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

Literature Review

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Colophon

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Preface

This literature report is part of the EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems Expanding the Distribution Band of the Gas Quality in the Netherlands". The working title of this project is "Effects of Wide Band Gases on Materials". It is part of the EDGaR program sub theme 1.2.

The following partners are involved in this project:

- Enexis
- Liander
- Stedin
- Gasunie
- Kiwa

Kiwa is the project leader.

This project is closely related to the research project with working title "Effects of Narrow Band Gases on Materials" and "Impact of Sustainable Gases on Joints used in Gas Distribution Systems". The literature reports for these projects are numbered GT-110204 and GT-110207 respectively.

Summary

The existing Dutch gas infrastructure has been designed for distribution of (pseudo) Groningen gas (G-gas). Network operators explore the possibilities to make the gas supply more sustainable and to extend the variety of gas sources. Because the process of upgrading sustainable raw gases to narrow band gases is expensive, the next step will likely be minimizing this process. This will save costs, but it will also lead to new gas compositions. These gases are called wide band gases and are researched in this EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems Expanding the Distribution Band of the Gas Quality in the Netherlands".

The following main research question will be answered:
What are the maximum allowable concentrations of gas components in wide band gases when using the existing Dutch gas infrastructure for the transport of these gases?

In the first phase of this project several scientific and technological date sources of relevant literature have been studied. All the results of this literature review are summarised in the table below.

	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	unknown		probably none		unknown			probably none		unknown	possibly	none, unless liquid (impact resistance)		probably none	unknown
PE	unknown		probably none		unknown			probably none		unknown	none	none, unless liquid		none	probably none
NBR	unknown	possibly	probably none		none	possibly		probably none		none		possibly, if unsaturated	probably none, unless liquid	none	
Steel	with water: possibly		probably none						with H_2S and water: possibly	with water: possibly		probably none		with water: possibly	none
Cu	with water: possibly, depending on their mutual influence			probably none	with water: possibly	probably none			unknown		with water: possibly	probably none		with water: possibly	unknown
Al	unknown			probably none	none	probably none			unknown		with water: possibly	probably none		none	unknown

🟢	=	The effect is unknown, but is expected to be very small or non existent.
🟩	=	This component in wide band has no effect on the material.
🟧	=	The effect is unknown.
🟥	=	Deleterious effects are under some conditions to be expected.

It is too early to conclude anything about the maximum allowable concentrations of gas components in wide band gases, because a deleterious effect of various components in wide band gas cannot be excluded for some of the most important materials in the Dutch gas network.

Additional experimental work, focussed on gases with a possible negative effect, will therefore be performed in the following phase of this EDGaR research project.

Contents

1 Introduction

1.1 Goal

In this project the following main research question will be answered:

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

In this respect the following sub questions are relevant:

a) What exactly are wide band gases?
b) What are the gas component-material combinations which are most likely to show premature failure within the desired lifetime?

In order to study the gas component–material combinations, the following sub questions have to be answered:

c) What are the critical failure mechanisms of the pipeline materials under study?
d) Can these failure mechanisms be modelled to establish maximum gas component concentrations?

The main goals in this project therefore are:

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

Although life expectancy of assets is not only limited by technical aging [1], the present literature review will only be focussed on this aspect. It will give a summary of the published knowledge about the resistance of the main materials, used in gas networks, to components in wide band gases. It will also indicate possible gaps in the knowledge, in which area further research is necessary.

Please note that the objective of this literature review is not to be exhaustive with respect to the components in wide band gas and the materials used in the Dutch gas distribution network. Therefore various trace components may be absent in answering sub question a) and it is emphasised that only the most important materials are discussed.

The effects of wide band gases on the Dutch gas transport network are investigated by Gasunie / Kema, and will be summarised in a separate report.

1.2 Background

To make the gas supply more sustainable and to extend the variety of gas sources, the network operators explore the possibilities to use the existing gas infrastructure, to which almost all customers in the Netherlands are connected, for transport and distribution of gases originating from these many sources. In this way sustainable gas supply can make use of the full existing natural gas infrastructure (pipeline systems, appliances, industrial installations, etc.), in the most cost-effective manner.

Due to the tendency to replace fossil fuels by sustainable gases, such as biogas, SNG et cetera, a rapidly expanding variety of gases should preferably be transported and distributed through the above-described gas infrastructure. The introduction of these sustainable gases is likely to start with upgraded (narrow band) gases, which are cleaned before they are fed into the natural gas grid. In several countries, national specifications for these narrow band gases are valid [2]. These upgraded and cleaned gases have comparable compositions and properties as the natural gas used to date (Groningen gas or G-gas), though some components may deviate in concentration from those in G-gas. The limits made for narrow band gases are however arbitrary and a solid foundation is missing. Research may lead to adjustments of these limits. This research is performed in another project ("Effects of Narrow Band Gases on Materials used in Gas Distribution Networks - Literature Review", report GT-110204).

Because the process of upgrading sustainable raw gases to narrow band gases is expensive, the next step will likely be minimizing this process. This will save costs, but it will also lead to new gas compositions. These gases are called wide band gases and do not fulfil the requirements used for narrow band gases as mentioned in report GT-110204.

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

Table 1. Definition of narrow band and wide band gases with Groningen gas.

G-gas	**narrow band gas**	**wide band gas**
Groningen gas (used as reference gas)	Pseudo - Groningen gas, e.g. upgraded biogas to "green gas" quality (see report GT-110204)	All other sustainable gases, e.g. raw biogases, partially upgraded sustainable gases, SNG and other natural gases (e.g. H-gas)

In the present literature review the focus will be on the effects of the transport of wide band gases on materials used in gas distribution systems. Two other reports will review the influence of narrow band gas on the Dutch gas distribution network and the influence of sustainable gases on joints and connections, respectively. Another literature review performed by Gasunie will discuss the effects of transport of wide band gases on materials used in gas transport systems.

1.3 Approach

Several sources of relevant literature have been studied:

- Literature already available in the literature database of Kiwa Technology
- The (now disappeared) Dutch monthly magazine “Gas”
- References present in the proceedings of technical conferences, such as:
    - Plastics Pipes I until XVI
    - AGA Plastic Fuel Gas Pipe Symposia
    - Plastic Pressure Pipes conferences
    - International Gas Research Conferences
- The scientific database STN Easy (FIZ Karlsruhe)
- International and national standards

The references that have been used in this report are listed in Appendix VI: References.

Next, these literature sources were evaluated in the light of the questions a) until d) and the main goals A and B listed in section 1.1. Many sources contain results that are not completely in the compositional area of interest in the present literature review. Therefore in many cases assumptions and extrapolations had to be made. Moreover, some sources reported contradictory results. To resolve this, differences in exposure parameters, evaluation (testing) procedures and the concentration range of influential chemical components and their combinations had to be taken into account. In case that was unsuccessful, assumptions were made or it was proposed to perform additional tests.

1.4 Reading Guide

In chapter 2 sub question a), the definition of wide band gases, is defined. To answer sub question b) it is important to know what kind of materials are used in the Dutch gas distribution network. This is discussed in chapter 3. In this chapter practical failure data is analysed as well to review the failure mechanisms of the most important materials. These answers partly sub question c).

Chapters 4 and 5 answer sub question c) in more detail focussing on the failure mechanisms of polymeric materials and metals respectively. These chapters also include a discussion on sub question d) if these failure mechanisms can be modelled. At the end of each section the conclusions will be presented.

It will not be possible yet to answer the main goals A and B dealing with components in wide band gases resulting in unacceptable lifetime reductions of certain materials. Answering this question will be the aim of the experimental testing programme that is foreseen as the next phase of this EDGaR project. This experimental work will not only lead to answers about the influence of certain components in wide band gases but also gives information on these effects under practical circumstances of long-term exposure and what the limiting concentrations need to be.

This literature review ends with the overall conclusions in chapter 6.

2 Definition of Wide Band Gas

Wide band gas is defined as all sustainable gases, including raw gases and partially upgraded sustainable gases. This means that the physical properties (like Upper Calorific Value and Wobbe index) and the chemical composition of wide band gases are different from narrow band gas or G- gas and that the composition ranges can be very broad.

Possible wide band gases are:
- Gas from anaerobic digestion
- Syngas/SNG
- Imported natural gases
- Hydrogen

These gases are discussed in the paragraphs 2.1 until 2.4. In paragraph 2.5 a comparison in composition is made between the various wide band gases and G-gas.

2.1 Gas From Anaerobic Digestion

In the anaerobic conversion of biomass and waste, organic materials are microbiologically converted to methane (CH_4), carbon dioxide (CO_2) and water (H_2O). This gas is also called "biogas". The rate of the anaerobic digestion is determined by the composition of the reaction mixture and the temperature. The rate of reaction increases with higher temperatures. This increase of the reaction rate is limited by the stability of the microbiological agents in this process. Temperatures up to 55 °C are however feasible.

Examples of anaerobic conversion processes for the production of biogas are:
- Sewage treatment plants. Many sewage treatment plants produce methane rich gases in the sludge fermentation stage. Utilisation of methane from sewage plants is used on a large scale in many countries.
- Landfills. All landfills produce methane rich gases. Collection and utilisation of the gases is reasonably widely applied.
- Cleaning of organic industrial waste streams. Anaerobic digestion processes are often successfully applied to clean the waste streams of agricultural processing industry.
- Mesofilic and thermophilic digestion of organic waste (farm biogas plants). Compact installations convert at higher temperatures organic waste to methane rich gases. The main difference between the two methods is the digestion temperature (35 °C in the mesofilic process and 55 °C in the thermofilic process).

Although the biological processes are the same for the different methods, the chemical composition of the gases is different. Landfill gas mainly consists of components of biological origins, but contaminants that are present in the landfill such as solvents, propellants and chemicals, can lead to unusual and unwanted trace gas components. Gas from sewage sludge digestion has less harmful components. However, traces of halogenated hydrocarbons and organo-silicon components do occur. Gas from mesofilic and thermophilic digestion contains high concentrations of hydrogen sulphide (H_2S) and other sulphur containing compounds, but contains almost no other polluting components. Appendix I shows the compositions of the different gases from anaerobic digestion.

2.2 Syngas/SNG

Syngas (from synthetic gas or synthesis gas) is a gas mixture that contains varying concentrations of carbon monoxide (CO) and hydrogen (H_2). Examples of production methods include steam reforming of natural gas or liquid hydrocarbons to produce hydrogen, the gasification of coal, biomass and the use of some types of waste-to-energy gasification facilities [3,4]. Syngas is used as intermediate in creating substitute natural gas (SNG) and for producing ammonia or methanol.

Substitute natural gas (usually abbreviated to SNG, also known as synthetic natural gas) is a generic term for natural gas substitutes that are produced by chemical processes. SNG can be made of various hydrocarbons, which could originate from heavy fractions of oil refining, coal or biomass. Using biomass it is called bio-SNG. [5]

2.3 Imported natural gases

This group includes all gases that are transported to the Netherlands. This could be by pipeline or as LNG. Liquefied natural gas (LNG) is natural gas that has been converted temporarily to liquid form for ease of storage and transport. Imported natural gas will not have the same physical properties or chemical composition like Groningen gas (G-gas), because the natural gas could come from all over the world and every natural gas well (including shale gas) has its own composition.

2.4 Hydrogen

Although there are still numerous questions about the actual realization of a possible transition towards a hydrogen economy, hydrogen could play an important role in the future energy supply. Currently the dominant technology for direct hydrogen production is steam reforming from hydrocarbons, which is less sustainable than for instance electrolysis of water using wind or solar power.

2.5 Chemical Composition of the Different Wide Band Gases

In Table 2 a global overview of the concentrations of different chemicals, which have been found in anaerobic digested gas, SNG, gas that has been transported to the Netherlands by LNG or pipeline, are given. This is compared to the known concentrations in G-gas [6]. The main differences between the wide band gases and G-gas can be found in the concentrations of CO, CO_2 and H_2 and various chemicals, which can especially be found in anaerobic digestion gases, such as ammonia, oxygen, aromatic hydrocarbons (including BTX), H_2S and organo-silicons.

For safety reasons G-gas is been odorized in the Netherlands by using tetrahydrothiophene (THT). Mercaptans, used in other countries as odorant, are not used for this purpose in the Netherlands. THT is a heterocyclic organic compound consisting of a five-membered ring containing four carbon atoms and a sulphur atom. The nominal content of THT in G-gas in the Netherlands is 18 mg/m^3 (n). For now THT is not added to wide band gases.

The dew point mentioned in Table 2 is the water dew point. Gas is cooled down at a certain pressure to remove moisture and other components that can condensate. A lower temperature or higher pressure will make the gas 'dryer'. How much dryer the gas will be is unknown. The required water dew point for G-gas is -12 °C at 40 bar pressure, while for instance LNG is cooled down to -162 °C at pressures up to 60 bar [7]. It is unknown what this means for the risk on condensation of not only water, but all components that can condensate. It is clear that gases without such a drying procedure (such as gas from anaerobic digestion and SNG) will be 'wetter' and the risk of condensation is increased. This is very important in view of corrosion of metallic pipes.

