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Impact of Sustainable Gases on Joints used in Gas Distribution Networks

Final Report

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Colophon

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Preface

This report is part of the results of the EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems within the Current Distribution Band for Natural Gas in the Netherlands". The working title of this project is "Impact of sustainable gases on jointability". 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 Technology

Kiwa Technology is project leader.

This project is closely related to the research projects with the working titles "Effects of Narrow Band Gases on Materials" and "Effects of Wide Band Gases on Materials".

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 possible influence of sustainable gases on distribution gas pipe materials is covered in two other EDGaR projects. However, every pipeline contains joints and, because a pipeline system is only as strong as its weakest link, the possible influence of sustainable gases on joints in these pipelines must also be addressed.
This final report investigates the impact of sustainable gases on joints. This was carried out by evaluating the integrity of existing joints and by examining the ability to make new joints for maintenance, repair or to extend the existing gas distribution network in which sustainable gases are distributed.

This project answers the following two research questions:

A. *Are the most important joint types currently used in the Dutch gas distribution grids resistant to sustainable gases?*
B. *Are the existing, well-established maintenance, repair and extension methods for pipelines still feasible for pipelines containing (admixed) sustainable gases?*

The project made use of relevant scientific and technological literature and involved experiments of 600 days in duration. The results are summarised in Table 1 (existing joints) and Table 2 (joints made during maintenance, repair or extension of the Dutch gas distribution grid).

Table 1 shows that the answer to research question A) depends on whether water is present in the gas distribution grid or not. Without water, corrosion of metallic materials (steel, copper and aluminium) or the chemical attack on POM materials cannot occur. This means that only a few restrictions on the maximum allowable concentrations of gas components in sustainable gases are necessary.

Table 2 shows that the answer to research question B) is:
Yes, the existing, well-established maintenance, repair and extension methods for plastic and metal piping systems are still appropriate for pipelines containing (admixed) sustainable gases.

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

- Increasing the distribution pressure to 100 mbar(g). At 100 mbar(g) gas pressure the risk of ground water entering the gas grid (water ingress) is significantly lower than at 30 mbar(g) gas pressure.
- Decreasing the water dew temperature of the gas at gas entry points. In other words, the gas must be dried (the relative humidity must be lowered) before it enters the gas distribution grid. This solution deserves a prominent role in the processing of sustainable 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 sustainable 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 sustainable gases is limited to 800 ppm.

Table 1. The effect of components present in sustainable gases on existing joints in the Dutch gas distribution grid based on literature review and experiments.

Existing joints														
	Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
PVC coupler with sealing ring	🟩 none (up to 160 ppm)		░ probably none		🟩 none			░ probably none		▒ unknown	🟩 none	🟩 none, unless liquid		🟩 none	🟩 none (up to 20 mol%)
PE heat fused joints	🟩 none (up to 160 ppm)		░ probably none		🟩 none			░ probably none		▒ unknown	🟩 none	🟩 none, unless liquid		🟩 none	🟩 none (up to 20 mol%)
POM coupler with sealing ring	🟩 none (up to 160 ppm)		░ probably none		🟩 none			🟧 water	▒ unknown		🟩 none	░ probably none			🟩 none
steel welded joints & steel threaded joints	🟩 water, CO_2		░ probably none						🟧 with H_2S and water: possibly	▒ unknown	🟩 water, H_2S	░ probably none		🟧 water, (H_2S), CO_2	🟩 none
	🟧 water, CO_2 and O_2										🟧 water, (H_2S) and O_2				
Com-pression brass fittings	🟩 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_2S, and O_2			🟧 water, H_2S, CO_2	
threaded aluminium joints	🟩 water and CO_2		░ probably none		🟩 none	░ probably none			▒ unknown		🟩 none	░ probably none		🟩 none	🟩 none (up to 20 mol%)
	🟧 water and O_2													🟧 water, H_2S	

Table 2. The effect of components present in sustainable gases on joints made in plastic piping systems during maintenance, repair and extension based on literature review and experiments.

Joints made during maintenance, repair and extension																
Material	Siloxanes	Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chloride containing components	Fluoride containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
PVC piping systems	🟩 none	🟩 none (up to 160 ppm)		░ probably none		🟩 none			░ probably none		▒ unknown	🟩 none	🟩 none, unless liquid		🟩 none	🟩 none (up to 20 mol%)
PE piping systems	🟩 none	🟩 none (up to 160 ppm)		░ probably none		🟩 none			░ probably none		▒ unknown	🟩 none	🟩 none, unless liquid		🟩 none	🟩 none (up to 20 mol%)

░	=	The effect is unknown but is expected to be very small or non-existent.
🟩	=	This component in sustainable gases does not affect joints.
▒	=	The effect is unknown.
🟧	=	Deleterious effects are expected under some conditions.

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 H_2S). 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 the gas components may be possible. It is therefore recommended that HCN and CO should be prevented from entering the gas distribution grid or that their concentration should at least be kept as low as possible. It is recommended to limit the maximum concentration of H_2S to 160 ppm.

Finally, the literature was inconclusive about the effects of H_2 on some materials. The effects of H_2 were tested up to 20 mol%, while the concentration in sustainable gases could be as high as 62 mol%. Therefore, the effect of H_2 at higher concentrations remains unknown for PVC, PE, copper and aluminium. It is therefore recommended that the maximum concentration of H_2 be limited to 20 mol%.

The above-mentioned recommendations are summarised in Table 3 where water is not present in the existing Dutch gas distribution grid. Limiting values for other gas components in sustainable gases are not required.

Table 3. Recommended limiting values for several gas components in sustainable gases where water is not present in the gas distribution grid or in sustainable 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 joint materials. Although only traces of these substances are currently found in sustainable 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 joints 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_2S	The effect of H_2S 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 joints used in the Dutch gas distribution grid, it is recommended that the maximum concentration of H_2S 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 joints. 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 H_2S, CO_2 and O_2 may lead to severe corrosion in steel, copper and aluminium. The combination of HCl and high humidity also causes damage to POM materials.

For POM materials it is therefore important to keep the relative humidity of the gases low to prevent the condensation of water. Furthermore, it is recommended that the concentration of HCl be kept as low as possible. A limiting value of 0.1 ppm is recommended for HCl.

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

- H_2S should be limited to 34 ppm
- CO_2 should be limited to 10.3 mol%
- O_2 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 CO_2. More research using low CO_2 concentrations is therefore recommended.

Finally, the effects of NH_3 on brass fittings were tested at concentrations of up to 50 ppm in humid gas. The literature was inconclusive about the effects of 100 ppm NH_3 (which may occur in sustainable gases) on copper and brass fittings. The effects of NH_3 at concentrations of up to 100 ppm is therefore currently unknown for copper materials with brass fittings. More research using higher NH_3 concentrations is recommended.

When water is present in the gas grid or in sustainable gases additional recommendations to the ones given in Table 3 are needed and given in Table 4. Limiting values for other components in sustainable gases are not required.

Table 4. Additional recommended limiting values for several gas components in sustainable gases where water is present in the gas distribution grid or in sustainable gases.

Limiting value	**Reason**
< 34 ppm H_2S	The combination of H_2S, 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	
< 0.1 ppm HCl	Where low concentrations of HCl occur in combination with the condensation of water, the formation of acidic water cannot be ruled out. This acidic water has a destructive effect on POM materials. It is therefore recommended that the concentration of HCl in sustainable gases be limited as much as possible.
< 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_2S and O_2 come into contact with aluminium or copper in the absence of CO_2, severe corrosion may occur. It is unknown if CO_2 must also be present for the above proposed limiting values. More research using low CO_2 concentrations is therefore recommended.

Contents

List of Symbols and Abbreviations

General

DSO	distribution system operator

Gases

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

Organo-silicons

L1	trimethyl silanol
D4	octamethylcyclotetrasiloxane
D5	decamethylcyclopentasiloxane

Materials

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

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* Nowadays Pipelife

Test-related

ESC	environmental stress cracking
HAZ	heat-affected zone
MAC	maximum accepted concentration
T_{BD}	brittle-ductile transition temperature
σ	standard deviation
$\sigma_{100\%}$	stress at 100 % elongation (sometimes called “modulus”)
σ_y	upper yield stress
σ_{UTS}	ultimate tensile strength
$\varepsilon_{F\%}$	elongation at break
ε_{Fmm}	displacement at break
v_{corr}	corrosion rate
mm/y	millimetre per year, a unit of corrosion rate
MPa	megapascal, a unit of stress
bar(a)	bar absolute, a unit of absolute pressure, i.e. pressure in bars above absolute vacuum
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
wt%	mass percentage, a unit of composition
°C	degree Celsius, a unit of temperature

1 Introduction

1.1 Background

The possible influence of sustainable gases on gas distribution pipe materials is covered in two other EDGaR projects ("Effects of Narrow Band Gases on Materials" [4] and "Effects of Wide Band Gases on Materials" [5]). These two projects only consider pipes and pipe segments.
However, every pipeline also contains many joints. Because a pipeline system is only as strong as its weakest link, the possible influence of sustainable gases on joints in pipelines must also be addressed.

In the present context, it is crucial to understand that the term "joints" refers not only to pre-existing joints in pipelines but also to normal maintenance, repair and extension works on existing networks, since such activities almost inevitably involve making joints. Therefore, it is necessary to assess whether long-term contact with sustainable gases may influence or hamper the applicability of well-established, everyday asset management operations on pipelines.
It is necessary to ascertain whether, in the case of the long-term use of (admixed) sustainable gases, the existing maintenance, repair and extension methods are still adequate or whether they need to be altered in special cases or in special regions.

1.2 Goal

This project provides answers to the following two research questions:

A. *Are the most important joint types currently used in the Dutch gas distribution grids resistant to sustainable gases*?*
B. *Are the existing, well-established maintenance, repair and extension methods for pipelines still feasible for pipelines containing (admixed) sustainable gases?*

Within the above two categories, the following sub-questions are relevant:
A. Existing joints.
    a) What are the most important joint types currently used?
    b) What are the critical (long-term) failure mechanisms for these most important joints where sustainable gases are present?
    c) What are the maximum allowable concentrations of various gas components in sustainable gases when using the existing Dutch gas distribution infrastructure for the transport of these gases?
B. Maintenance, repair and extension methods.
    d) What are the most important maintenance, repair and extension methods currently used?
    e) Which of these methods could be influenced or hampered most when applied to grids that have been or will be exposed to sustainable gases?
    f) What are the maximum allowable concentrations of gas components in sustainable gases when using the above-mentioned maintenance, repair and extension methods?

The main goals of this project are therefore:

- To determine which gas components and which concentrations of certain components in sustainable gases may be harmful to the joints used in the existing Dutch gas distribution infrastructure.
- To assess which of the well-established repair, maintenance and network extension methods used at present are also feasible for grids containing sustainable gases.

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* Sustainable gases are wide band gases as defined in the EDGaR project "Effects of Wide Band Gases on Materials" [5], including LNG, SNG, raw gases and partially upgraded gases.

- To provide detailed technical information on the maximum allowable concentrations of certain components in sustainable gases when using the above-mentioned repair, maintenance and extension methods.

Although the life expectancy of assets is limited by more than technical aging [6] alone, the present literature review will focus on this aspect only. It is primarily concerned with the effects of the transport of sustainable gases on existing and "future maintenance" joints.

It is important to note that the experiments performed were not intended to be exhaustive with respect to the components present in sustainable gases or the jointing 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 joints are discussed.
The experimental work in this report focussed on gases that may lead to negative effects on the materials used in the gas distribution network. Gases that (are expected to) have no negative effect were generally not used.
Questions regarding joints in transmission pipelines are addressed in a separate project entitled: *From mono-gas to multi-gas: "Effect of narrow and wide band gases on the integrity and safety of the Dutch gas grid.* [7]

1.3 Approach

The first phase of the project involved the study of relevant literature. This literature was evaluated with regard to sub-questions a) to f) in section 1.2. For some gas component/material combinations it was not possible to draw solid conclusions as to whether deleterious effects could be expected under certain conditions. In these cases it was decided 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 sustainable gases on existing joints and the making and maintenance of joints in 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 (joints in plastic piping systems) and chapter 4 (joints in metal piping systems) discuss the effects of sustainable gases on existing joints. Chapter 5 (joints in plastic piping systems) and chapter 6 (joints in metal piping systems) consider the effects of making joints using normal maintenance, repair and extension methods on piping systems that have been exposed to sustainable gases.
In each section, the importance of a specific joint in the Dutch gas distribution network (more information can be found in [1]) is highlighted. 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 joint 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 joint to sustainable gases.
This report ends with overall conclusions in chapter 7 and recommendations for the distribution system operators (DSOs) in chapter 8.

2 Literature Review & Experimental Setup

This chapter explains the approach of the EDGaR research project "Impact of Sustainable Gases on Joints used in Gas Distribution Systems", which was performed to evaluate the influence of sustainable gases on joints used in the Dutch gas distribution networks. 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 and joints 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.

In plastic piping systems, the most important pipe materials are PE and PVC. The main jointing techniques in these systems are:

- PVC couplers with rubber sealing (mechanical fitting, not end-load resistant)
- Fused PE joints (electro-fusion and butt fusion)
- POM couplers with rubber sealing (mechanical fitting, full end-load resistant)

In metal piping systems, the principle materials are steel and copper. Aluminium is widely used in gas pressure regulators and gas meters. Most aluminium components feature threaded joints for connection to the gas distribution system. The main joint types employed in metal piping systems are:

- Welded steel joints (made by gas metal arc welding (GMAW) or shielded metal arc welding (SMAW))
- Threaded steel joints
- Brass mechanical fittings used in copper piping systems
- Threaded aluminium joints

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, narrow band gases and wide band gases. G-gas, or so-called Groningen gas, is natural gas from the large gas field near Slochteren in the Netherlands. This gas has a relatively high nitrogen content in comparison to other gas fields. Narrow band gases are defined as upgraded or downgraded gases that have the same physical properties (e.g. Wobbe index, Calorific value) as G-gas. The concentration limits for the composition of narrow band gases are based on the additional terms and conditions applicable to Dutch biomethane producers [9]. Differences in chemical composition between G-gas and narrow band gases are mainly found in the levels of CO_2 and H_2S. Differences also exist in the concentrations of trace components such as those containing halogens.

Wide band gases are defined as all sustainable gases (those containing gas from anaerobic digestion, SNG and imported natural gases). This means that the physical properties and the chemical composition of wide band gases may be very 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.

Table 5. The average concentrations of various chemical components in G-Gas, the limiting values of these components for narrow band gases and the maximum concentrations of these components found for wide band gases.

Chemical compound/mix	**G-gas average [8]**	**Narrow band gases limiting value [4]**	**Wide band gases max. found concentration [5]**	**Unit**
Sulphur (total)	6.7	45	-	mg/m^3 (n)
Inorganically bound sulphur (H_2S)	0.4	5	4 300 mg/m^3 (n)	ppm
Mercaptane	< 1.0	10	-	mg/m^3 (n)
Odorant value (*THT*)	17.7	> 10; nom 18; < 40	-	mg/m^3 (n)
Chlorine-containing compounds	< 0.1	50	735	mg/m^3 (n)
Fluorine-containing compounds	< 0.1	25	256	mg/m^3 (n)
Ammonia (NH_3)	< 0.1	4	100	ppm
Hydrogen chloride (HCl)	< 1.0	1	Traces (ppb)	ppm
Hydrogen cyanide (HCN)	< 1.0	10	Traces (ppb)	ppm
Carbon monoxide (CO)	< 100	10 000	700 000	ppm
Carbon dioxide (CO_2) in dry gas	8 900	103 000	59.0 mol%	ppm
Aromatic hydrocarbons	800 (max. value [9])	10 000	Traces (ppm)	ppm
Benzene	-	500	11.4	ppm
Toluene	-	-	76.2	ppm
Oxygen (O_2) in dry gas	< 100	5 000	26 000	ppm
Hydrogen (H_2)	< 0.01	12	62	mol%
Methane (CH_4)	81.29	-	99.8	mol%
Nitrogen (N_2)	14.32	-	50.9	mol%
Ethane (C_2H_6)	2.87	-	2	mol%
Organo-silicons	< 0.1	5	20	mg/m^3 (n)

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 sustainable gases in order to determine whether deteriorating influences could be expected at these concentration levels on the materials present in the gas distribution network. The survey focused primarily on the effect of these gases on existing joints and joints made during the maintenance, repair or extension of plastic or metal piping systems.

For existing joints in plastic piping systems, the effect on environmental stress cracking (ESC) in PVC, PE, POM and rubber (SBR/NBR) was the primary focus. ESC in polymeric materials is considered to be the most important failure mechanism when these materials are exposed to sustainable gases. For joints that are made during maintenance, repair or extension of plastic piping systems attention was primarily given to the absorption of these sustainable gases in PVC and PE. Absorption may lead to swelling, which could in turn give rise to problems if push fittings can no longer be connected to the PVC or PE pipes. Negative effects on the fusibility of PE pipes as a result of the absorption of certain gaseous components could also lead to problems.

For existing joints in metallic materials (steel, copper and aluminium), the focus was primarily on the effect on corrosion rate. The same applied to welded joints (for maintenance, repair or extension) in steel piping systems. Corrosion in metallic materials is considered to be the most important failure mechanism when these materials are exposed to sustainable gases. The occurrence of stress corrosion is an important factor for brass fittings in copper piping systems.

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

Table 6. The effect of sustainable gases on the most important gas distribution joints based on literature review.

Existing joints

Joint	Material	Sulphur-containing components	H_2S	Mercaptans	Odorant	Ammonia	Chloride-containing components	Fluoride-containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
Coupler body material	PVC	unknown		probably none		unknown			probably none		unknown	possibly	none, unless liquid (impact resistance)		probably none	unknown
	POM	unknown		probably none		possibly				unknown			probably none		unknown	
Coupler sealing ring	NBR	unknown	possibly	probably none		none	possibly		probably none		none		probably none, unless liquid		none	
	SBR	unknown	possibly	probably none		none	possibly		probably none		none		possibly		probably none	none
Electro-fusion and butt fusion	PE	unknown		probably none		unknown			probably none		unknown	none	none, unless liquid		none	probably none
Welded	Steel	with water: possibly		probably none			Unknown				with water: possibly		probably none		with water: possibly	none
Press and compression	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

Maintenance, repair and extension methods

Joint	Material	Sulphur-containing components	H_2S	Mercaptans	Odorant	Ammonia	Chloride-containing components	Fluoride-containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
Coupler and pipe	PVC	unknown		probably none		unknown	possibly		probably none		unknown	possibly	none, unless liquid		unknown	
Electro-fusion and butt fusion	PE	unknown		probably none		unknown			probably none		possibly		none, unless liquid		none	unknown
Welded	Steel	with water: possibly		probably none			unknown				with water: possibly		probably none		with water: possibly	probably none
Compression	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

▧	=	The effect is unknown but is expected to be very small or non-existent.
🟩	=	This component in sustainable gases does not affect joints.
▨	=	The effect is unknown.
🟧	=	Deleterious effects are expected under some conditions.

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

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

2.2 Experimental Setup

The literature survey demonstrated that the knowledge available at present is sometimes inconclusive. For existing joints in plastic piping systems in particular, little was known about the influence of gases containing sulphur, fluorine or chlorine components, CO_2, ammonia or H_2. The effect of the combination of H_2S, O_2 and CO_2 at different concentration levels on joints in metal piping systems in an aqueous environment was also unknown. Lab experiments focused 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 sustainable 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 sustainable 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. For joints in plastic piping systems, the fusibility of PE after possible absorption of certain gaseous components in PE pipe required particular attention. To this aim special tests have been carried out.

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 sustainable 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 same applied to welded joints in steel piping systems. Stress corrosion is also important for brass fittings in copper piping systems. This was further investigated by special tests.

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 gas concentration leads to a higher partial pressure and thus a higher absolute. This could increase the effect of the chemical component on the material.

2.2.1 Testing the Effect of Sustainable Gases on Existing Joints in Polymeric Piping Systems and Joints made during Maintenance, Repair and Extension

The effect of sustainable gases on existing polymeric joints was tested by means of environmental stress cracking (ESC) experiments. Many different ESC methods have been described in literature and have been standardised [10]. 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 rubber (SBR/NBR) rings over oversized pipes under constant strain (Figure 4). 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).

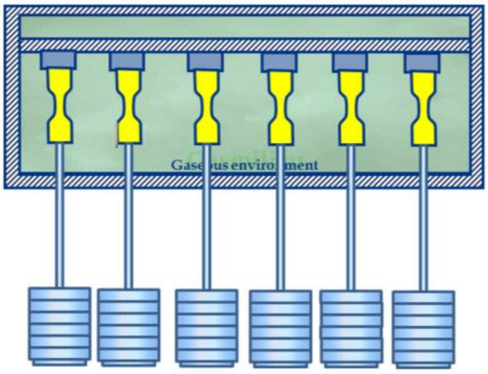

Figure 1. Schematic view of the constant load equipment for testing PE and PVC samples.

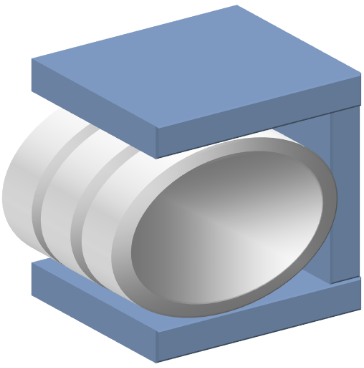

Figure 2. Principle of a U-clamp test on PE and POM rings.

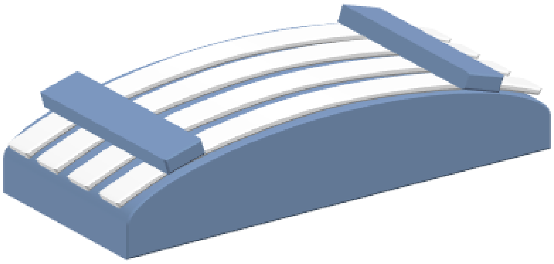

Figure 3. Principle of a Marbon clamp test on POM tensile test bars.

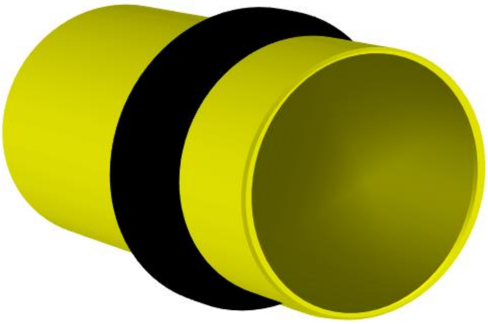

Figure 4. Setup used to expose stressed rubber rings to a particular gaseous environment using an oversized pipe.

