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6 March 2012

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

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## Colophon

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# Preface

This literature review is part of the EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems within the Current Distribution Band for Natural Gas in the Netherlands". The working title of this project is "Effects of Narrow Band Gases on Materials". It is part of the EDGaR program sub theme 1.2.

The following partners are involved in this project:

- Enexis
- Liander
- Stedin
- Gasunie
- Kiwa

Kiwa is project leader.

This project is closely related to the research projects with working title "Effects of Wide 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-110205 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. For this reason the effects of the change to narrow band gases are researched in this EDGaR research project "Effects of Sustainable Gases on Materials used in Gas Transmission and Distribution Systems within the Current Distribution Band for Natural Gas in the Netherlands".

In this project the following main research question will be answered:  
*Are the most important materials used in the Dutch gas distribution network resistant to narrow band gases?*

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

	Sulphur containing components	H <sub>2</sub> S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydro-carbons	Aromatic hydro-carbons	O <sub>2</sub>	H <sub>2</sub>
PVC	probably none	none	probably none			unknown		probably none		unknown	possibly	none, unless liquid (impact resistance)		probably none	unknown
PE	probably none	none	probably none	none	probably none	unknown		probably none		unknown	none	none, unless liquid		none	
NBR	probably none				none	unknown		probably none		none		probably none, unless liquid		none	
Steel	with water: possibly		probably none						with H <sub>2</sub> S and water: possibly		with water: possibly	probably none		with water: possibly	none
Cu	with water: possibly, depending on their mutual influence		probably none		with water: possibly	probably none			unknown		with water: possibly	probably none		with water: possibly	unknown
Al	unknown		probably none		none	probably none			unknown		with water: possibly	probably none		none	unknown

	=	The effect is unknown, but is expected to be very small or non existent.
	=	This component 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.

It is too early to conclude anything about the concentration limits given in the current tentative specification for narrow band gas, because a deleterious effect of various components in narrow 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.

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# 1 Introduction

## 1.1 Goal

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

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

In this respect the following sub questions are relevant:

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

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 narrow 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 narrow 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 narrow band gases on the Dutch gas transport network are investigated by Gasunie / Kema and will be summarised in a separate report.

## 1.2 Background

Network operators explore the possibilities to make the gas supply more sustainable and to extend the variety of gas sources. In this respect the use of the existing gas infrastructure, to which almost all customers in the Netherlands are connected, for transport and distribution of gases originating from these various sources should be evaluated. 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.

The existing Dutch gas infrastructure has been designed for transport and distribution of (pseudo) Groningen gas (G-gas). However, this situation will change. Natural gases from other sources, biogas and SNG, have to be transported as well. This rapidly expanding variety of gases should preferably be transported and distributed through the existing natural gas infrastructure, because (partial) replacement of this infrastructure will result in very high costs. Therefore, network companies consider even partial degradation as highly unwanted. Despite the fact that these gases generally have a composition different from the natural gas used to

date, the distribution network should not suffer from increased materials problems when used to transport these gases.

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

To be able to distinguish between the various possible gases that will be injected into the gas network, the following three types of gas compositions are distinguished (Table 1).

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 chapter 2)	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 narrow band gases on materials used in gas distribution systems. Two other reports will review the influence of wide band gas on materials and the influence of narrow and wide band gases on joints and connections, respectively. Another literature review performed by Gasunie/Kema will discuss the effects of transport of narrow 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 Gas 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 III: References

Next, these literature sources were evaluated in the light of the questions a) until e) 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 narrow band gases, is defined.

Chapter 3 discusses first sub question b), which deals with the most important materials used in the Dutch gas network. Then practical failure data is analysed to review the failure mechanisms of the most important materials. This answers partly sub question c).

Chapter 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), which focuses on the components in narrow band gases that can influence the mentioned failure mechanisms. At the end of each section the conclusions will be presented.