Table 2. The minimum and maximum contents of chemicals found in anaerobic gas, SNG and imported natural gas, compared to the average chemical composition of G-Gas. Some values in mol % and mg/m³ have been converted to ppm for comparison.

Quality	**G-gas Average [6]**	**Gas from anaerobic digestion***	**SNG [8]**	**Imported natural gases [8]**	**Unit**
Dew point	-12 (at 40 bar)	n.a.	n.a.	various	°C
Temperature (of feed in gas)	10	0 - 50	n.a.	n.a.	°C
Sulphur (total)	6.7				mg/m³ (n)
Inorganically bound sulphur (H_2S)	0.4	4 300			mg/m³ (n)
Mercapthene	< 1.0				mg/m³ (n)
Odorant value (*THT*)	17.7	n.a.	n.a.	n.a.	mg/m³ (n)
Chlorine containing compounds	< 0.1	0 - 735			mg/m³ (n)
Fluorine containing compounds	< 0.1	0 - 256			mg/m³ (n)
Ammonia	< 0.1	0 – 100			ppm
Hydrogen chloride (*HCl*)	< 1.0	Traces			ppm
Hydrogen cyanide (*HCN*)	< 1.0	Traces			ppm
Carbon monoxide (*CO*)	< 100		10 000 – 700 000		ppm
Carbon dioxide (CO_2) in dry gas	8 900	240 000 – 520 000	20 000 – 590 000	0 - 1000	ppm
Aromatic hydrocarbons	500	Occasional traces		Occasional traces [9]	ppm
Benzene		0 – 11.4			ppm
Toluene		0 – 76.2			ppm
Oxygen (O_2) in dry gas	< 100	0 – 26 000			ppm
Hydrogen (H_2)	< 0.01	0 – 190 mg/m³	7 - 62		vol %
Methane (CH_4)	81.29	40 – 68	0 – 43	70 - 99.8	mol%
Nitrogen (N_2)	14.32	0 – 17	0 – 50.9	0.01 – 1.8	mol%
Ethane (C_2H_6)	2.87		0 – 2	0.06 - 15	mol%
C_2H_y (except C_2H_6)			1 – 25		mol%
C_3H_y	0.38			0 - 10	mol%
C_4H_y	0.15			0 - 3.5	mol%
$C_{5+}H_y$	0.09		0 - 0.3	0 - 0.6	mol%
C_xH_y			0 - 0.3		mol%
Phosphine	technically free	0 – 0.7			mg/m³ (n)
Organo-silicons	< 0.1	0 – 20			mg/m³ (n)
Volatile organic compounds (VOC)		Traces			ppm
Metals (copper, mercury)		Occasional traces			ppm

* In appendix I a broader overview is given about the chemical composition of the gases from anaerobic digestion processes.

n.a. = not applicable
blank cell = not measured

3 Materials and Failure Data

To answer sub question b) of section 1.1, the most important materials used in the Dutch distribution network are identified. Furthermore, the practical failure data of these materials is analysed to identify the failure mechanisms of the most common materials. The next chapter discusses failure mechanisms in more detail, which have been well-documented in scientific and technological sources. This partially answers sub question c) of section 1.1.

3.1 Most Important Materials

3.1.1 *Distribution Mains*

The Dutch distribution network contains about 124 000 km of mains, which are mainly made from either polymeric materials (PE and PVC) or from steel (carbon steel, grey and nodular cast iron). Asbestos cement (AC) was also used in certain areas. In Table 3 the length of each material in the distribution network in 2010 can be found.

Table 3. Length and MOP of distribution mains in 2010 for different types of materials [10].

Material	**(Sub)total length (km)**	**Length (km)**	**MOP* (bar)**	**Material standard**
Polyvinyl chloride (PVC)	75 062			
High Impact PVC (PVC-HI)		*53 996*	0.1	[11]
Unplasticized PVC (PVC-U) †		*21 066*	0.1	-
Steel	27 484			
Carbon steel		*19 228*	16	[12,13]
Grey cast iron †		*6 241*	1	[14]
Nodular cast iron		*2 015*	8	[15]
Polyethylene (PE)	19 529			
2nd and 3rd generation PE		*14 422*	8 §	[16]
1st generation PE †		*5 107*	4 §	-
Other	1 918			
Asbestos cement (AC) †		*1 719*	0.1	[17]
Unknown		*199*	-	-
Total	**123 993**			

* *MOP = Maximum Operating Pressure*

† *Not allowed for new pipelines*

§ *Value may be lower. This depends on the SDR (Standard Dimensional Ratio) and the type of PE (PE80 or PE100). See references for more information.*

This table shows that PVC is the most used material in the Dutch gas network. Because materials are often used below their MOP, by far the largest part of the network (about 100 500 km, 81%) consists of low pressure distribution mains with operating pressures of 30 or 100 mbar. The rest of the network are high pressure distribution mains (operating pressure 1, 4 or 8 bar) in which the majority (about 14 000 km) is used at an operating pressure of 8 bar.

3.1.2 *Service Lines*

With more than seven million connections to residential houses, industries, etcetera, connecting almost 99 % of the Netherlands to gas, service lines are an important part of the gas network. The materials of service lines (SL) are mainly steel, copper and PE (see Table 4). Based on an average length of approximately ten meter of the service line, the total length in the Netherlands is about 70 000 km.

Table 4. The materials used as service line. [18]

Material
Polyethylene (PE)
PEKO (copper pipe with PE sleeve)
Copper (without PE sleeve)
Steel

3.1.3 Pressure Regulators

Pressure regulators are used for the reduction of the pressure of the natural gas. The pressure regulators in houses and gas stations are made from steel (including carbon steel, stainless steel, steel castings, cast iron, etc.) or aluminium (including silumin) and contain a elastomeric membrane, which is used as diaphragm [19].The typical elastomeric material used as diaphragm in gas pressure regulators is nitrile butadiene rubber (NBR i.e. Perbunan®, Buna-N®) [19].

3.1.4 Conclusions

The most important materials used in the Dutch distribution mains are: PVC, PE and steel (carbon steel, grey cast iron and nodular cast iron). The service lines consist of steel, copper (with and without PE sleeve) and PE. The most important materials in pressure regulators are steel, aluminium and elastomeric materials.

This means that the most important materials that are discussed in this literature report are steel, PVC, PE, copper, aluminium and elastomeric materials. The polymeric materials are discussed in chapter 4 and the metals are discussed in chapter 5. Carbon steel, stainless steel and cast iron are all discussed in section 5.1 "Steel".

3.2 Failure Data

Failure data of Nestor [20] shows that the most important cause of disturbance in gas supply is excavation (about 30 %) and corrosion/aging (about 20-25 %). The failures due to excavation indicate that the impact resistance of the pipe materials should be high to prevent failures as much as possible. Metals are by nature stronger than polymeric materials such as PVC and PE. Because PVC can fracture brittle, while the failure mode upon impact for PE will be ductile, impact resistance is most important for this material. This will be discussed further in section 4.1.1.
The failure data from field practice about corrosion/aging is not specific enough to conclude anything about the degradation of the material caused by harmful components in the gas.

The Nestor Database further shows that disturbed gas supply in a distribution main or service line is caused by point loadings in 5 % of all cases. These pipelines are made from a polymeric material, because metals usually do not fail due to point loadings (exceptions for grey cast iron). Point loadings introduce extra stress on polymeric pipe material, possibly initiating stress cracking (see chapter 4).

Next to this information on practice, most information on failure mechanisms is known from well-documented scientific and technological data sources. This will be discussed in more detail in chapters 4 and 5.

4 Effects on Polymeric Materials

4.1 Polyvinyl Chloride (PVC)

Unplasticized PVC (PVC-U) was introduced in the Dutch gas network in the late 1950s and was subsequently used on a large scale. In the late 1960s high-impact PVC (PVC-HI) was introduced on the market. Impact modifiers used are chlorinated PE (PVC-CPE) and butyl-acrylate (PVC-A). These materials are not only more resistant to impact loadings; they also have a higher resistance to the formation and growth of crazes. Crazes are the precursors of environmental stress cracking (ESC). Therefore the GIVEG quality mark for PVC-U gas pipes was withdrawn in 1974 and PVC-U gas pipes were no longer installed [21].
However, to date still many old PVC-U gas pipes are in operation in the Netherlands (see Table 3). [22-24]

4.1.1 Failure Mechanisms

4.1.1.1 Long-Term Failure

Because PVC is used in the Netherlands for networks up to 100 mbar only, internal gas pressure loading does not result in the initiation and growth of cracks in the material within 50 years. However, failure may occur due to impact forces (see section 3.2), external stresses, such as point loadings, or as a result of the environment in combination with mechanical loading (environmental stress cracking, ESC). Failure caused by ESC is well known in literature on PVC-U, but it is hardly encountered in practice.

In the 1980s questions were raised about the ESC behaviour of PVC-HI pipes. Many researches [23-31] were subsequently performed, which are discussed below.

A precondition for the formation of crazes is mechanical stress. If long-term failure occurs, it is almost always preceded by craze initiation and craze growth (see Figure 1). However, craze initiation does not always lead to failure. An aggressive environment can accelerate the craze initiation and craze growth.

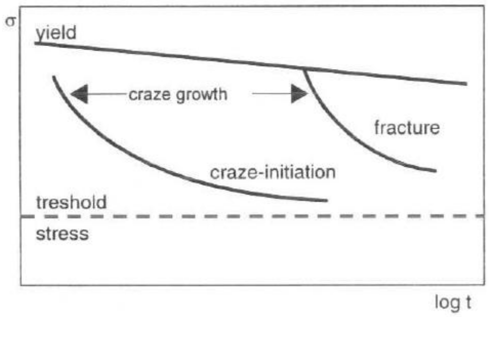

Figure 1. Craze initiation, craze growth, yield and fracture in PVC [27]

Crazes initiate on local stress concentrations, such as small imperfections, and are formed faster by simultaneous absorption of certain components from the environment. The stress needed for craze initiation is time-dependent. A threshold stress can be defined, below which no crazes will initiate, even after a very long time (see Figure 1). This threshold in air is 20 MPa [23,25], which is higher than stresses induced by normal soil loads in practice. However, high local stresses due to point loadings may occur. So point loadings are very important and can result in craze initiation, craze growth and eventually failure.

After initiation a craze will grow, which is controlled by stress concentration and stress relaxation at the craze tip. Crazes do not grow linearly because of the

viscoelastic behaviour (creep) of the material, such as (local) necking. Neighbouring crazes also influence the craze growth. Swelling could even cause crazes to stop growing. The extent of sorption is again dependent on the local stress, making craze growth a very complex phenomenon.
A crack grows when a fibril in a craze breaks. Additionally the stress in the craze tip increases, causing the craze to grow and new fibrils to be formed. Therefore, crack growth is strongly connected with craze growth.

Failure occurs when the stress in the crack formed exceeds a certain critical stress intensity. This stress intensity is a function of the shape of the craze and the size of the plastic zone around the craze tip. This is also dependent on the absorbed chemical component, thus influencing the time to failure.

Some gaseous environments accelerate craze initiation and lower the threshold stress for crazing. This is caused by absorption, diffusion and the interaction of the medium with the polymer. If diffusion occurs quickly, the absorption and weakening effects will take place over larger areas and homogeneous yielding may arrest possible craze growth processes. On the other hand, a medium with a slow diffusion and strong interaction results in a stronger stress corrosion effect.

4.1.1.2 *Impact Loadings*

Because third party damage, caused by digging activities, is the most important cause of failure for gas pipeline systems (see section 3.2), the resistance to impact loadings is very important for PVC. By testing the pipe with an instrumented falling weight test [32], the energy to fracture can be calculated when a weight is dropped from a certain height on the plastic pipe. A ductile failure results in a high amount of absorbed energy. Pipes with brittle failures are unwanted, because such pipes can shatter when handled or hit during digging.

The type of failure is largely dependant on the temperature. At lower temperatures more brittle failures will be observed. The brittle-ductile transition temperature for PVC-U is about 0 °C, while the transition temperature for PVC-HI is much lower i.e. between -10 °C and -20 °C [24,33]. In practice, the temperature during for instance repairs can be near 0 °C. This means that PVC-U can behave brittle under these circumstances.

The sorption of vapours and liquids by PVC can cause plasticization or embrittlement. This will result in a shift in the brittle-ductile transition temperature, possibly making PVC pipes brittle when handled.

4.1.2 *The Influence of Wide Band Gases on PVC*

4.1.2.1 *Effects of Hydrocarbons*

Natural gas contains many different aromatics and aliphatics. Appendix IV gives the composition of natural gas condensate. However, wide band gases also introduce 'new' aromatic and aliphatic components, such as limonene, which is present in various citrus fruits. The effects of all these individual components on PVC are unknown, but research with model gases gives a general idea for this class of gas components.