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 PVC, PE, POM and rubber materials, newly fabricated materials were used. These materials were fabricated in 2012. Both NBR and SBR were taken from the sealing rings of new PVC couplers (suitable for gas and water respectively). For the field test, additional NBR rings were taken from POM couplers. The POM homopolymer samples (hPOM) were milled from POM couplers, while the POM copolymer samples (cPOM) were cut from POM plates.

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 sustainable gases. An explanation of the concentration levels is given on the next pages and also shown in Table 8.

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	HDPE 50	Old and used	PE 2012-058	1973	Constant load	4 MPa
					U-clamp	1.9%
	MDPE 80	Old and not used	PE 3	1990	Constant load	8 MPa
					U-clamp	1.9%
	HDPE 100	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
POM	hPOM	New, from couplers	POM 2012-024 (lab) POM 2012-003 (field)	2012	U-clamp	3.1 %
					Marbon clamp	3.1 %
	cPOM	New, from plates	POM 2012-004	2012	Marbon clamp	3.1 %
Rubber	NBR	New, from PVC gas couplers	OV 2012-071	2012	Ring over pipe	Undefined
	NBR	New, from POM couplers	none	2012	Ring over pipe	Undefined
	SBR	New, from PVC water couplers	OV 2012-072 & OV 2012-073	2012	Ring over pipe	Undefined

Of all the chlorine-containing and fluorine-containing components that may occur in the gases under consideration, it is known that dichloromethane (DCM) is one of the most aggressive halogenated organics as regards its effect on PVC. It was therefore decided to use DCM as a model gas for all halogen-containing materials. The highest concentration of chlorine-containing components found is 50 mg/m^3 in narrow band gases and 735 mg/m^3 in wide band gases. For fluorine-containing components, this figure is 25 mg/m^3 and 256 mg/m^3 respectively. It was therefore decided to use dichloromethane (DCM) as a model gas for halogen-containing gas at concentrations of 75 mg/m^3 and 1000 mg/m^3 for respectively narrow and wide band gases.

Sulphur-containing components may also be present in a wide variety of gases. H_2S 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 H_2S 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 H_2S is 3 085 ppm. However, this level of H_2S 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 H_2S over an exposure period of eight hours to be acceptable. The MAC value of H_2S is 1.6 ppm. It was therefore decided to use H_2S at a concentration of 160 ppm as a model gas for sustainable gases.

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

After the period of exposure the environmental stress cracking samples were subjected to non-destructive (visual changes) and destructive testing. This will be discussed in the separate sections covering the individual materials.

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, Rubber, POM	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.
Rubber	5 ppm H_2S	0.03	The maximum allowable concentration of H_2S in narrow band gases is 5 ppm.
Rubber	80 ppm H_2S	0.03	This concentration is between that of the wide and narrow band gases.
PE, PVC, Rubber POM	160 ppm H_2S	0.03	The concentration of 160 ppm H_2S for wide band gases was chosen by the Dutch DSOs as acceptable (= 100 times the MAC value for eight hours).
		8.0	
PE, PVC, Rubber POM	75 mg/m^3 DCM	0.03	The maximum allowable concentration of halogen-containing chemicals in narrow band gases is 75 mg/m^3.
Rubber	550 mg/m^3 DCM	0.03	This concentration is between that of wide and narrow band gases.
PE, PVC, Rubber, POM	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, Rubber, POM	100 ppm NH_3	0.03	The maximum concentration of NH3 found in wide band gases is 100 ppm.
		8.0	
PE, PVC, Rubber, POM	59 mol% CO_2	0.03	The maximum concentration of CO2 found in wide band gases is 59 mol%.
PE	A mixture of organo-silicons	0	A mixture of L1, D4 and D5 was used. These organo-silicons are most common in sustainable gases.
SBR	Natural gas	0.03	G-gas was used for reference purposes with SBR for joints [ref].
Rubber	2 mol% propene	0.03	The maximum concentration of propene found in wide band gases is 2 mol%.
POM	62 mol% H_2	8.0	The maximum concentration of H_2 found in wide band gases is 62 mol%.
POM	3 ppm HCl	8.0	The maximum allowable concentration of HCl in narrow band gases is 1 ppm. Nevertheless, a stable concentration of 1 ppm in a gas cylinder is not achievable. This meant that 3 ppm was chosen.

* *A type 2 test was used in order to determine the effect of H_2S and DCM on NBR.*

Some samples were only used to test the influence of sustainable gases on joints during maintenance, repair and extension. These samples were not exposed to stress and were used to determine mass or dimensional changes of the polymeric materials. In the case of PE piping systems, the ability to weld joints while saturated with certain gas components was tested.

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

2.2.2 *Testing the Effect of Sustainable Gases on Existing Joints in Metal Piping Systems and Joints during Maintenance, Repair and Extension*

Testing the effect of sustainable gases on existing joints on metal piping systems 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 joints used in the experiments were produced using strips taken from plates that had the same metallic structure as pipes and that had been welded using gas metal arc welding (GMAW).

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 5 shows an illustration of the experimental setup.

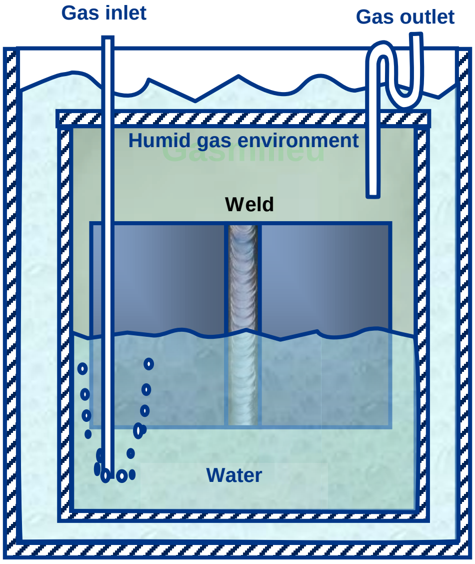

Figure 5. Experimental setup (autoclave) for corrosion testing of metals.

Table 9 gives an overview of the metallic materials tested, the used gaseous environments and the test pressures. The concentration levels were based on the "white spots" and the limits derived from the literature survey [1]. The matrix gas was N_2 in all cases.

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 effects of O_2) that may increase or decrease the corrosion rate were unknown. The gas conditions and quantities were determined using the methodology of Design of Experiments (DoE) [11]. Table 9 also includes an explanation of the specified concentration levels.

During the period of exposure the corrosion rate was followed by measuring the material thickness and mass at set intervals. The effect of each gaseous concentration on the corrosion rate was calculated and trend lines were constructed to determine 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.

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

Joint	**Gas Number**	**Gas conditions**				**Pressure (bar(g))**	**Explanation of the concentration levels (see also Table 5)**
		Relative Humidity (%)	**CO_2 (mol%)**	**O_2 (mol%)**	**H_2S (ppm)**		
welded steel joints, threaded steel joints, brass mechanical fittings & threaded aluminium joints	1	100	50	0.01	160	0.03	Worst case wide band gases with low O_2 level, low pressure
		100	50	0.01	160	8.0	Worst case wide band gases with low O_2 level, high pressure
		50	50	0.01	160	0.03	Worst case wide band gases 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_2S worst case wide band gases 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 gases without H_2S
	6	100	0	0.5	34	0.03	O_2 and H_2S inside narrow band gas limits
	7	100	10	0.5	34	0.03	CO_2, O_2 and H_2S inside narrow band gas limits
	8	100	10	0.1	34	0.03	Effects of low O_2 levels were unknown, therefore this concentration was chosen
	9	100	10	0.01	34	0.03	Effects of low O_2 levels were unknown, therefore this extremely low concentration was chosen
brass mechanical fittings	10	50 ppm NH_3, using different torques				0.03	100 ppm is the maximum concentration found in wide band gases. However, due to the mixing process 50 ppm in humid gas was eventually used.

Additionally, brass fittings in copper pipes were exposed to gas number 10. The brass joints were made in accordance with the installation instructions. Since the stress level is also important for ammonia, exposure to this gas took place with brass joints tightened to various torques (as prescribed, hand tightened (too loose) and 1.5 and 2 times the prescribed torque (too tight)). The experiments were performed at room temperature.

More detailed information about the experimental setup for testing the influence of sustainable gases on joints in 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 sustainable 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 6 shows some PE and PVC dumbbell samples clamped in their holders before the constant load experiments were started. Figure 7 shows PE ring samples in U-clamps.

Figure 8 and Figure 9 show details of the test rig for the polymeric samples under constant load (PE and PVC) and constant strain (NBR). Figure 10 and Figure 11 show the complete 30 mbar(g) and 8 bar(g) test rigs.

Figure 6. PE and PVC dumbbell samples clamped for ESC experiments.

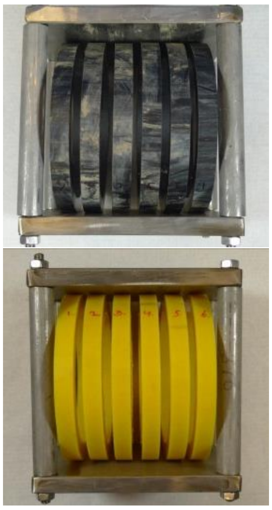

Figure 7. PE ring samples in U-clamps.

Figure 8. Constant load experiments on PVC dumbbell samples.

Figure 9. Constant load experiments on PE dumbbell samples and constant strain experiments on NBR samples that have been placed over oversized pipes.

Figure 10. Full-scale test rig for 30 mbar(g). Inside the test rigs, the materials are exposed to various gases.

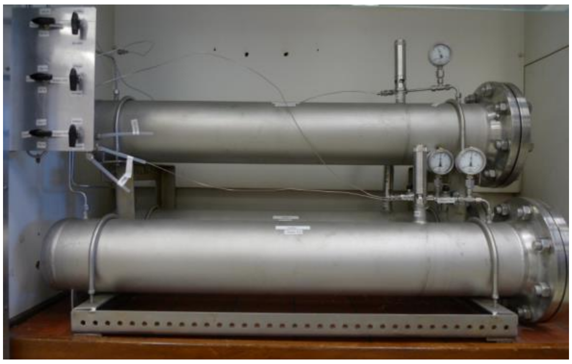

Figure 11. Full-scale test rig for 8 bar(g). Inside the test rigs, the materials are exposed to various gases.

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

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

Polymeric materials	**Gaseous environments**	**Pressure bar(g)**	**Exposure time**		
			Start date	**End date**	**Total (days)**
PE, PVC, POM, rubber	100 mol% N_2	0.03	18-1-2013	22-9-2014	612
rubber	5 ppm H_2S	0.03	7-2-2013	9-10-2014	609
rubber	80 ppm H_2S	0.03	7-2-2013	9-10-2014	609
PE, PVC, POM, rubber	160 ppm H_2S	0.03	30-1-2013	29-9-2014	607
		8.0	8-2-2013	16-10-2014	615
rubber	75 mg/m^3 DCM	0.03	22-1-2013	8-9-2014	594
rubber	550 mg/m3 DCM	0.03	7-2-2013	9-10-2015	609
PE, PVC, POM, rubber	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, POM, rubber	100 ppm NH_3	0.03	29-1-2013	13-10-2014	622
		8.0	8-2-2013	25-9-2014	594
PE, PVC, POM, rubber	59 mol% CO_2	0.03	23-1-2013	20-10-2014	635
rubber	G-gas	0.03	7-2-2013	9-10-2014	609
rubber	2 mol% propene	0.03	7-2-2013	9-10-2014	609
POM	62 mol% H_2	8.0	7-2-2013	8-10-2014	608
POM	3 ppm HCl	8.0	7-2-2013	10-10-2014	610
PE	A mixture of organo-silicons	0.0	Each working day, PE pipes were sprinkled with a mixture of organo-silicons (L1, D and D5) for a total of 90 days		

In order to determine the effect of sustainable gases on the heat fusion of PE pipes, additional experiments were performed. PE pipe samples were exposed (both inside and outside) to 59 mol% CO_2 at 30 mbar(g) or were sprinkled with a mixture of organo-silicons. After exposure, the PE pipes were directly fused by means of butt fusion and electro-fusion. The joints were made in accordance with NEN 7200 [12] (butt fusion) and the manufacturer's instructions (electro-fusion). In the case of electro-fusion, PE100 couplers manufactured by Georg Fischer were used.

The quality of the butt fusion joints was tested visually in accordance with NEN 7200, (semi) non-destructively tested with the bead bend back test (BBBT) and destructively tested with the tensile test in accordance with ISO 13953 [13]. The quality of the electro-fusion joints was tested visually in accordance with VM 102 [14], non-destructively tested with an ultrasonic phased array [15] and destructively tested with the peel test in accordance with ISO 13954 (≥ 90mm) [16] or with the crush test in accordance with ISO 13955 (< 90 mm) [17] (see Table 11).

Table 11. Experiments performed after heat fusion of PE pipes exposed to components from sustainable gases.

Heat fusion technique	**Visual examination**	**(semi) non-destructive technique**	**Destructive technique**
Butt fusion	NEN 7200	bead bend back test	ISO 13953
Electro-fusion	VM 102	Ultrasonic – Phased Array	ISO 13955 (< 90 mm) ISO 13954 (≥ 90 mm)

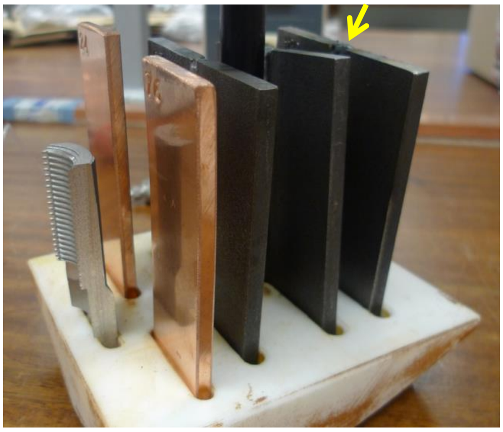

Figure 12. Metallic samples in a special PTFE holder for the corrosion test. The steel joint is located at the yellow arrow.

Figure 13. Complete setup for the corrosion tests.

Figure 14. Impression of the experimental setup (right photo: EDGaR/Jan Buwalda).

Figure 12 shows the metallic materials in a special PTFE holder used to place them in the test rig (the steel joints are indicated with a yellow arrow), while Figure 13 shows the entire test rig for the corrosion experiments. Figure 14 shows an impression of the experimental setup used during the exposure period of 600 days.

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 ºC. 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 O_2 concentration at the outlet was ~30 ppm. It is unknown whether the oxygen was introduced at the gas sampling point or elsewhere in the setup.

2.4 Implementation of Field Experiments

In addition to the laboratory tests, field experiments were also performed. The purpose of these tests was to determine whether narrow band gases have any adverse effects that had not previously been foreseen from tests at variuous gaseous environments in the laboratory. For the field experiments, two rigs were inserted into the Dutch distribution grid; one was installed directly after a biomethane feed (meaning narrow band quality, see Figure 15), whereas the other was installed in a pipeline carrying G-gas quality only (Figure 16). The G-gas test rig was installed for reference purposes.

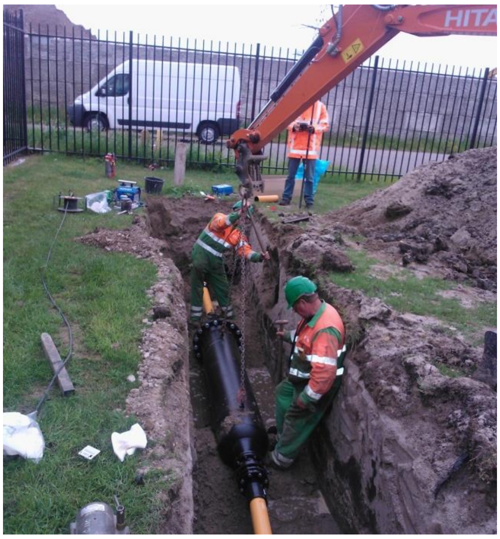
Figure 15. Test rig under biomethane conditions (narrow band gases).


Figure 16. Test rig under G-gas conditions.

The test rigs were filled with the same material types as used in the laboratory experiments. However, the grades of these material types were different from that used in the laboratory experiments. This means that comparison between laboratory and field experiments was not straightforward. Figure 17 gives an overview of the different materials used in the test rigs for exposure to G-gas and narrow band gas for a period of two years. In the test rigs several materials were under tension.

Where applicable, the materials were exposed to G-gas and narrow band gases under the same applied stresses as mentioned in the lab conditions. Table 12 gives an overview of the sample design at the applied stress or strain, where applicable.

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

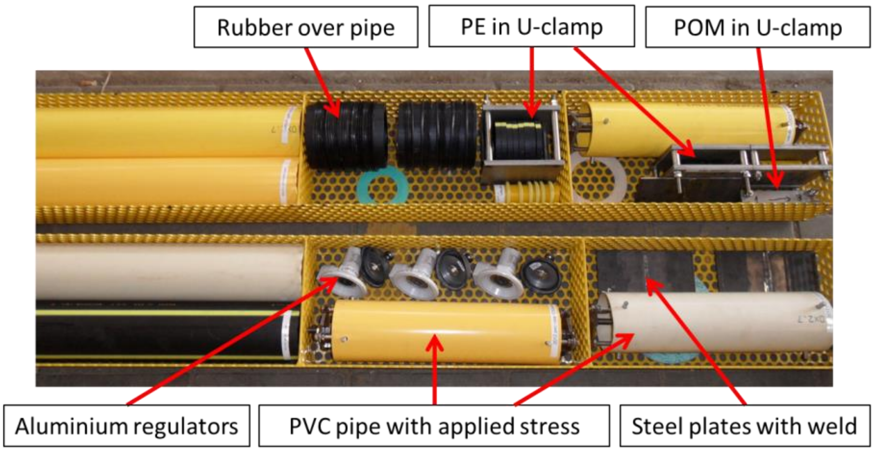

Figure 17. An overview of the materials placed in the test rigs for field exposure to G-gas and narrow band gas for a period of two years.

Table 12. Overview of materials and their applied stress/strain in the test rigs for field exposure.

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

2.5 Results

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

PART I EXISTING JOINTS

3 Effects on Existing Joints in Plastic Piping Systems

In plastic piping systems, the most important pipe materials are PE and PVC. The main jointing techniques in these systems are:

- PVC couplers with rubber sealing (see 3.1);
- Fused PE joints (see 3.2);
- POM couplers with rubber sealing (see 3.3).

These joints are discussed further in this chapter.

3.1 PVC Couplers with Elastomeric Sealing Rings

PVC couplers with elastomeric sealing rings consist of a casing with sealing rings. The casings of existing joints are made of PVC-U or PVC-HI. The sealing rings are made of NBR or SBR materials.

3.1.1 PVC Body

It is assumed that the effects of sustainable gases on PVC casing materials will be the same as the effects on PVC pipe materials. Therefore no further experiments on PVC casing materials have been performed. The effects of sustainable gases on PVC pipe materials (PVC-HI and PVC-U) are described in [5].

3.1.2 Elastomeric Sealing Rings

3.1.2.1 The Importance of Elastomeric Sealing Rings in PVC Couplers

There are two main rubber types in use for the elastomeric sealing rings in the existing pipeline infrastructure: NBR and SBR. After around 1978 (4 years after the transition from PVC-U to PVC-HI), SBR compounds were replaced by NBR. This is because SBR sealing rings have a lower resistance to methane and other hydrocarbons than NBR [18].

3.1.2.2 Test Method

The experimental setup as described in chapter 2 was used to expose NBR and SBR to various components in sustainable gases over a period of 600 days.

The following six tests were performed on NBR and SBR materials directly after exposure:

- Mass change.
- Hardness (IRHD). The hardness was measured in accordance with ISO 48 [19].
- Tensile tests. The stress at 100% elongation, elongation at break and tensile strength were measured in accordance with ISO 37 using type 2 samples [20].
    - Stress at 100% elongation (sometimes called “modulus”) ($\sigma_{100\%}$)
    - Elongation at break ($\varepsilon_{F\%)}$
    - Ultimate Tensile Strength (σ_{UTS})
- Dimensional change, measured before exposure, directly after exposure and one hour after exposure.
    - Inner diameter
    - Outer diameter
    - Thickness

In each test, two rings from each condition were tested. The exception was the mass change test, 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 [19,20].
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 [21].

3.1.2.3 The Influence of Sustainable Gases on Elastomeric Sealing Rings

Effects of Hydrocarbons

The literature [1] had already indicated that, due to the low concentrations of aromatic hydrocarbons found in sustainable gases, no effect on the elastomeric seals was expected from these components . However, the presence of any liquid aromatic hydrocarbons will negatively affect the mechanical properties, including the sealing force, of both SBR and NBR.

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

Furthermore, for both rubbers, there was no statistically significant difference between samples exposed to G-gas and the reference samples exposed to nitrogen as regards hardness, stress at 100% elongation, strain at fracture or tensile strength (see Figure 18 for a visual comparison of the average values for SBR).

However, the average ultimate tensile strength of SBR seemed to have been reduced considerably (see Figure 18). The experimental scatter in the results for nitrogen means that this is not statistically significant.

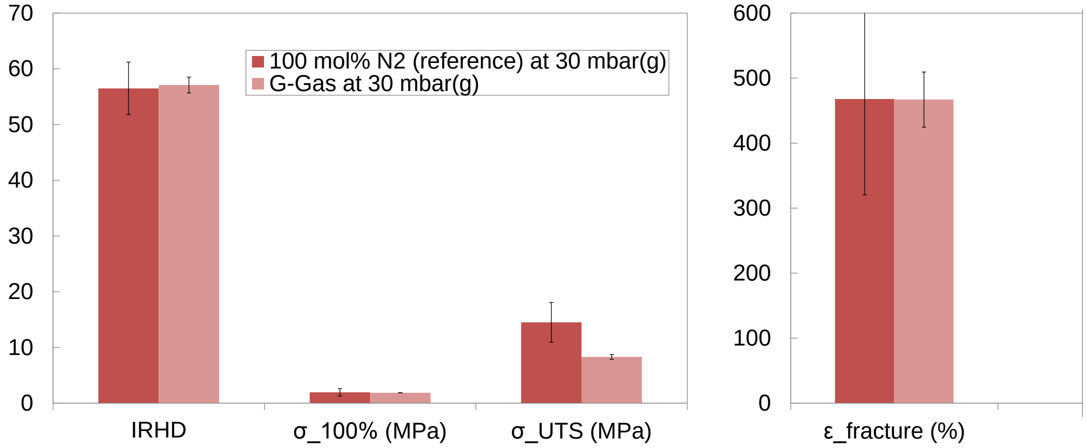

Figure 18. Comparison of the average values of hardness (IRHD), stress at 100 % elongation ($\sigma_{100\%}$) and tensile strength (σ_{UTS}) (left) and strain at fracture ($\varepsilon_{F\%}$) (right) for four SBR rings exposed to N_2 (reference) and two SBR rings exposed to G-gas (natural gas). The data for NBR can be found in [5] and appendix II.3

No profound change in dimensions was observed for NBR either. All NBR 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 within the same range for all rings.

