].

IV.1.1 Mass Change

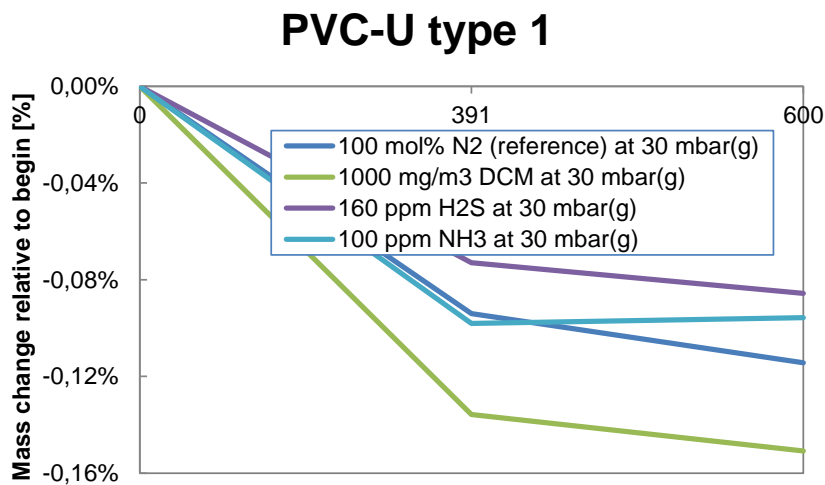


Figure 61. Mass change of PVC-U type 1 materials which had been exposed for a period of 600 days to 1000 mg/m³ DCM, 160 ppm H₂S, 100 ppm NH₃ and N₂ (reference).

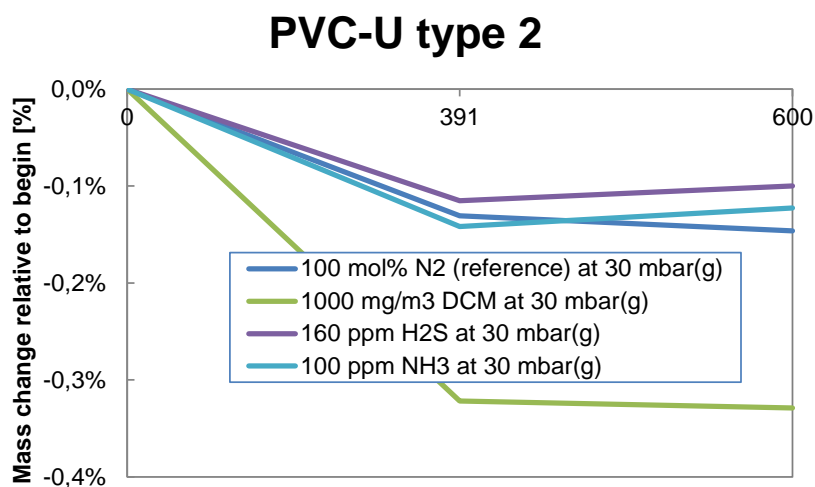


Figure 62. Mass change of PVC-U type 2 materials which had been exposed for a period of 600 days to 1000 mg/m³ DCM, 160 ppm H₂S, 100 ppm NH₃ and N₂ (reference).



PVC-CPE

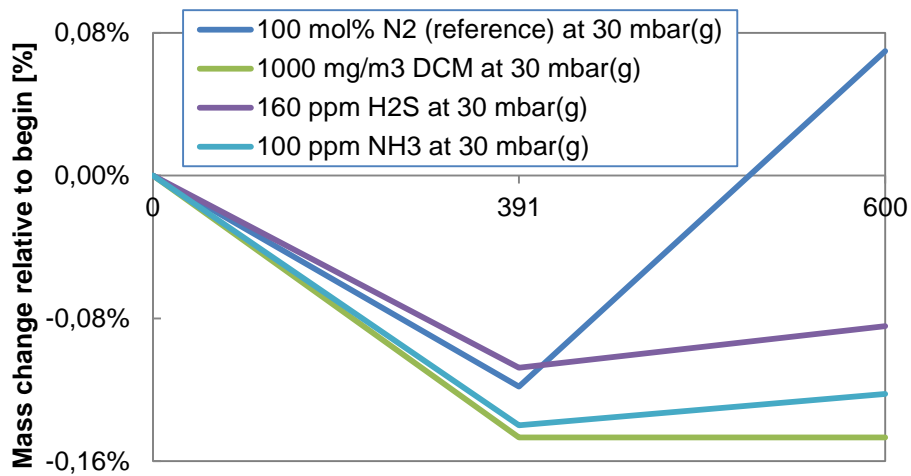


Figure 63. Mass change of PVC-CPE materials which had been exposed for a period of 600 days to 1000 mg/m³ DCM, 160 ppm H₂S, 100 ppm NH₃ and N₂ (reference).

PVC-A

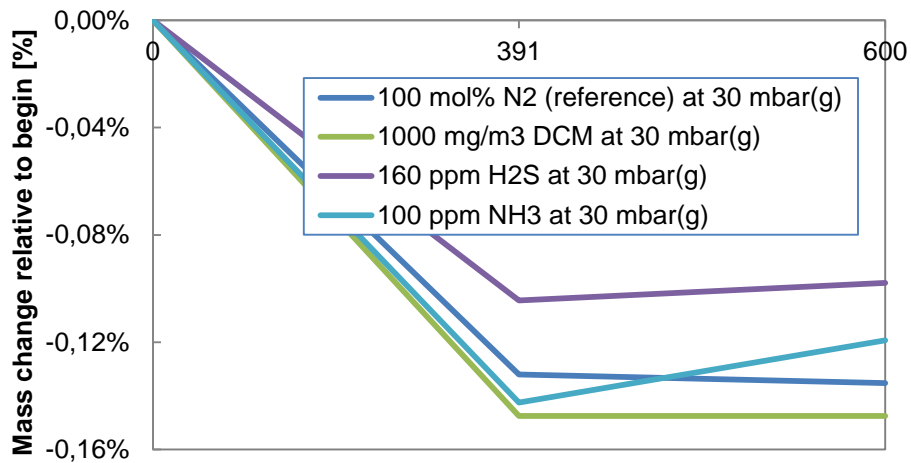
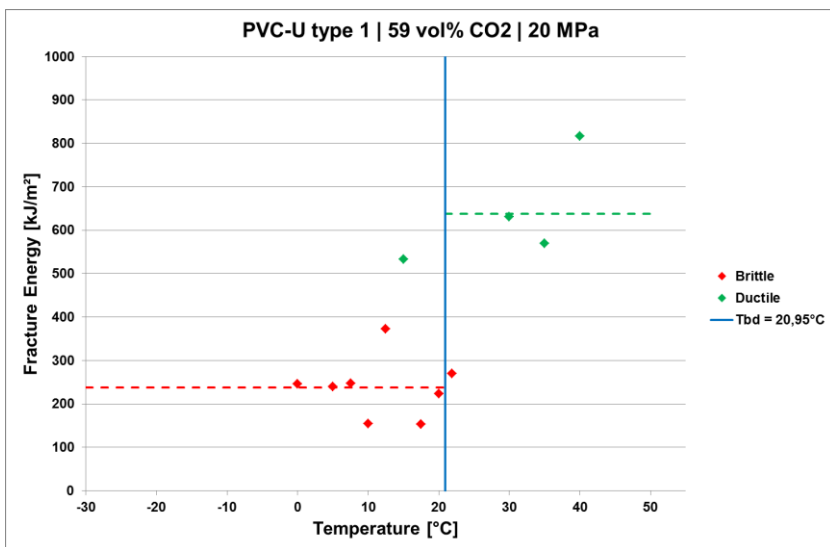
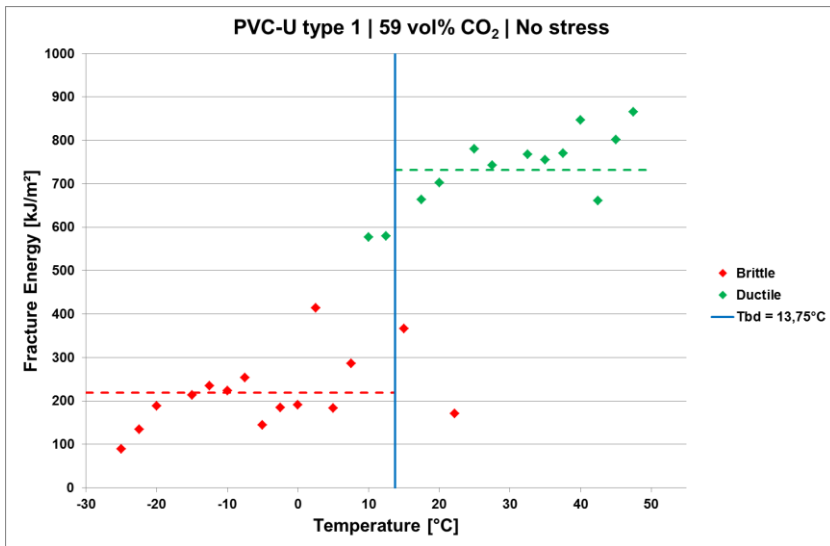
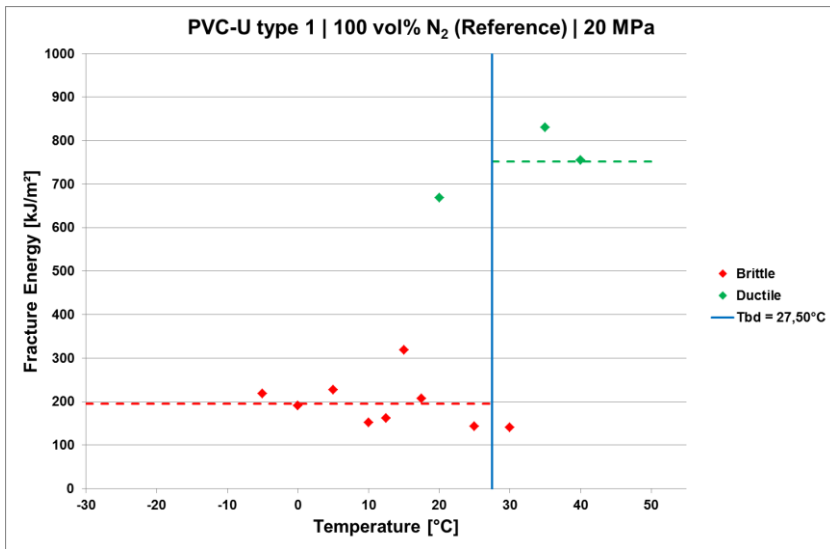
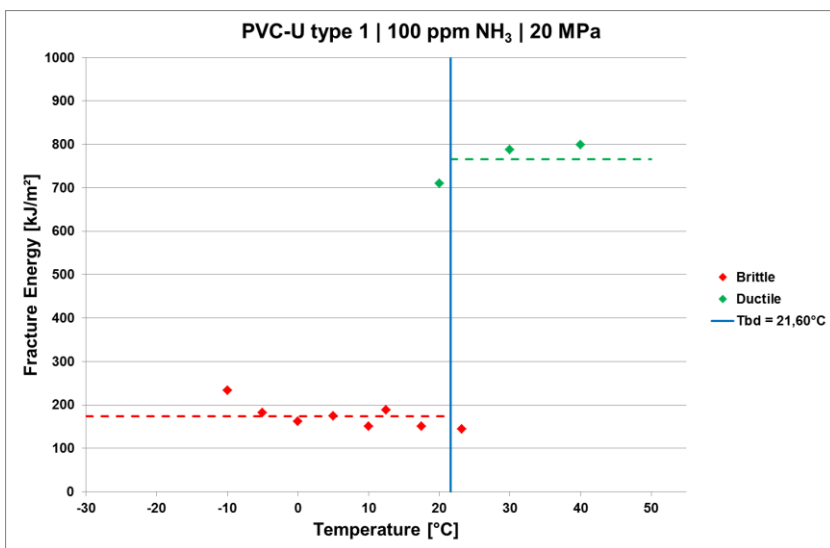
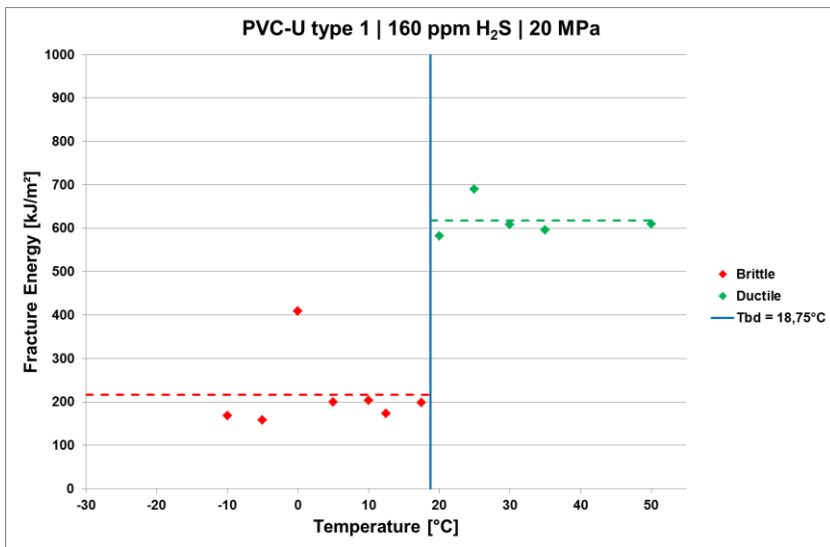
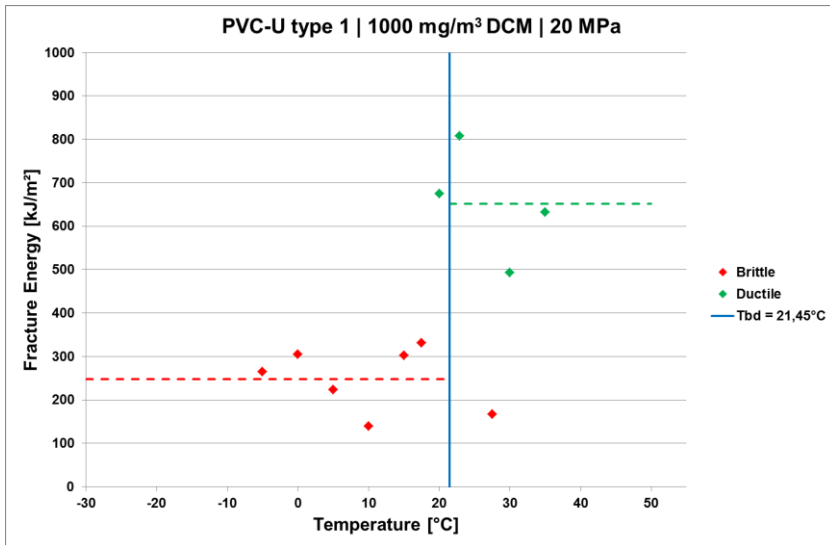