The effects of aromatic components on PVC are strongly related to the relative degree of saturation (r.s.) of aromatics in natural gas. The r.s. is the percentage of aromatics the natural gas can hold under certain conditions. This means that r.s. not only changes with respect to the absolute concentration, but also with temperature and pressure.

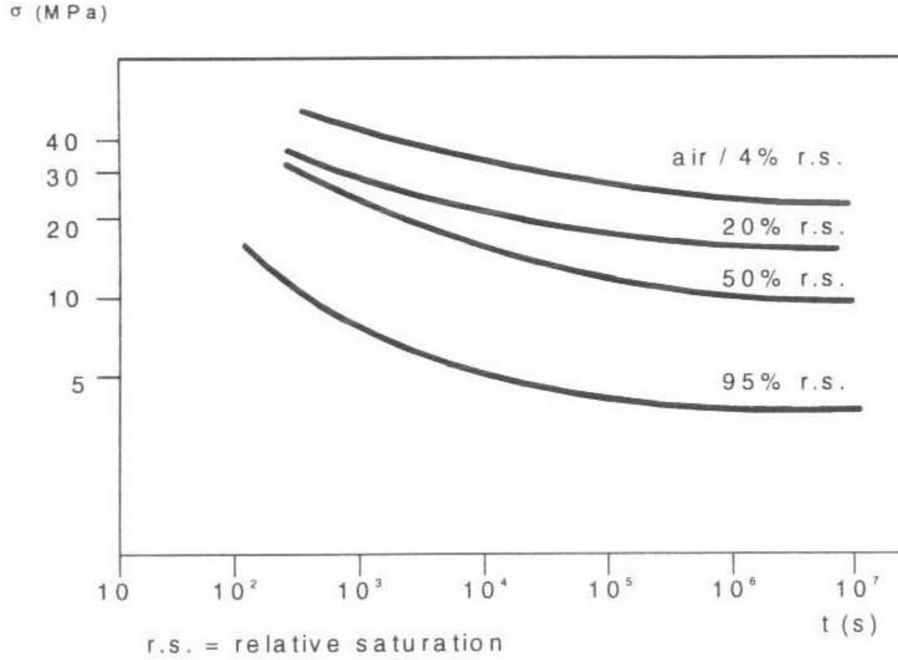

Figure 2. Craze initiation in PVC under constant loading in natural gas with various contents of benzene. 10^7 seconds is almost 4 months. [27]

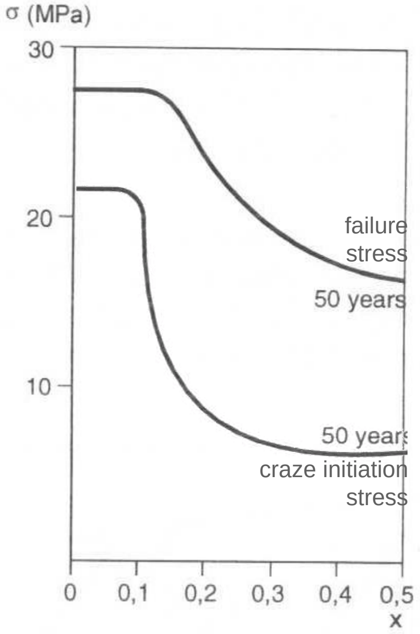

Figure 3. 50-year craze initiation stress and failure stress as a function of relative degree of aromatic concentration.
x = 0,1 equals 10 000 ppm. [27]

Craze initiation is accelerated considerably at high benzene concentrations (see Figure 2). It was found that an r.s. of aromatics of 4 % is not high enough to result in any effect on craze initiation [27]. 4 % r.s. is about 5000 ppm (at 20 °C and 100 mbar). Higher concentrations will form crazes in less time or at a lower stress.

The results of limited tests were extrapolated to 50 years. No significant change in craze initiation stress and long-term failure stress up to about 0.1 % (±10 000 ppm) was found (see Figure 3) [27].

In other experiments a mixture of benzene, toluene and xylene (BTX) until a maximum concentration of about 1000 ppm BTX was used. Extrapolating the results of the experiments at elevated temperatures also showed no detrimental long-term effect when used for 50 years at 20 °C [23].

The concentration of aromatics for SNG and imported natural gas is not provided (see Table 2), so it is not known whether these gases have an aromatic content below 10 000 ppm or even 1000 ppm. Gases from anaerobic digestion have only occasional traces of aromatic components. The maximum concentration of toluene is 287 mg/m^3(n), which corresponds to 76 ppm [34]. Also the concentration of benzene is much lower than 10 000 ppm. G-gas has 500 ppm of aromatics (mainly BTX: benzene, toluene and xylene) and has therefore the highest (known) concentration. Based on these known concentrations, the concentration of aromatics in wide band is far below the problematic concentration.

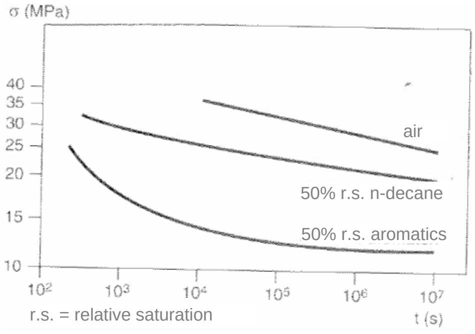

Figure 4. Craze initiation in different gas environments.[23]

Aliphatics have a much lower effect on craze initiation than aromatics at the same concentration (see Figure 4), because the interaction between aromatics and PVC is much stronger than the interaction between aliphatics and PVC. Molecules of aromatic components can therefore penetrate between PVC molecules. This plasticizes the PVC and causes local yielding, forming crazes quicker. However, the rate of stress relaxation is also increased at the craze tip, slowing craze growth down. Alifatic molecules will only fill up the free space between the PVC molecules. Therefore stress relaxation is no longer possible and a brittle fracture can occur relatively fast. [23]

Aromatics and aliphatics in the liquid phase (condensate) have the same effect on craze initiation and failure behaviour as saturated vapour (100 % r.s.) [27].
It is also known from other literature sources [35] that environmental stress cracking (ESC) in PVC-U is highest in ketones and aromatic components and less in esters and alcohols. Any effect is almost absent for aliphatic components. Turpentine gives some cracking at high deformation, due to the presence of an aromatic fraction. No differences are observed between PVC-HI and PVC-U.
ESC may therefore only be found if the following two extreme conditions occur simultaneously [27]:

1. a condensate has been present in the gas pipe for quite some time;
2. a very high stress is present locally due to a point or line load.

The simultaneous exposure of PVC-U to condensate and mechanical loading had only marginally changed the brittle-ductile transition temperature. This means that the impact resistance decreases only slightly. The transition temperature of PVC-HI showed a clear increase. The impact resistance can therefore strongly be decreased to values that are comparable to those of PVC-U.

4.1.2.2 *Effects of Carbon Dioxide*

The sorption of vapours and liquids by PVC can cause plasticization or embrittlement. This will not only result in a shift in the brittle-ductile transition temperature, but also in the glass transition temperature (T_g). CO_2 is considerably more soluble than methane or inert gases like He, N_2 and Ar. Exposure of small samples to 20 bars CO_2 up to equilibrium resulted in a decrease of T_g of 18 °C, while the low soluble gases resulted in no noticeable reduction in T_g [36].
Similar to the effect of aromatic components to PVC, the plasticizing effect of CO_2 may cause a faster formation of crazes which may influence the impact strength, although this is still to be confirmed. Due to the high concentrations of CO_2 in wide

band gases (up to 62 mol %, see Table 2) the plasticizing effect needs to be investigated.

4.1.2.3 *Effects of Hydrogen Sulphide*

In experiments with 1000 ppm hydrogen sulphide (H_2S) in sewer systems concrete pipes were compared with PVC pipes. The surface of the PVC pipe revealed very low pH values of 0.4. Nevertheless, after 8 months of testing no (mechanical) failures in the PVC pipe whatsoever were reported, although mechanical properties were not measured [37].

H_2S causes a colour change (dark brown to black) at the surface of lead stabilised PVC pipes. Also, the stability of the PVC-U is decreased after exposure to 3 ppm H_2S [38]. However, only a very small layer at the surface is discoloured. There is no significant difference in impact resistance between exposed and non-exposed PVC-U samples [39].

The maximum known concentration of H_2S in wide band gas is 4300 mg/m^3(n) (see Table 2), which corresponds to 3085 ppm. Therefore the results in the literature are not conclusive if these concentrations are allowable. Even the effects of the currently proposed lower concentration of 160 ppm H_2S [40] are unclear. Therefore further research is needed.

4.1.2.4 *Effects of Chlorine and Fluorine Containing Components*

It is known that some organic chlorides can dissolve PVC. For instance dichloromethane is specifically used for dissolving PVC in the dichloromethane test (DCMT) as described in ISO 9852 [41]. ISO/TR 10358 [42] confirms the low resistance of PVC against dichloromethane: "The pipes are seriously attacked: they shall not be used for either pressure or non-pressure applications."
Organic fluorides may have the same effect on PVC as organic chlorides. In wide band gases traces of these compounds have been found, especially in gases from anaerobic digestion. It is unknown if these traces are high enough to negatively affect the long-term and impact resistance properties of PVC.

4.1.2.5 *Effects of Odorant*

In a test requirement of 1976 for PVC-U and PVC-CPE a stress corrosion test is described with 75 mg/m^3 THT [43], which is more than four times as high as the average concentration in G-gas (see Table 2). From the DSO's it is known that sometimes as much as 80 ppm (288 mg/m^3 [34]) is added to the sustainable gas to overcome other odours in the gas. Effects on PVC with these concentrations are unknown.

4.1.2.6 *Effects of Other Components*

Practically no literature about the effect of other components present in wide band gases was found. Only traces of HCN and HCl can be found in wide band gases and therefore the deleterious effect is unlikely.

4.1.3 *Conclusions*

The concentrations of aromatic and aliphatic components in wide band gas are not high enough to result in any effect on craze initiation or craze growth for PVC-U and PVC-HI. The brittle-ductile transition temperature of PVC-HI may increase slightly when exposed to condensate. It is not expected however, that impact resistance of PVC materials will be reduced due to the rather low concentrations of aromatic constituents in wide band gases.

It should be noted that although the concentration of hydrocarbons in wide band gases is similar to G-gas, the required water dew point for wide band gas is different than that for G-gas or even absent (see chapter 2). Due to this difference with G-gas the risk of condensation of not only water, but all components that can condensate, in wide band gas may be higher than that of G-gas. This includes (aromatic) hydrocarbons. Condensate will have a deleterious effect on PVC.

The concentrations of H_2S in wide band gases exceed the levels investigated in known experiments. Experiments are necessary to determine that PVC pipelines are not affected.

CO_2 may have some effect on long-term strength as well as on impact resistance.

The influence of other components is not known and since the concentration levels in wide band gas are unknown for most components, experiments are needed to determine if these components affect PVC.

These conclusions are summarised in the table below.

Table 5. The effect of components present in wide band gas on PVC. Some components will have no deleterious effect (green) or no or little deleterious effect is expected (light green). The effect of other components is unknown (light orange) or a deleterious effect may be present (orange)

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

4.2 Polyethylene (PE)

In the Netherlands PE is used for gas pipes since 1968. Different types exist, such as a medium or high density PE (MDPE and HDPE respectively), PE with a different pressure class (e.g. PE 80 and PE 100) or mono- and bimodal PE. In this literature review no distinction between the PE types is made.

4.2.1 *Failure Mechanisms*

4.2.1.1 *Long-Term Failure*

When there is enough stress for a small defect to grow, PE may ultimately fail. The crystalline parts in the PE, the lamellae, will be pulled apart caused by the stress. Only the so called tie molecules keep the lamellae together (see Figure 5). From this moment two types of failures can occur.

1. If the stress is above a threshold value, the lamellae break up, or undergo a stress-induced phase change and renucleate. This will continue and ends with a ductile failure. Ductile failures normally do not occur in practice, because the pressures used in the Dutch gas network are not high enough.
2. If the stress is below a threshold value the tie-molecules, still keeping the lamellae together, untangle and relax until they ultimately fail. The PE fails macroscopically brittle in this case [44].This brittle failure process is called slow crack growth (SCG) and is the failure mechanism which determines the

lifetime for PE gas pipes, if the pipe did not fail due to other external causes such as excavation or third party damage.