The SBR rings showed a similar return to almost their original dimensions when removed from the oversized pipe. However, in contrast to NBR, the outer diameter remained relatively deformed and did not decrease as much as did the NBR samples after one hour (see Figure 19). On the other hand, the inner diameter was deformed by 24 % when placed over the oversized pipe. This means that the ring still came close to returning to its original dimensions.

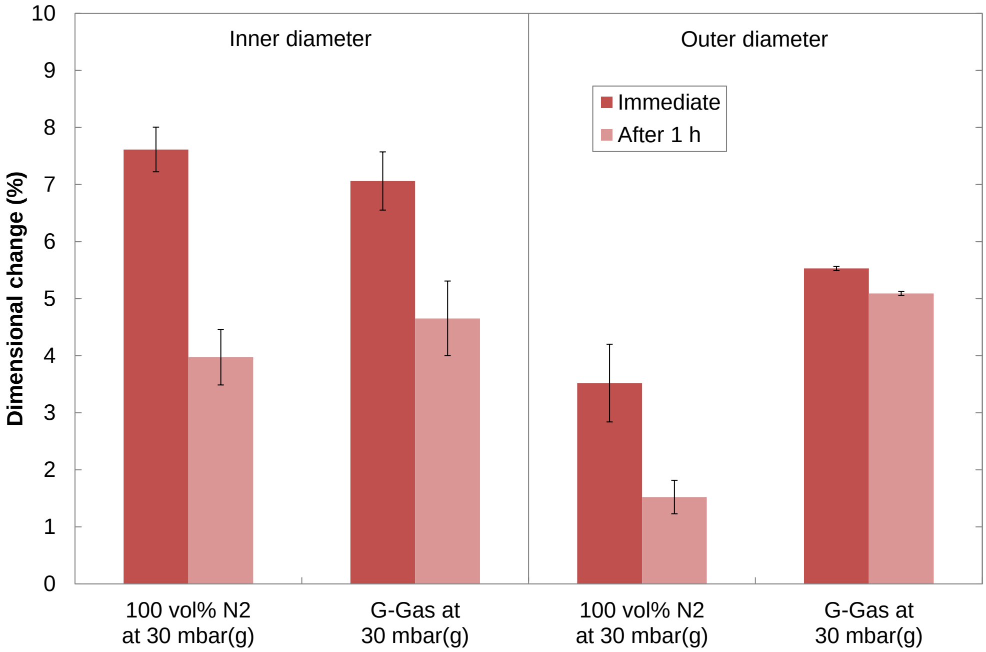

Figure 19. The difference in inner diameter (left) and outer diameter (right) of SBR rings after 600 days of exposure to N_2 (reference) and G-gas (natural gas). The dimensions were measured immediately after removing the rings from the oversized pipe (125 mm) and after 1 hour and were subsequently compared to the original dimensions before exposure.

Because no large decrease in mechanical quality after exposure was proven for SBR rings, the results confirm that SBR is suitable for use in G-gas. When SBR comes into contact with liquid hydrocarbons, a large difference with respect to NBR can be observed [18].

Since G-gas currently has the highest concentration of hydrocarbons, the change to sustainable gases will have no influence on the performance of SBR sealing rings with respect to hydrocarbons. However, it is recommended that the concentration of aromatic hydrocarbons be limited to 800 ppm (the maximum found concentration of aromatic hydrocarbons in G-gas of the last ten years) in order to prevent future extremes.

Because no noteworthy difference in dimensional change between N_2 and G-gas was found for NBR, no effect on the functioning of NBR sealing rings is expected.

The literature also revealed that NBR can experience negative effects once in contact with unsaturated chemical compounds (e.g. propene, C_3H_6, and butadiene, C_4H_8) [1]. Experiments with 2 mol% propene (at 8 bar(g)) resulted in no mass change for either NBR or SBR after 600 days. Furthermore, there was no statistically significant difference (according to the t-test) between the NBR and SBR samples in propene and the reference samples exposed to N_2 as regards hardness, stress at 100% elongation, strain at fracture or tensile strength. The same results were found when compared to the reference samples exposed to G-gas.

Figure 20 shows these results graphically for the ultimate tensile strength. For SBR (red) there was once again a reduction in average ultimate tensile strength when nitrogen was compared to G-gas and propene. For SBR the average ultimate tensile strength for G-gas and propene is almost identical.

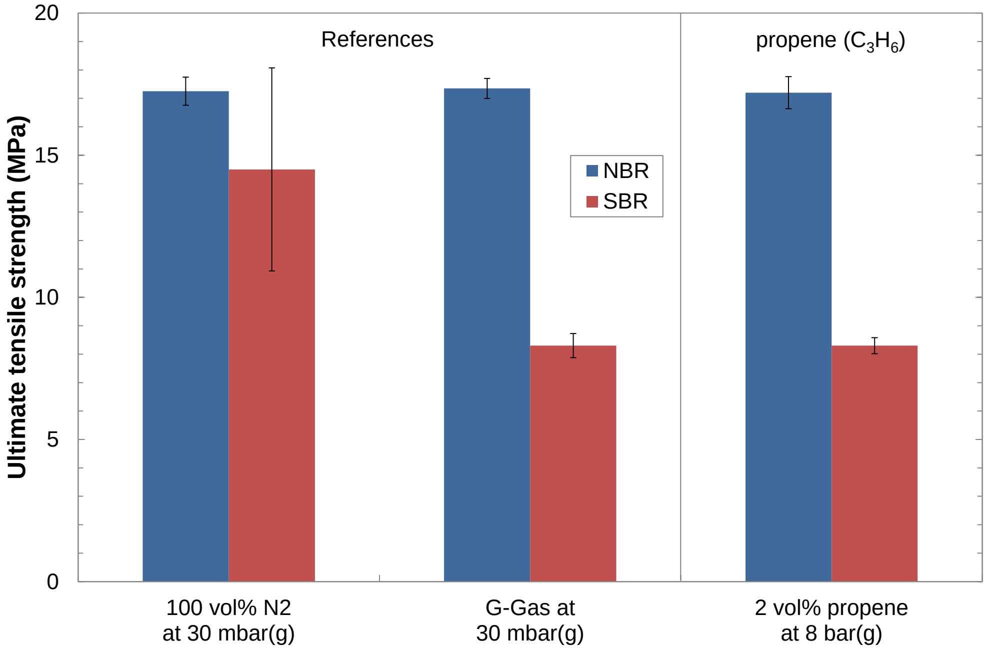

Figure 20. Ultimate tensile strength (σ_{UTS}) of NBR (blue) and SBR (red) exposed for a period of 600 days to the reference gases (nitrogen (N_2) and G-gas) and 2 mol% propene at 8 bar(g). The results for SBR rings exposed to propene deviate statistically from those for SBR rings exposed to N_2 but are virtually identical to those for the SBR rings exposed to G-gas.

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

Research on NBR rings submerged in liquid limonene showed a high degree of absorption of the fluid and severe mechanical degradation [22]. 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.
SBR was not tested but is expected to have similar or even worse effects.

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

Effects of Carbon Monoxide, Carbon Dioxide and Hydrogen

It was concluded on the basis of the studied literature [1] that no deleterious effect could be expected for CO, CO_2 or H_2. The effects of 59 mol% CO_2 were also tested in the experiments (see chapter 2).

The experiments resulted in no mechanical or dimensional change [5] for NBR after 600 days of exposure. No mass change was measured for SBR. It can therefore be concluded that no significant absorption or depletion occurred.

For SBR, there was no statistically significant difference (t-test) between the SBR samples exposed to CO_2 and the reference samples exposed to nitrogen as regards hardness, stress at 100 % elongation, strain at fracture or tensile strength. The same results were found when compared to reference samples exposed to G-gas. The only exception was the tensile strength test, which did reveal a statistical difference. However, the tensile strength for CO_2 increased when compared to natural gas (see Figure 21). This is not therefore considered to be a deterioration with exposure to G-gas.

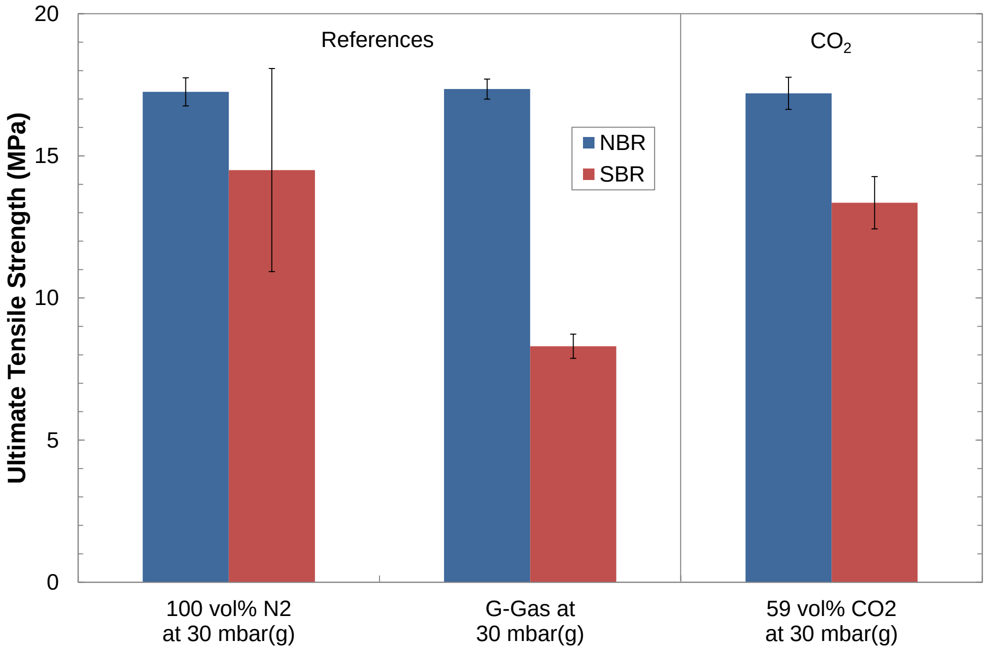

Figure 21. Ultimate tensile strength (σ_{UTS}) of NBR (blue) and SBR (red) exposed for a period of 600 days to the reference gases (nitrogen (N_2) and G-gas) and to 59 mol% CO_2. The results for SBR rings exposed to 59 mol% CO_2 deviate statistically from those of SBR rings exposed to G-gas but are still within the range of SBR rings exposed to N_2.

No profound dimensional change was observed either. The results for the NBR and SBR rings exposed to 59 mol% CO_2 were similar to those for the rings exposed to nitrogen and G-gas. No effect on the functioning of elastomeric sealing rings is therefore expected.

The detailed results of all tests can be found in appendix II.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 sustainable gases.

Effects of Sulphur-Containing Components (H_2S, S and THT)

The studied literature [1] revealed that the effect of high concentrations of sulphur-containing components (up to 4 300 mg/m^3) was unknown. The effects remain unclear even at the currently proposed lower concentration of 160 ppm H_2S. Therefore additional experiments have been carried out.

The experiments resulted in no noteworthy mass changes in either NBR or SBR after 600 days of exposure. No significant absorption or depletion therefore occurred.

For NBR, the only statistical significant difference (ANOVA) between the results of samples exposed to 160 ppm H_2S at 8 bar(g) and results of samples exposed to G-gas was in hardness. However, the difference was small and there was no clear trend (a lower hardness with increasing concentration), but rather one differing result [5].

For SBR, the only statistical significant difference (ANOVA) between the results of samples exposed to 160 ppm H_2S at 8 bar(g) and the results of samples exposed to G-gas was in tensile strength. Graphically (see Figure 22), a trend can also be seen: the tensile strength increases with increasing concentration. However, this trend is not seen for strain at fracture or stress at 100 % elongation. There are also indications for a trend in hardness (a lower hardness with increasing concentration) (see Figure 23). Nevertheless, the differences are about the same of the SBR rings exposed to nitrogen. The effect up to 160 ppm H_2S is small and therefore no deleterious effects on NBR and SBR are expected.

There was no statistical significant difference (ANOVA) between the results of SBR samples exposed to H_2S and the results of SBR samples exposed to G-gas as regards hardness, stress at 100% elongation or strain at fracture.
There was also no statistical significant difference (ANOVA) between the results of SBR samples exposed to H_2S and the results of SBR reference samples exposed to N_2 as regards hardness, stress at 100 % elongation, strain at fracture or tensile strength.

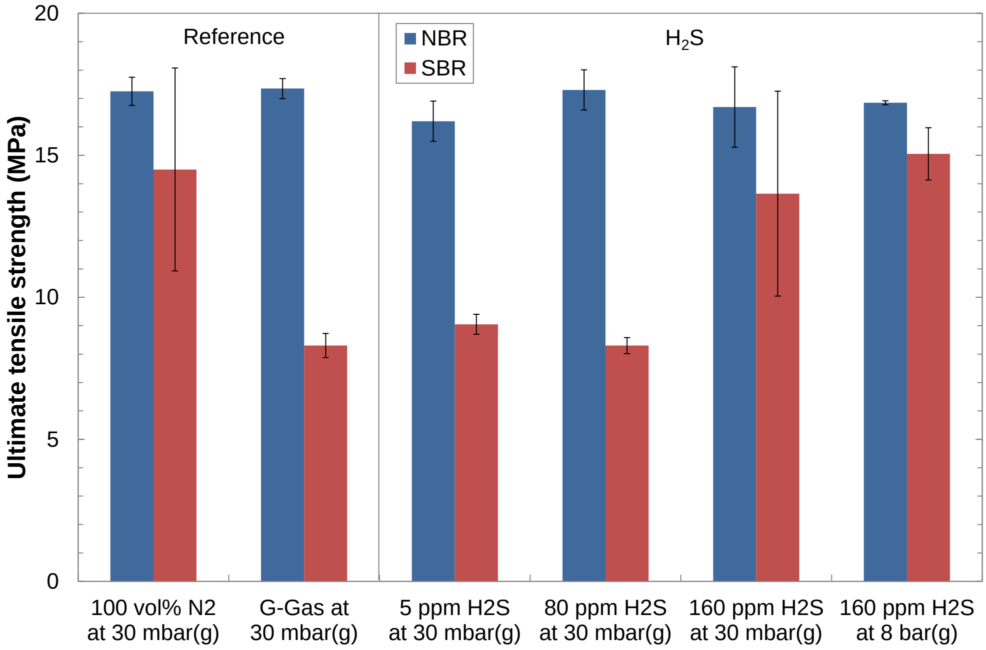

Figure 22. Ultimate tensile strength (σ_{UTS}) of NBR (blue) and SBR (red) exposed for a period of 600 days to the reference gases (N_2 and G-gas) and H_2S at various concentrations. There may be a trend of increasing σ_{UTS} with increasing concentration for SBR rings. The values are however still within the range of SBR rings exposed to N_2.

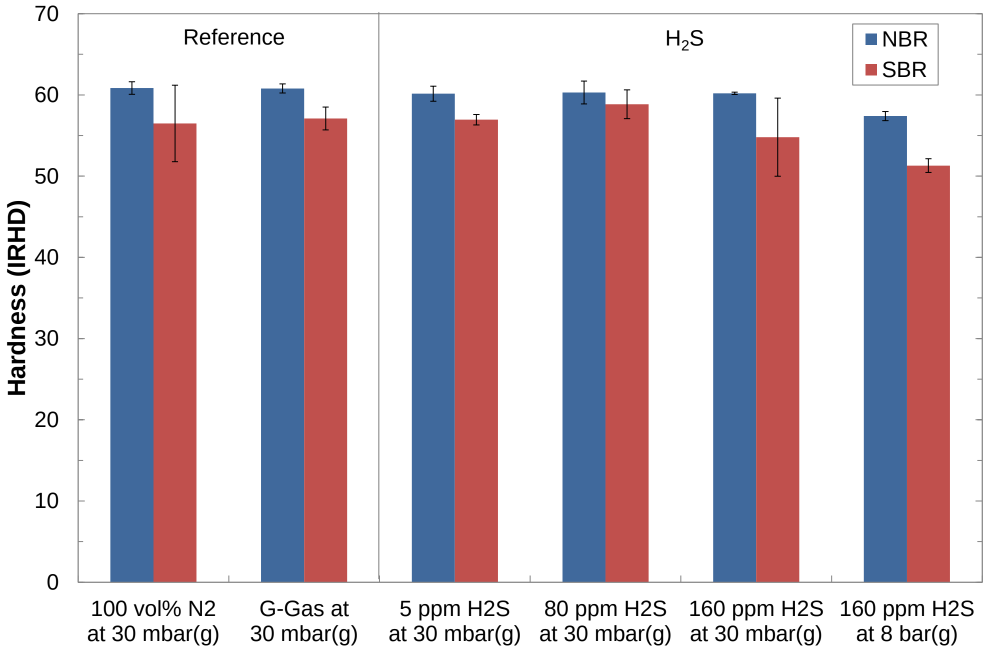

Figure 23. Hardness (IRHD) of NBR (blue) and SBR (red) exposed for a period of 600 days to the reference gases (N_2 and G-gas) and H_2S at various concentrations. There may be a trend of decreasing IRHD with increasing concentration for SBR. The effect is however small.

No profound dimensional change was observed for NBR. The dimensions of the rings exposed to H_2S were similar to the dimensions of the rings exposed to N_2 and G-gas. No effect on the functioning of NBR elastomeric sealing rings is therefore expected. On the other hand, a clear trend is visible for the dimensions of the SBR rings. With increasing H_2S concentrations, the SBR rings remained more deformed after being removed from the oversized pipe. This trend is visible in both the inner diameter (Figure 24) and to a lesser extent in the outer diameter (Figure 25) for both cases immediately and one hour after removal from the oversized pipe. However, the remaining dimensional changes are still within the range of the dimensional changes after exposure to the reference gases (N_2 and G-gas).Therefore, no effect on the functioning of the elastomeric sealing rings is expected for sulphur-containing components at up to 160 ppm.

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

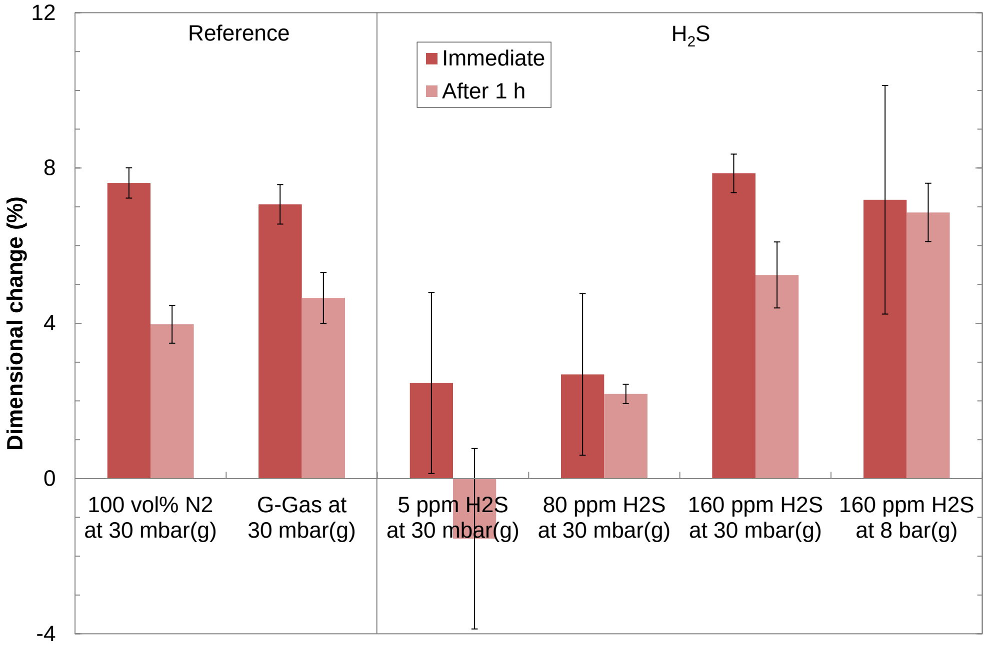

Figure 24. The difference in inner diameter of SBR rings after 600 days of exposure to the reference gases (nitrogen (N_2) and G-gas) and H_2S at various concentrations. The dimensions were measured immediately after removing the rings from the oversized pipe (125 mm) and after 1 hour and were subsequently compared to the original dimensions before exposure.

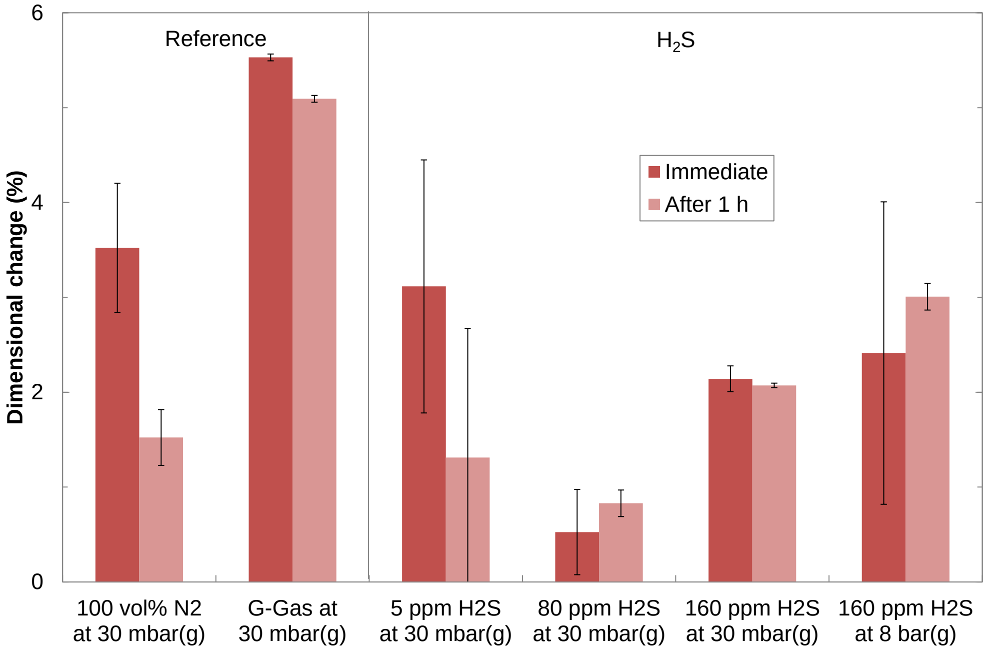

Figure 25. The difference in outer diameter of SBR rings after 600 days of exposure to the reference gases (nitrogen (N_2) and G-gas) and H_2S at various concentrations. The dimensions were measured immediately after removing the rings from the oversized pipe (125 mm) and after 1 hour and were subsequently compared to the original dimensions before exposure.