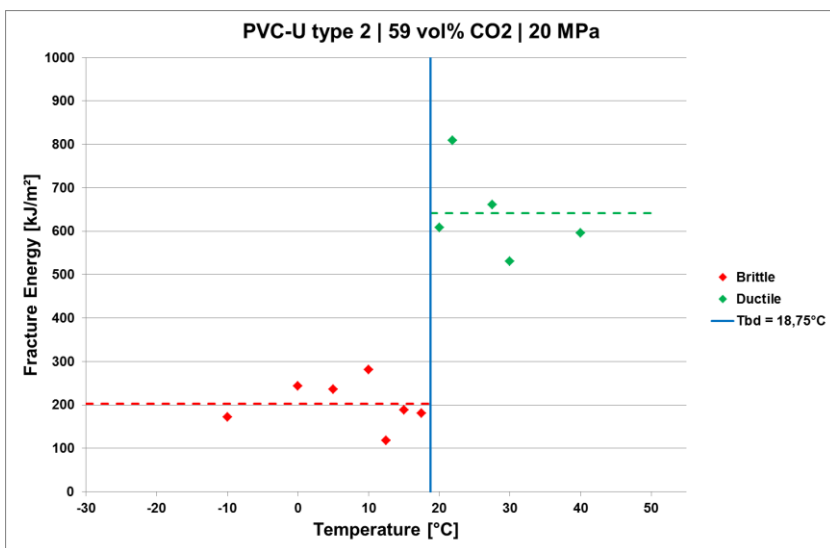
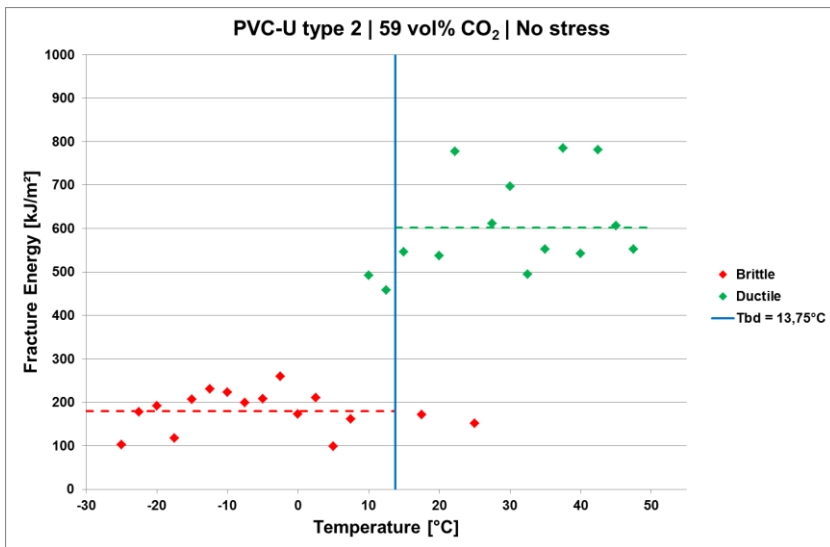
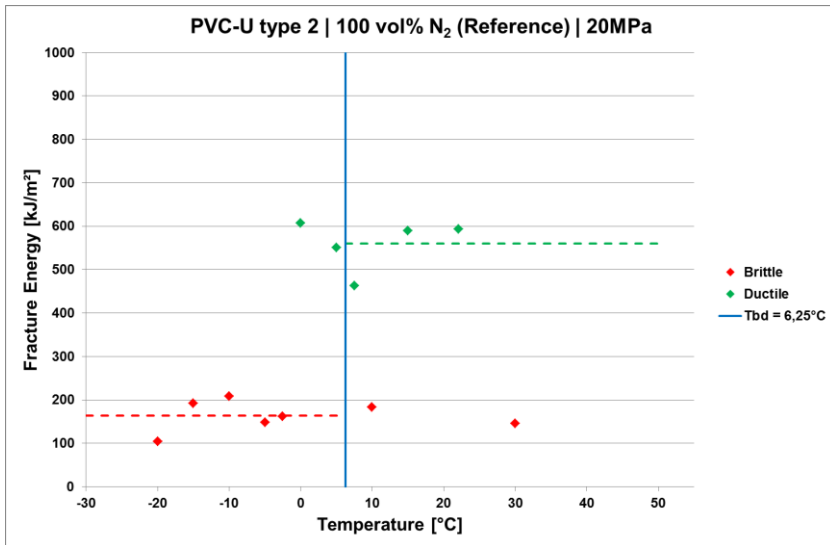
Figure 64. Mass change of PVC-CPE materials which had been exposed for a period of 600 days to 1000 mg/m³ DCM, 160 ppm H₂S, 100 ppm NH₃ and N₂ (reference).

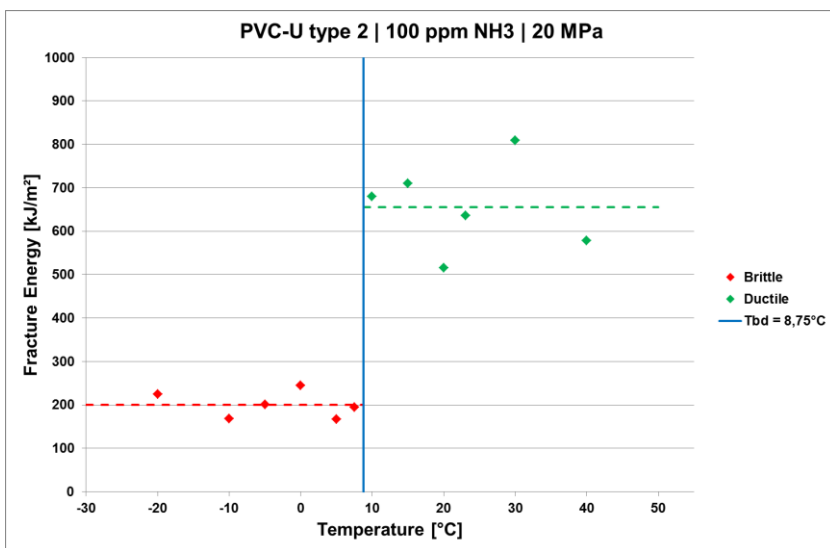
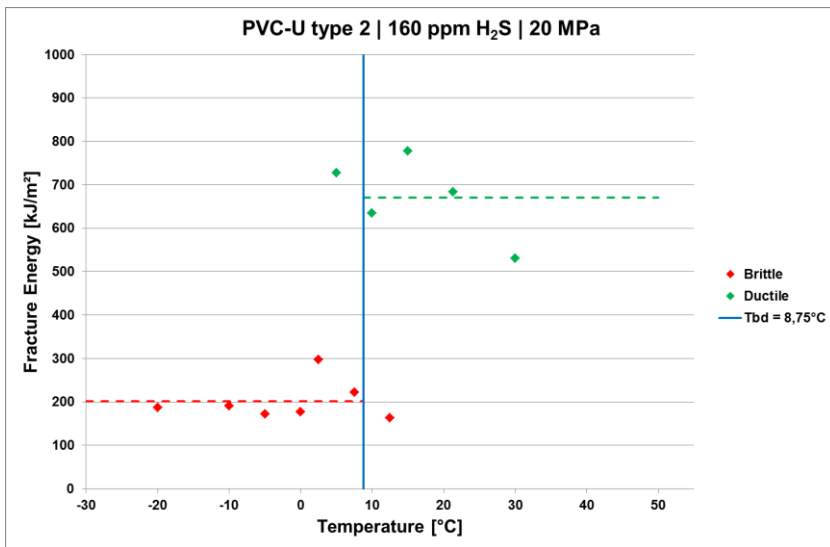
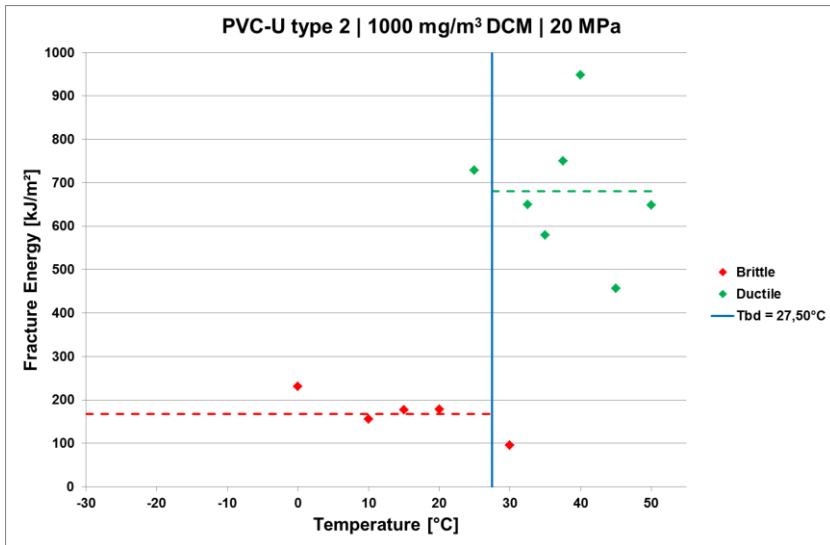