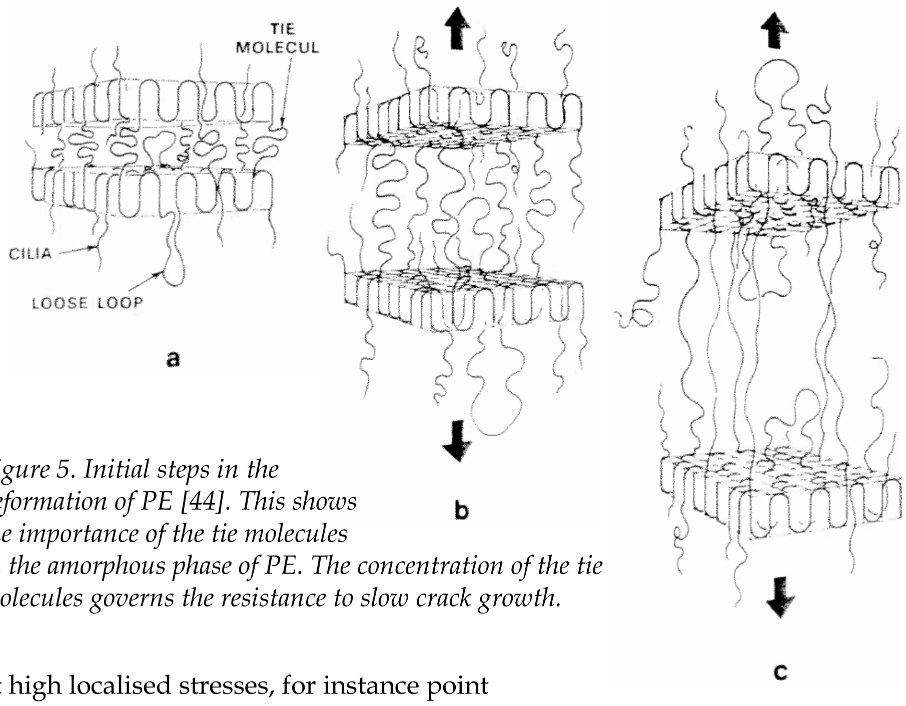

Figure 5. Initial steps in the deformation of PE [44]. This shows the importance of the tie molecules in the amorphous phase of PE. The concentration of the tie molecules governs the resistance to slow crack growth.

At high localised stresses, for instance point loadings, SCG is enhanced which causes premature failure. This is the experience of Kiwa Gas Technology and established in various researches (e.g. [45]).
The resistance to SCG was improved spectacularly during the last 40 years. This is not only due to better processing, but especially due to increased levels of tie molecules in the molecular structure of more modern PE types [45,46].

Tie molecules are only found occasionally and randomly in first generation PE. By introducing a comonomer, which marks the second generation PE, the tie molecules are built in the polymeric structure on purpose. Third generation PE is produced using a two step polymerisation process, positioning the comonomer mainly at the longer PE chains, increasing the concentration and effectiveness of the tie molecules. [45,46]
Because tie molecules are very important to the resistance to SCG, any effect of components in wide band gas on these molecules will directly have an influence on the remaining lifetime.

For determining the lifetime, the resistance to SCG was traditionally tested by determining the long term hydrostatic strength using internal water pressure tests according to the procedure described in ISO 9080 [47]. However, this way of testing ignores any effects of external forces such as point loads. Because point loads produce locally high stresses, this should be taken in consideration when the effects of components in wide band gas on the SCG behaviour of PE is reviewed.

4.2.1.2 *Impact Loadings*

Although third party damage is the most imported cause of failure for gas pipeline systems (see section 3.2), the type of failure (brittle or ductile) is of much less importance for PE than for PVC, because PE always fails ductile when handled or hit during digging. Moreover, in the literature no information is found about the effect of various components in wide band gases on the impact resistance of PE pipelines.

4.2.2 *The Influence of Wide Band Gases on PE*

4.2.2.1 *Effects of Hydrocarbons*

Using internal water pressure testing, it was determined that G-gas had no negative effect on the short-term and long-term strength of first generation PE [22,25]. The concentration of aromatics for SNG and imported natural gas is not provided (see Table 2), so it is not known whether these gases have an aromatic content below 10 000 ppm or even 1000 ppm. Gases from anaerobic digestion have only occasional traces of aromatic components. The maximum concentration of toluene is 287 mg/m^3(n), which corresponds to 76 ppm [34]. Also the concentration of benzene is much lower than 10 000 ppm. G-gas has 500 ppm of aromatics (mainly BTX: benzene, toluene and xylene) and has therefore the highest (known) concentration. The effect of 'new' hydrocarbons, for instance limonene, is expected to be comparable, but this still has to be confirmed. It is therefore not expected that gaseous hydrocarbon components in wide band gas will have a deleterious effect on PE.

On the other hand, it is well known that PE will soften and weaken when it comes in contact with liquid aromatic hydrocarbons (including BTX) and/or liquid higher hydrocarbons [48,49]. PE can absorb about 7 wt.% of natural gas condensate [26] (the composition is given in Appendix IV). This lowers the yield strength of a MDPE from about 19 MPa to 15 MPa [25,26] and it drastically reduces the long-term strength measured by internal water pressure testing [22,25]. If the condensate can desorb, the original strength will return, unless additives are leached from the PE [25,26].

Because synthetic condensate (a mixture of 50 vol% n-decane and 50 vol% tri-methyl benzene) results in a similar decrease of yield strength and long-term strength as gas condensate, a requirement for the resistance to gas constituents has been added to ISO 4437 [22,50].
It should be noted that although the concentration of hydrocarbons in wide band gases is similar to G-gas, the required water dew point for wide band gas is different than that for G-gas or even absent (see chapter 2). Due to this difference with G-gas the risk of condensation of not only water, but all components that can condensate, in wide band gas may be higher than that of G-gas. This includes (aromatic) hydrocarbons.

There are no indications for the occurrence of stress cracking phenomena in PE caused by the combined influence of stress and environment (condensate, other gas constituents) [25,26].

4.2.2.2 *Effects of Oxygen, Carbon Dioxide and Nitrogen*

Gases like oxygen (O_2), carbon dioxide (CO_2) and nitrogen (N_2) can have an influence on the mechanical behaviour of polymers. However, this is only valid at very low temperatures (e.g. 78 K or -195 °C). At a critical temperature above the boiling temperature of a gas, these gases will loose its influence [51]. This critical temperature increases as the gas pressure increases. Since O_2, CO_2 and N_2 have an effect only at very low temperatures, these gases are not an important factor in influencing the lifetime of a PE gas pipeline [52].

4.2.2.3 *Effects of Hydrogen*

No macroscopic differences were found between unexposed PE and PE exposed to H_2 for 6 months. However, there were some indications that the elongation in the tensile test increased, but more samples are needed to confirm these suspicions [53]. More recent experiments with H_2 diffusion at pressures up to 100 bar for 12 months, revealed no influence on the tensile strength [54]. Any effect of hydrogen on PE is therefore not expected.

4.2.2.4 *Effects of Hydrogen Sulphide*

The same experiments with H_2S in sewer systems for PVC (see section 4.1.2.3) have been performed on PE. Similar results were obtained: after 8 months of testing (1000 ppm H_2S), no (mechanical) failures whatsoever were reported [37]. However, the maximum concentration for H_2S in wide band gas is 3085 ppm (chapter 2). Since the aim of the above described experiment was not the long-term strength of PE, even the effects of the currently proposed lower concentration of 160 ppm H_2S are unclear [40].

4.2.2.5 *Effects of Chlorine and Fluorine Containing Components*

ISO/TR 10358 [42] classifies PE as having a low resistance against the organic chloride dichloromethane: "The pipes are seriously attacked: they shall not be used for either pressure or non-pressure applications."
Organic fluorides may have the same effect on PE as organic chlorides. In wide band gases traces of these compounds have been found, especially in gases from anaerobic digestion. It is unknown if these traces are high enough to negatively affect the long-term strength and impact resistance properties of PE.

4.2.2.6 *Effects of Other Components*

The effect of various other components in wide band gases, such as sulphur, mercaptanes, ammonia, HCN, HCl and CO on PE is still unknown. Only traces of HCN and HCl can be found in wide band gases and therefore the deleterious effect is unlikely.

4.2.3 *Conclusions*

Liquid aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), and liquid higher hydrocarbons will lower the yield strength drastically and reduce the long-term strength measured with the internal water pressure test. Such influences are tested according to ISO 4437.
Condensate, including liquid aromatic hydrocarbons, is much more likely to occur in wide band gas than in G-gas, because water is not always actively removed.

Gases like nitrogen (N_2), oxygen (O_2) and carbon dioxide (CO_2) will have no deleterious effect on PE. Although it is not certain what the effects of higher concentrations of H_2 are, it is expected that the effects, if there are any, will be rather small. It is unknown what kind of long-term effects other components, such as sulphur, H_2S, mercaptans, ammonia, chlorine and fluorine containing compounds, HCl, HCN and CO, have on PE.

These conclusions are summarised in the table below.

Table 6. The effect of components present in wide band gas on PE. Some components will have no deleterious effect (green) or no or little deleterious effect is expected (light green). The effect of other components is unknown (light orange).

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

4.3 Elastomeric Materials

Elastomeric materials, especially rubber, are used in gas pressure regulators as diaphragms (see section 3.1.3). Rubber used in other components of the Dutch gas network, such as a sealing ring in PVC joints, will be discussed in "Impact of Sustainable Gases on Joints used in Gas Distribution Systems" (report GT-110207).

4.3.1 Failure Mechanisms

The most common causes of failure of diaphragms in e.g. pressure regulators are wear and fatigue. The constant bending of the membrane causes wear crackles. There are a number of factors that can influence the growth rate of these wear crackles. These are:

- Type of rubber material.
- Excessive temperature development causing the rubber to harden and lose its elastic properties. (For example high temperatures may result from external environmental factors and friction)
- Excessive squeeze due to over tightening of adjustable glands.
- Incomplete curing (vulcanization) of the rubber material during production.
- Volume swell of the elastomeric seal due to transported medium and especially condensate.
- Introduction of gas-components incompatible with the elastomeric material.

In the comparison between the influence of G-gas and wide band gas on the elastomeric diaphragms, the most important factors that could have an influence are the latter two mentioned. Therefore the focus of this report will be on these aspects.

4.3.2 The Influence of Wide Band Gases on Rubber

4.3.2.1 Effects of Hydrocarbons

In wide band gases concentrations of hydrocarbons (e.g. ethane, propane, etc) can be higher, especially in SNG, compared to G-gas.
According to ISO DTR 762 [55] no negative effect of alkanes is suspected towards NBR. NBR can undergo a moderate effect once in contact with unsaturated chemical compounds (e.g. propene and butadiene) [55] Due to the high concentrations of C_2H_y and C_3H_y in wide band gases (propene may be up to 2 % in SNG [56]), NBR can experience negative effects of these gases.

In several studies, it has been shown that NBR will swell in contact with aromatic hydrocarbons [25,57-59]. The effect of swelling by liquid aromatic hydrocarbons (condensate) and – after vaporisation of the condensate - subsequent extraction of plasticizer and other additives from the elastomeric components has been studied using exposure to pentane and synthetic condensate (70 % iso-octane, 30 % toluene) [58,59]. For NBR the reduction of the mechanical properties (e.g. tensile strength, elongation at break, hardness) was up to 60 %. After extraction, the mechanical properties re-gained up to 90 % of the initial values.
The influence of benzene, toluene and xylene (BTX) is classified by ISO DTR 7620 as severe [55]. This means that the hardness will change more than 30 IRHD and/or the

volume will increase over 60 %. But this is investigated when the NBR compound was fully submerged in one of the chemicals.

Due to the low concentrations of aromatic hydrocarbons in wide band gas (see section 2.5) it is not expected that these components in wide band gases will affect the elastomeric diaphragms in e.g. pressure regulators. However, the presence of any liquid aromatic hydrocarbons will negatively affect the mechanical properties.

4.3.2.2 *Effects of Carbon Monoxide, Carbon Dioxide and Hydrogen*

ISO DTR 7620 [55] states that there is little or no adverse effect on NBR expected by CO, CO_2 and H_2. This is confirmed by NBR producers [60-62].
Also in research by the former VEG-Gasinstituut it was concluded that no deleterious effect would be expected for CO, CO_2 and H_2 [63]. This conclusion is based on the low solubility of these gases, because the solubility is an important aspect with respect to any deleterious effect. The solubility, and thus the risk on a deleterious effect, is higher when the rubber is already affected by hydrocarbons [63].

4.3.2.3 *Effects of Oxygen*

Although O_2 has a low solubility in NBR as well, oxidation can cause a degradation of the rubber [63]. O_2 will not be harmful as long as the compound is well protected with an antioxidant and the temperature is low. Nevertheless, problems may arise if the rubbers are thin and are exposed to large deformations.

According to ISO DTR 7620 [55] and NBR producers [60-62] no negative effect by O_2 is to be expected.

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

According to ISO DTR 7620 [55] a severe deleterious effect of H_2S (saturated solution) and sulphur (S) on NBR can be expected if the material is fully submerged in one of these chemicals.