Effects of Chlorine-Containing and Fluorine-Containing Components

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

The experiments resulted in no noteworthy mass change for all concentrations in both NBR and SBR after 600 days. No significant absorption or depletion therefore occurred.

For NBR, there was no statistical significant difference (ANOVA) between results of the samples exposed to DCM and the reference samples in N_2 or G-gas as regards mechanical properties [5].

For SBR, the only statistical significant difference (ANOVA) between the results of samples exposed to 75 mg/m^3 DCM and samples exposed to G-gas was in tensile strength. Graphically there was no clear trend and the average ultimate tensile strength of SBR rings exposed to 75 mg/m^3 DCM was about the same as the SBR rings exposed to N_2 (see Figure 26).
There may be a trend in the strain at fracture (a lower strain at fracture with increasing concentration) in the results of the samples exposed to DCM (see Figure 27). However, there was no statistical significant difference (ANOVA).The differences are small and therefore no deleterious effect from halogen-containing components at concentrations of up to 1000 mg/m^3 is expected.

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

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

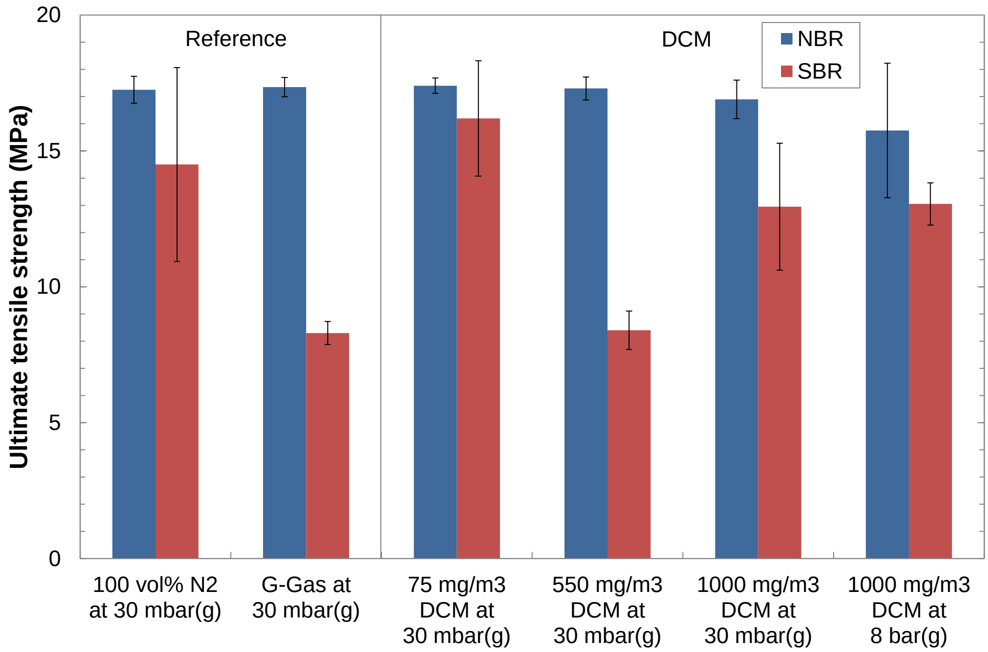

Figure 26. Ultimate tensile strength (σ_{UTS}) of NBR (blue) and SBR (red) exposed for a period of 600 days to the reference gases (100 mol% N_2 and G-gas) and DCM at various concentrations. The results for SBR rings exposed to 75 mg/m^3 DCM deviate statistically from those of the SBR rings exposed to G-gas but are about eh same as for the results of SBR rings exposed to N_2.

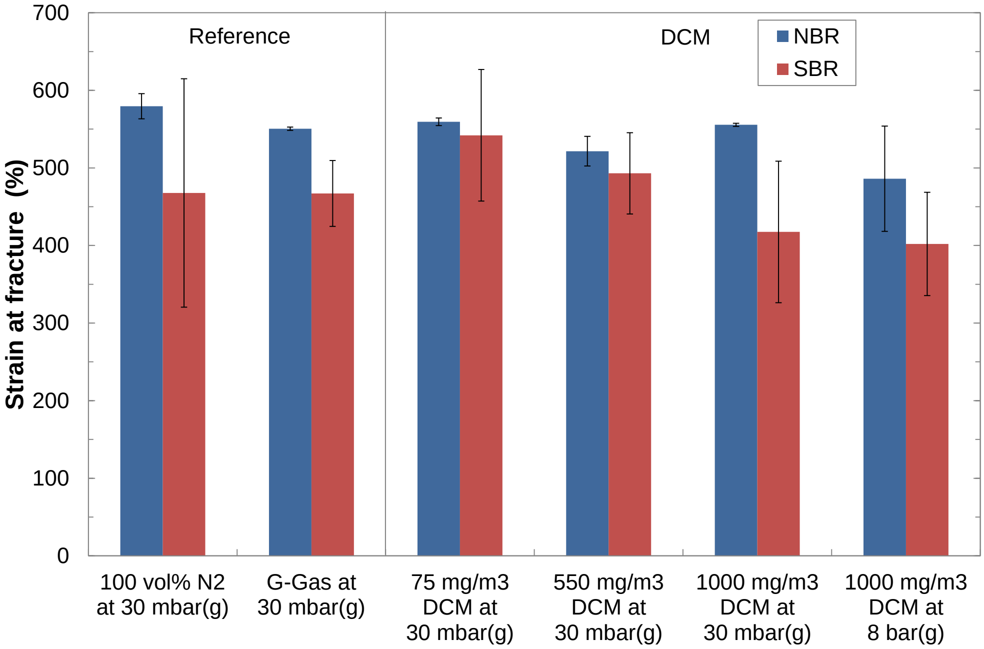

Figure 27. Strain at fracture ($\sigma_{F\%}$) of NBR (blue) and SBR (red) after exposure for 600 days to the reference gases (100 mol% N_2 and G-gas) and DCM at various concentrations. There may be a trend for the SBR rings, but the effect is small.

Effects of Other Components

It was concluded on the basis of the studied literature [1] that no deleterious effect was expected for ammonia. 100 ppm NH_3 was also tested in the experiments (see chapter 2).

The experiments resulted in no noteworthy mass change for either SBR or NBR after 600 days. No significant absorption or depletion therefore occurred.

Furthermore, there was no statistically significant difference (ANOVA) between the results of the samples exposed to NH_3 and the results of the reference samples exposed to N_2 as regards stress at 100% elongation, strain at fracture or tensile strength.
There was however a difference in hardness: both the NBR and SBR samples exposed to 100 ppm NH_3 at 30 mbar(g) had a slightly lower hardness (see Figure 28). 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 this is probably just an individual deviation. The same results were found when compared to the reference samples in G-gas.

For SBR, there was also a statistically significant difference (ANOVA) between the results of the SBR samples exposed to NH_3 (both 30 mbar(g) and 8 bar(g)) and the results of the SBR samples exposed to G-gas in tensile strength (see Figure 29). However, the average ultimate tensile strength of SBR rings exposed to 100 ppm NH_3 was still within the same range as the SBR rings exposed to N_2.

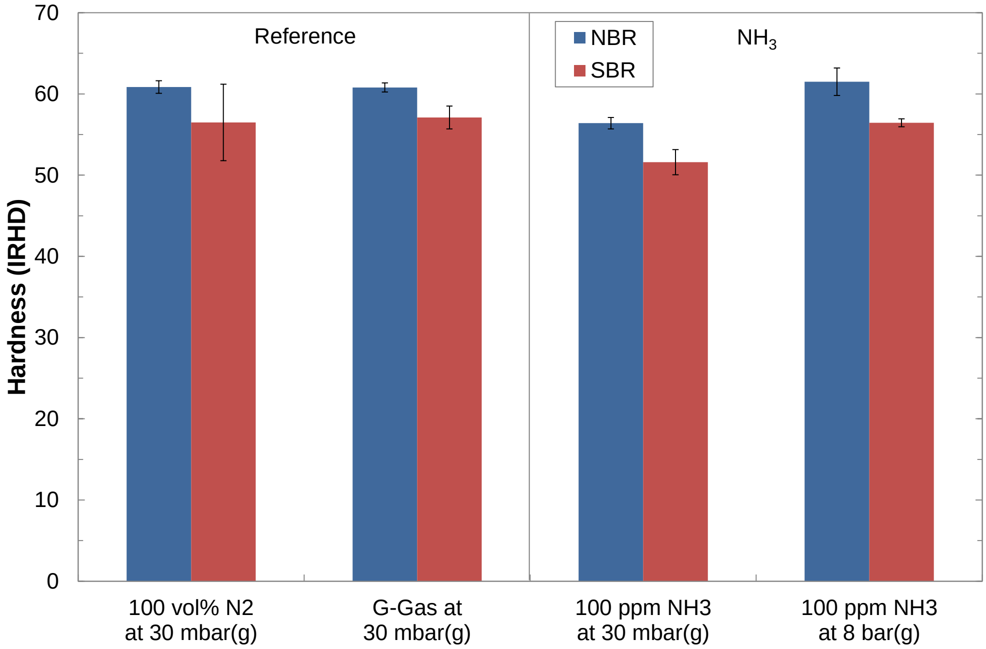

Figure 28. Hardness (IRHD) of NBR (blue) and SBR (red) exposed for a period of 600 days to the reference gases (nitrogen (N_2) and G-gas) and 100 ppm NH_3 at 30 mbar(g) and 8 bar(g). For both NBR and SBR, the hardness for the rings exposed to low pressure NH_3 deviates statistically from the reference gases.

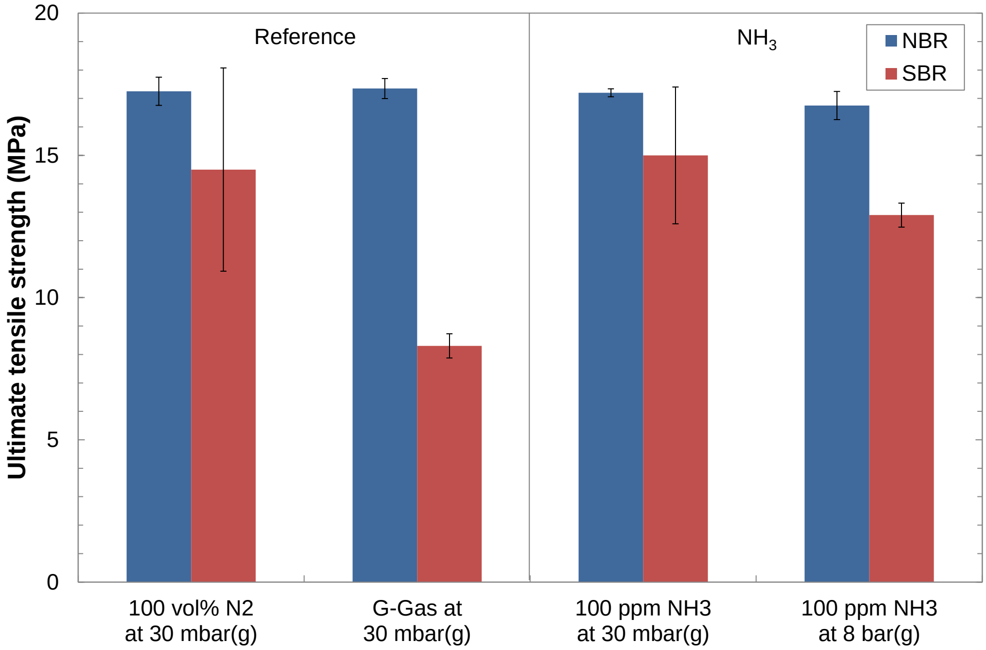

Figure 29. Ultimate tensile strength (σ_{UTS}) of NBR (blue) and SBR (red) exposed for a period of 600 days to the reference gases (nitrogen (N_2) and G-gas) and 100 ppm NH_3 at 30 mbar(g) and 8 bar(g). The σ_{UTS} of SBR rings exposed to NH_3 deviates statistically from that of the SBR rings exposed to natural gas but is still within the same range as that of the SBR rings exposed to nitrogen.

No profound dimensional change was observed for either SBR or NBR. The results for the rings exposed to the two concentrations of 100 ppm NH_3 were similar to the results for the rings exposed to 100 vol% N_2 and G-gas. No effect on the functioning of elastomeric sealing rings is therefore expected when exposed to 100 ppm NH_3.

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

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

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

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

3.1.3 Conclusions

The literature and experiments led to the conclusion that no deleterious effect for H_2S (up to 160 ppm), halogen-containing components, ammonia, CO_2 or O_2 in sustainable gases is expected for PVC couplers with sealing rings. Field tests furthermore demonstrated that H_2 at up to 20 mol% has no effect on PVC couplers. (Aromatic) hydrocarbons are not expected to have a negative effect on the mechanical and physical properties either. However, liquid aromatic hydrocarbons (e.g. BTX and terpenes) will negatively affect the mechanical properties of PVC and elastomeric sealing rings made of NBR. SBR will be affected to an even greater extent.

Since the concentrations of HCl and HCN in sustainable 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 no problems arise as a result of the current concentrations of these components in the distribution grid. Finally, the effects of CO have not been investigated and remain unknown.

These conclusions are summarised in Table 13.

Table 13. The effect of components present in sustainable gases on PVC couplers (PVC, NBR and SBR). Most components will have no deleterious effect (green). For some components, little or no deleterious effect is expected (light green).

	Sulphur-containing components	H_2S	Mercaptans	Odorant	Ammonia	Chlorine-containing components	Fluorine-containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
PVC	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid (impact resistance)		none	none (up to 20 mol%)
NBR	none (up to 160 ppm)		probably none		none			probably none		None		none, unless liquid		None	
SBR	none (up to 160 ppm)		probably none		none			probably none		None		none, unless liquid		None	
PVC coupler with sealing ring	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)

3.2 Heat-fused Joints

The two most commonly used heat fusion jointing methods in PE piping systems are butt fusion and electro-fusion. Both methods melt the PE material to obtain a strong bond after solidification. The solidified PE in both joint types is similar to the PE used for pipes. The failure mechanism for heat fusion joints will also be slow crack growth (SCG), as is the case for PE pipes. It is therefore expected that the effect of sustainable gases on existing thermal fused joints will be comparable to the effect of sustainable gases on PE pipe materials. The effects of wide band gases on PE pipe materials are described in "Effects of Wide Band Gases on Distribution Materials" [5].

3.2.1 Conclusion

The experiments and literature led to the conclusion that no deleterious effects on PE in sustainable gases were found for H_2S and sulphur-containing components (at up to 160 ppm), ammonia, halogen-containing components, CO_2 or O_2. Field tests furthermore demonstrated that H_2 at up to 20 mol% has no effect on PE materials either. No negative effects on material properties were found in literature for (aromatic) hydrocarbons in gaseous form. However, liquid aromatic hydrocarbons (e.g. BTX and terpenes) will negatively affect the mechanical properties of PE.

Since the concentrations of HCl and HCN in sustainable 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 no problems arise as a result of the current operation of these components in the distribution grid. Finally, the effect of CO has not been investigated and remains unknown.

The conclusions of this report are summarised in Table 14.

Table 14. The effect of components present in sustainable gases on PE heat-fused joints. Some components will have no deleterious effect (green), while for others little or no deleterious effect is expected (light green). The effect of CO is unknown (light orange).

	Sulphur-containing components	H_2S	Mercaptans	Odorant	Ammonia	Chlorine-containing components	Fluorine-containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
PE heat fused joints	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)

3.3 POM Couplers with NBR Sealing Rings

Mechanical fittings with a body made from polyoxymethylene (POM) are mostly used in service lines operated at low pressures (≤ 200 mbar(g)). POM couplers are used as a transition fitting (PE-steel/PE-PVC) and also to connect PE pipes with a small diameter (≤ 63 mm). These couplers are full end-load resistant, which is mandatory in service lines. The exact number of POM couplers in use in service lines is unknown. What is known is that the quantities involved are substantial. Almost every DSO in the Netherlands uses these couplers.

The couplers were introduced in the late 1970s and were at first used only in the water industry. A few years later, the use of POM couplers in gas distribution systems was also permitted. All POM couplers fitted today are made of homopolymer POM (hPOM). Nevertheless, copolymer POM (cPOM) may also be used in the future due to its improved mechanical characteristics.

The coupler contains a rubber ring that acts as a sealant and a grip ring made of POM materials. Modern POM couplers for gas systems contain an NBR ring that is yellow in colour indicating that it is for use with gas. POM couplers with blue NBR rings are used in water distribution systems.

3.3.1 POM Body

3.3.1.1 Test Method

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

The following five tests were also performed on POM:

1. Mass change. The mass of POM dumbbell specimens not subject to stress was compared before and after exposure to various components in sustainable gases.
2. Dimensional changes. The dimensions of POM dumbbell specimens and rings not subject to stress were compared before and after exposure to various components in sustainable gases
3. The Ultimate Tensile Strength (σ_{UTS}). POM dumbbell specimens and rings subject to stress under constant load were tested using tensile tests.
4. Elongation at Break ($\varepsilon_{F\%}$). POM dumbbell specimens subject to stress under constant load were tested using tensile experiments to determine the elongation at break.
5. Displacement at break (ε_{Fmm}). POM rings subject to tension stress under constant load were tested using tensile experiments to determine the displacement at break.

The mechanical characteristics σ_{UTS} and $\varepsilon_{F\%}$ of the dumbbells were determined by performing tests in accordance with ISO 527-4 [23]. The mechanical characteristics σ_{UTS} and ε_{Fmm} of the rings were determined by performing tests in accordance with ISO 8496 [24].

Where applicable, eight dumbbells and eight rings were tested. The results were evaluated using the ANOVA method in the statistical software package SigmaPlot [25]. With this package it can be assessed whether the differences that are noted in some cases are statistically significant or not (95 % confidence level). The software calculates this using the scatter in the data and the averages.

3.3.1.2 The Influence of Sustainable Gases on POM Materials under Lab Conditions

The mass and dimensional changes of the exposed dumbbells and rings are low. Usually, there is a mass loss less than 0.2 %. The dimensional changes are usually also low, a few hundreds of a millimetre.

The ultimate tensile strength of the hPOM rings after exposure for a period of 600 days to six gases (100 mol% N_2 (as reference), 75 mg/m^3 DCM, 1000 mg/m^3 DCM, 59 mol% CO_2, 160 ppm H_2S and 100 ppm NH_3) at 30 mbar(g) is presented in Figure 30.
The largest change in σ_{UTS} can be found for the hPOM rings exposed to 59 mol% CO_2. However, it transpires that neither σ_{UTS} (Figure 30) nor $\varepsilon_{F\%}$ (not shown) changed in a statistically significant manner. This means that no influence for the five tested chemicals on the rings was found. Even the increased σ_{UTS} after exposure to 59 mol% CO_2 gas was not statistically significant.

Figure 31 shows the ultimate tensile strength after exposure of hPOM and cPOM dumbbell specimens to the same chemicals and concentrations as mentioned in Figure 30 for a period of 600 days. The only difference between Figure 30 and Figure 31 is that the former shows results for rings, while the latter figure shows results for dumbbell specimens. In none of the investigated gases (75 mg/m^3 DCM, 1000 mg/m^3 DCM, 59 mol% CO_2, 160 ppm H_2S and 100 ppm NH_3) was a statistically significant difference (ANOVA) with respect to the reference gas (100 mol% N_2) observed.

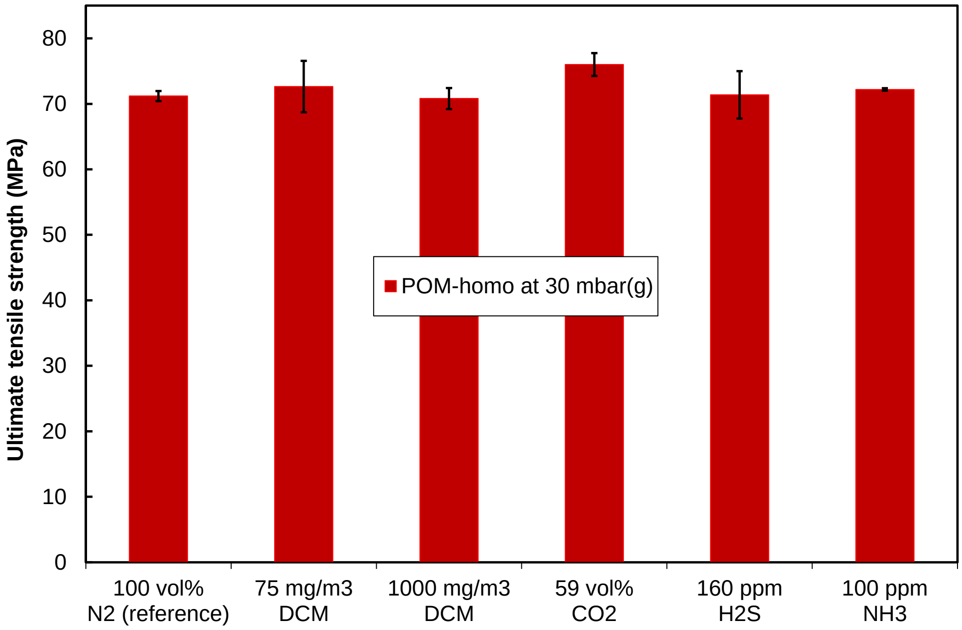

Figure 30. Average ultimate tensile strength (σ_{UTS}) of hPOM rings exposed to various gases at 30 mbar(g).