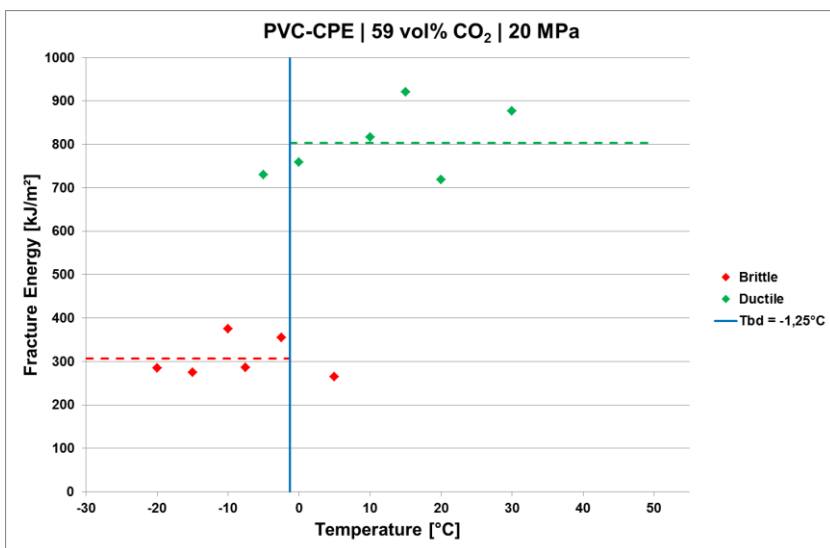
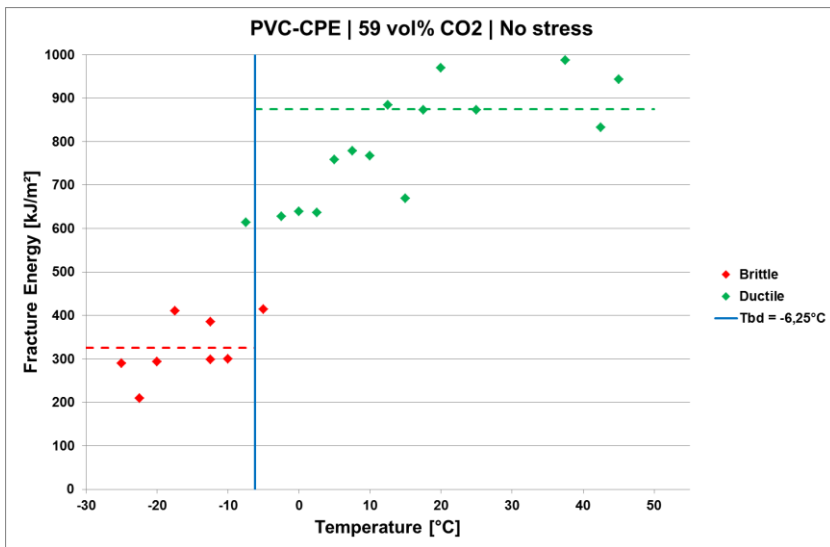
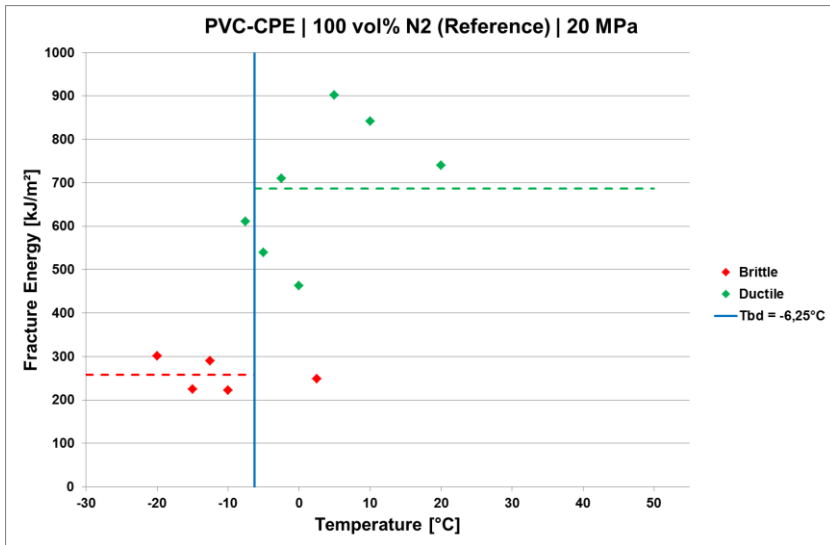
IV.1.2 Brittle-Ductile Transition Temperature

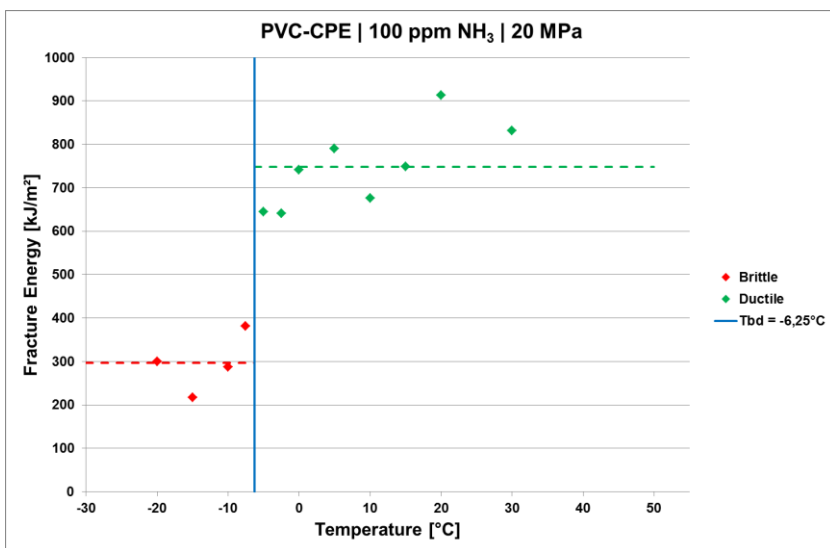
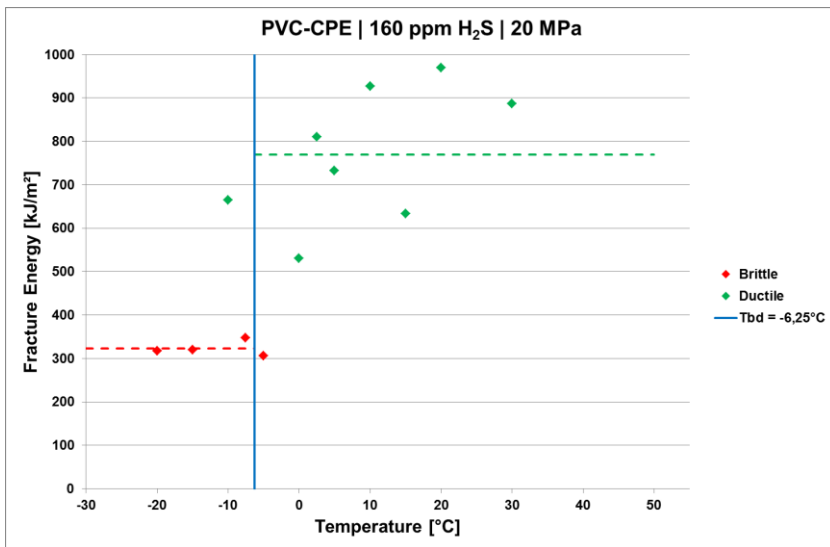
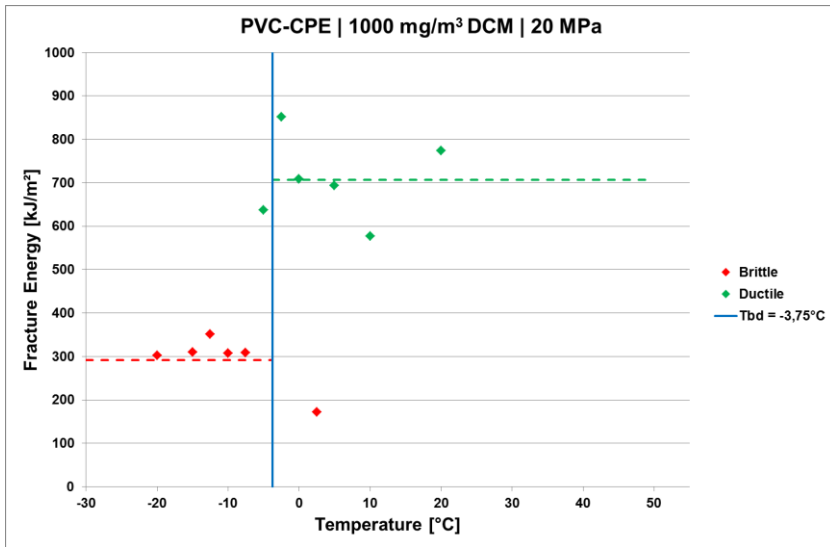


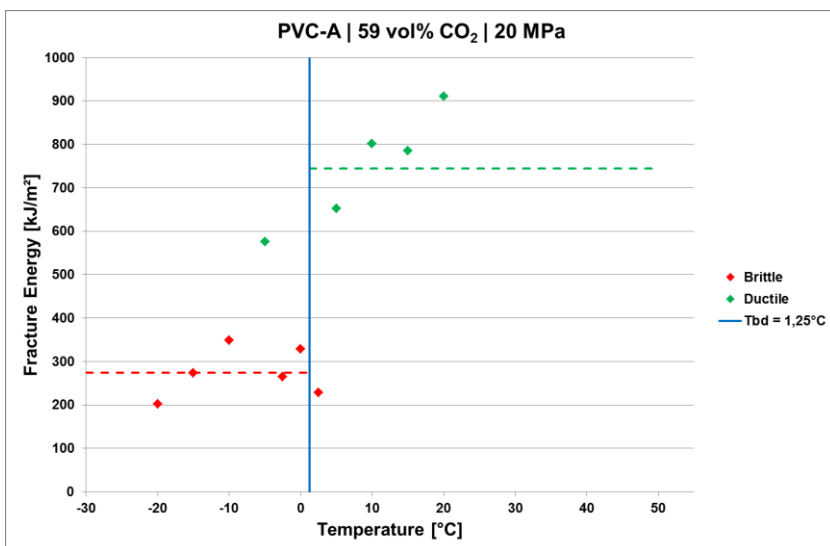
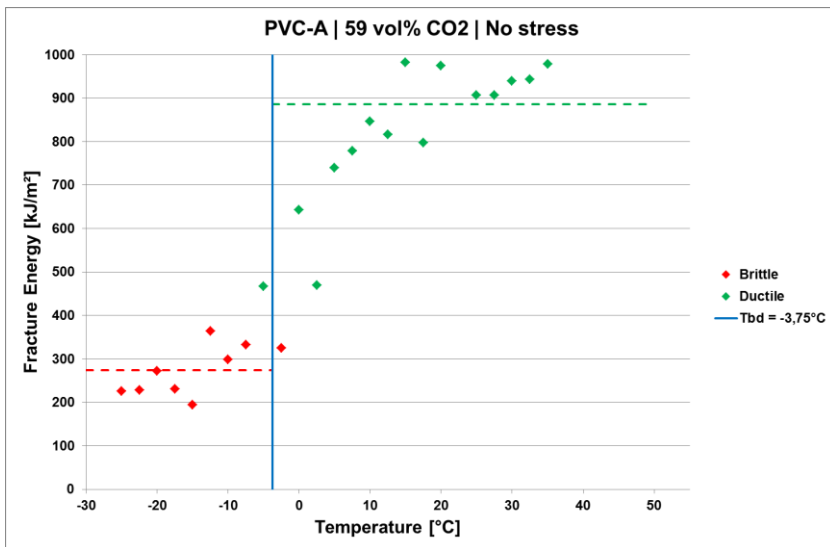
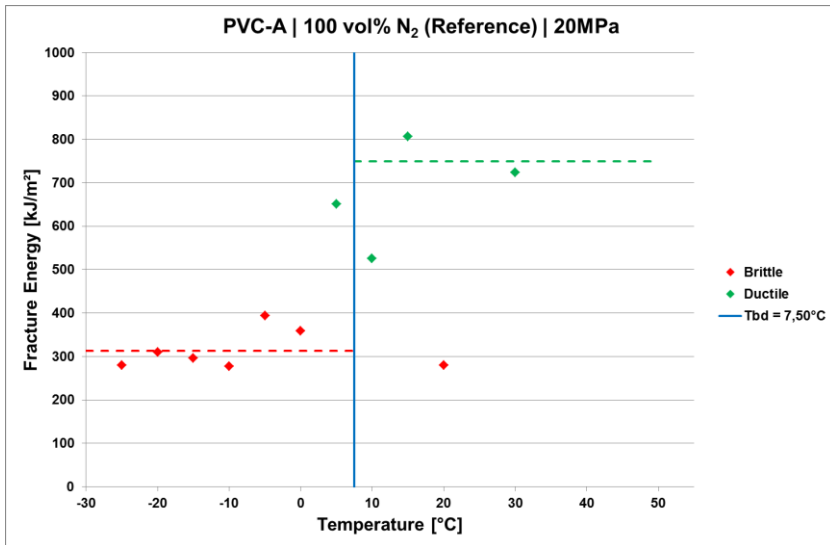