On the other hand according to NBR producers, NBR diaphragms are relatively resistant to H_2S [60-62]. This was also concluded after a research led by the former VEG-Gasinstituut [63]. Nevertheless these results were based on low concentrations of H_2S (≤ 5 mg/m^3). The concentrations of sulphur containing chemicals (especially H_2S) are in wide band gas much higher (up to 4300 mg/m^3 for H_2S). The impact of this concentration is unknown. Even the effects of the currently proposed lower concentration of 160 ppm H_2S [40] are unclear. Therefore further research is needed.

4.3.2.5 *Effects of Halogen Containing Components*

All halogen containing components can have a severe effect on the mechanical properties of NBR components, according to ISO DTR 7620 [55]. Also NBR producers [60-62] warn their customers to be careful using NBR products with halogen containing components.
Although only traces of halogen containing compounds are found in wide band gases, deleterious effects on NBR by these chemicals can therefore not be excluded.

4.3.2.6 *Effects of Other Components*

NBR has a moderate resistance when fully submerged in HCN according to ISO DTR 7620 [55]. Because only traces of HCN chemicals are found in wide band gases, the negative effects are expected to be very low.

According to ISO DTR 7620 [55] NBR has an outstanding resistance against refrigerant ammonia. The relatively low concentration of ammonia in wide band gases (up to 100 ppm) is therefore not high enough to have a deleterious effect of the NBR.

4.3.3 Conclusions

The major cause for failure of elastomeric diaphragms is wear and fatigue, which is caused by the constant bending of the membrane. Swelling of the membrane and the introduction of gas-components which are incompatible to the elastomeric diaphragms accelerate the process of failure.

Based on among others various data sheets, no deleterious effect of ammonia, CO, CO_2, O_2 and H_2 is expected. H_2S, halogens and higher aromatic, but also unsaturated chemical compounds causes swelling of elastomeric diaphragms resulting in a decrease of functionality and possibly the failure time. Therefore special attention should be paid to the concentrations of these gases. However, it is unknown above which concentrations certain chemicals could affect the NBR rubbers. This should be investigated further.

This is summarised in the table below.

Table 7.The effect of components present in wide band gas on NBR. Some components will have no deleterious effect (green) or no or little deleterious effect is expected (light green). The effect of other components is unknown (light orange).

Sulphur containing components	H_2S	Mercaptans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydrocarbons	Aromatic hydrocarbons	O_2	H_2
unknown	possibly	probably none		none	possibly		probably none		none		possibly, if unsaturated	probably none, unless liquid	none	

5 Effects on Metals

5.1 Steel

The natural gas distribution infrastructure includes a considerable number of steel pipes, fittings and other equipment. Due to the variety of components and their varying age a large variety of steel qualities has been applied. In the gas distribution infrastructure the applied steel qualities range from cast iron (nodular and grey cast iron), basic steel grades like St 37 and modern steel grades like ASTM A106 gr. B and API 5L gr. B to stainless steels.

5.1.1 Failure Mechanisms

The main failure mechanism for steel is 'third party damage' (see section 3.2). The gas composition is the main factor influencing the corrosion related failure mechanisms which can occur in steel gas distribution materials. Corrosion related failure mechanisms include general corrosion, pitting and stress corrosion cracking mechanisms.
The corrosion mechanisms as described in this chapter are in general applicable to the plain carbon steel and cast iron grades applied in the natural gas distribution infrastructure. However, the susceptibility to corrosion and the aggressivity of a corrosive medium can be highly dependent on the specific properties of a specific steel type.

5.1.2 The Influence of Wide Band Gases on Steel

5.1.2.1 Effects of Water

The presence of water in the gas infrastructure is one of the preconditions for the occurrence of corrosion. Natural gas with a relative humidity less than 100 % is considered non-corrosive [64], however some literature is available in which corrosion problems are described at a relative humidity of 60 – 70 % [65,66]. A relative humidity of 70% is considered critical, as above this relative humidity corrosion becomes rapid [67]. This means that even in conditions with a relative humidity below 100% corrosion can be expected, and a relative humidity above 70 % should be avoided.

The specified water dew point in the distribution of narrow band gas at 8 bar pressure is -10 °C. As there are no specifications for the dew point for wide band gasses condensation of water in the natural gas infrastructure may occur for wide band gas (see Table 2). Except for the humidity of the transported gas there are other possible sources of water in the gas infrastructure such as leaking joints in low pressure distribution systems and incomplete draining after pressure tests.

Once liquid water is present in the gas infrastructure, a corrosive medium can result from the dissolutions of constituents of the transported gases in the water. The composition of the liquid water determines to a large extent whether the scale formed due to the corrosion of the metal is protective and, once formed, prevents the metal underneath from further corrosion. The concentration (or more precisely the partial pressure) of the gas components is decisive for the rate of corrosive attack and the type of scale formed. Besides the gas composition also the mineral content of the water may determine the properties of the formed scale. The presence of chlorides in the water may decrease the protective properties of iron-carbonate layers as formed

in corrosion of steel by carbon dioxide [65]. The gas constituents with a known influence on the corrosion of steel are oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO) and hydrogen sulphide (H_2S), which are discussed in the following sections.
To prevent the occurrence of corrosion, a relative humidity above 70 % should be avoided. Above a relative humidity of 70 % corrosion may occur as a result of the presence of gas components like CO_2, O_2 and H_2S.

5.1.2.2 *Effects of Carbon Dioxide*

The natural gas distributed in the Netherlands to date is considered non corrosive [64]. The average concentration of CO_2 in G-gas is 0.89 mol%, while the observed maximum concentration of CO_2 in wide band gas in dry gas distribution systems is 62 mol% (see Table 2).

The effect of CO_2 on the corrosion rate of steel in the natural gas infrastructure has been studied extensively. Generally, gases with a higher CO_2 partial pressure are increasingly corrosive [64-81]. This means that, with a given gas composition, the gas becomes more corrosive at higher pressure due to the increased partial pressure of the corrosive components at higher pressure.

The corrosivity of gases containing CO_2 is based on the easy dissolution of CO_2 in water. After dissolution in water carbonic acid is formed. This causes the pH of the water to decrease to pH 4 at a CO_2 partial pressure around 1 bar. It has been observed that, in an oxygen free environment, carbonic acid is more corrosive than strong acids like hydrochloric acid (HCl) [65].
Various models have been proposed to predict the corrosion rate, dependent on the concentration of CO_2 and the temperature, of which the model by De Waard and Milliams, as shown in Figure 6, is the most well known [74]. For wide band gas, with a maximum concentration of CO_2 of 62 mol% (see chapter 2), in gas distribution systems with a pressure of 8 bar(g) and a gas temperature of 7 °C, the De Waard and Milliams model predicts a corrosion rate of 1.5 mm/year. The formation of protective scales may however lead to a decrease of the corrosion rate, therefore increasing the service life of the steel components of the gas distribution systems compared to the service life predicted based on the corrosion rate models [65].

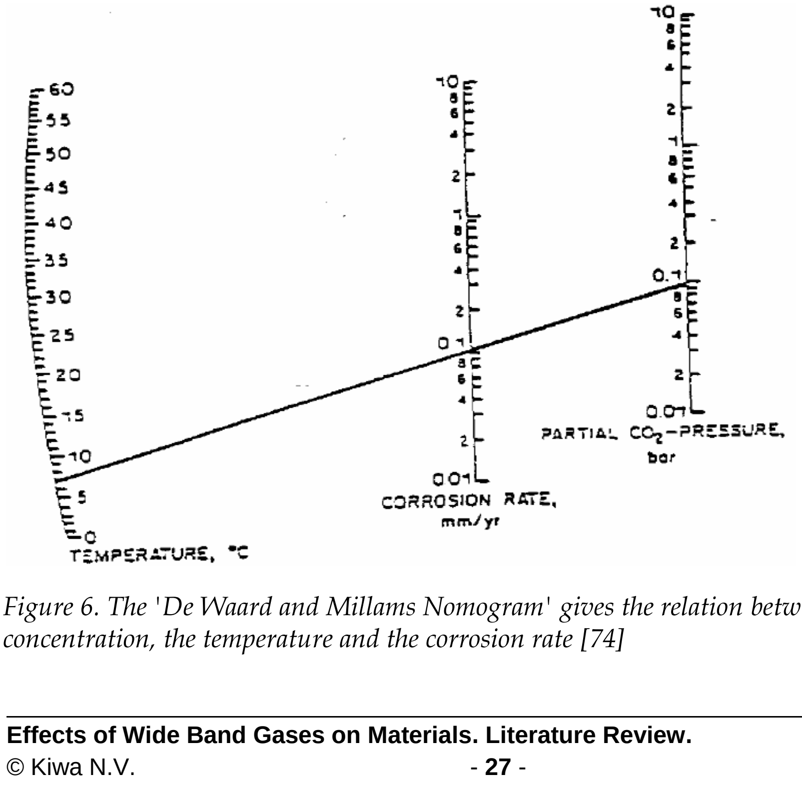

Figure 6. The 'De Waard and Millams Nomogram' gives the relation between the CO_2 concentration, the temperature and the corrosion rate [74]

A limitation of the known corrosion rate models is that that only very limited interactions between different gas components have been included in the experimental setup.

Based on corrosion rate models, with liquid water present in gas distribution systems the maximum concentration of CO_2 in wide band gas may lead to a corrosion rate limiting the service life of steel components. In practice however the corrosion rate may be limited due to the formation of protective scales. Therefore the importance to minimize the risk of the presence of liquid water in the gas distribution system should be emphasised. Interactions between different gas components may affect the corrosion rate to a great extent as is described in section 5.1.2.5 and 5.1.2.6.

5.1.2.3 Effects of Oxygen

For low O_2 concentrations (from ppm level to 0.5 mol%) the effect of the presence of oxygen on the corrosion rate is not entirely unambiguously described in literature. Part of the literature describes a linear relation between the corrosion rate and low oxygen concentrations in aqueous media, but also aqueous media with chlorides or sodium sulphate (Na_2SO_4) [66-69,72,82]. This means that the corrosion rate increases with the concentration of O_2. Other literature sources report little effect of the presence of O_2 concentrations below 100 ppm [75,81], while also an improvement of the resistance to carbon dioxide corrosion is sometimes reported at an oxygen concentration of 2 ppm [71] and 0.5 - 2.5 mol% [65]. This is explained by an improved protectivity of the scales formed due to the presence of low oxygen concentrations [65,71].

For O_2 concentrations higher than 0.5 % unacceptable corrosion has been observed under wet conditions, however the corrosion rate decreases with increasing O_2 content due to the formation of protective scales at higher O_2 content [64]. In a condensing environment the corrosion rate is not dependent on the O_2 content [64].

With liquid water present in gas distribution systems it is unclear whether the maximum concentration of O_2 in wide band gas of 2.6 mol% results in a corrosion rate limiting the service life of steel components. Low oxygen concentrations may improve the corrosion resistance due to the improved protectivity of the scales formed. Interactions with other gas components may affect the corrosion rate to a great extent as is described in section 5.1.2.5 and 5.1.2.6.

5.1.2.4 Effects of Hydrogen Sulphide

The presence of H_2S in an aqueous environment results in a corrosive medium. The presence of H_2S can result in various corrosion mechanisms. H_2S can increase the general corrosion rate. Due to the dissociation of H_2S dissolved in water, H^+ ions are formed. The electrons formed during dissolution of steel, can be consumed in the formation of molecular hydrogen (H_2) from the hydrogen ions. In general corrosion due to the presence of H_2S, iron sulphide (FeS) scales are formed that can decrease the corrosion rate. However, small defects in the FeS scale may cause occurrence of localised corrosion because the scale is cathodic compared to the steel [83]

The major risk of the presence of H_2S however is not the general corrosion, but the occurrence of stress corrosion cracking mechanisms related to hydrogen embrittlement. Atomic hydrogen is formed in the reduction of hydrogen ions. Atomic hydrogen can either recombine to molecular hydrogen (H_2) or can penetrate into the metal as adsorbed hydrogen. In the presence of H_2S the equilibrium between recombination and adsorption shifts strongly towards adsorption.

Typical hydrogen embrittlement mechanisms are environmentally induced mechanisms like Hydrogen Induced Cracking (HIC) and stress corrosion mechanisms Sulphide Stress Corrosion Cracking (SSCC) [80]. Generally stress corrosion mechanisms in steel are associated with hard zones in the material, caused by cold working (e.g. bending) or welding. The susceptibility to stress corrosion cracking increases with the H_2S concentration and with increasing acidity of the medium. Based on the pH of the solution and the partial pressure four regimes can be identified with increasing severity of stress corrosion cracking, as is shown in Figure 7. For an 8 bar gas distribution system at a partial pressure of H_2S of 3 mbar there is a transition from region 0 (no stress corrosion) to the stress corrosion regions. A partial pressure of 3 mbar at a pressure of 8 bar(g) corresponds with a H_2S concentration of 333 ppm. [84, 85] At lower gas pressures the transition shifts towards higher concentrations of H_2S, because the partial pressure of H_2S required forms an increasing part of the gas pressure. For high pressure gas transport the transition shifts towards lower concentrations.