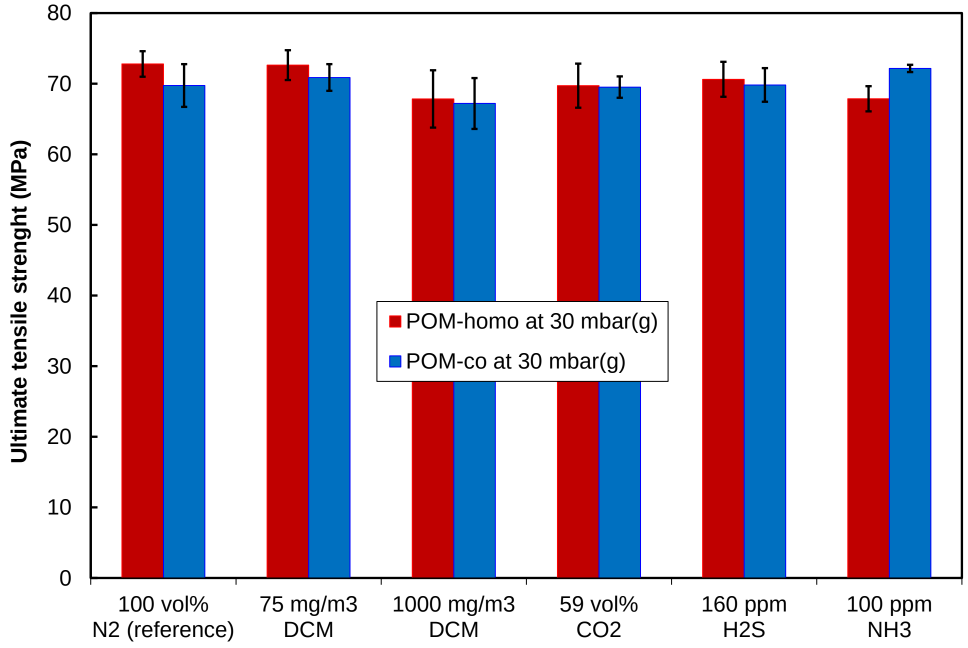

Figure 31. Average ultimate tensile strength (σ_{UTS}) of hPOM and cPOM dumbbells exposed to various gases at 30 mbar(g).

The ultimate tensile strength after exposure of hPOM and cPOM dumbbells to 6 chemicals (100 mol% N_2, 62 mol% H_2, humid 3 ppm HCl, 1000 mg/m^3 DCM, 160 ppm H_2S and 100 ppm NH_3) at high pressure (8 bar(g)) for a period of 600 days is presented in Figure 32. The only statistically significant change is for humid 3 ppm HCl gas. For hPOM the reduction is -12 %.
The negative effect noted for the hPOM dumbbells was also found for the cPOM dumbbells, but the extent of the quality reduction was much larger than that of the hPOM dumbbells (-54 %).

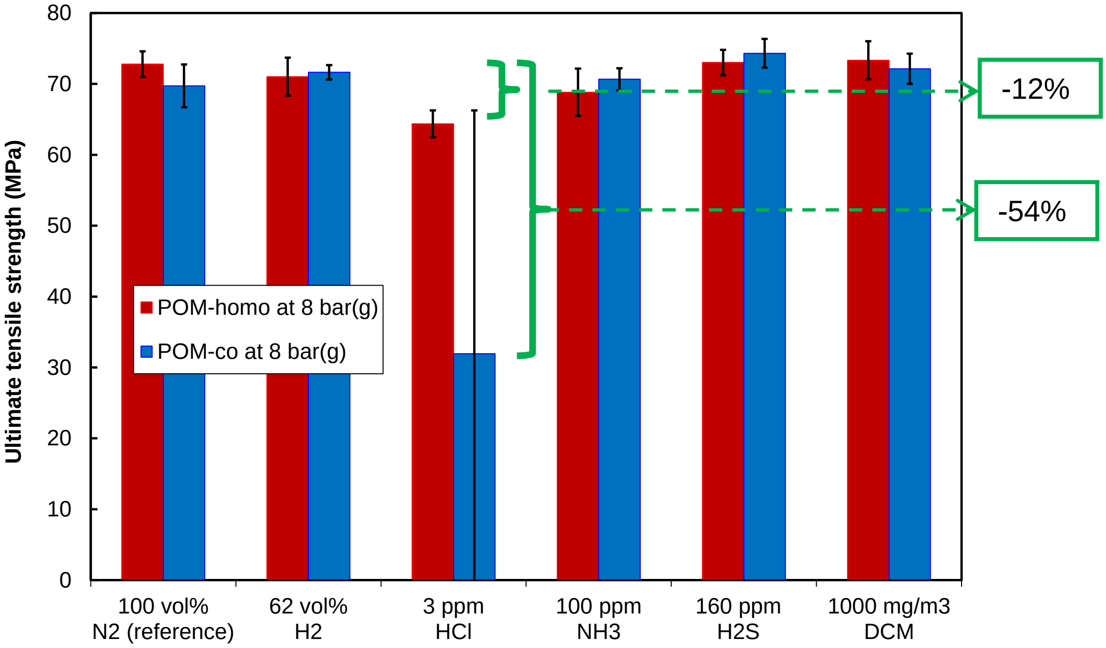

Figure 32. Average ultimate tensile strength (σ_{UTS}) of hPOM and cPOM dumbbells exposed to various gases at 8 bar(g).

Microscopy of the exposed dumbbells revealed more about the origin of this effect. After exposure to most chemicals, no detrimental effects on the POM materials were observed using optical microscopy, except in one case: after exposure to humid 3 ppm HCl gas at 8 bar(g). Obvious but local attack was noted in this condition. Some hPOM dumbbell specimens proved to contain circular or oval holes or pits caused by chemical attack. Such local attack of a hPOM dumbbell by 3 ppm HCl vapour can be seen in Figure 33. The holes seemed to have been “burned” into the hPOM material. This occurred down to a certain depth at certain spots on the external surface of some dumbbell specimens. These “pits” were generally isolated defects. Some of the products of degradation were discoloured.

Figure 34 shows several cPOM dumbbells that had already failed during exposure to 3 ppm HCl vapour. This effect did not occur in the hPOM dumbbells. Figure 35 shows a microscopic image in which severe cracking at several locations in three cPOM dumbbells can be observed.

Figure 36 shows severe “pitting” of a cPOM dumbbell. It would seem that the effect of 3 ppm HCl vapour gas is much larger for cPOM materials than for hPOM materials.

This degradation of POM by HCl is consistent with the fact that hydrogen chloride vapour, being a very acidic component, degrades POM materials. In essence, a so-called hydrolysis occurs, which means breakage of the long polymer chains due to chemical attack by the acid. This process is not reversible. When liquid water is present this process may occur gradually, depending on the concentration of dissolved HCl.
At a relative humidity (RH) of approximately 82 %, HCl vapour can promote the condensation of water from such a humid environment. The HCl can then dissolve in the condensed water. During water re-evaporation, the water droplets shrink in volume. Quite a large increase in acidity occurs, which is high enough to cause appreciable degradation. Appendix I gives more details about this process.

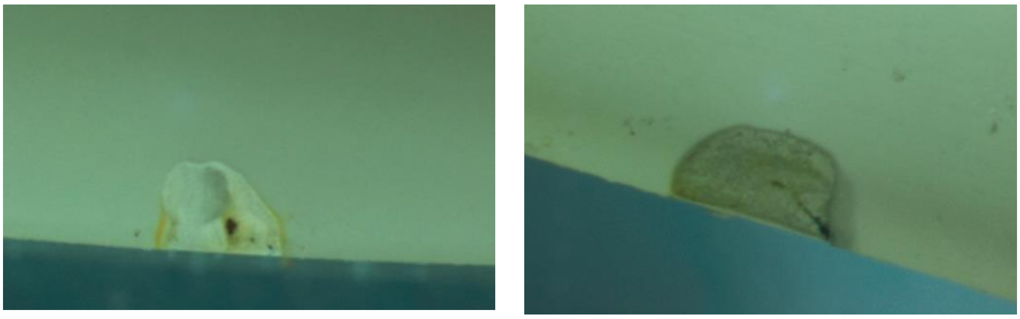

Figure 33. Chemical attack of hPOM in humid 3 ppm HCl vapour.

Figure 34. Three cPOM dumbbells, still mounted in the test rig, which broke during the exposure period of 600 days to humid 3 ppm HCl vapour.

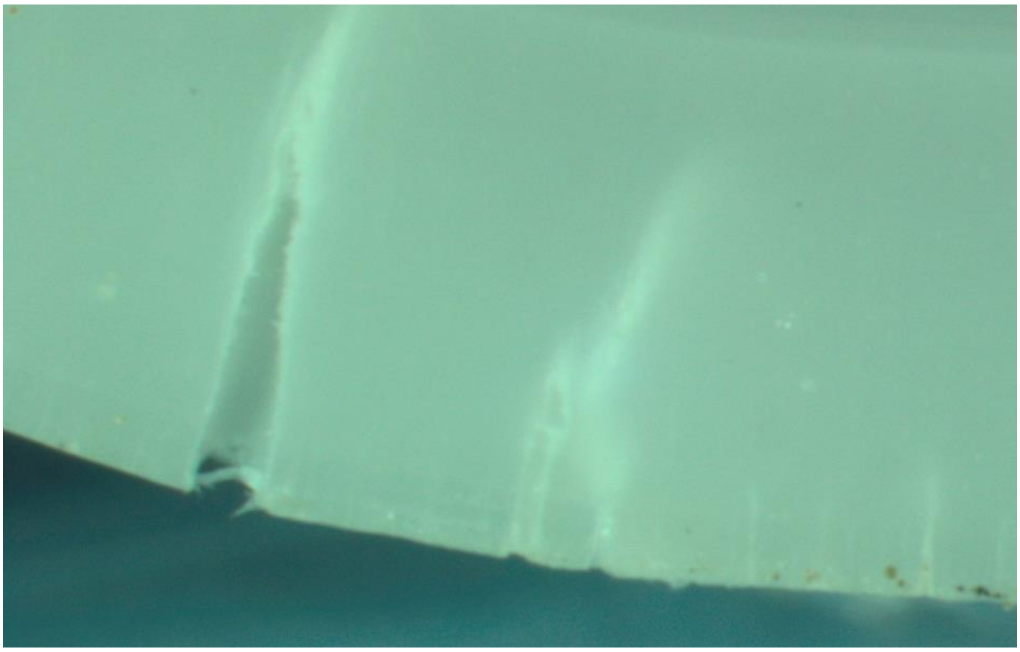

Figure 35. Microscopic image of one of the cracked cPOM dumbbells after 600 days of exposure to humid 3 ppm HCl vapour.

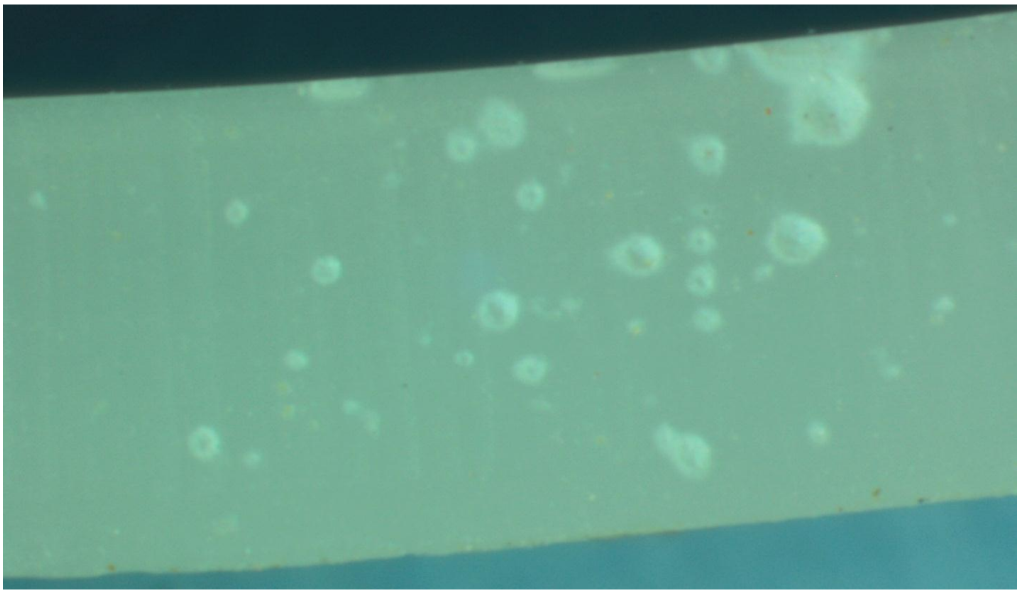

Figure 36. Round "pitting" holes caused by chemical attack of cPOM dumbbells after 600 days of exposure to humid 3 ppm HCl gas at 8 bar(g).

POM products must therefore not be used in gas with a high water content, since the condensation of acidic water cannot be ruled out in this case.

It remains to be explained why cPOM material is more severely attacked by HCl gas than hPOM material. During the period of exposure, the same hPOM that was tested in the present EDGaR project and three cPOM materials were tested another research project [26]. The results revealed that hPOM is vulnerable to the aggressive zinc chloride solution. This effect is well known. For cPOM materials, a lower

vulnerability to this stress crack agent was expected. This did indeed prove to be the case for two cPOM materials. However, one of the cPOM materials, which was the same as tested in the present EDGaR project, was even more vulnerable to zinc chloride than hPOM. This was unexpected at the time these results became available. It later became known that several international customers also experienced disappointing results with this cPOM material. The manufacturer subsequently removed its copolymer POM resin from the market. However, the EDGaR project tests on hPOM and cPOM were well underway.
It is now possible to understand why this cPOM material was more severally attacked by HCl gas than hPOM. Had one of the other two cPOM materials been selected for the EDGaR project, degradation by HCl gas would probably have been lower for these copolymers than for hPOM.

3.3.1.3 The Influence of Sustainable Gases on POM Materials under Field Conditions

hPOM rings were also tested in a field test (see chapter 2). The results of the tests for mechanical characteristics (ultimate tensile strength (σ_{UTS}) and displacement at break (ε_{Fmm})) of the hPOM materials are given in Figure 37 and Figure 38.
It must be emphasised that the rings used in the field tests and the rings used in the lab tests did not have the same dimensions (see Table 15). This had a great deal of influence on the results.

Table 15. Dimensions of the hPOM rings after exposure in the lab and after field tests. The constant deformation was 3.1% in all cases.

	Lab tests on hPOM rings	Field tests on hPOM rings
Diameter (mm)	40	40
Wall thickness (mm)	2.0	3.5

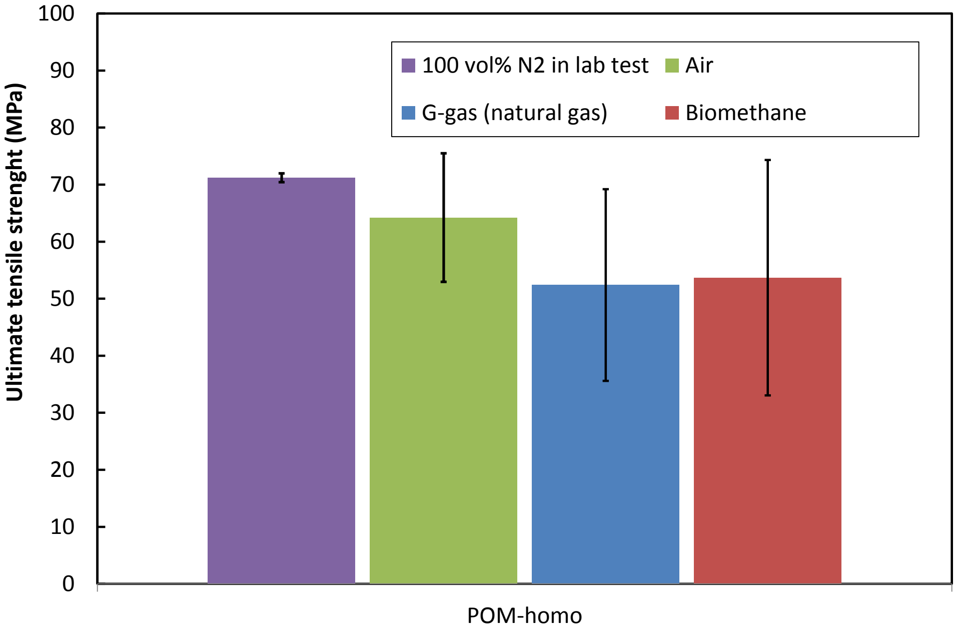

Figure 37. Average ultimate tensile strength (σ_{UTS}) of hPOM rings (3.5 mm wall thickness) that had been exposed to air, G-gas and biomethane for a period of two years compared to hPOM rings with a wall thickness of 2.0 mm (reference from the lab test).

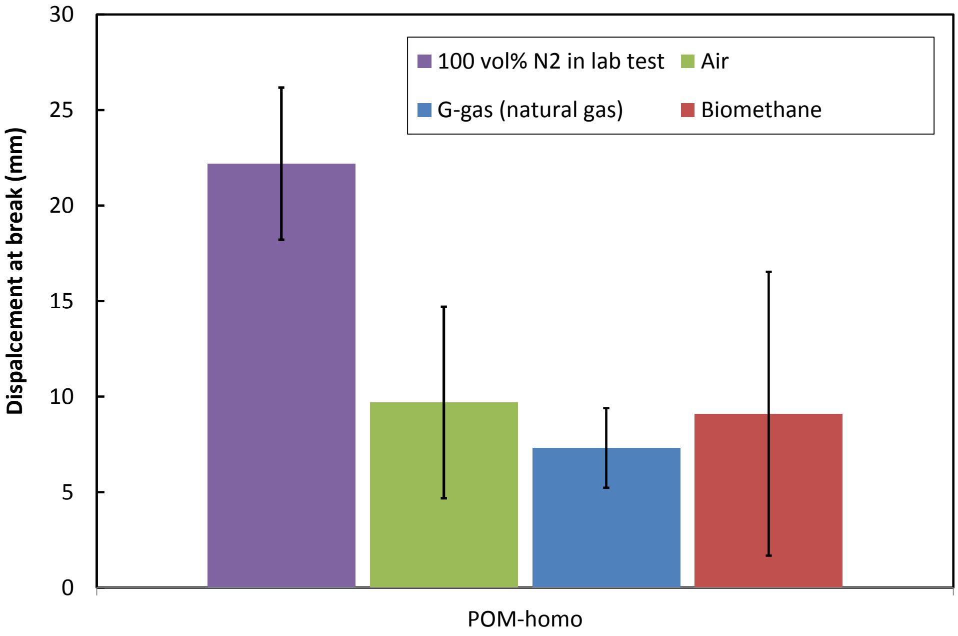

Figure 38. Average displacement at break (ε_{Fmm}) of hPOM rings (wall thickness of 3.5 mm) that had been exposed to air, G-gas and biomethane for a period of two years compared to hPOM rings with a wall thickness of 2.0 mm (reference from the lab test).

Several obvious differences can be noted. The average σ_{UTS} of the rings tested in air in the field test (green column) is lower than the average σ_{UTS} of the rings tested in nitrogen in the lab (purple column). The scatter in the first case is also much higher. The rings exposed to G-gas (blue column) and biomethane (red column) show an even lower average σ_{UTS} and once again have a high scatter. However, there are no statistically significant differences among the three conditions when only the field test results are compared. This is mainly due to the noted high scatter in the data.

The displacement at break for the three conditions in the field tests (G-gas, narrow band gases, air) is similar, but only about 50 % of the reference (100 % N_2) in the lab tests. These differences are statistically significant.

All external diameters were 40 mm and the applied deformations (%) in the U-clamp were the same (3.1 %) in all cases. However, the wall thickness of the rings exposed in the lab (2.0 mm) and the rings exposed in the field tests (3.5 mm) were different. This difference is very important.

During the ring tensile tests, the thick-walled rings showed more of a so-called “plane strain condition” whilst the thin-walled rings showed more of a “plane stress condition”. The rings with the thicker wall did not deform as easily as the thin-walled rings. In the thick-walled rings, ductile behaviour was suppressed. This can be seen in Figure 38.
Consequently, the noted differences are mostly the result of differences in the wall thickness of the tested rings. As regards ε_{Fmm}, no statistically significant influence for the exposure conditions of the thick-walled rings could be noted.

As regards the differences in Figure 38, the fact that the thick-walled rings showed less ductile behaviour also leads to additional stresses in the rings and a higher overall (“von Mises”) stress. Thicker-walled rings are simply more heavily loaded than thin-walled rings. The former are therefore more easily damaged by mechanical stress during exposure, even in air. This explains the differences between the green and the purple column in this figure. The other two exposure conditions led to an even lower average σ_{UTS}. However, due to the high scatter, these differences are not statistically significant.

Consequently, the differences noted in Figure 37 and Figure 38 are the result of the difference in wall thickness of the exposed rings.
There is no proof that there was a statistically significant effect for G-gas or biomethane on the POM rings exposed in the field tests.

3.3.2 NBR Sealing Rings

In addition to the results described in section 2.1.2, NBR sealing rings from POM couplers were tested in the field test (see chapter 2). These experiments resulted in virtually no mass change after two years. Furthermore, there was no statistically significant difference between the results of the samples exposed to biomethane feed (narrow band quality) and the results of the samples exposed to natural gas (G-gas) as regards hardness, stress at 100% elongation, strain at fracture or tensile strength. Virtually no dimensional change could be observed either.
These results do not alter the conclusions as mentioned in section 2.1.2 for NBR sealing rings.

3.3.3 Conclusions

On the basis of the literature and experiments, no deleterious effect from H_2S (up to 160 ppm), halogen-containing components, ammonia or H_2 in sustainable gases is expected for POM couplers with sealing rings. (Aromatic) hydrocarbons are not expected to have a negative effect on the mechanical and physical properties either. However, liquid aromatic hydrocarbons (e.g. terpenes and BTX) will negatively affect the mechanical properties of elastomeric sealing rings made of NBR. Finally, the effects of HCN and CO were not investigated due to safety reasons and remain unknown.

For low concentrations of HCl in combination with water vapour, the condensation of acidic water cannot be ruled out. This acidic water has a destructive effect on POM materials and therefore also on POM couplers with sealing rings.

These conclusions are summarised in Table 16 below.

Table 16. The effect of components present in sustainable gases on POM couplers with sealing rings (POM and NBR). Most components will have no deleterious effect (green). For some components little or no deleterious effect is expected (light green).