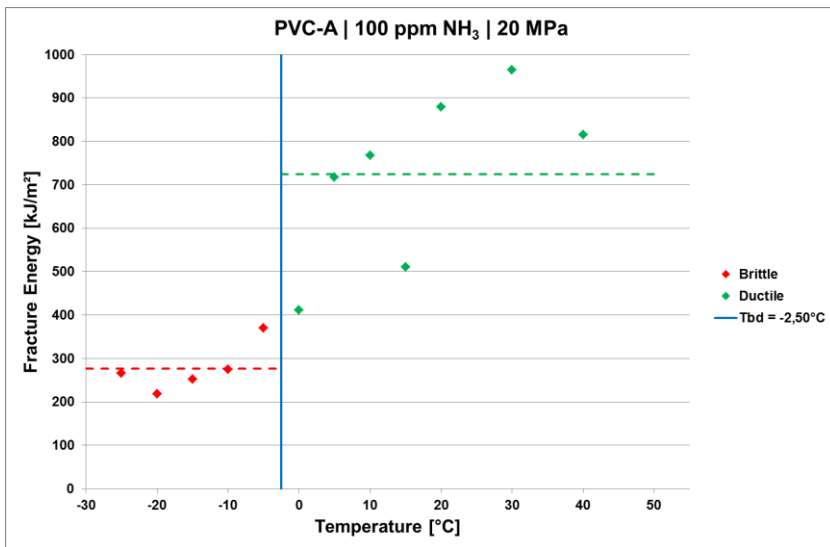
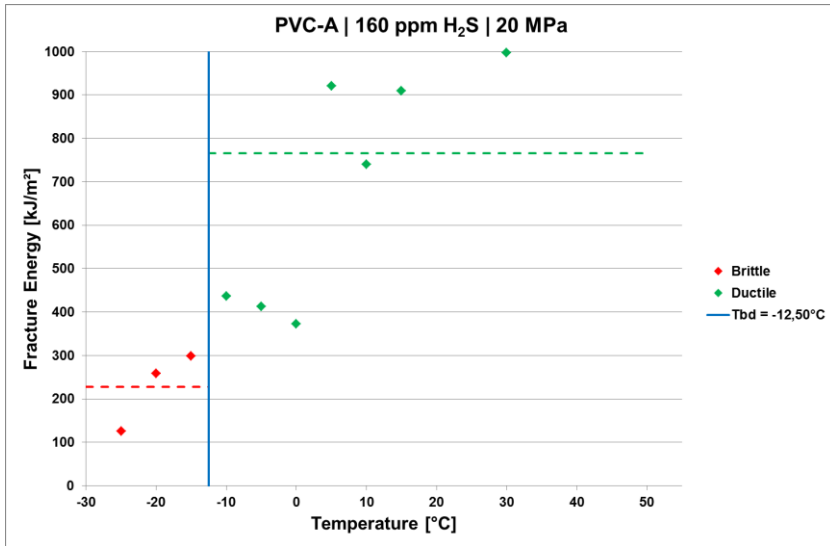
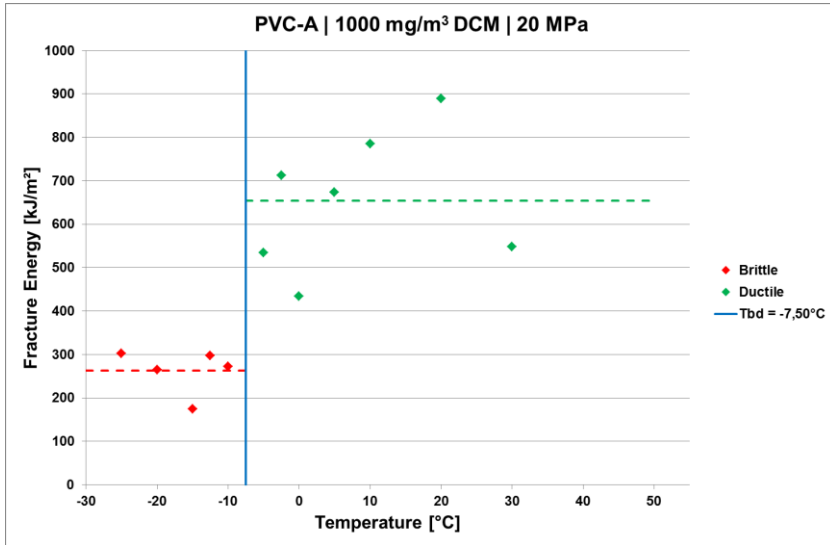














IV.2 Polyethylene (PE)

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

IV.2.1 Mass Change

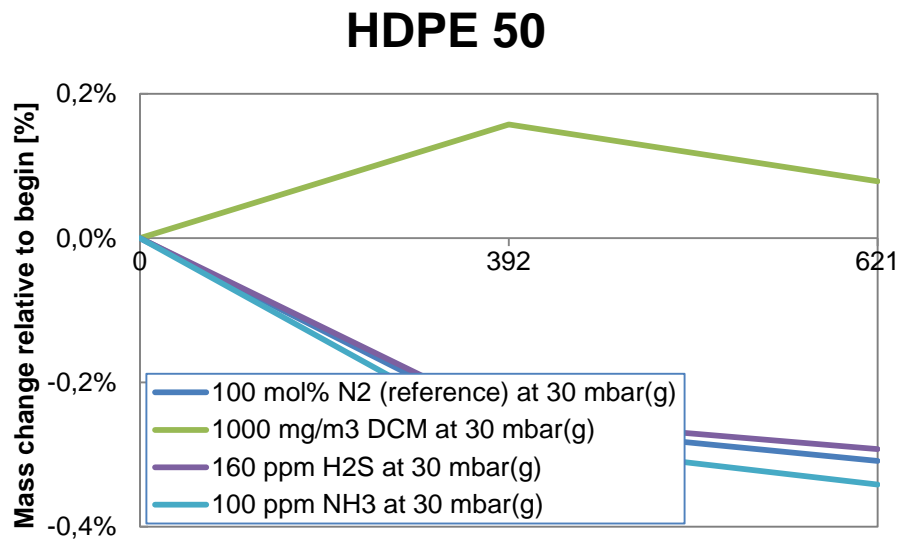


Figure 65. Mass change of HDPE 50 materials which had been exposed for a period of 600 days to 1000 mg/m³ DCM, 160 ppm H₂S, 100 ppm NH₃ and N₂ (reference).

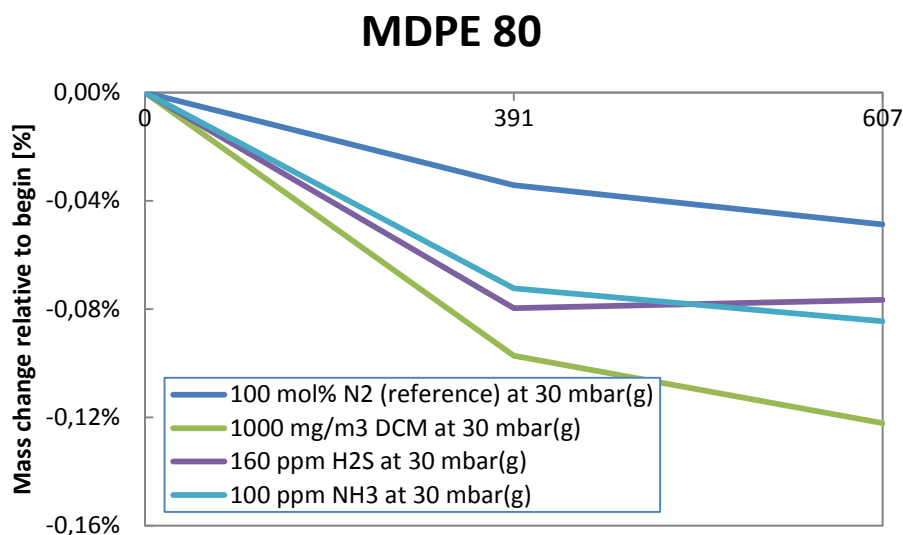


Figure 66. Mass change of MDPE 80 materials which had been exposed for a period of 600 days to 1000 mg/m³ DCM, 160 ppm H₂S, 100 ppm NH₃ and N₂ (reference).



HDPE 100

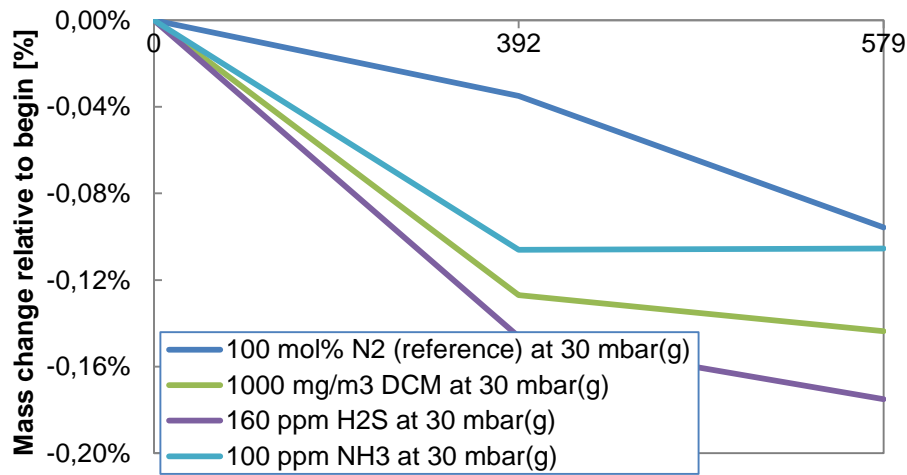


Figure 67. Mass change of HDPE 100 materials which had been exposed for a period of 600 days to 1000 mg/m³ DCM, 160 ppm H₂S, 100 ppm NH₃ and N₂ (reference).

IV.2.2 Mechanical Properties

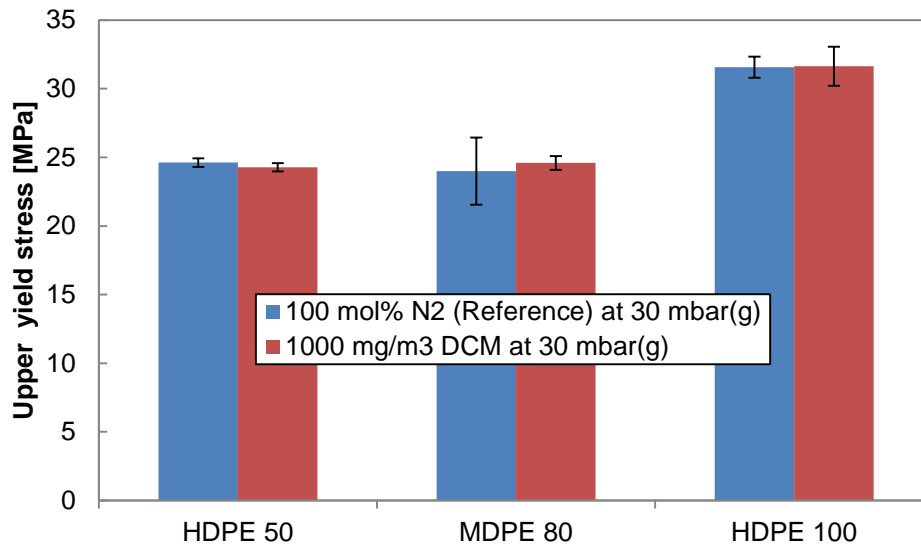


Figure 68. Upper yield stress of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 1000 mg/m³ DCM and N₂ (reference).

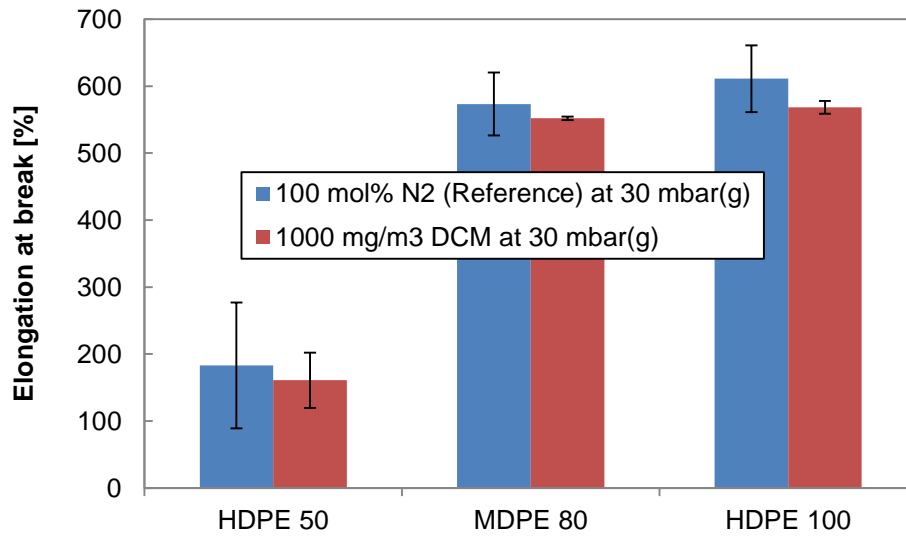


Figure 69. Elongation at break of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 1000 mg/m³ DCM and N₂ (reference).