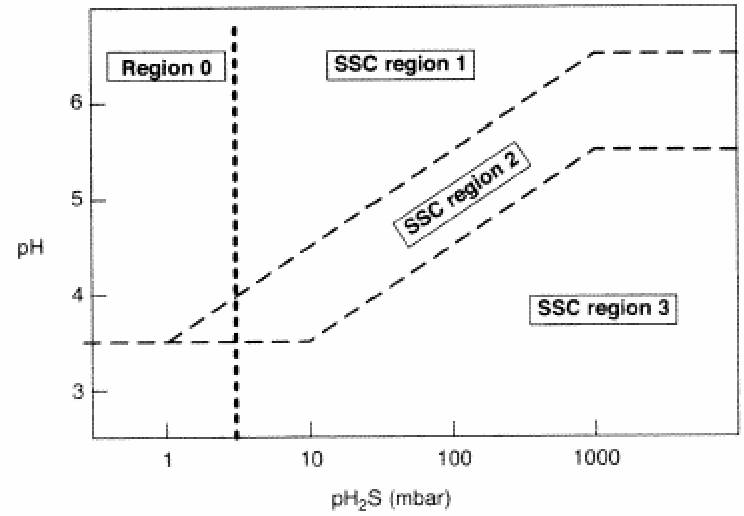

Figure 7. Regimes for stress corrosion cracking mechanisms in sour service [85]

With the maximum concentration of H_2S in wide band gas the risk of stress corrosion cracking is low (region 0). For wide band gases no stress corrosion cracking is expected. As far as general corrosion is concerned iron sulphide (FeS) scales are formed that can decrease the corrosion rate. However, small defects in the FeS scale may cause occurrence of localised corrosion because the scale is cathodic compared to the steel. With the low allowed concentration of 160 ppm H_2S in wide band gases only a limited influence on general corrosion is to be expected, although the risk is higher than for narrow band gasses. Interactions with other gas components may affect the corrosion rate to a great extent as is described in section 5.1.2.5.

5.1.2.5 *Effects of Interactions between CO_2, O_2 and H_2S*

At temperatures below 60 °C, as in the natural gas infrastructure, the presence of H_2S in combination with CO_2 can increase the corrosion rate because the H_2S prevents the formation of protective iron carbonate ($FeCO_3$) scales [77].

The presence of both H_2S and O_2 in the natural gas infrastructure may, additionally to the possible corrosion reactions that were previously described, lead to other conditions that increase the corrosion rate, through the formation of elemental sulphur (S). The formation of elemental sulphur can occur in moist circumstances, as

well as in dry systems. In dry systems iron oxide ('rust') already present on the steel surface, acts as a catalyst in the formation of sulphur. Elemental sulphur is a strong oxidiser.
Once the elemental sulphur has been formed, in the presence of moisture highly localised corrosion (pitting) can occur. Small quantities of sulphur can also be transported in the gas flow and precipitate in pressure regulators [86,87]. Operational problems with pressure regulators may occur for example by clogging of restrictions by the precipitating sulphur [88].

The combined presence of O_2, CO_2 and H_2S in an aqueous environment results in a highly corrosive medium [89]. The combined effect of O_2, CO_2 and H_2S on the corrosion rate has been modelled, using gas compositions in the range of narrow band gases [81]. However, the model has been based on short term (2 weeks) corrosion experiments only. In these experiments the highest corrosion rate has been observed in the gaseous phase for partially immersed specimens (CO_2 1 %, O_2 100 ppm, H_2S 3.8 ppm, T = 15 °C) [81]. In recent experiments [90] to model the corrosion behaviour in carbon capture and storage (CCS) systems, also indications are found that traces (ppm level concentrations of oxygen and/or H_2S) may lead to detrimental corrosion rates for carbon steel and even some alloyed steel types, while considerable but lower corrosion rates are observed at higher concentrations. Additional work to further examine the effect of traces of O_2 and H_2S on the corrosion rate has to be performed.

5.1.2.6 *Effects of Interactions between O_2, CO and CO2*

The combined presence of CO and CO_2 in an aqueous environment may result in the occurrence of stress corrosion [84,91,92]. The presence of oxygen is reported to mitigate the stress corrosion process [84], while another study reports a promotion of the stress corrosion process by the presence of oxygen [92]. In some experiments stress corrosion was observed at a partial pressure of 0.07 bar for CO as well as CO_2. In another study stress corrosion cracking was observed at a partial pressure of CO_2 above 2.4 bar and a CO partial pressure above 0.3 bar [92]. For the distribution of G-gas no failures due to CO stress corrosion are known.

Given the expected partial pressures of CO and CO_2 for wide band gases (see Table 2), based on the above mentioned experimental results, the occurrence of stress corrosion due to the presence of CO may be possible. The observed concentration of CO in high band gas is relatively high compared to the concentration of CO in Groningen gas. Therefore the occurrence of stress corrosion cannot be completely ruled out for wide band gases (especially SNG). It is therefore important to prevent the occurrence of moisture (water) in the gas distribution network.

5.1.2.7 *Effects of Ammonia*

Steel is often used for the transport and storage of ammonia. However, at high concentrations ammonia can cause stress cracking in carbon steel. The presence of O_2 or a combination of O_2 and CO_2 is an essential precondition for the occurrence of ammonia stress cracking. Stress cracking due to ammonia is especially found in cold formed or welded materials [84]. The concentration of ammonia found in wide band gases is very low (up to 100 ppm (70 mg/m^3) (see chapter 2)). Because the concentration is low compared to the conditions where stress corrosion is observed, the effect on steel is unknown but is expected to be negligible.

5.1.2.8 *Effects of Hydrogen*

Hydrogen Stress Cracking (HSC) can occur if steel is exposed to H_2, but this only occurs at high stresses in steel types, like high strength steel and in highly stressed materials, e.g. near welds or cold deformation. No serious problems occurred during the town gas period, when concentrations up to 50 % H_2 were transported through steel mains, at low pressures (probably around 30 mbar). In town gas storage tanks operated at pressures of 8 bar, however, HSC has been detected. [25] Furthermore, hydrogen can have an adverse effect on the ductility and fracture toughness of steel. Besides that, the fatigue crack growth rate is accelerated by the presence of hydrogen [93]. Compared to the crack growth rates in air, the largest effect of hydrogen is found for high values for the stress intensity factor (ΔK) as is illustrated in Figure 8 [94].

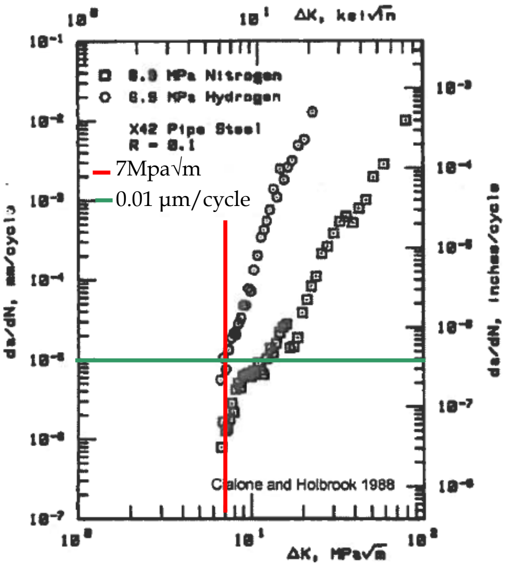

Figure 8: Fatigue crack growth rate (da/dN) as a function of the stress intensity factor (ΔK) for hydrogen and nitrogen for API X42 steel [93]

The presence of oxygen has been shown to reduce the effect of hydrogen on the crack growth rate. In the presence of H_2S the effect of hydrogen on the crack growth rate was observed to increase [94]. An analysis of the stress situation for gas distribution infrastructure showed that the ΔK values are relatively low (7 MPa√m). The results and assumptions of this analysis are summarised in Appendix V. This means that for loads as applicable to the gas distribution infrastructure the effect of hydrogen on the fatigue crack growth is negligible (0.01 µm/cycle), irrespective of the concentration of hydrogen. Therefore the expected concentrations of H_2 in wide band gas are not expected to have no deleterious effects is expected on steel in the gas distribution infrastructure.

5.1.2.9 *Effects of Chlorine and Fluorine Containing Components*

Chlorine and fluorine containing components can have an adverse effect on the protective iron carbonate scales [92], but this effect is only expected for components which dissociate to ions in aqueous solutions, resulting in chloride and fluoride. The concentration limit for chlorine and fluorine containing components in wide band gas is low (see Table 2). The expected components are stable. Therefore no effect on the integrity of steel pipes is expected.

The maximum concentration of HCl in wide band gas is limited. Traces of HCl are not expected to limit the service life of steel gas distribution materials.

Also the concentration of chlorides in the ground water is rather limited (max ca 300 mg/l at a depth of 1 m) and is in the same order of magnitude as for potable drinking water (max 150 mg/l). This is not considered detrimental to the steel gas distribution mains, as cast iron is to date applied without large corrosion problems in water distribution mains.

5.1.2.10 *Effects of Hydrogen Cyanide*

In aqueous solution, hydrogen cyanide (HCN) dissociates to H^+ and CN^-. In the presence of the CN^- ion, the passivating film layer of FeS, formed in general corrosion in the presence of H_2S, is not formed. Even when the passivating film of FeS has already been formed, the layer is destroyed by the presence of CN^- ions. The acceptable level of cyanides in water is 10-20 ppm [95]. Another effect of cyanide is the promotion of the adsorption of atomic hydrogen in steel in favour of the recombination of atomic hydrogen to hydrogen gas molecules. The adsorption of atomic hydrogen can cause the occurrence of hydrogen induced cracking (HIC) [96].

5.1.2.11 *Effects of Hydrocarbons*

In practice metals including steel are extensively used in combination with (aromatic) hydrocarbons without any problem. Therefore effects of (aromatic) hydrocarbons, including BTX, on steel are not expected.

5.1.2.12 *Effects of Other Components*

Because the expected concentrations for other components in wide band gas are low, deleterious effects by these components seem unlikely.

5.1.3 Conclusions

The most important factor in the corrosion of steel pipelines is the presence of water. Without water no corrosion problems are to be expected. With water present the severity of the material degradation by corrosion is affected mainly by the concentrations of oxygen, carbon dioxide and hydrogen sulphide. The effect of these constituents individually was examined extensively for CO_2, and also the effect of the presence of H_2S is well understood. Generally the corrosion rate increases with increasing concentration of CO_2 and with temperature, as is described in well known corrosion models like the de Waard and Milliams nomogram. Also for O_2, generally the corrosion rate increases with the concentration. From sour service applications in the Oil and Gas industry it is well known that H_2S can cause stress corrosion cracking. H_2S may also cause corrosion problems through a mechanism where elemental sulphur is formed. The maximum allowable concentration of H_2S in wide band gases is limited and given the current chemical specification for wide band gas no detrimental corrosion of steel gas pipes is expected H_2S alone.

Some corrosion problems may occur however as a result of the interaction between several gas constituents. The corrosion rate may be increased by the combined presence of H_2S and CO_2. The presence of CO_2 and CO may cause stress corrosion cracking, which however is a greater risk for high pressure gas transport than for low pressure gas distribution networks. The effect of the presence of traces of O_2 in combination with CO_2 is not known exactly, as the literature is not unambiguous. There are indications that traces of oxygen may have a large effect on the corrosion rate compared to higher concentrations. It is therefore proposed to perform corrosion experiments to further quantify the risk of corrosion focussing on the interactions between CO_2, O_2 and H_2S.

Based on the literature and the experience with hydrogen during the town gas period no effect of hydrogen on steel in the gas distribution infrastructure is expected. Because the expected concentration for other components in wide band gas is low, a deleterious effect is unlikely.

These conclusions are summarised in the table below.

Table 8. The effect of components present in wide band gas on steel. Some components will have no deleterious effect (green) or no or little deleterious effect is expected (light green). Other components may have a deleterious effect (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
with water: possibly		probably none						with H_2S and water: possibly	with water: possibly		probably none		with water: possibly	none

5.2 Copper

In gas distribution mainly copper tubes manufactured from Cu-DHP (deoxidised high phosphorus) are used. Copper tubes are only used at low pressures.

The material can be divided into three classes (see Table 9) which have different mechanical properties.

Table 9. Three classes of copper.