<table>
<tr><th></th><th>Sulphur-containing components</th><th>H_2S</th><th>Mercaptans</th><th>Odorant</th><th>Ammonia</th><th>Chloride-containing components</th><th>Fluoride-containing components</th><th>HCl</th><th>HCN</th><th>CO</th><th>CO_2</th><th>Hydrocarbons</th><th>Aromatic hydrocarbons</th><th>O_2</th><th>H_2</th></tr>
<tr><td>POM</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">none</td><td>water</td><td colspan="2">unknown</td><td>none</td><td colspan="3">probably none</td><td>none</td></tr>
<tr><td>NBR</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">none</td><td colspan="2">probably none</td><td colspan="2">none</td><td colspan="2">none, unless liquid</td><td colspan="2">none</td></tr>
<tr><td colspan="16"></td></tr>
<tr><td>POM coupler with sealing ring</td><td colspan="2">none
(up to 160 ppm)</td><td colspan="2">probably none</td><td colspan="3">none</td><td>water</td><td colspan="2">unknown</td><td>none</td><td colspan="2">probably none, unless liquid</td><td>probably none</td><td>none</td></tr>
</table>

4 Effects on Existing Joints in Metal Piping Systems

The principle materials used in metal piping systems are steel and copper. Aluminium is also widely used in gas pressure regulators and gas meters. Most aluminium components contain threaded joints to allow connection to the gas distribution system. Four main joint types are employed in metal piping systems:

- Welded steel joints (see 4.1);
- Threaded steel joints (see 4.2);
- Brass mechanical fittings (see 4.3);
- Threaded aluminium joints (see 4.4).

These joints are discussed further in this chapter.

4.1 Welded Steel Joints

4.1.1 *The Importance of Steel in the Dutch Gas Distribution Network*

The Dutch gas distribution network contains about almost 27 500 km of steel mains (see also Table 17). Steel pipelines are mostly in use as high pressure gas distribution materials in the 8 bar(g) network. Grey cast iron pipes are used in rather old, 1 bar(g) pipelines and have to be replaced in the coming years. Welding and threaded joints are the most commonly used methods of connecting steel pipes.

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

Material	Length (km)	MOP* (bar)	Material-standard
Carbon steel	*19 228*	16	[27,28]
Grey cast iron[§]	*6 241*	1	[29]
Nodular cast iron	*2 015*	8	[30]
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 sustainable gases (see also Table 18). for a period up to 19 months. Cast iron materials were not tested but these materials are expected to corrode in a similar manner as steel.

Table 18. Gas compositions to which steel was exposed.

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

After the experiments, the corrosion samples were cleaned using cleaning methods as described in ASTM G1 [31] 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 Sustainable Gases on Welded Steel Joints in Lab Conditions

Welded steel specimens were used for all experiments. The welds were not in general attacked preferentially. In the high pressure (8 bar(g)) experiment with gas number 1 (50 mol% CO_2, 0.01 mol% O_2 and 160 ppm H_2S), a preferential attack was observed above the waterline in the heat-affected zone (HAZ), i.e. the base material affected by the heat input of the welding process. The same effect was observed in the low pressure (30 mbar(g)) experiment with gas number 1. However, the severity of the attack was far less than that of the high-pressure experiment. In addition, during the exposure to gas number 7 (10.3 mol% CO_2, 0.5 mol% O_2 and 34 ppm H_2S), the heat-affected zone and the root of the weld were attacked preferentially on some samples.

The attack of the material in the heat-affected zone above the waterline for gas number 1 is a remarkable result as the most severe attack was expected either in the water phase or at the waterline. A possible explanation is the formation of a moist, thick grey/white coloured layer in the gaseous phase, as illustrated in Figure 39. The attack in the gaseous phase for gas number 1 is therefore likely to be the result of the combination of a high CO_2 concentration (50 mol%), low O_2 concentration (100 ppm) and high humidity (100 % RH).

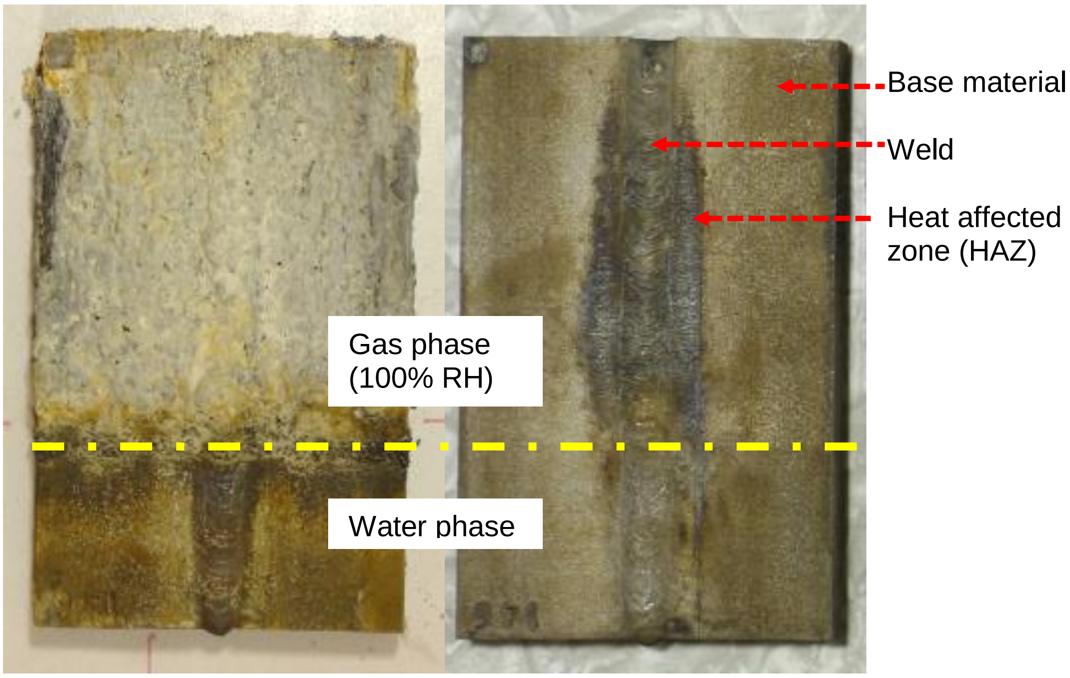

Figure 39. Corrosion sample from the experiment with gas number 1 at 8 bar(g). The as exposed sample (left) shows a moist, thick grey/white coloured layer of ferrous hydroxides in the gas phase, while the cleaned sample (right) shows the preferential attack in the heat-affected zone (HAZ).

For gas number 5 (50 mol% CO_2, 3 mol% O_2, no H_2S), pitting was observed both in the base material and in the weld. As the severity of the attack in the base material and the weld was comparable, the effect was therefore not specific to the welded joint. However, some preferential attack was observed in the HAZ in the water phase for the 6-month exposure only. It is unclear why this was only observed for the 6-month exposure and not for the longer and shorter exposure periods. See the wide band report [5] for more detailed information on the test results obtained for the steel base material.

4.1.4 The Influence of Sustainable Gases on Welded Steel Joints in Field Conditions

Steel welded joints were also tested in a field test (see chapter 2). The samples exposed to biomethane showed a similar degree of superficial corrosion to the reference samples. The field test therefore led to the conclusion that there are no additional effects to be expected from narrow band gases on steel welded joints other than those observed in the laboratory experiments.

4.1.5 Conclusions

Because no preferential attack of the welds occurred, the conclusions arising from the exposure of steel to narrow band and wide band gases also apply to existing steel welded joints exposed to sustainable gases.

The presence of water is obviously of great influence on the corrosion of steel as a result of the interaction of O_2, CO_2 and H_2S. 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% CO_2, 100 ppm O_2 and 160 ppm H_2S), for which the strongest attack was observed in the moist gas phase. The corrosion tests were conducted with a maximum H_2S concentration of 160 ppm, which is the maximum permitted concentration of H_2S in the gas distribution network. 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 H_2S concentrations exceeding the tested H_2S concentrations. In order to be able to transport raw biogas, a minimum treatment of removing H_2S and drying the gas is required.

For all conditions (except for gas number 5) the weight loss of the corrosion samples showed a linear trend with time. This justifies the extrapolation of the test results for longer exposure times.

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

At high concentrations of CO_2 (50 mol%) and H_2S (160 ppm) with low O_2 concentrations (100 ppm), high corrosion rates are possible in the gaseous phase with 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 O_2 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 O_2 with 50 mol% CO_2 and 160 ppm H_2S / gas number 9: 100 ppm O_2 with 10 mol% CO_2 and 34 ppm H_2S) did not result in a corrosion rate limiting the lifespan of steel to less than 50 years. However, the corrosion rate showed a local maximum between 0.01 and 0.5 mol% O_2. It is therefore recommended that the effect of low oxygen concentrations on the integrity of steel in the gas distribution network be further investigated.

At high concentrations of CO_2 (50 mol%) and O_2 (3 mol%), the presence of H_2S seems to lead to superficial pitting (0.31 mm/y), while the absence of H_2S 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 CO_2 and O_2 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].

These conclusions are summarised in Table 19 below.

Table 19. The effect of components present in sustainable gases on joints in steel piping systems. 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_2S	Mercaptans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
Steel welded joints	water, CO_2		probably none						with H_2S and water: possibly	unknown	water, H_2S	probably none		water, (H_2S), CO_2	none
	water, CO_2 and O_2										water, (H_2S) and O_2				

4.1.6 *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 CO_2 and O_2 concentrations in the absence of H_2S (for example in biogas generation directly after the H_2S 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 O_2, CO_2 and CO have not been studied. The conclusion therefore remains unchanged: stress corrosion cracking in a gaseous environment containing these components is possible in the presence of water.

4.2 Steel Threaded Joints

No specific experiments were carried out for steel threaded joints in steel piping systems. It is expected that the effects of sustainable gases on steel threaded joints will be the same as the effects on steel pipe materials, since the joint material has the same characteristics as the pipe material. The effects of wide band gases on steel threaded joints will therefore be the same as the effects on steel pipes. These are described in "Effects of Wide Band Gases on Distribution Materials" [5].

These conclusions are summarised in Table 20.

Table 20. The effect of components present in sustainable gases on steel threaded joints. 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_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
Steel threaded joints	water, CO_2		probably none						with H_2S and water: possibly	unknown	water, H_2S	probably none		water, (H_2S), CO_2	none
	water, CO_2 and O_2										water, (H_2S) and O_2				

4.3 Brass Compression and Press Fittings in Copper Piping Systems

4.3.1 The Importance of Copper in the Dutch Gas Distribution Network

While copper is used in service lines, its most common use is in domestic applications. These are not part of the gas distribution network but represent a high degree of risk if severe attack were to occur. The most common methods of connecting copper pipes are compression press brass fittings and POM couplers used as transition couplers (copper to PVC or PE). These are discussed in chapter 3.3.

4.3.2 Test Method

The experimental setup as described in chapter 2 was used to expose copper and brass materials to various components in sustainable gases (see also Table 21) for a period of 19 months.

Table 21. Gas compositions to which copper and brass were exposed.

Gas number	CO_2 (mol%)	O_2 (mol%)	H_2S (ppm)
1	50	0.01	160
2	50	0	160
3	0	3	160
4	50	3	160
5	50	3	0
6	0	0.5	34
7	10	0.5	34
8	10	0.1	34
9	10	0.01	34
10	50 ppm NH_3 with 50 % RH		

After the experiments, the corrosion samples were cleaned using cleaning methods as described in ASTM G1 [31] 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 Sustainable Gases on Compression Fittings in Copper Piping Systems under Lab Conditions

4.3.3.1 Effects of Interactions between CO_2, O_2 and H_2S

It is expected that the effects of sustainable gases on compression brass fittings in copper piping systems will be the same as the effects on copper pipes as described in "Effects of Wide Band Gases on Distribution Materials" [5].

4.3.3.2 Effects of Ammonia

The literature [1] revealed that stress corrosion due to ammonia in sustainable gases cannot be ruled out.

No stress corrosion cracking was observed in copper tubes or brass mechanical fittings after 19 months of exposure to gas number 10 with 50 ppm NH_3 and a relative humidity of 50 % at different stress levels exceeding the stress level of normal installation (see chapter 2).

4.3.4 The Influence of Sustainable Gases on Compression Fittings in Copper Piping Systems under Field Conditions

Compression brass fittings were also tested in a field test (see chapter 2). The samples exposed to biomethane showed a similar degree of influence from the gases as the reference samples. Therefore, for compression fittings, it can be concluded from the field experiments that no effects are expected from narrow band gas, other than those observed in the laboratory test rig.

4.3.5 Conclusions

For copper, the combination of H_2S and O_2 can result in a high corrosion rate in a gaseous environment with high humidity. CO_2 increases the corrosion rate as a result of the combined presence of H_2S and O_2. The same effect can be expected for brass compression fittings. The combination of high O_2, CO_2 and H_2S concentration is typical for raw biogas. The use of copper and brass mechanical fittings should therefore be avoided in raw biogas applications.

No effect was observed for the ammonia concentrations found in sustainable gases and the applied stress levels in copper piping with brass mechanical fittings. No effect for ammonia is therefore expected at concentrations of up to 50 ppm, especially if only dry gas is distributed.

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].

The conclusions are summarised in Table 22 below.

Table 22. The effect of components present in sustainable gases on compression brass fittings. 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).

<table>
<tr><th></th><th>Sulphur containing components</th><th>H_2S</th><th>Mer-captans</th><th>Odorant</th><th>Ammo-nia</th><th>Chlorine containing components</th><th>Fluorine containing components</th><th>HCl</th><th>HCN</th><th>CO</th><th>CO_2</th><th>Hydro-carbons</th><th>Aromatic hydro-carbons</th><th>O_2</th><th>H_2</th></tr>
<tr><td rowspan="2">Compression fittings</td><td colspan="3">water, CO_2</td><td rowspan="2">probably none</td><td rowspan="2">none (with water up to 50 ppm)</td><td colspan="3" rowspan="2">probably none</td><td colspan="2" rowspan="2">unknown</td><td>water, O_2</td><td colspan="2" rowspan="2">probably none</td><td>water, CO_2</td><td rowspan="2">none (up to 20 mol%)</td></tr>
<tr><td colspan="3">water, CO_2 and O_2</td><td>water, H_2S, and O_2</td><td>water, H_2S, CO_2</td></tr>
</table>

4.4 Threaded Joints in Aluminium Components

4.4.1 The Importance of Aluminium in the Dutch Gas Distribution Network

Aluminium is present in the Dutch G-gas transport and distribution network and 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. Most aluminium components contain threaded joints for connection to the gas distribution system.

4.4.2 Test Method

The experimental setup as described in chapter 2 was used to expose aluminium threaded joints to various components in sustainable gases (see also Table 23) for a period of 19 months.

Table 23. Gas compositions to which aluminium threaded joints were exposed.

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

After the experiments, the corrosion samples were cleaned using cleaning methods as described in ASTM G1 [31] 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.

4.4.3 The Influence of Sustainable Gases on Threaded Aluminium Joints under Lab Conditions

No specific experiments were carried out for aluminium threaded joints in existing gas distribution systems. It is expected that the effects of sustainable gases on aluminium threaded joints will be the same as the effects on aluminium materials, since the joint material has the same characteristics as the base material. The effects of sustainable gases on aluminium threaded joints will therefore be the same as the effects on aluminium materials. These are described in "Effects of Wide Band Gases on Distribution Materials" [5].

This report notes that pitting corrosion was observed at machined surfaces (sides of the samples as well as the thread) for gas numbers 3 (no CO_2, 160 ppm H_2S, 3 mol% O_2) and 6 (no CO_2, 34 ppm H_2S, 0.5 mol% O_2), as shown in Figure 40.

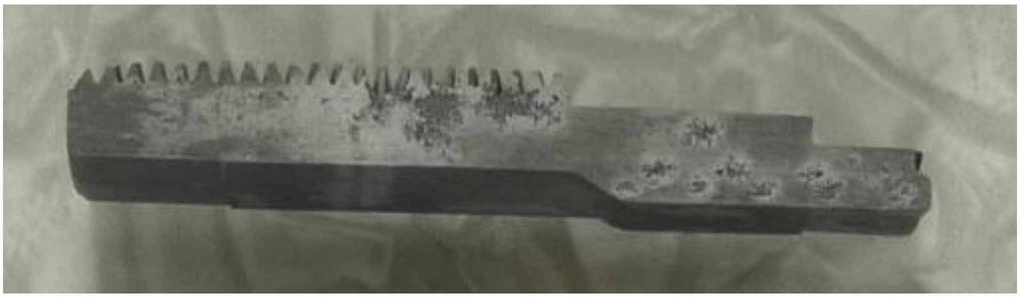

Figure 40. Pitting corrosion on machined surfaces of the corrosion sample after 19-month exposure to gas number 3.

Furthermore, while the highest pitting corrosion rate was observed with gas number 3, the corrosion rate with gas number 6 was also substantial. The corrosion mainly occurred at machined surfaces (both cutting planes and thread), and was rather localised. The number of corrosion pits formed with gas number 3 was higher than with gas number 6. Corrosion was only observed in the water phase. In the field, severe damage to the thread may cause leakage at the threaded connections of components made of aluminium such as the service governor and gas meter bracket.

The corrosion rate increased with increasing H_2S and O_2 concentration. As O_2 does not in itself cause corrosion problems with aluminium, it is assumed that the observed increase in corrosion rate was caused by the increased concentration of H_2S. This was not observed in the presence of CO_2.

The condensation of water in gases containing H_2S without CO_2 may therefore cause corrosion problems with aluminium. Failure of the aluminium components may occur as the result of penetration of the wall thickness and loss of function of the thread of the components.

4.4.4 The Influence of Sustainable Gases on Aluminium under Field Conditions

Disassembled domestic aluminium pressure regulators (service governors) were tested in a field test with biomethane. The samples exposed to biomethane, G-gas and reference samples that were stored in a conditioned laboratory during the field test all showed no attack. It can therefore be concluded that, for aluminium components used in piping systems, no effects are expected from narrow band gas other than those observed in the laboratory test rig.

4.4.5 Conclusions

In the presence of O_2 and absence of CO_2, significant pitting corrosion due to H_2S was observed. This was most prominent on machined surfaces such as the threaded joints of aluminium components. On the basis of the experiments it was concluded that, in the presence of CO_2, no corrosion due to the presence of H_2S will take place. The use of aluminium with gases containing H_2S where CO_2 is not present should therefore be avoided.

The literature revealed that corrosion due to CO_2 alone is also possible. However, this was not investigated experimentally. No negative effect from CO_2 in combination with O_2 was observed for aluminium.

Corrosion was observed in the water phase and was localised on machined surfaces only. As regards aluminium, the importance of drying the gas and preventing water ingress into the low-pressure distribution network must once again be emphasised

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].

The conclusions are summarised in Table 24 below.

Table 24. The effect of components present in sustainable gases on threaded aluminium joints. Some components will have no deleterious effect (green), while for others little or no deleterious effect is expected (light green). The effect of other components is unknown (light orange) or a deleterious effect may be present (orange).

	Sulphur containing components	H_2S	Mercaptans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
Threaded aluminium joints	water and CO_2			probably none	none	probably none			unknown		none	probably none		none	none (up to 20 mol%)
	water and O_2													water, H_2S	

PART II MAINTENANCE, REPAIR AND EXTENSION METHODS

5 Effects during the Maintenance, Repair and Extension of Plastic Piping Systems

5.1 PVC Piping Systems

The literature [1] indicated that the possible negative effects of sustainable gases on PVC piping systems during maintenance, repair or extension are:

- Swelling: the absorption of gases may alter the dimensions of PVC pipes, causing push fittings to no longer fit.
- Embrittlement: when PVC pipes are cut, for example during maintenance, they should not break in a brittle manner over a certain length.

The effect of sustainable gases on both failure mechanisms has already been discussed in "Effects of Wide Band Gases on Distribution Materials" [5] and is therefore not repeated here. The conclusions are summarised in Table 25 below.

Table 25. The effect of components present in sustainable gases on PVC piping systems during maintenance, repair or extension. Some 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).

Material	Sulphur containing components	H_2S	Mer-captans	Odorant	Ammonia	Chloride containing components	Fluoride 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%)

5.2 PE Piping Systems

The literature [1] indicated that the possible negative effects of sustainable gases on PE piping systems during maintenance, repair or extension are:

- Formation of holes and voids during heat fusion welding of PE pipes: absorbed gases may form voids in PE if the temperature is raised for heat fusion of a saddle or electro-fusion coupler.
- Swelling: the absorption of gases may alter the dimensions of the PE pipe, causing mechanical fittings to no longer fit.
- A lower resistance to slow crack growth: when PE pipes are squeezed, for example during maintenance, small cracks can develop. Lack of resistance to slow crack growth will therefore be the main failure mechanism in this case.

The effect of sustainable gases on the last two failure mechanisms has already been discussed in "Effects of Wide Band Gases on Distribution Materials" [5] and is therefore not repeated here. The remainder of this chapter discusses heat fusion welding only.

5.2.1 Heat Fusion Welding of PE Pipes

5.2.1.1 Effects of Aromatics and Aliphatics

PE can absorb about 7 wt% of natural gas condensate [1] and about 6-7 wt% of terpenes. These absorbed gases may be released during the heat fusion process. Research conducted by Kiwa technology [32]has led to the conclusion that an existing PE piping system (HDPE 100) could be electro-fused even if 1 wt% of limonene was dissolved in the PE material. It is unknown if PE can still be fused where higher concentrations of limonene are dissolved. It is therefore recommended that liquid hydrocarbons be prevented from forming in the gas distribution grid.

5.2.1.2 *Effects of Hydrogen*

The studied literature [1] indicated that the effect of hydrogen is unknown. PE materials were tested in the field at concentrations of up to 20 mol% H_2 [33]. No effect for H_2 at up to this concentration level on PE materials was measured. PE does not absorb hydrogen to any great extent. It is therefore not expected that absorbed hydrogen will form holes and voids at the welding zone during heat fusion.

5.2.1.3 *Effects of Hydrogen Sulphide, Chlorine and Fluorine Containing Components and Ammonia*

The experiments [5] performed resulted in no noteworthy mass or dimensional changes in the PE materials after 600 days of exposure. This indicates that no significant absorption or secretion occurred. It is therefore not expected that H_2S, halogen-containing components or ammonia will cause problems during heat fusion.

5.2.1.4 *Carbon Monoxide and Carbon Dioxide*

It is known from experiments at Kiwa Technology that the permeation rate of CO_2 is higher than that of CH_4 in PE pipes. This is mainly because the solubility of CO_2 is higher, which means that more CO_2 can be absorbed by the PE. CO_2 may be released during heat fusion, which may result in holes and voids at the welding zone.

The effect of these gases in combination with the fusion of PE has therefore formed the basis for experiments (see chapter 2). All joints made in the experiments passed the criteria for the various tests performed (see Table 11). This means that PE pipes that have been exposed to 59 mol% CO_2 can be heat fused.

5.2.1.5 *Siloxanes or silicones*

It is well known that silicones (e.g. silicon grease) have a negative influence on the welding performance of PE segments [34]. Silicon grease is normally not found in sustainable gases, but is sometimes used by the constructer for lubrication purposes.