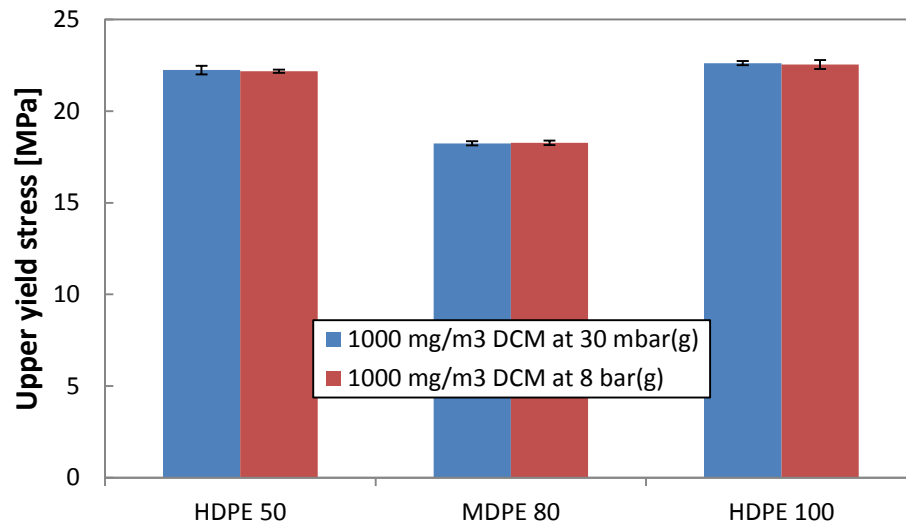


Figure 70. Upper yield stress of PE rings (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 1000 mg/m³ DCM at 30 mbar(g) and 8 bar(g).

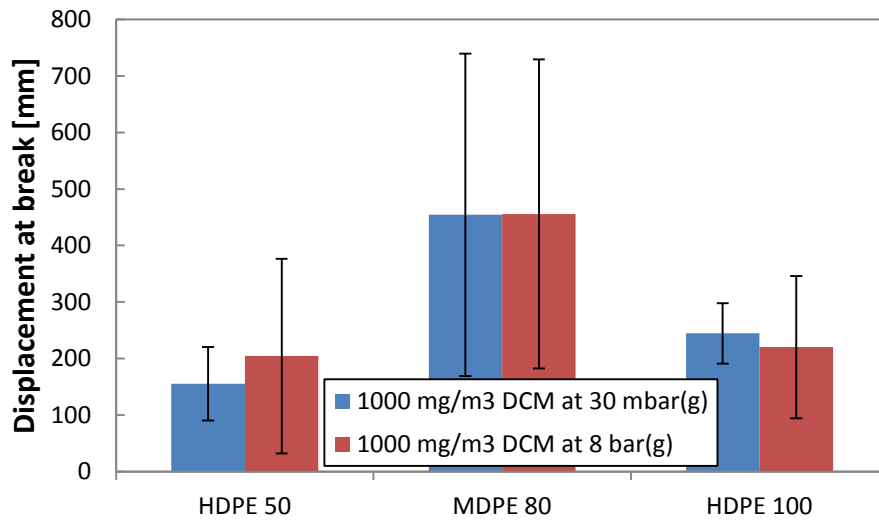


Figure 71. Displacement at break of PE rings (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 1000 mg/m³ DCM at 30 mbar(g) and 8 bar(g).

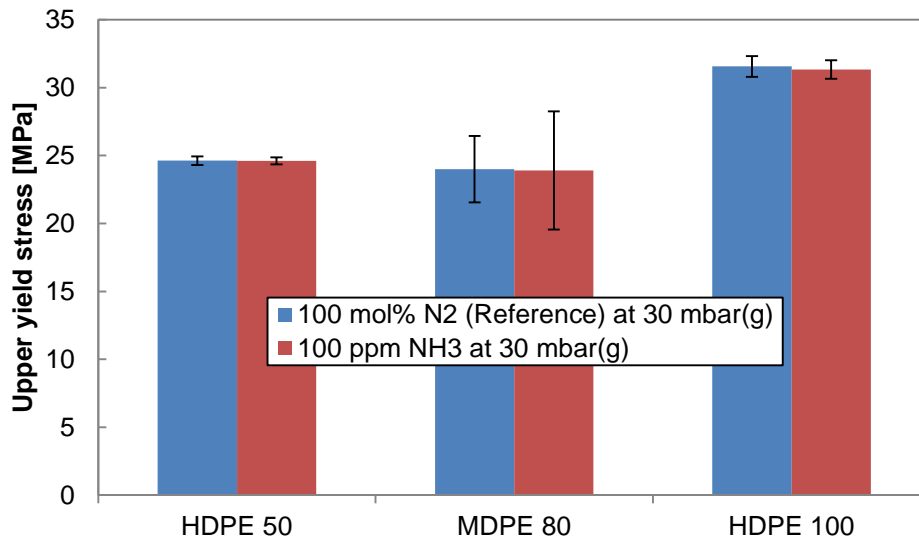


Figure 72. Upper yield stress of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 100 ppm NH₃ and N₂ (reference).

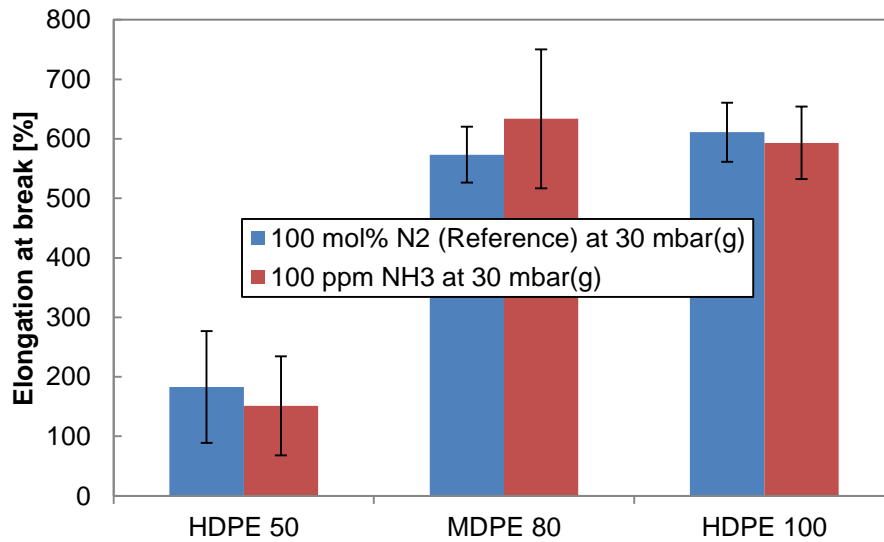


Figure 73. Elongation at break of dumbbell PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 100 ppm NH₃ and N₂ (reference).

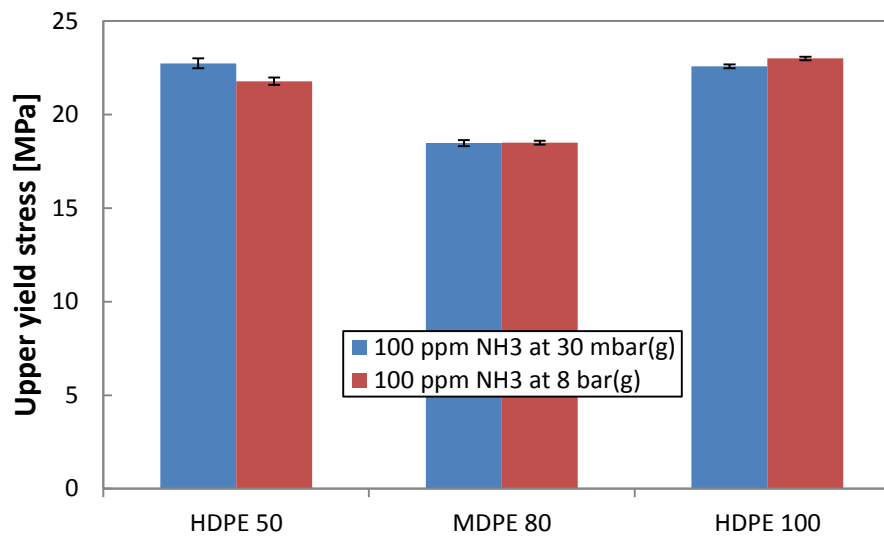


Figure 74. Upper yield stress of ring PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 100 ppm NH₃ at 30 mbar(g) and 8 bar(g).

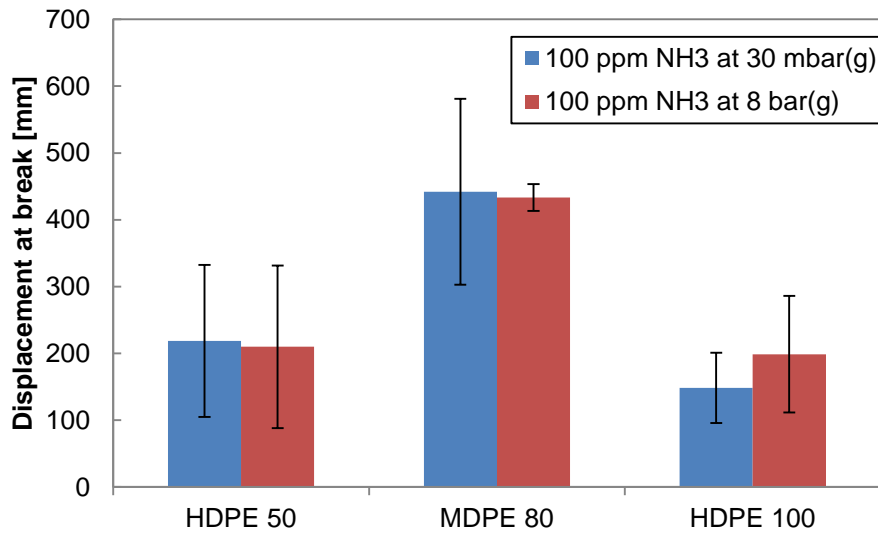


Figure 75. Displacement at break of ring PE specimens (HDPE 50, MDPE 80 and HDPE 100) which had been exposed for a period of 600 days to 100 ppm NH₃ at 30 mbar(g) and 8 bar(g).

IV.3 Elastomeric Materials (NBR)

In this appendix the results of the experiments on NBR are given. The results of the field experiments are left out and can be found in [5] and [6].

IV.3.1 Mass Change

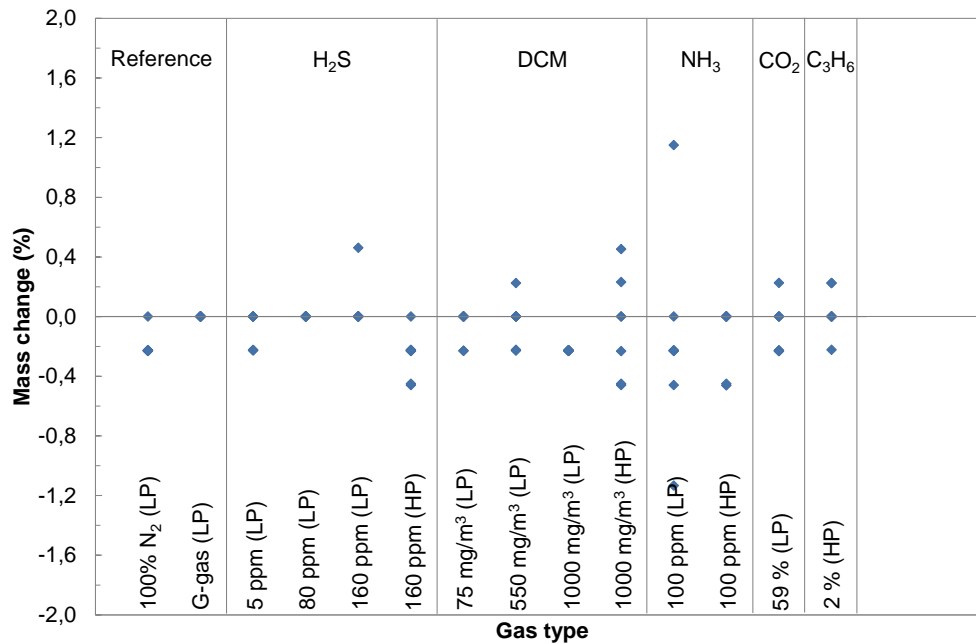


Figure 76. Mass change of NBR samples which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.