Class	**Annealed (R220)**	**Half hard (R250)**	**Hard (R290)**
Tensile strength	> 220 MPa	> 250 MPa	> 290 MPa
Elongation at fracture	> 40 %	> 30 %	> 3 %

5.2.1 *Failure Mechanisms*

The corrosion mechanisms described in this chapter are generally applicable to the copper applied in the Dutch natural gas distribution network.
In general the susceptibility to corrosion and the aggressivity of a corrosive medium are highly dependent on the specific properties of the copper.

Copper can be affected by homogeneous corrosion but also stress corrosion [70]. Stress and environment must be present, from which stress is the most distinctive, for stress corrosion [97].

5.2.2 *The Influence of Wide Band Gases on Copper*

5.2.2.1 *Effects of Water*

The presence of water is one of the preconditions for the occurrence of corrosion. Condensation of water in the natural gas distribution network is possible in wide band gases. Except for the humidity of the transported gas there are other possible sources of water in the gas infrastructure such as leaking joints in the low pressure distribution system and incomplete draining after pressure testing.

Once water is present in the gas distribution network, a corrosive environment can result from the constituents of the transported gasses. The concentration of the gas constituents is determining the aggressiveness and the type of corrosion mechanism that takes place. Copper corrosion products and water containing minerals can form protective scales on the copper [98].

The gas constituents with a known influence on the corrosion of copper are oxygen (O_2), carbon dioxide (CO_2), hydrogen sulphide (H_2S), sulphur (S) and ammonia (NH_3), which are discussed in the following sections.

5.2.2.2 *Effects of Carbon Dioxide and Oxygen*

The cause of the corrosiveness of gases containing CO_2 is the dissolution in water. After dissolution in water carbonic acid is formed which causes the pH of the water to decrease. This leads to degradation of metallic pipes. Copper has a better corrosion resistance compared to carbon steel. However, copper will also degrade when oxygen is present as well [70]. If no carbon dioxide is present, the oxygen will contribute to the formation of a protective scale on the copper.

5.2.2.3 *Effects of Sulphur Containing Components*

Copper corrosion experiments according to ASTM 1838 reveal the (mutual) influence of sulphur (S) and hydrogen sulphide (H_2S). In the presence of both H_2S and S more corrosion is seen in comparison to the presence of the individual components [99].
A concentration of 0.35 ppm H_2S or 2 ppm sulphur lead to corrosion of copper while the combination of sulphur and hydrogen sulphide decreases the threshold value for corrosion to 0.12 ppm H_2S and 0.5 ppm S.
An increasing concentration of sulphur will further lower the threshold value for corrosion of copper by H_2S.

The presence of ethyl mercaptan (CH_3-CH_2-SH) up to a concentration of 100 ppm does not lead to degradation. In the presence of both mercaptan and H_2S it is observed that mercaptan has a protective effect on the degradation by H_2S. In the presence of mercaptan and sulphur it is the other way around. In this case the mercaptan promotes the degradation by sulphur. This leads to degradation at sulphur concentrations at which no degradation was expected. [99]
The presence of water accelerates the possible reactions. In order to prevent corrosion there has to be strived to have gas without H_2S. If this is impossible the water content should be as low as possible [99].
In the Dutch gas distribution network no mercaptans are used as odorant, but tetra hydro thiophene (THT) (see chapter 2). The effects of THT on copper are unknown; however to date no negative influences of THT on copper using dry G-gas have been observed. An adverse effect is therefore not expected.

5.2.2.4 *Effects of Ammonia*

Ammonia is one of the most well-known causes of stress corrosion in copper [97]. The conditions under which ammonia stress corrosion can occur are a combination of the following factors:

- Ammonia
- Moisture (water)
- Oxygen
- Internal stress in the material from various causes.

Ammonia stress corrosion can only occur if all these factors are present. Local differences in internal stress inside the material can lead to local degradation of the material because of the important role of the internal stresses [97].
Internal stress in the materials can have different causes. One of the most important causes of internal stress lies in the production process. Especially the combination of

forming and (insufficient) heat treatment can result in high levels of internal stress. Also the construction of a network made of copper pipes can result in internal stress. For example: the cold forming of bends in copper pipes. [97]
Wide band gases (which could contain up to 100 ppm ammonia) in combination with water and internal stress can cause corrosion.

5.2.2.5 *Effects of Hydrocarbons*

In practice metals including copper are extensively used in combination with (aromatic) hydrocarbons without any problem. Therefore any effects of (aromatic) hydrocarbons, including BTX, on copper are not expected.

5.2.2.6 *Effects of Chlorine and Fluorine Containing Components*

The effect of chlorine and fluorine containing components on copper are unknown, but any effect is only expected for components which dissociate into ions in aqueous solutions, resulting in chloride and fluoride. Because the expected concentration for chlorine and fluorine containing components in wide band gas is low (see Table 2), and the expected components are stable, no adverse effect on the integrity of copper gas distribution materials is expected. The maximum concentration of HCl in wide band gas is limited. Because of the limited concentration the presence of traces of HCl are not expected to limit the service life of copper gas distribution materials.

5.2.2.7 *Effects of Hydrogen Cyanide*

The effect of HCN on copper is unknown. One erosion corrosion failure of copper has been reported related to cyanides. The corrosive medium consisted of hydrocarbon vapours with contaminations of ammonia and cyanides [100]. Therefore it is unknown whether the effect can be contributed to the presence of the cyanides.

5.2.2.8 *Effects of Other Components*

In literature no record of effects of CO or H_2 on copper has been found. Therefore these effects are unknown.

5.2.3 Conclusions

The most important factor in the corrosion of copper is the presence of water. With water present corrosion is affected mainly by the concentrations of oxygen, carbon dioxide, sulphur containing components and ammonia. On the basis of the literature review effects of the other components in wide band gases on the corrosion of copper can not be predicted. Therefore corrosion caused by wide band gases can not be excluded. Additional experimental work is therefore needed.

These conclusions are summarised in the table below.

Table 10. The effect of components present in wide band gas on copper. No or little deleterious effect is expected of some components (light green). The effect of other components is unknown (light orange) or a deleterious effect may be present (orange).

Sulphur containing components	H_2S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO_2	Hydro-carbons	Aromatic hydro-carbons	O_2	H_2
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

5.3 Aluminium

The Dutch natural gas transportation and distribution network contains some aluminium used in gas pressure regulators and gas meters.

5.3.1 *Failure Mechanisms*

Aluminium possesses a very thin oxide layer (ca. 50 Å) on its surface by nature. In case of damage the layer will recover rapidly preventing further degradation. An important condition for the formation of the oxide layer is the presence of oxygen in the system. This oxide layer results in an excellent corrosion resistance of aluminium. However, in certain environments aluminium can corrode [80,101].

5.3.2 *The Influence of Wide Band Gases on Aluminium*

5.3.2.1 *Effects of Water*

The presence of water is one of the preconditions for the occurrence of corrosion. Except for the humidity of the transported gas there are other possible sources of water in the gas infrastructure such as leaking joints in the low pressure distribution system and incomplete draining after pressure testing.

Once water is present in the gas distribution network, a corrosive environment can result from the constituents of the transported gases. The concentration of the gas constituents is determining the aggressiveness of the corrosion.

5.3.2.2 *Effects of Carbon Dioxide*

The gas constituent with a known influence on the corrosion of aluminium is carbon dioxide (CO_2). In combination with water the presence of CO_2 can lead to corrosion problems of aluminium by affecting the protective oxide layer [101].

At low pH levels the oxide layer will dissolve and the underlying material can be affected. This can occur at pH levels below 4. Also at pH levels above 9 similar effects can occur. Therefore low levels of CO_2 will not lead to problems, although higher levels of CO_2 in combination with moisture can lead to corrosion problems of aluminium parts by lowering the pH [101].
In a CO_2/H_2O system at 25 °C a pH level of 4 will be reached at pCO_2 of 0.35 bar [69]. The maximum concentration of CO2 in Wide band gases is up to 60 mol% and lies higher then this partial pressure. Therefore at these concentrations negative effects can occur.

5.3.2.3 *Effects of Chlorine and Fluorine Containing Components*

The presence of chloride ions in combination with aerated aqueous solutions can cause pitting corrosion to aluminium by affecting the protective oxide layer [101]. This effect is only expected for components which dissociate into ions in aqueous solutions, resulting in chloride and fluoride. Because the expected concentration for chlorine and fluorine containing components in wide band gas is low (see Table 2), and the expected components are stable, no adverse effect on the integrity of copper gas distribution materials is expected. The maximum concentration of HCl in wide band gas is limited. Because of the limited concentration the presence of traces of HCl are not expected to limit the service life of copper gas distribution materials.

5.3.2.4 *Effects of Ammonia*

Aluminium alloys have a good resistance against aqueous phases of amines and NH_3 [80].

5.3.2.5 Effects of Other Components

In practice metals including aluminium are extensively used in combination with aromatic hydrocarbons without any problem. Therefore effects of aromatic hydrocarbons, including BTX, on aluminium are not expected. The same applies for the odorant THT used in the Netherlands. To date no effects of THT on aluminium have been observed.

In literature no record of effects of HCN, CO, or H_2, on aluminium has been found. Therefore the effects are unknown.

5.3.3 Conclusions

Aluminium has an excellent corrosion resistance. The most important factor in the corrosion of aluminium is the presence of water. With water present corrosion is affected mainly by the concentrations of carbon dioxide or the presence of chloride ions. Based on the literature the corrosion effects on aluminium caused by the constituents in wide band gasses can not be predicted. However the possible existence of large concentrations of carbon dioxide makes corrosion likely if water is present. Therefore corrosion caused by wide band gasses can not be excluded.

Aluminium alloys have a good resistance against ammonia. Effects of aromatic hydrocarbons, including BTX, are not expected.

These conclusions are summarised in the table below.

Table 11. The effect of components present in wide band gas on NBR. Some components will have no deleterious effect (green) or no or little deleterious effect is expected (light green). The effect of other components is unknown (light orange) or a deleterious effect may be present (orange).

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

6 Conclusions

All the results of this literature review are summarised in the table below.

	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	unknown		probably none		unknown			probably none		unknown	possibly	none, unless liquid (impact resistance)		probably none	unknown
PE	unknown		probably none		unknown			probably none		unknown	none	none, unless liquid		none	probably none
NBR	unknown	possibly	probably none		none	possibly		probably none		none		possibly, if unsaturated	probably none, unless liquid	none	
Steel	with water: possibly		probably none						with H_2S and water: possibly	with water: possibly		probably none		with water: possibly	none
Cu	with water: possibly, depending on their mutual influence			probably none	with water: possibly	probably none			unknown		with water: possibly	probably none		with water: possibly	unknown
Al	unknown			probably none	none	probably none			unknown		with water: possibly	probably none		none	unknown

▨	=	The effect is unknown, but is expected to be very small or non existent.
🟩	=	This component within the concentrations of narrow band has no effect on the material.
🟨	=	The effect is unknown.
🟧	=	Deleterious effects are under some conditions to be expected.

The following main conclusions can be drawn from this literature review:

- A negative effect of (aromatic) hydrocarbons (including BTX) on is not expected due to the low concentrations in wide band gas. Liquid aromatic hydrocarbons (including BTX) may have a negative effect on the impact resistance of PVC-HI.
  The effects of the high concentrations of H_2S in wide band gas are unknown. CO_2 may have an influence on the impact resistance of PVC, because CO_2 has a plasticizing effect on PVC. For the same reason it may also cause a faster initiation of crazes and thus possibly negatively affect the long-term strength. The influence of other components is not known and since the concentration levels in wide band gas are unknown for most components, experiments are needed to determine allowable concentration levels.

- Liquid aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), and liquid higher hydrocarbons will lower the yield strength of PE drastically and reduce the long-term strength measured with the internal water pressure test. These liquids are more likely to occur in wide band gas than in G-gas, because water is not always actively removed.
  Gases like nitrogen (N_2), oxygen (O_2) and carbon dioxide (CO_2) will have no deleterious effect on PE. Although it is not certain what the effects of higher concentrations of H_2 are, it is expected that the effects, if there are any, will be rather small. It is unknown what kind of long-term effects other components, such as sulphur, H_2S, mercaptans, ammonia, chlorine and fluorine containing compounds, HCl, HCN and CO, have on PE

- No deleterious effect of ammonia, CO, CO_2, O_2 and H_2 on NBR is expected. H_2S, halogens and higher aromatic, but also unsaturated chemical compounds causes swelling of elastomeric diaphragms resulting in a decrease of functionality and possibly the failure time

- The most important factor in the corrosion of steel pipelines is the presence of water. With water present the severity of the material degradation by (stress) corrosion is affected mainly by the concentrations of O_2, CO_2 and H_2S. Additionally, some negative influence of CO and sulphur containing components on steel cannot be excluded.

- Water is the most important factor in the corrosion of copper. With water present corrosion is affected mainly by the concentrations of oxygen, carbon dioxide, sulphur containing components and ammonia. On the basis of the literature review effects of the other components in wide band gases on the corrosion of copper cannot be predicted.