Siloxanes can be present in sustainable gases. These silicon-containing components may have a negative effect on the heat fusibility of PE pipes. Although it is necessary to scrape the outer layer of the pipe for electro-fusion (mainly for oxidation purposes), it is possible that absorbed siloxanes could affect the weld quality. Another hazard is that the cloth used by the welder to clean the outer surface of the pipe may come into contact with the interior of the pipe, thus transferring siloxanes to the welding surface.

The effect of these gases in combination with the fusion of PE has therefore formed the basis for experiments (see chapter 2). All joints made in the experiments passed the criteria for the various tests performed (see Table 11). This means that PE pipes that have been exposed to a mixture of organo-silicons can be heat fused.

5.2.1.6 *Effects of Other Components*

The literature [1] did not indicate that problems with the fusion of PE materials as the result of other components present in sustainable gases were expected.
PE pipes were nonetheless also tested in a field test. Several heat fusion joints were also made using exposed PE pipes (see chapter 2). All joints made in the experiments passed the criteria for the various tests performed (see Table 11). This means that PE pipes that were exposed to biomethane (narrow band gases) can be heat fused.

5.2.2 Conclusions

The overall results for the effect of components present in sustainable gases on slow crack growth (SCG), dimensions (swelling) and heat fusion (fusion) for polyethylene (PE50, PE 80 and PE 100) are given in Table 26.

Table 26. The effect of components present in sustainable gases on PE piping systems during maintenance, repair or extension. Some 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).

	siloxanes	Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chloride containing components	Fluoride containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
PE *(scg)*	None	none (up to 160 ppm)		probably none		None			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
PE *(swelling)*	None	none (up to 160 ppm)		probably none		None			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
PE (fusion)	None	none (up to 160 ppm)		probably none		None			probably none		unknown	none	none, unless liquid		none	probably none

6 Effects during the Maintenance, Repair and Extension of Metal Piping Systems

In order to maintain, repair or extend metallic piping systems, the metallic materials involved must have a suitable wall thickness. The mechanical strength of these metallic materials is dependent only on the material quality and wall thickness. An inspection of the metallic materials prior to maintenance, repair or extension should therefore be performed in order to determine whether the planned work can be executed. If the material has insufficient wall thickness as a result of corrosion, then the pipe cannot be welded and must be replaced.

Because the ability to maintain, repair and extend existing metallic piping systems is dependent on the quality of the existing piping as determined through inspections prior to planned work, the composition of a “traffic light diagram” for the different gas components is not useful. No concluding tables are therefore given in this chapter.

6.1 Steel Piping Systems

6.1.1 Welding

As the pipe wall is cleaned and bevelled by grinding prior to welding, which removes any impurities on the pipe surface, no specific effects on the weldability of steel for the gas components under consideration is expected. The severity of corrosion resulting from the gas components is described in the narrow band and wide band reports [4,5].

6.1.2 Threaded Joints

Threaded joints in steel piping system are not usually loosened and refitted after initial mounting. Where a threaded joint that has been corroded as a result of exposure to gas components is loosened and refitted, difficulties may occur in obtaining a tight joint. This will however be noticed during either installation or pressure testing of the joints.

6.2 Copper Piping Systems

Brass compression and press fittings in copper piping system are not usually loosened and refitted after initial mounting. Where a joint that has been corroded as a result of exposure to gas components is loosened and refitted, difficulties may occur in obtaining a tight joint. This will however be noticed during either installation or pressure testing of the joints.

6.3 Threaded Joints in Aluminium Components

Threaded joints in aluminium components can be loosened and refitted after initial mounting for maintenance or repair. Where a joint that has been corroded as a result of exposure to gas components is loosened and refitted, difficulties may occur in obtaining a tight joint. This will however be noticed during either installation or pressure testing of the joints.

7 Conclusions

The influence of various components in sustainable gases on existing joints in the Dutch gas distribution grid is summarised in Table 27. The influence of components present in sustainable gases on joints made during the maintenance, repair or extension of plastic piping systems is summarised in Table 28.

Table 27. The effect of components present in sustainable gases on existing joints in the Dutch gas distribution grid based on literature review and experiments.

Existing joints															
	Sulphur containing components	H_2S	Mercaptans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
PVC coupler with sealing ring	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
PE heat fused joints	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
POM coupler with sealing ring	none (up to 160 ppm)		probably none		none			water	unknown		none	probably none			none
steel welded joints & steel threaded joints	water, CO_2		probably none						with H_2S and water: possibly	unknown	water, H_2S	probably none		water, (H_2S), CO_2	none
	water, CO_2 and O_2										water, (H_2S) and O_2				
Compression brass fittings	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_2S, and O_2			water, H_2S, CO_2	
threaded aluminium joints	water and CO_2		probably none		none	probably none			unknown		none	probably none		none	none (up to 20 mol%)
	water and O_2													water, H_2S	

Table 28. The effect of components present in sustainable gases on joints made in plastic piping systems during maintenance, repair and extension based on literature review and experiments.

Joints made during maintenance, repair and extension																
Material	Siloxanes	Sulphur containing components	H_2S	Mercaptans	Odorant	Ammonia	Chloride containing components	Fluoride containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
PVC piping systems	none	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)
PE piping systems	none	none (up to 160 ppm)		probably none		none			probably none		unknown	none	none, unless liquid		none	none (up to 20 mol%)

⬜	=	The effect is unknown but is expected to be very small or non-existent.
🟩	=	This component in sustainable gases does not affect joints.
🟨	=	The effect is unknown.
🟧	=	Deleterious effects are expected under some conditions.

For the most important existing joints in polymeric materials (PVC/POM coupler with sealing ring and heat-fused joints) used in the Dutch gas distribution grid, no negative effects are expected for any component at levels up to the maximum concentrations found in sustainable gases. This is valid with the following exceptions:

- Due to health and safety reasons, the effect of H_2S at higher concentration then 160 ppm in sustainable gases on the most important polymeric materials and joints was not tested. Although no deleterious effect on PVC, PE, POM and rubber 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 sustainable gases on polymeric materials and joints was not tested. The effect of this gas component is therefore still unknown.
- Due to health and safety reasons, the effect of HCN in sustainable gases on POM was not tested. The effect of this gas component is therefore still unknown for POM materials and joints.
- The presence of any liquid aromatic hydrocarbons will negatively affect the mechanical properties of the most important polymeric materials and joints.
- Low concentrations of HCl in combination with water vapour can have a destructive effect on POM materials and joints.
- The effect of H_2 at higher concentration than 20 mol% in sustainable gases on PVC and PE materials and joints was not tested. Although no deleterious effect on these materials and joints was measured at this concentration level, the effect of this gas component at higher concentrations is still unknown.

For the most important existing joints in metallic materials (steel welded joints, steel threaded joints, brass compression and press fittings and aluminium threaded joints) 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 brass joints, 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 of the above-mentioned joints. When this combination of gas components occurs an acceptable corrosion rate on steel joints 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 acceptable 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 joints. Completely removing O_2 from the humid gaseous environment is also a good solution for these materials and joints. However, a wider composition range is permissible for copper and aluminium joints. For both copper and aluminium joints it is also effective to completely remove H_2S. For copper and especially aluminium joints 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 or joints. The minimum concentration level of CO_2 to prevent this severe corrosion is unknown. For brass fittings the influence of 50 ppm NH_3 in humid gas had no negative effect.

Based on literature corrosion due to CO_2 alone is also possible for both copper and aluminium joints. However, this was investigated further in the experiments carried out.

The effect of HCN and CO in sustainable 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 joints. The effects of HCN on copper and aluminium joints remain unknown. Also the effect of CO on all three metals is still unknown.

Sustainable gases had no effects (e.g. swelling and desorption during fusion) on the performance of joints made during maintenance, repair or extension in plastic piping systems. Therefore, no extra precautions are needed in addition to the ones mentioned earlier. This also applies to joints made during the maintenance, repair or extension in metal piping systems.

8 Recommendations

The most significant recommendation that would enable the existing Dutch gas distribution grid to transport sustainable 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) or vapour condensation of acidic water, which is destructive to POM, cannot occur. Only a few restrictions on the maximum allowable concentrations of gas components in sustainable gases are recommended.

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

- Increasing the distribution pressure to 100 mbar(g). At 100 mbar(g) gas pressure the risk of ground water entering the gas grid (water ingress) is significantly lower than at 30 mbar(g) gas pressure.
- Decreasing the water dew temperature of the gas at gas entry points. In other words, the gas must be dried (the relative humidity must be lowered) before it enters the gas distribution grid. This solution deserves a prominent role in the processing of sustainable 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 sustainable 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 sustainable 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 H_2S). 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 the gas components may be possible. It is therefore recommended that HCN and CO should be prevented from entering the gas distribution grid or that their concentration should at least be kept as low as possible. It is recommended to limit the maximum concentration of H_2S to 160 ppm.

Finally, the literature was inconclusive about the effects of H_2 on some materials. The effects of H_2 were tested up to 20 mol%, while the concentration in sustainable gases could be as high as 62 mol%. Therefore, the effect of H_2 at higher concentrations remains unknown for PVC, PE, copper and aluminium. It is therefore recommended that the maximum concentration of H_2 be limited to 20 mol%.

The above-mentioned recommendations are summarised in Table 29 where water is not present in the existing Dutch gas distribution grid. Limiting values for other gas components in sustainable gases are not required.

Table 29. Recommended limiting values for several gas components in sustainable gases where water is not present in the gas distribution grid or in sustainable 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 joint materials. Although only traces of these substances are currently found in sustainable 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 of 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 joints 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_2S	The effect of H_2S 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 joints used in the Dutch gas distribution grid, it is recommended that the maximum concentration of H_2S 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 joints. 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 H_2S, CO_2 and O_2 may lead to severe corrosion in steel, copper and aluminium. The combination of HCl and high humidity also causes damage to POM materials.

For POM materials it is therefore important to keep the relative humidity of the gases low to prevent the condensation of water. Furthermore, it is recommended that the concentration of HCl be kept as low as possible. A limiting value of 0.1 ppm is recommended for HCl.

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

- H_2S should be limited to 34 ppm
- CO_2 should be limited to 10.3 mol%
- O_2 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 CO_2. More research using low CO_2 concentrations is therefore recommended.

Finally, the effects of NH_3 on brass fittings were tested at concentrations of up to 50 ppm in humid gas. The literature was inconclusive about the effects of 100 ppm NH_3 (which may occur in sustainable gases) on copper and brass fittings. The effects of NH_3 at concentrations of up to 100 ppm is therefore currently unknown for copper materials with brass fittings. More research using higher NH_3 concentrations is recommended.

When water is present in the gas grid or in sustainable gases additional recommendations to the ones given in Table 29 are needed and given in Table 30. Limiting values for other components in sustainable gases are not required.

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

Limiting value	**Reason**
< 34 ppm H_2S	The combination of H_2S, 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	
< 0.1 ppm HCl	Where low concentrations of HCl occur in combination with the condensation of water, the formation of acidic water cannot be ruled out. This acidic water has a destructive effect on POM materials. It is therefore recommended that the concentration of HCl in sustainable gases be limited as much as possible.
< 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_2S and O_2 come into contact with aluminium or copper in the absence of CO_2, severe corrosion may occur. It is unknown if CO_2 must also be present for the above proposed limiting values. More research using low CO_2 concentrations is therefore recommended.

I The Influence of HCl Vapour on POM

In this appendix the question will be answered why 3 ppm HCl vapour attacks hPOM and especially cPOM to such an extent. The reason why the tested cPOM was attacked more than hPOM is already discussed in 3.3.1.2. This resin showed less favourable mechanical characteristics compared to other cPOM resins and was therefore removed from the market by the manufacturer.

The HCl partial pressure was 3 ppm at ambient pressure (1 bar(a)). It is assumed that at 3 ppm and 1 bar(a) pressure the partial pressure of HCl is $3/10^6$ bar is 3×10^{-6} bar. At 8 bar(g), the absolute pressure is 9 bar(a). This means that at 8 bar(g) the HCl partial pressure becomes 9 multiplied 3×10^{-6} bar, which makes 2.7×10^{-5} bar.

The relative humidity (RH) inside the testing cabinet was approximately 82 %. However, at certain moments, during a certain time, condensation of water vapour to form small droplets of liquid water was possible. If such a water droplet forms on the surface of the POM test bars, hydrochloric acid will readily dissolve into it. This acid dissolves so well, that its concentration in water will be become higher than in nitrogen, which is used as matrix gas.

It can be calculated how much increase in concentration this is, by using the Henry partition (or distribution) coefficient [35]. Henry's Law [35] describes the relation between the partial pressure of a gas or vapour above a liquid and the concentration of this gas of vapour when it is dissolved in that same liquid. For hydrogen chloride vapour and water the equation is:

$$\textit{Partial Pressure of HCl (bars)} = \textit{HC} * \textit{concentration of HCl in water (mol/m}^3\textit{)} \qquad (1)$$

The value of this Henry's Law constant (*HC*) for hydrogen chloride vapour is 19 mol/(litre×bar) [36].

It can now be calculated what the concentration of hydrochloric acid in a water droplet becomes, if such a water droplet is formed by condensation. According to [36] it is:

$$\begin{aligned} \text{Concentration of HCl in a water droplet} &= 19 * 2.7 \times 10^{-5} \text{ mol/litre} \\ &= 5.13 \times 10^{-4} \text{ mol/litre.} \end{aligned}$$

The pH value inside a droplet can now be calculated:

$$\begin{aligned} \text{pH} &= -\log(5.13 \times 10^{-4}) \\ \text{pH} &= 3.3 \end{aligned}$$

This pH value is rather acidic. HCl gas dissolves rather readily in water.

At certain moments in time the humidity may fall below 100 % and then the water droplets will want to evaporate again. This evaporation may be retarded by the HCl that is dissolved (boiling point elevation by dissolved substances) but eventually the droplets may evaporate completely. However, during this process, as the water droplet shrinks very much in size, the concentration of HCl in it may rise very quickly, and the pH might drop well into the very acidic region ($pH < 1$). It is unknown how low pH values can be reached and how long these low pH values will have prevailed. However, it is very likely that condensation of water droplets containing dissolved HCl and evaporation of the droplets followed by a period of very high acidity in a shrinking droplet occur.
Under these circumstances it is understandable that clear degradation of hPOM and cPOM by HCl can occur, but only at a shrinking droplet and not at other locations. This is exactly what is seen in Figure 33 and Figure 36.

Apparently, after about 600 days of exposure and in the presence of relatively acidic water droplets, hPOM is attacked.
The high Henry coefficient and the “condensation effect” explain why the average ultimate tensile strength of the POM tests bars after exposure to only 3 ppm HCl is reduced to an statistically significant extent and the standard deviation is larger than for the reference (as received) dumbbells.

II 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.

II.1 Polyvinyl Chloride (PVC)

For the results of all PVC experiments, see [4] and [5].

II.2 Polyethylene (PE)

For the results of all PE experiments, see [4] and [5].

II.3 Elastomeric Materials (NBR)

II.3.1 Mass Change

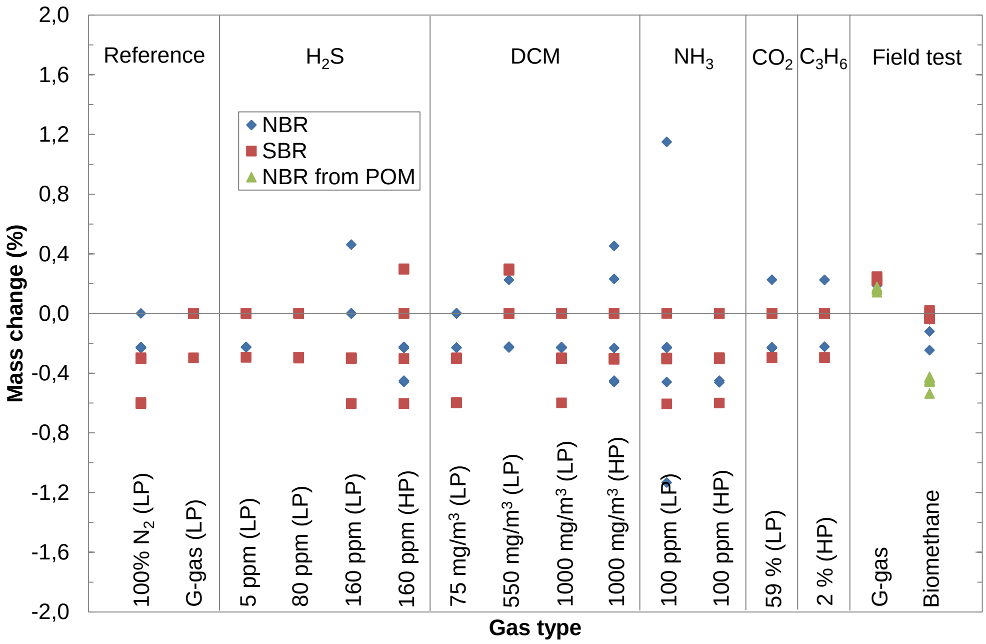

Figure 41. Mass change of NBR (blue), SBR (red) and NBR from POM couplers (green) samples which had been exposed for a period of 600 days to various sustainable gases. LP is low pressure. HP is high pressure.

II.3.2 Mechanical Properties

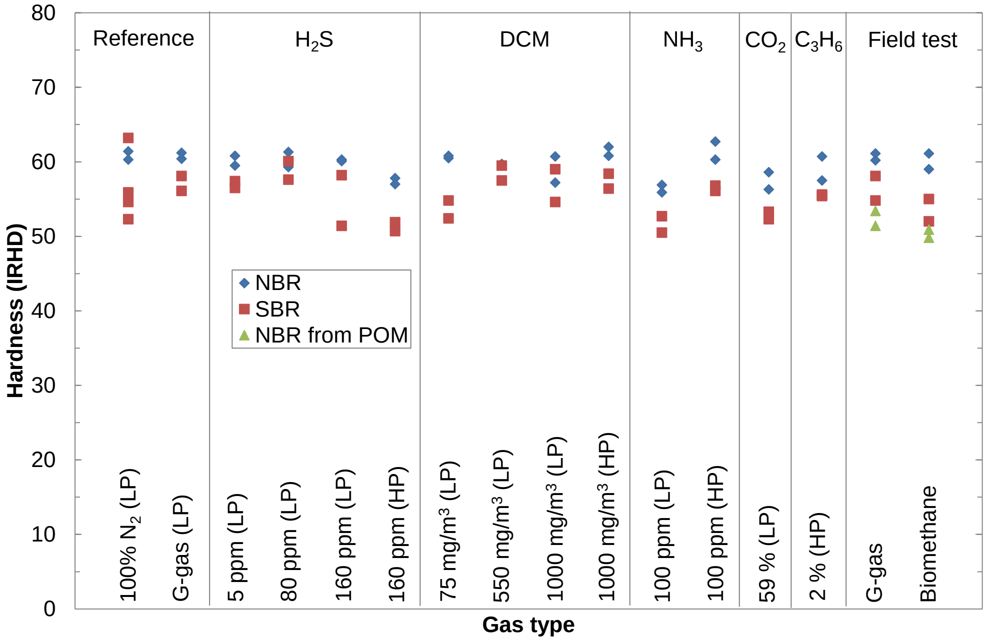

Figure 42. Hardness of NBR (blue), SBR (red) and NBR from POM couplers (green) samples which had been exposed for a period of 600 days to various sustainable gases. LP is low pressure. HP is high pressure.

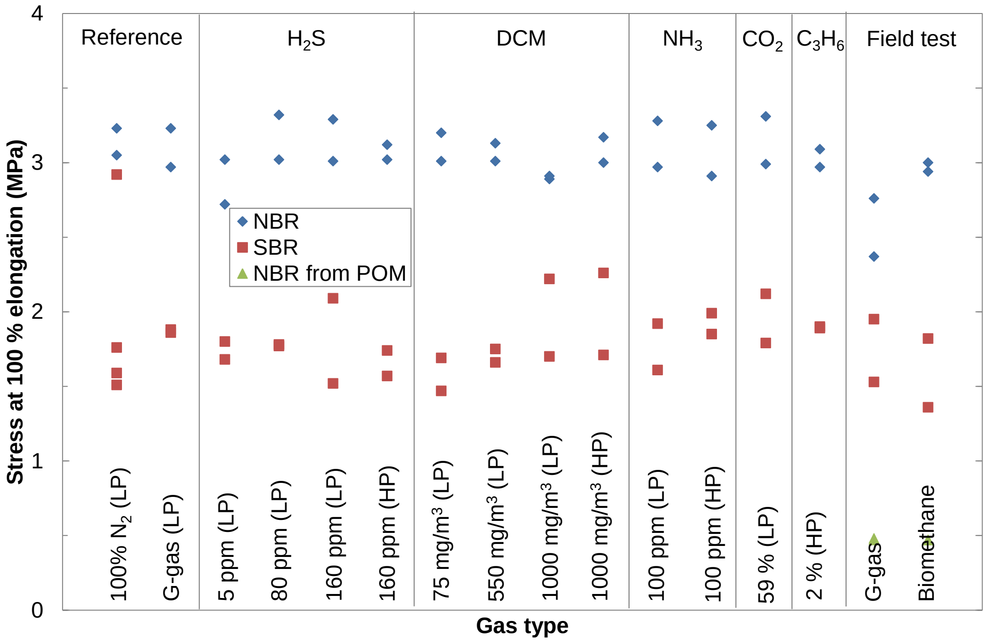

Figure 43. Stress at 100 % elongation of NBR (blue), SBR (red) and NBR from POM couplers (green) samples which had been exposed for a period of 600 days to various sustainable gases. LP is low pressure. HP is high pressure.