IV.3.2 Mechanical Properties

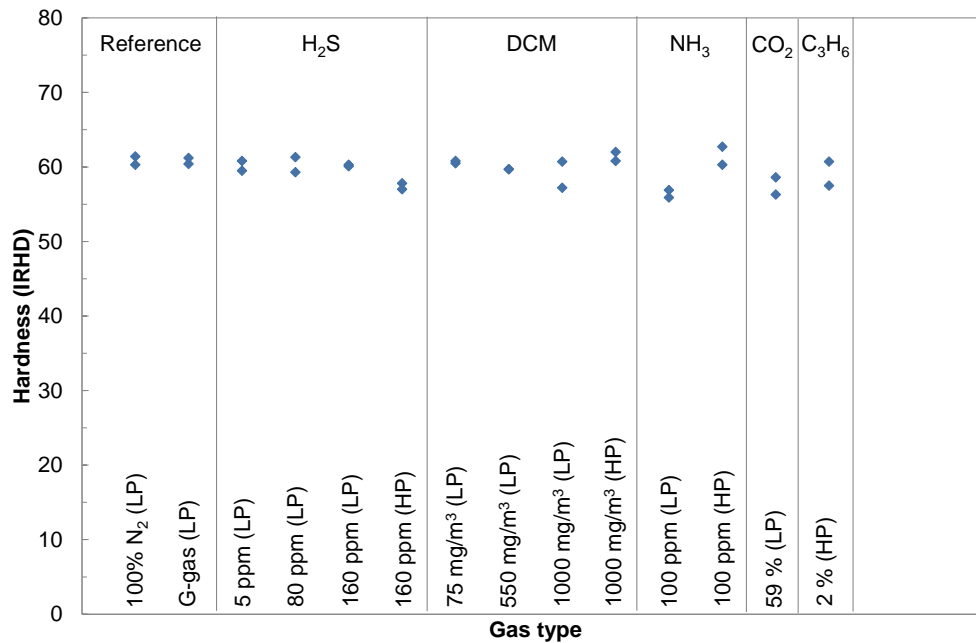


Figure 77. Hardness of NBR samples which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

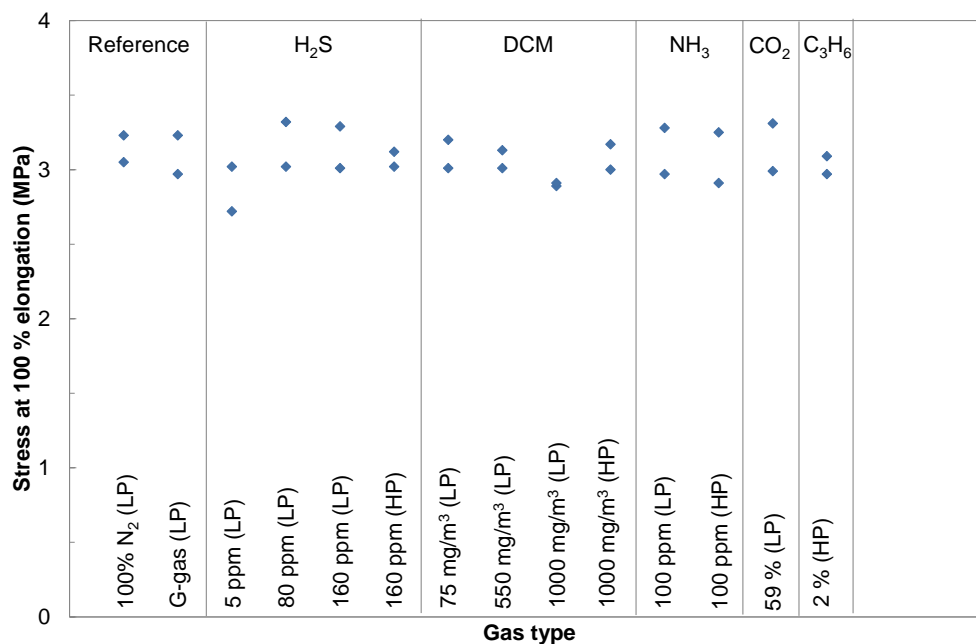


Figure 78. Stress at 100% elongation of NBR samples which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

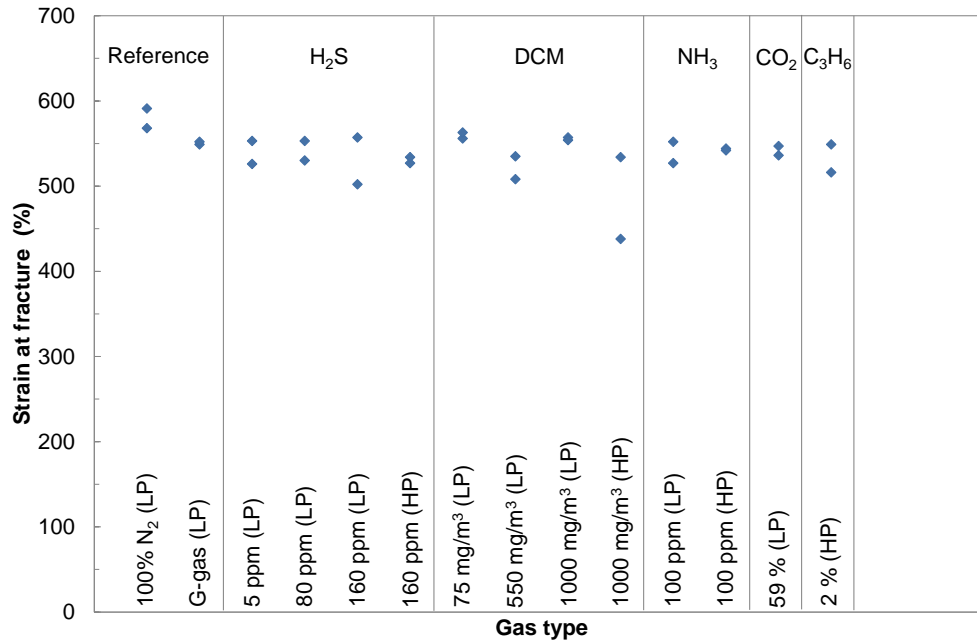


Figure 79. Elongation at break of NBR samples which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

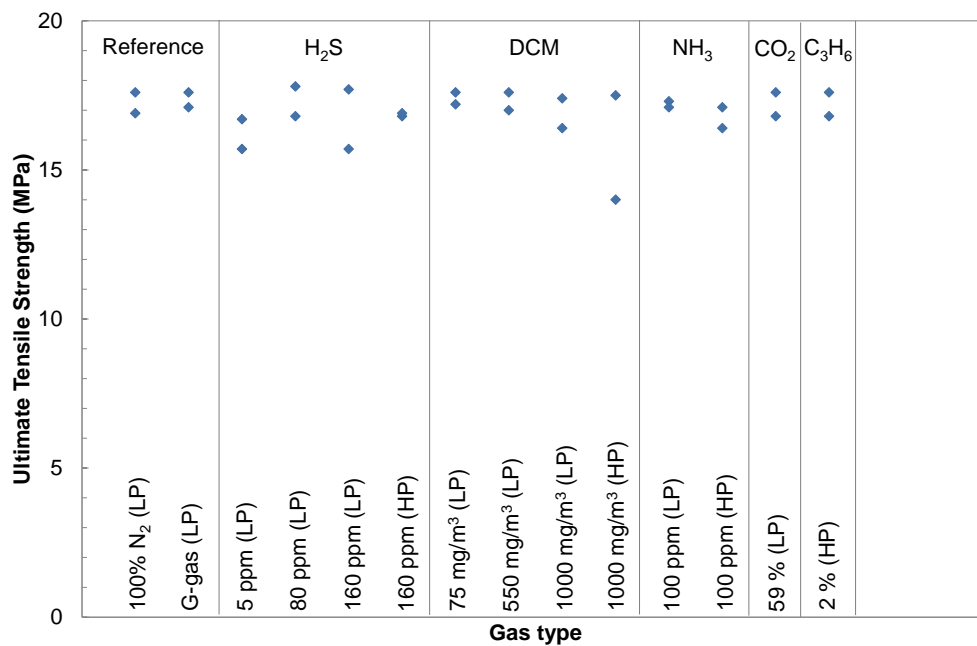


Figure 80. Ultimate tensile strength of NBR samples which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

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.

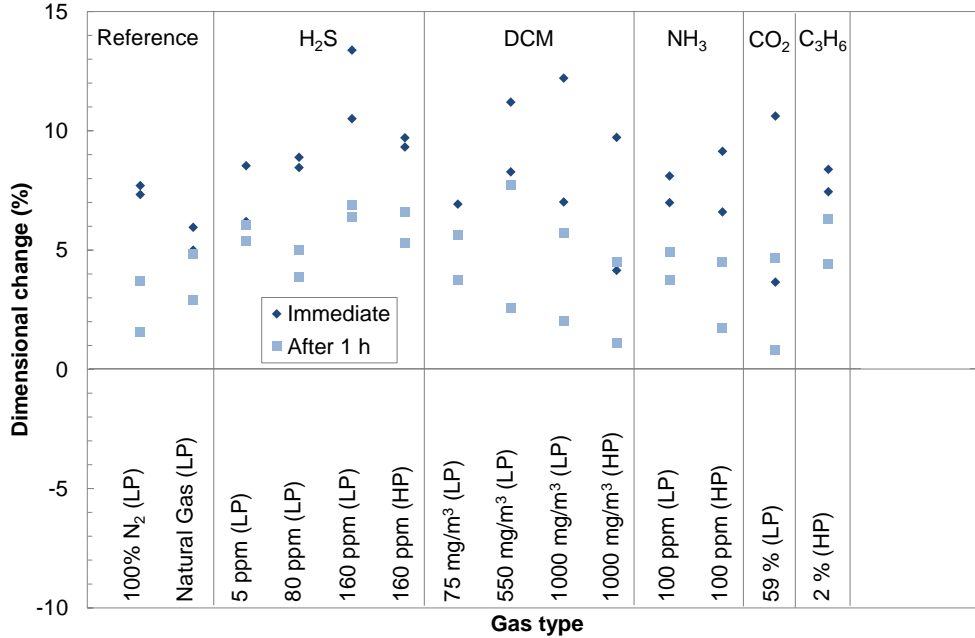


Figure 81. The difference in inner diameter of NBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

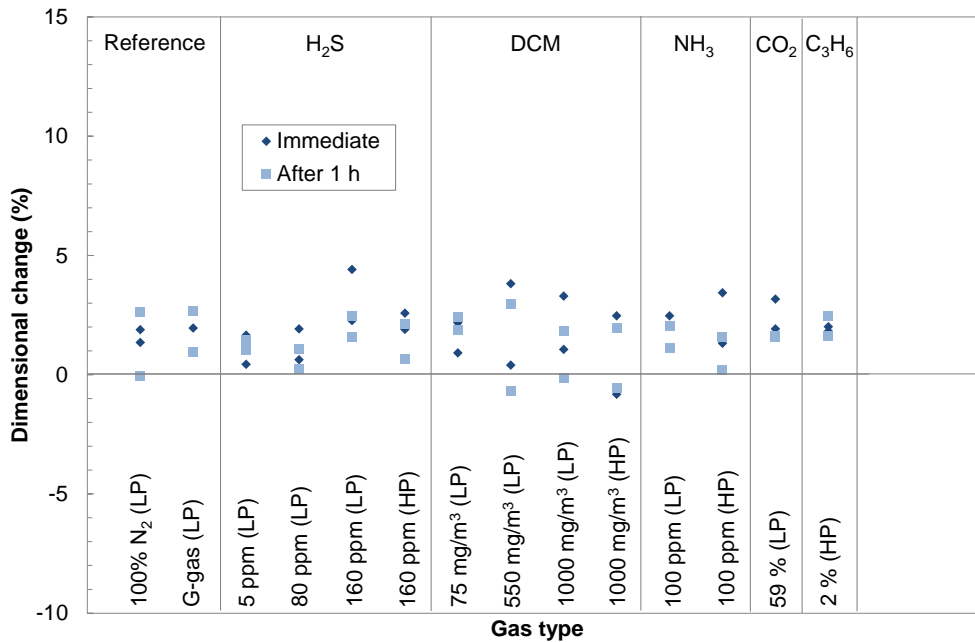


Figure 82. The difference in outer diameter of NBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