- Aluminium has an excellent corrosion resistance. Again, the most important factor in the corrosion of aluminium is the presence of water. With water present corrosion is affected mainly by the concentrations of carbon dioxide or the presence of chloride ions. Aluminium alloys have a good resistance against ammonia. The effect of other components in wide band gases on aluminium is unknown.

It is too early to conclude anything about the maximum allowable concentrations of gas components in wide band gases. Additional experimental work, focussed on gases with a possible negative effect, is needed. This will be done in the following phase of this EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems Expanding the Distribution Band of the Gas Quality in the Netherlands".

I Gas composition of different anaerobic digestion installations

Biogas	**CH_4 (mol%)**	**CO_2 (mol%)**	**O_2 (mol%)**	**N_2 (mol%)**	**H_2S (ppm)**	**Benzene (mg/m^3)**	**Toluene (mg/m^3)**	**Hydrogen (mg/m^3)**	**Ammonia (mg/m^3)**	**Organo-silicons (mg/m^3) (see also Appendix III)**	**Other traces (see also Appendix II)**	**Reference**
Landfill	47 – 57	37 - 41	< 1	< 1 - 17	36 - 115	0.6 - 2.3	1.7 - 5.1					[102]
Sewage Digester	61 – 65	36 - 38	< 1	< 2	n.a.	0.1 - 0.3	2.8 - 11.8					
Farm biogas Plant	55- 58	37 - 38	< 1	< 1 - 2	32 - 169	0.7 - 1.3	0.2 - 0.7					
Landfill	59 – 68	30 - 39	n.a.	n.a.	15 - 428	21.7 - 35.6	83.3 - 171.6					
Landfill	37 - 62	24 - 29	< 1	n.a.	n.a.	<0.1-7	10 - 287					
Landfill	56	37	< 1	n.a.	n.a.	3.0	55.7					
Landfill	44	40	2.6	13.2	250	n.a.	65.9					
Sewage digester	58	39	0	3.7	63	n.a.	n.a.					
Sewage digester	63	37	n.a.	n.a.	n.a.	n.a.	n.a.					
Sewage digester	58	34	0	8.1	24	n.a.	n.a.					
Farm biogas plant (manure 33%, Crops 67%)	53.13	42.32	0.1	4.42	0.03				Traces	Traces	• Halogen components • Phosphine	[103, 104]
Farm biogas plant (manure 50%, Crops 50%)	51.54	43.82	0.1	4.54	< 0.01				Traces	Traces	• Halogen components • Phosphine	
Farm biogas plant (Manure 100%)	62.84	34.86	0.05	3.57	0.04				Traces	Traces	• Halogen components • Phosphine	
Farm biogas plant (Manure 75%, Crops 25%)	57.46	37.99	0.09	4.46	< 0.01				Traces	Traces	• Halogen components • Phosphine	
Sewage Digester	61.94	37.86	0.04	0.49	-							

Biogas	**CH_4 (mol%)**	**CO_2 (mol%)**	**O_2 (mol%)**	**N_2 (mol%)**	**H_2S (ppm)**	**Benzene (mg/m^3)**	**Toluene (mg/m^3)**	**Hydrogen (mg/m^3)**	**Ammonia (mg/m^3)**	**Organo-silicons (mg/m^3) (see also Appendix III)**	**Other traces (see also Appendix II)**	**Reference**
Mixture of 12 farm biogas plants	60.42	35.5	0.74	3.08	3085	traces	Traces		0.004	Not detected	• Pesticides • Volatile organic compounds • Cupper • Mercury	[105]
Farm biogas plant (manure 100%)	40 - 57	32 - 58	0.75 - 2.5		0 - 1100 mg/m^3			0	Traces, max 70 mg/m^3	Traces, max 25 mg/m^3	• Halogen components • Aromatics • Volatile organic compounds	[106]
Farm biogas plant (Crops 100%)	45 - 64	33 - 51	0 - 9		0 - 450 mg/m^3			0 - 190	Traces, max 70 mg/m^3	Traces, max 25 mg/m^3		
Farm biogas plant (manure 50%, Crops 50%)	47 - 54	43 - 52			150 - 800 mg/m^3			0	Traces, max 70 mg/m^3	Traces, max 25 mg/m^3	• Halogen components • Aromatics • Volatile organic compounds	
Sewage Digester	63 - 67		0 - 1		0 - 50 mg/m^3					0 - 500		

II Halogen containing components

Component	Max. concentration		Reference
	ppbv	µg/m^3	
1,1,1-Trichloroethane		0.05	[107-109]
1,1,2-Trichloroethane		0.08	[107]
1,1-Dichloroethane	113	0.01	[107], [109], [110]
1,1-Dichloroethene	149	0.37	[107], [109], [110]
1,2-Dichlorobenzene		0.08	[107]
1,2-Dichloroethane	13	1.22	[107], [108], [110]
1,2-Dichloroethene	54	0.11	[107], [109]
1,3-Dichlorobenzene		0.01	[107]
1,3-Dichloropropene		0.07	[107]
1,3-Dichloropropylene	323	0.09	[110]
1,4-Dichlorobenzene		0.4	[107]
1-Chloro-1-fluoroethane			[108]
1-Chloropropane			[108]
Benzyl chloride			[111]
Bromobenzene	31		[110]
Bromoform	100		[110]
Bromomethane	319		[110]
Carbon tetrachloride	82	0.23	[107], [109], [110]
Chlorobenzene	339	0.12	[110], [111]
Chlorodifluoromethane			[109]
Chloroethane	973		[109], [110]
Chlorofluoromethane			[109]
Chloroform		0.16	[107], [110]
Chloromethane	1070		[110]
Dichlorodifluoromethane	10200		[109]-[111]
Dichloroethylene			[110]
Dichlorofluoromethane			[109]
Dichlorotoluene			[111]
Ethyl chloride			[108]
m-Dichlorobenzene			[111]
Methylene chloride	66	7.95	[107]-[111]
o-Dichlorobenzene			[111]
p-Dichlorobenzene			[111]
Tetrachloroethane		9.16	[107]
Tetrachloroethylene	68		[107]-[110]
Trichloroethene	34	62.91	[107], [109], [110]
Trichlorofluoromethane	270		[109], [110]
Trichlorotrifluoroethane	23		[109], [110]
Vinyl chloride	800		[110], [111]

Blank cell = traces have been found

III Organo-silicon components

Biogas	(L1)	(L2)	(D3)	(L3)	(D4)	(L4)	(D5)	Reference
	Maximum concentration (mg/m^3)							
Landfill	n.d.	6.07	0.49	0.32	12.53	n.d.	4.73	[112]
	3.2	0.9	0.44	n.d.	5.1	n.d.	0.65	[113]
	7.43	1.31	0.01	0.05	8.84	<0.01	1.09	[114]
	3.21	0.77	0.45	0.04	5.03	< 0.01	0.53	[114]
	12.0	5.0	0.84	n.d.	15.0	<0.1	3.3	[115]
	n.d.	0.87	0.088	n.d.	2.06	n.d.	47	[116]
	n.d.	0.14	0.083	n.d.	1.21	n.d.	0.40	[116]
	n.d.	0.12	0.81	n.d.	2.0	n.d.	3.33	[116]
	n.d.	0.23	-	n.d.	5.03	n.d.	0.83	[116]
	0.56	0.63	<0.1	< 0.01	< 0.67	n.d.	<0.3	[108]
	0.2	<0.2	<0.2	0.2	1.5	<0.2	22.3	[117]
Sewage sludge	n.d.	0.02	0.04	0.02	0.93	n.d.	6.03	[112]
	n.d.	0.08	0.42	n.d.	8.2	n.d.	15.5	[113]
	n.d.	<0.05	0.35	n.d.	7.7	n.d.	12.0	[113]
	0.15	0.05	0.17	0.03	6.98	0.15	9.65	[114]
	0.08	0.01	0.2	0.02	3.02	0.02	2.81	[114]
	0.07	0.008	<0.04	<0.2	0.87	<0.04	1.27	[108]
Max	**12.0**	**1.31**	**0.84**	**0.32**	**15.0**	**0.15**	**47**	

n.d.	= not detected
-	= not analyzed

L1 = Trimethyl silanol
L2 = Hexamethyldisiloxane
D3 = Hexamethylcyclotrisiloxane
L3 = Octamethyltrisiloxane
D4 = Octamethylcyclotetrasiloxane
L4 = Decamethyltetrasiloxane
D5 = Decamethylcyclopentasiloxane

IV Composition of a Natural Gas Condensate

Table 12. Composition of a G-gas natural gas condensate [25].

Component	Quantity (%)
n-decane	12.9
n-undecane	9.6
n-nonane	8.1
xylenes	6.5
cumarone	5.8
toluene	5.0
n-octane	4.2
n-dodecane	3.8
mesithylene	3.4
benzene	2.6
n-tridecane	2.5
n-heptane	1.8
n-tetradecane	1.5
cyclo-hexane	1.1
n-hexane	0.7
n-pentadecane	0.6
iso-heptanes	0.4
n-pentane	0.3
2.3 dimethyl-butane	0.3
2.2 dimethyl-butane	0.2
iso-pentane	0.18
neo-pentane	0.14
n-hexadecane	0.1
n-butane	0.05
iso-butane	0.03
n-heptadecane	0.02

Please note that the table above only contains the components that are measurable with a gas chromatograph. It is known from infrared spectroscopy measurements at Kiwa Gas Technology that the following aromatic components can occur in G-gas natural gas condensate as well:

- alkylbenzene
- cumene
- 1,2,4 trimethylbenzene
- naftalene
- p-cymene

V Analysis of the Stress State of the Steel Pipes in the Gas Distribution Infrastructure

The stress state in steel gas distribution pipes has been determined as well for longitudinal as for circumferential welds based on the following basic information and assumptions [118].

Basic information and assumptions

- Tube diameter: 60, 100, 200, 300, 400 and 500 mm
- Wall thickness: 3-20 mm
- Maximum difference in gas pressure 6 barg (minimum pressure of 2 barg in 8 barg network)
- Traffic load (lorry, 30 tons, speed 50 km/h): 20 MPa
- Traffic load (lorry, 30 tons, speed 15 km/h, speed ramp): 40 MPa
- Out of roundness of the tube (peaking longitudinal welds): max 2%
- High-low in circumferential welds: 2 mm

To be able to calculate the stress intensity factor (ΔK) the following defect has been assumed, with:

- $a = 0.25t$
- $2C = 6a = 3t$

(see Figure 9)

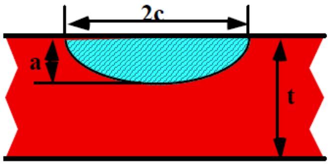

Figure 9. Assumed defect for calculation of the stress intensity factor.

The following loading frequencies have been assumed:

Source of load	Frequency [Hz]
Internal pressure changes	4×10^{-5}
Traffic (speed hump, 15 km/h)	1
Traffic (50 km/h)	10

Calculations

The stress intensity factor (ΔK) for different stress states has been calculated using the software program Signal as described in [118]. The above mentioned basic information and assumptions have been used.

Results

Source of load	Stress Intensity Factor, ΔK [MPa√m]
Internal pressure changes	0.5 - 1
Internal pressure with out of roundness	0.5 - 2
Internal pressure with out of roundness (peaking)	1 - 6
Internal pressure with high-low	1 - 7
Traffic loading	3

Conclusion

The maximum stress intensity factor is 7 MPa√m. At this stress intensity factor the fatigue crack growth rate for hydrogen loaded material reaches the threshold value of 0.01 µm/cycle as can be seen from Figure 10. This crack growth rate is considered acceptable to BS7910 [119]. Therefore it can be concluded that for the given conditions the fatigue crack growth is not influenced by hydrogen loading.

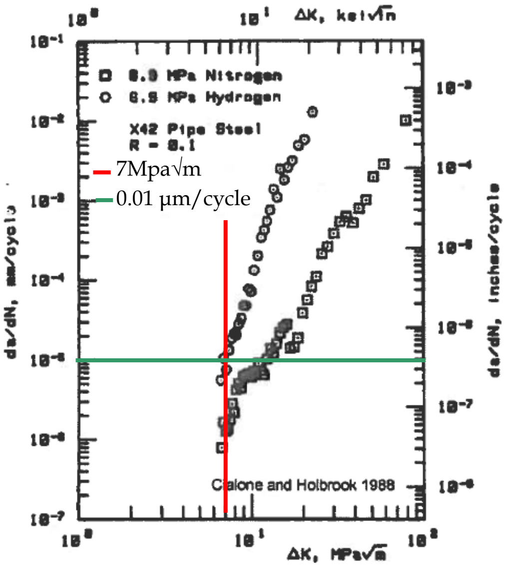

Figure 10. Fatigue crack growth rate (da/dN) as a function of the stress intensity factor (ΔK) for hydrogen and nitrogen for API X42 steel [93]

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