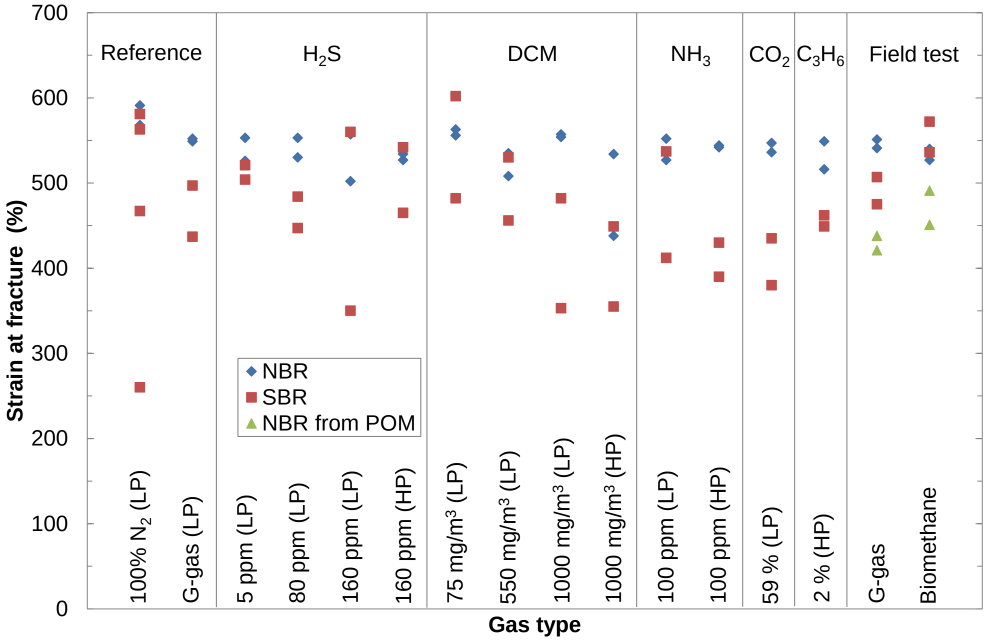

Figure 44. Strain at fracture of NBR (blue), SBR (red) and NBR from POM couplers (green) samples which had been exposed for a period of 600 days to various sustainable gases. LP is low pressure. HP is high pressure.

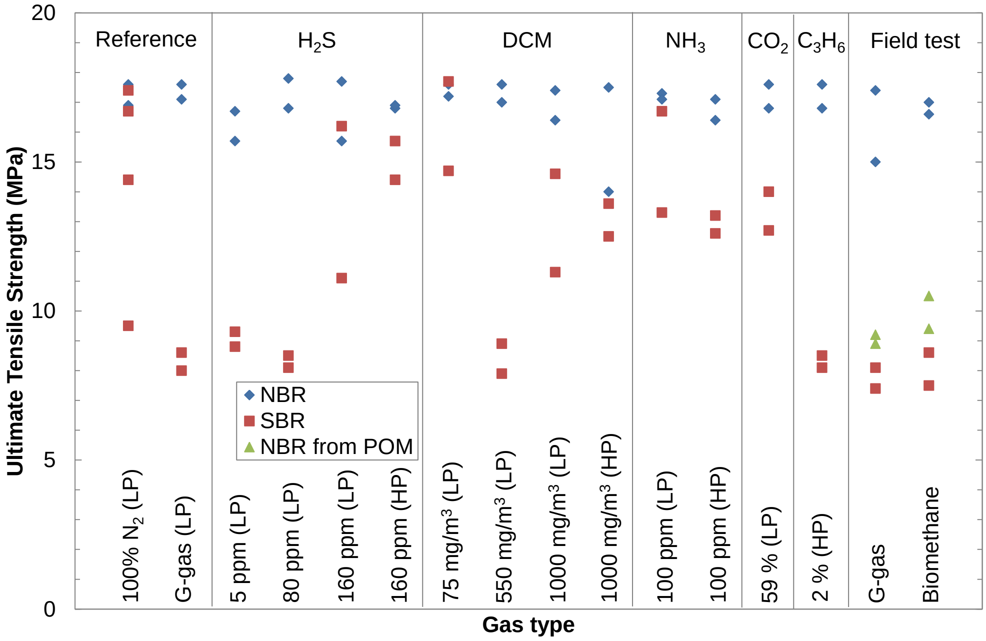

Figure 45. Ultimate tensile strength of NBR (blue), SBR (red) and NBR from POM couplers (green) samples which had been exposed for a period of 600 days to various sustainable gases. LP is low pressure. HP is high pressure.

II.3.3 Dimensional Change

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

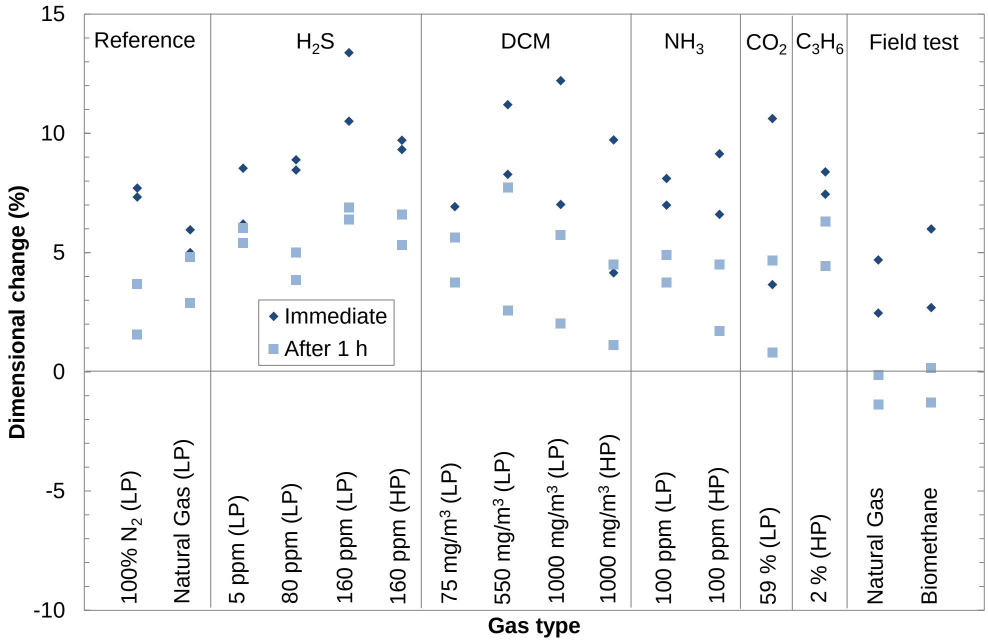

Figure 46. The difference in inner diameter of NBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

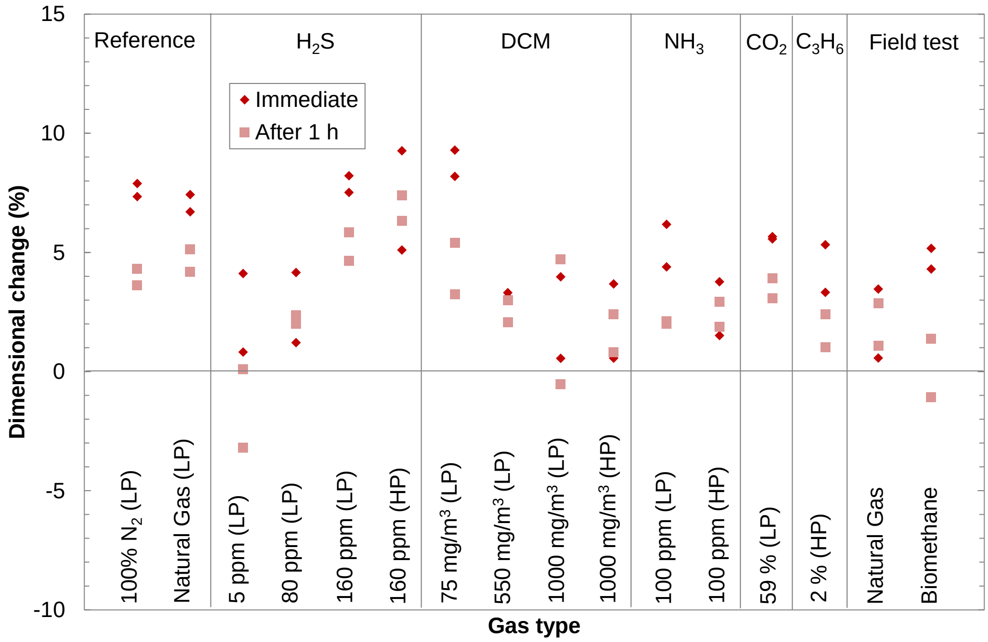

Figure 47. The difference in inner diameter of SBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

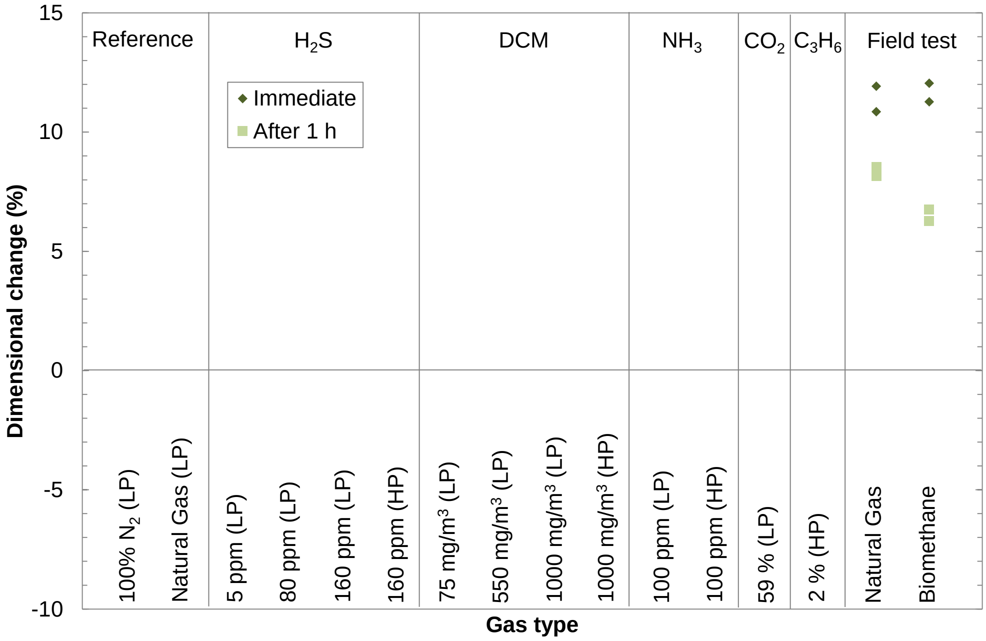

Figure 48. The difference in inner diameter of NBR rings from POM couplers which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

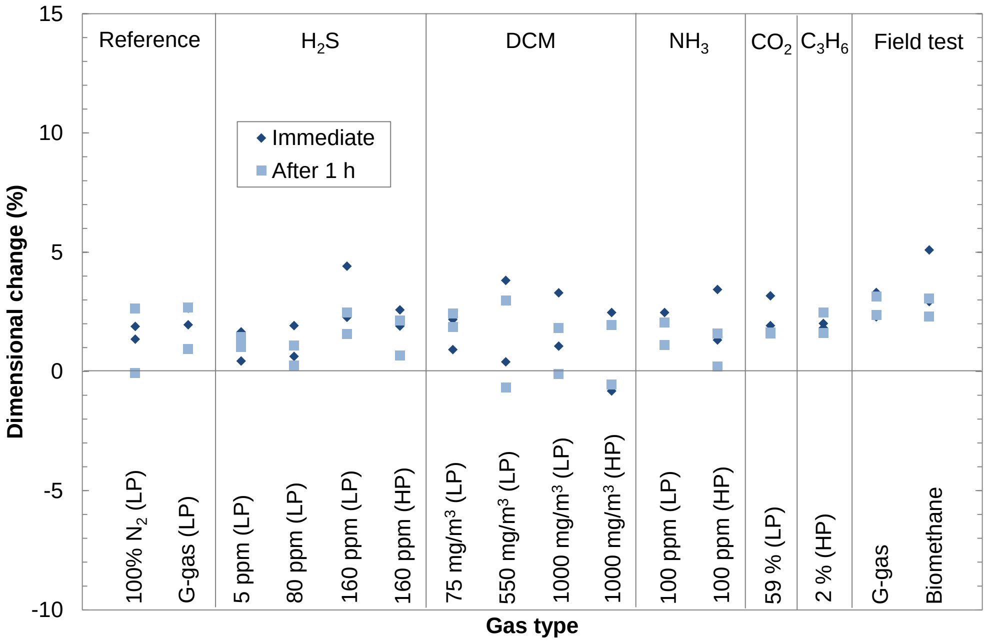

Figure 49. The difference in outer diameter of NBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

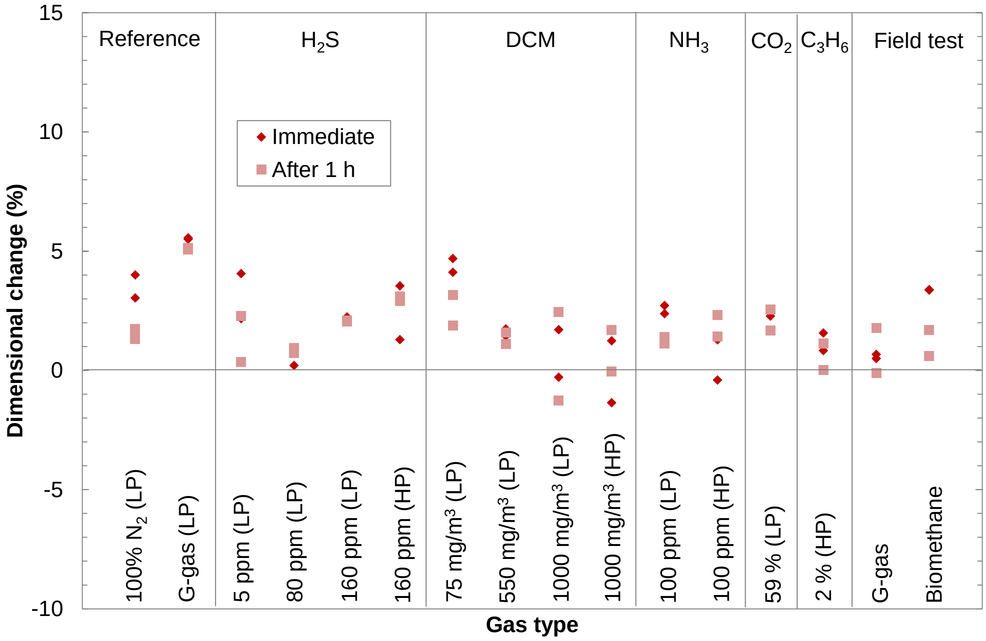

Figure 50. The difference in outer diameter of SBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

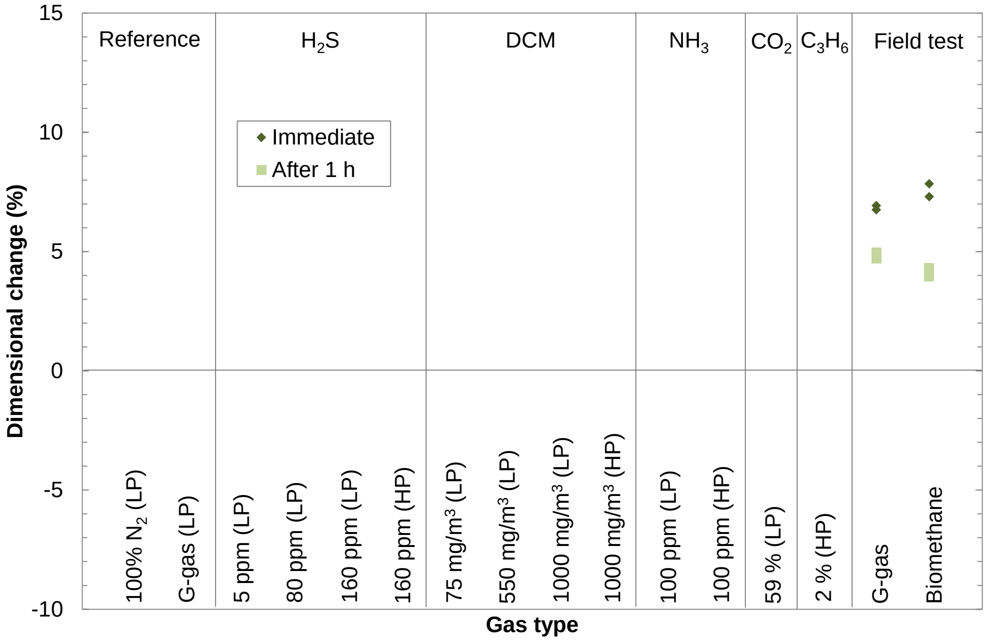

Figure 51. The difference in outer diameter of NBR rings from POM couplers which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

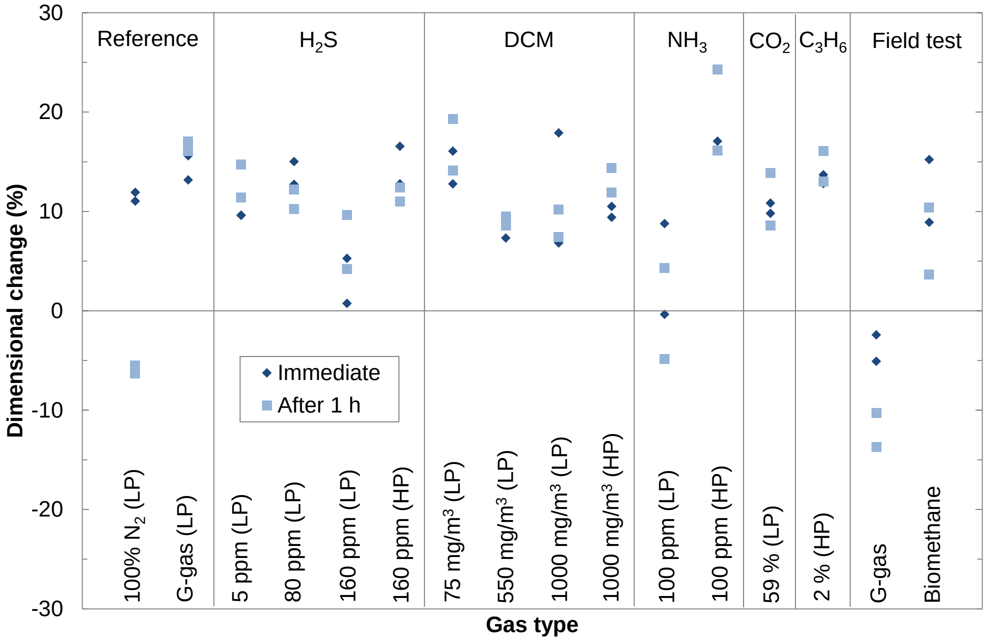

Figure 52. The difference in thickness of NBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

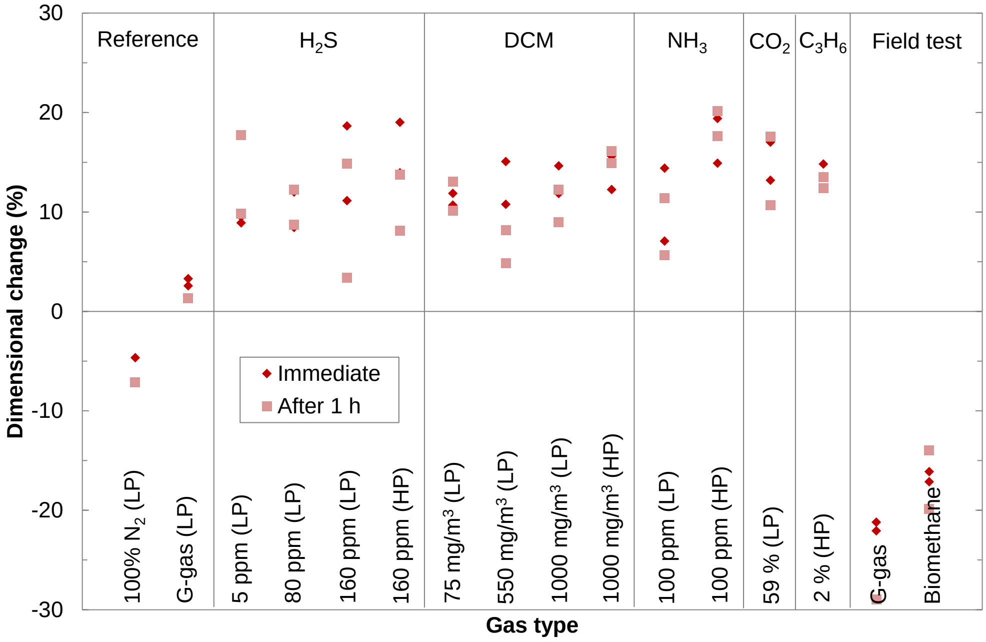

Figure 53. The difference in thickness of SBR rings which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

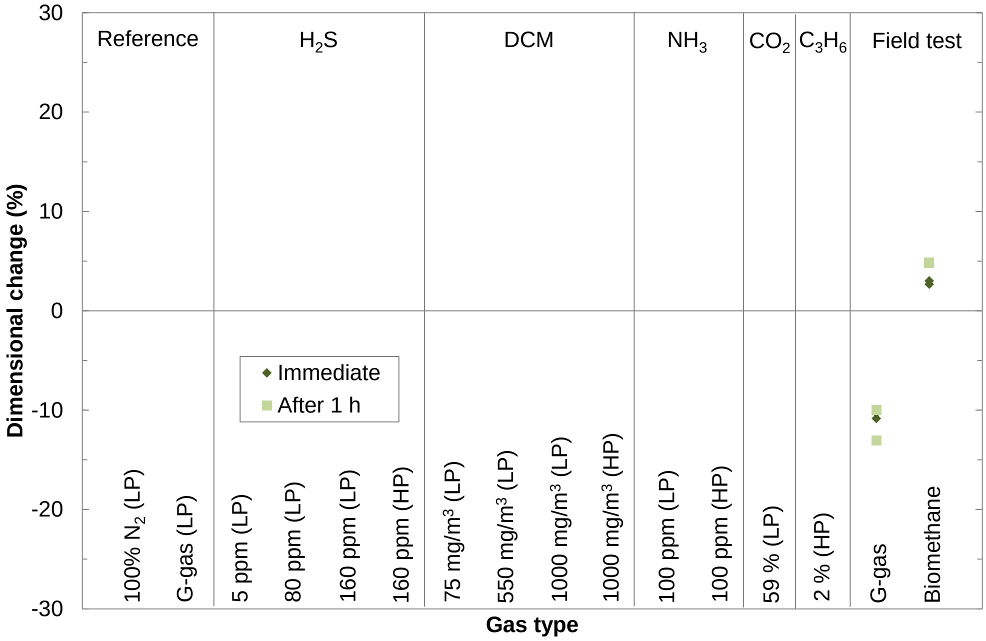

Figure 54. The difference in thickness of NBR rings from POM couplers which had been exposed for a period of 600 days to various wide band gases. LP is low pressure. HP is high pressure.

II.4 Steel

For the results of all steel experiments, see [5].

II.5 Copper

For the results of all copper experiments, see [5].

II.6 Aluminium

For the results of all aluminium experiments, see [5].

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