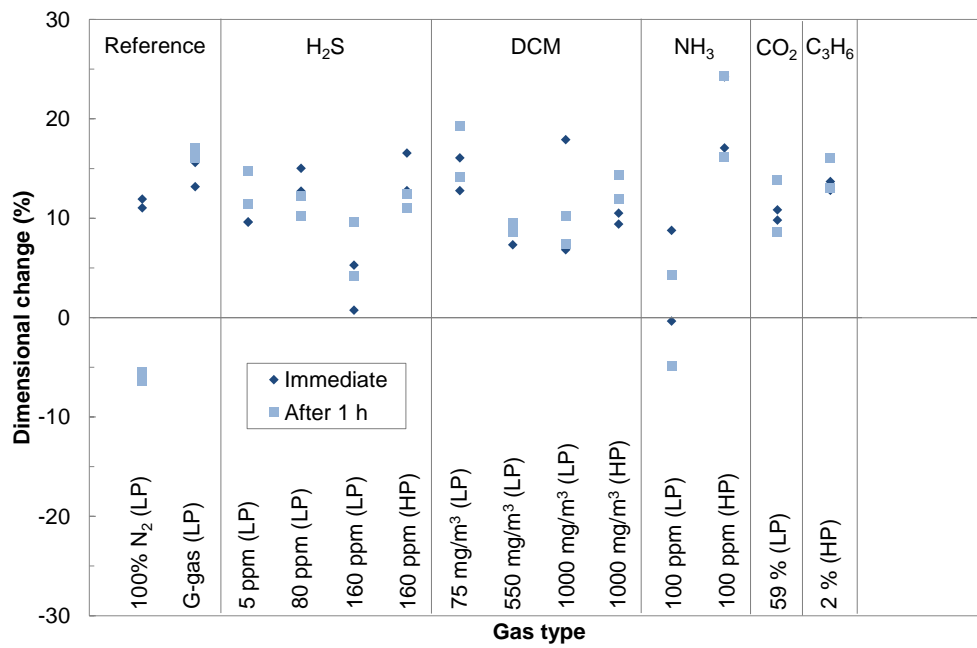
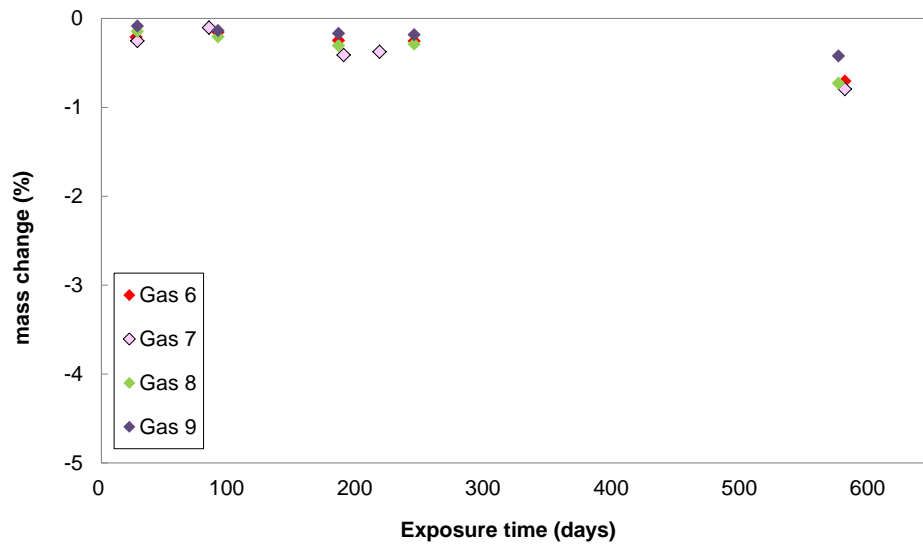
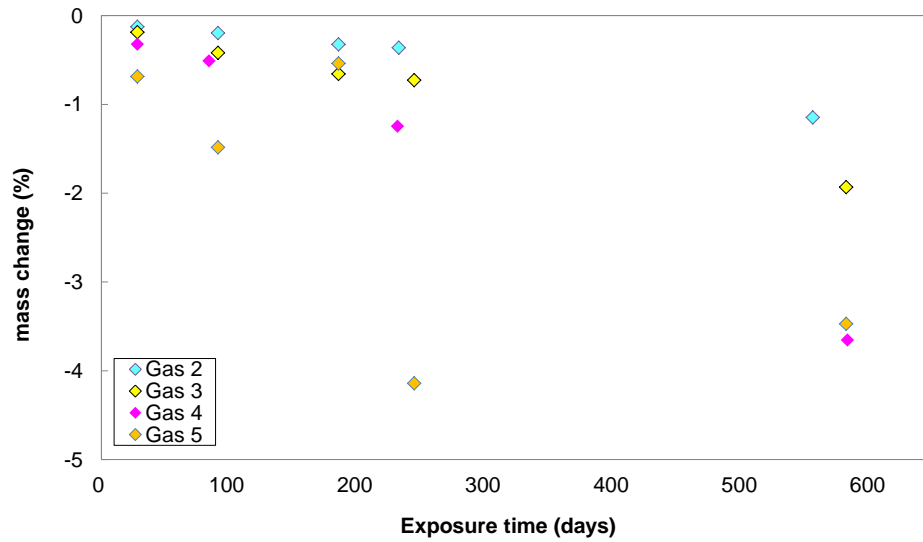
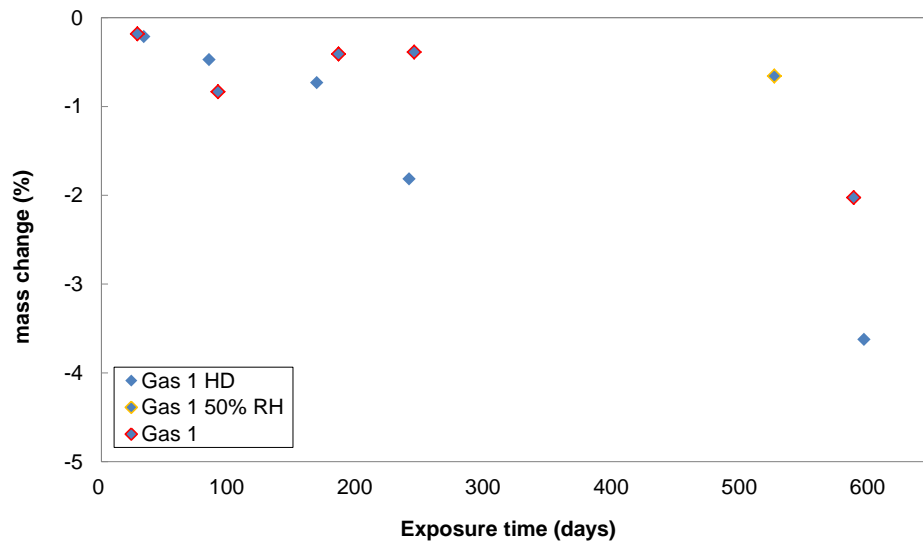


Figure 83. The difference in thickness of NBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

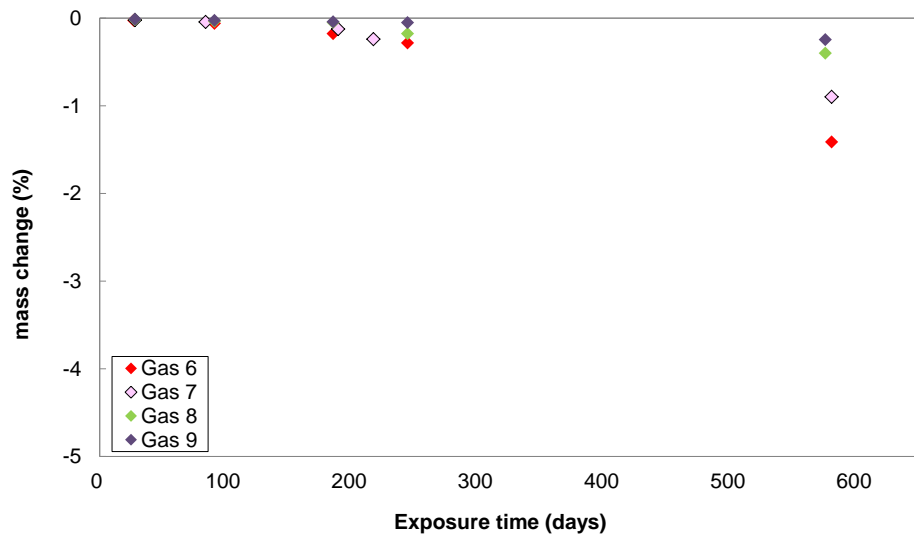
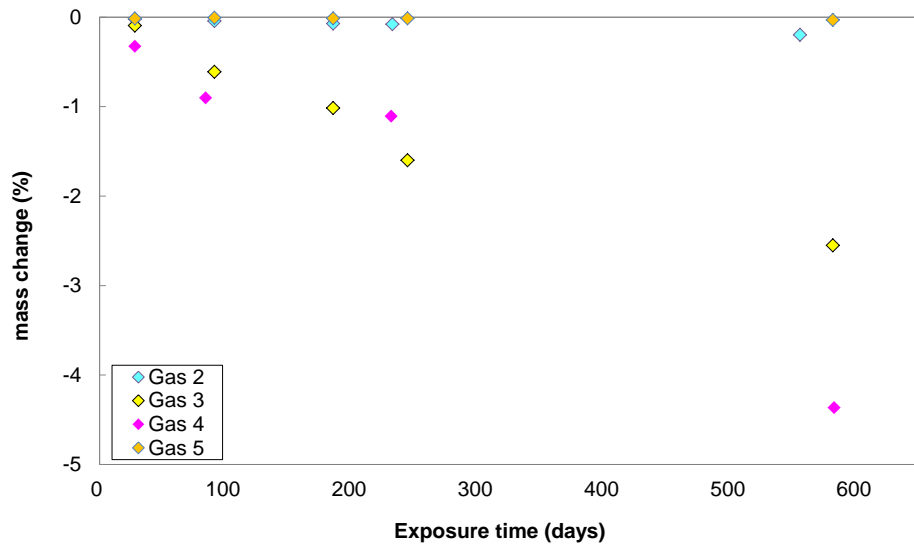
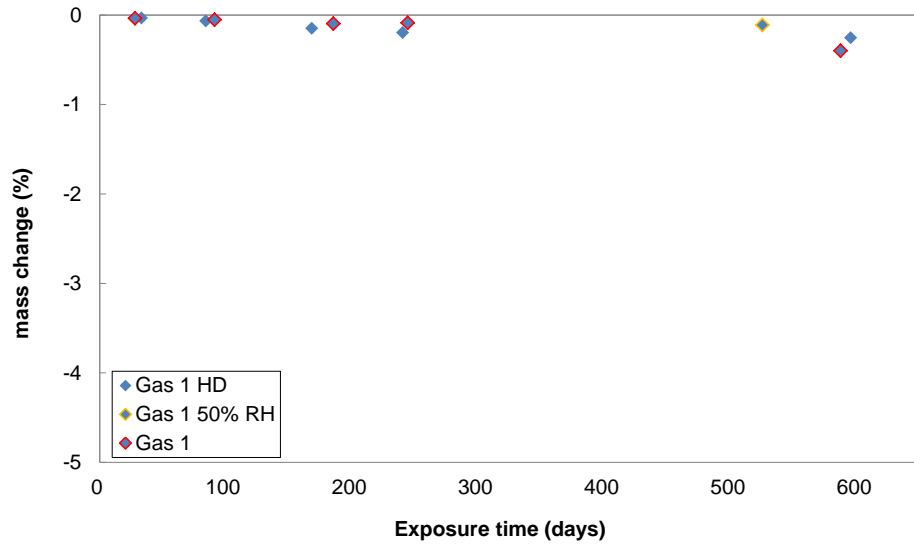


IV.4 Steel



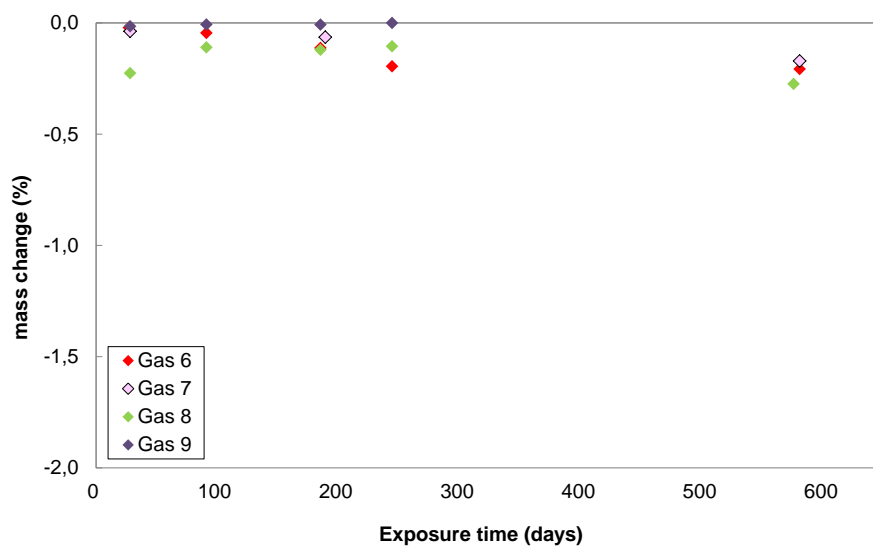
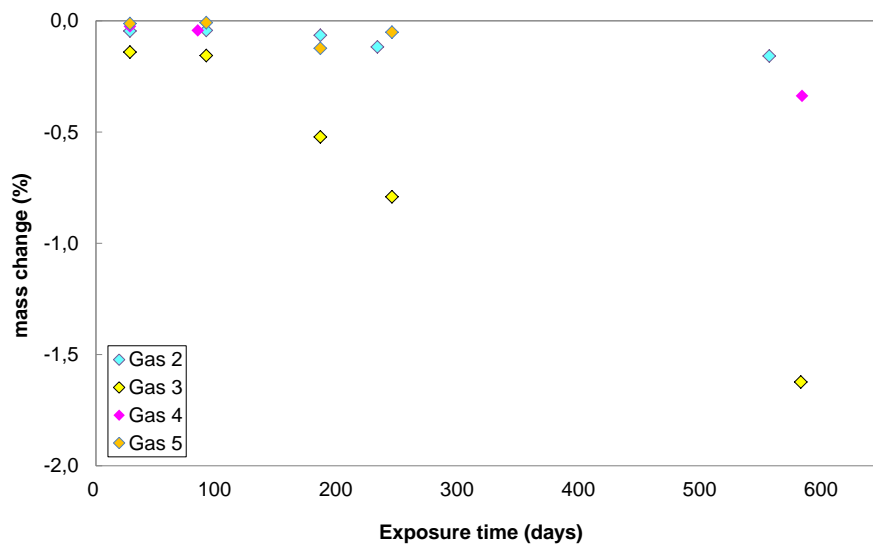
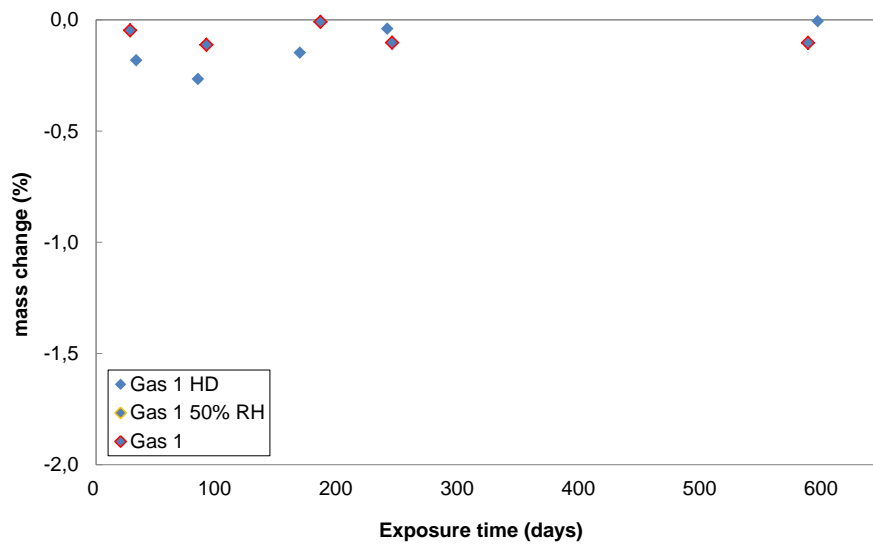


IV.5 Copper





IV.6 Aluminium





V References

- [1] de Bruin, Hermkens, Ophoff, Postma, Rittel, Scholten, van der Stok, *Effects of Wide Band Gases on Materials used in Gas Networks. Literature Review*, Kiwa Technology, **GT-110205**, (2012)
- [2] de Bruin, Heerings, Hermkens, Postma, Rittel, Scholten, van der Stok, *EDGaR – Experimental Procedures. Description of the experiments for testing the resistance of gas distribution materials to narrow band and wide band gases*, Kiwa Technology, **GT-120085**, (2012)
- [3] de Bruin, Heerings, Hermkens, Postma, Rittel, Scholten, van der Stok, *EDGaR – Experimental Procedures. Description of the experiments for testing the resistance of gas distribution materials to narrow band and wide band gases AMENDMENT*, Kiwa Technology, **GT-130116**, (2013)
- [4] Zwart, *R&D needs and recommendations for the production of high-efficient bioSNG*, Conference Gasification 2009 Gas Clean-up and Gas Treatment, October 22nd 2009, Stockholm.
- [5] de Bruin, Rittel, van der Stok, Weller, *Effects of Narrow Band Gases on Materials used in Gas Distribution Networks. Final Report*, Kiwa Technology, **GT-140281**, (2015)
- [6] de Bruin, Rittel, Scholten, van der Stok, Weller, *Impact of Sustainable Gases on Joints used in Gas Distribution Networks. Final Report*, Kiwa Technology, **GT-140283**, (2015)
- [7] Duyff, Hommes, *Samenstelling van nieuwe aardgassen en duurzame gassen*, (Dutch), KEMA Nederland, **GCS 11.R.51986**, (2011)
- [8] Hommes, Monsma, *Materiaalinventarisatie in het Gasunienetwerk*, (Dutch), KEMA Nederland, **GCS 11.R.52174**, (2011)
- [9] NV Nederlandse Gasunie, *Basisgegevens Aardgassen*, (Dutch), (1980), **39**, (Table A9)
- [10] Gas measurements over the last 10 years:
 - *Verificatie technische bepalingen 2004. Gasoverdracht LNB - RNB's*, (Dutch), Gastec, (2005)
 - *Verificatie technische bepalingen 2005. Gasoverdracht LNB - RNB's*, (Dutch), Kiwa Gastec Technology, (2006)
 - *Verificatie technische bepalingen 2006. Gasoverdracht LNB - RNB's*, (Dutch), Kiwa Gastec Technology, (2007)
 - *Verificatie technische bepalingen 2007. Gasoverdracht LNB - RNB's*, (Dutch), Kiwa Gastec Technology, (2008)
 - *Verificatie technische bepalingen 2008. Gasoverdracht LNB - RNB's*, (Dutch), Kiwa Gas Technology, (2009)
 - Brouwer, *Kwaliteitscontrole gastransport 2009. Verificatie naleving technische bepalingen met betrekking tot de gasoverdracht LNB-RNB's*, (Dutch), Kiwa Gas Technology, (10-03-2010)
 - van Heugten, *Kwaliteitscontrole gastransport 2010. Verificatie naleving technische bepalingen met betrekking tot de gasoverdracht LNB-RNB's*, (Dutch), Kiwa Gas Technology, (19-05-2011)
 - van Heugten, van Orizande, Bonestroo, *Kwaliteitscontrole gastransport 2011. Verificatie naleving technische bepalingen met betrekking tot de gasoverdracht LNB-RNB's*, (Dutch), Kiwa Gas Technology, (31-05-2012)
 - van Heugten, van Orizande, Bonestroo, *Kwaliteitscontrole gastransport 2012. Verificatie naleving technische bepalingen met betrekking tot de gasoverdracht LNB-RNB's*, (Dutch), Kiwa Gas Technology, **GT-130031**, (01-03-2013)
 - van Heugten, van Orizande, Bonestroo, *Kwaliteitscontrole gastransport 2013. Verificatie naleving technische bepalingen met betrekking tot de*



-
- gasoverdracht LNB-RNB's, (Dutch), Kiwa Gas Technology, **GT-140079**, (27-05-2014)
- van Heugten, Polman, *Kwaliteitscontrole gastransport 2014. Verificatie naleving technische bepalingen met betrekking tot de gasoverdracht LNB-RNB's*, (Dutch), Kiwa Gas Technology, **GT-150063**, (to be finalised)
- [11] Several methods for determining the influence of environmental stress cracking (ESC) have been standardised. The following list gives a brief overview:
- ISO 16241:2005, *Notch tensile test to measure the resistance to slow crack growth of polyethylene materials for pipe and fitting products (PENT)*
 - ISO 16770:2004, *Plastics -- Determination of environmental stress cracking (ESC) of polyethylene -- Full-notch creep test (FNCT)*
 - ISO 22088-2:2006, *Plastics -- Determination of resistance to environmental stress cracking (ESC) -- Part 2: Constant tensile load method*
- [12] Montgomery, *Design and Analysis of Experiments*, Seventh Edition, John Wiley & Sons, Inc. **ISBN 978-0-470-39882-1**, (2009)
- [13] Ophoff, *Methaanemissie door Gasdistributie. Rapportage over 2013 volgens het Monitoringsprotocol Methaanemissie Gasdistributie*, (Dutch), Kiwa Technology, **GT-140096**, (2014)
- [14] Mutter, Benjamin, *Spanningscorrosie in hard PVC en slagvast PVC (PVC/CPE) buizen in aardgasdistributienetten in Nederland*, (Dutch), GAS, **6**, (1974), 247-258.
- [15] Oranje L., Wolters M., *De invloed van gascomponenten op kunststoffen buismaterialen*, (Dutch), Gas, **5**, (1992), 244-250.
- [16] Wolters M., *Environmental Stress Cracking of PVC Pipe Materials*, Plastic Pipes **X**, Gothenburg, (1998).
- [17] Wales, *Crazing and Fracture project, Quarterly Progress Report No. 10*, TNO, **MRP IV 294'81**, August 1981)
- [18] Breen, *Onderzoek naar de spanningscorrosieve werking van aardgas op PVC-materialen van marginale kwaliteit*, (Dutch), TNO, **176'88**, (29-06-1988)
- [19] Scholten, Wolters, *Physical Ageing of uPVC Gas and Water Pipes*, **PVC 2011**, Brighton UK, British Plastics Federation, (2011).
- [20] Kippers, Ophoff, *Waterstof in aardgas op Ameland. De invloed van maximaal 20% waterstof in het aardgasdistributienet op materialen en gastoestellen; aangevuld met de ervaringen van bewoners*, (Dutch), Kiwa Technology, **GT-120092**, (2012)
- [21] Dolezel, Bretilav, *Die Beständigkeit von Kunststoffen und Gummi*, (1978), 1, (Table 1.0).
- [22] NEN-EN 1555:2010, *Plastics piping systems for the supply of gaseous fuels - Polyethylene (PE)*
- [23] ISO 527-4:1997, *Plastics -- Determination of tensile properties -- Part 4: Test conditions for isotropic and orthotropic fibre-reinforced plastic composites*
- [24] ISO 8496:2013, *Metallic materials -- Tube -- Ring tensile test*
- [25] SigmaStat version 3.5, Systat Software Inc., USA.
- [26] de Bruin, *Het effect van limoneen op PE en rubber*, (Dutch), Kenniscentrum Gasnetbeheer Nieuwsbrief **2012-2**, June 2012.
- [27] ISO 48:2010, *Rubber, vulcanized or thermoplastic -- Determination of hardness (hardness between 10 IRHD and 100 IRHD)*
- [28] ISO 37:2011, *Rubber, vulcanized or thermoplastic -- Determination of tensile stress-strain properties*
- [29] de Bruin, *Het effect van limoneen en cymeen op PE en rubber: Deel 2*, (Dutch), Kenniscentrum Gasnetbeheer Nieuwsbrief **2012-3**, September 2012.
- [30] NEN-EN 10208, *Steel pipes for pipelines for combustible fluids - Technical delivery conditions*, (01-04-2009).



-
- [31] NEN-EN 10220, *Seamless and welded steel tubes - Dimensions and masses per unit length*, (01-01-2003).
 - [32] NEN 3045, *Gietijzeren pijpen en hulpstukken voor drukleidingen*, (Dutch), (01-02-1957).
 - [33] NEN-EN 969, *Ductile iron pipes, fittings, accessories and their joints for gas pipelines - Requirements and test methods*, (01-04-2009).
 - [34] ASTM G1 - 03(2011), *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*.
 - [35] Weller, van der Stok, Hermkens, *Tensile Impact Experiments of PVC-U at a Wide Range of Temperatures*, Plastic Pipes **XVI**, (2012).