It will not be possible yet to answer sub question e) dealing with components in narrow 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 narrow 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 Narrow Band Gas

In this chapter sub question a) is answered by defining narrow band gas. Furthermore, a comparison is made with the reference: Groningen gas (G-gas). The Dutch gas distribution and transmission companies have decided that the physical properties of narrow band gas, such as the calorific value and Wobbe Index, should be within the range of G-gas. This means that narrow band gas can be used in the same appliances as G-gas. The main physical properties and their band width can be found in Table 2.

Table 2. Most important physical properties of Groningen gas.

Physical property	Band width	Unit
Calorific value	34.5 - 36.0	MJ/m <sup>3</sup> (n)
Wobbe index	43.46 - 44.41	MJ/m <sup>3</sup> (n)

These limiting physical properties require that sustainable gases need to be up- or downgraded to become narrow band gas. This means that the chemical composition has to be changed by gas upgrading technologies.

Furthermore, narrow band gas should not have a deteriorating effect on the gas network integrity. Therefore, a tentative specification of the chemical composition of narrow band gas has been made by the regional gas distribution companies in cooperation with GTS (operator of the transmission network). This specification, given in Table 3, gives limiting values to several constituents of narrow band gas. The tentative limiting concentrations of various constituents in narrow band gas are based to a great extent on those for G-gas. This EDGaR research project may lead to modifications of these specifications.

For comparison the limiting values to several constituents in G-gas have been given in Table 3 as well. In practice the concentration of various constituents in G-gas are far from these limiting values. Moreover, for a number of constituents, which may be present in narrow band gas, no limiting values have been specified for G-gas. This is caused by the fact that these constituents are not present in G-gas or only at very low (not harmful and sometimes not detectable) concentrations.

An example is CO<sub>2</sub>. In G-gas the concentration of CO<sub>2</sub> is always low (< 1 mol%). This low CO<sub>2</sub> content does not affect the combustion behaviour nor the pipeline integrity significantly. Therefore a limiting CO<sub>2</sub> value has not been specified for G-gas. However, CO<sub>2</sub> can be found in narrow band gas, in rather high concentrations (possibly above 10 mol%). These high CO<sub>2</sub> concentrations may affect the combustion behaviour as well result in the deterioration of certain materials. Therefore a limiting value should be specified. This limit is tentatively defined as 10.3 mol% (= 103 000 ppm).

For safety reasons G-gas is odorized in the Netherlands by using tetrahydrothiophene (THT). Mercaptans, used in some 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 for THT in G-gas in the Netherlands is 18 mg/m<sup>3</sup> (n). In order to fulfil the safety requirements, THT should be added to

Table 3. Specifications of narrow band gas and G-gas. Some values in mol % and mg/m<sup>3</sup> have been converted to ppm for comparison.

Quality	Narrow Band Limiting value [2]	G-gas Limiting value [3]	G-gas Average [4]	Unit
Dew point	-10 (at 8 bar)	-12 (at 40 bar)		°C
Temperature (of feed in gas)	0 – 20	0 – 20		°C
Sulphur (total)	45	45	6.7	mg/m <sup>3</sup> (n)
Inorganic bound sulphur (H <sub>2</sub> S)	5	5	0.4	mg/m <sup>3</sup> (n)
Mercaptans	10	10	< 1.0	mg/m <sup>3</sup> (n)
Odorant value (THT)	> 10; nom 18; < 40	> 10; nom 18; < 40	17.7	mg/m <sup>3</sup> (n)
Chlorine containing components	50	n.a.	< 0.1	mg/m <sup>3</sup> (n)
Fluorine containing components	25	n.a.	< 0.1	mg/m <sup>3</sup> (n)
Ammonia	4	n.a.	< 0.1	ppm
Hydrogen chloride (HCl)	1	n.a.	< 1.0	ppm
Hydrogen cyanide (HCN)	10	n.a.	< 1.0	ppm
Carbon monoxide (CO)	10 000	n.a.	< 100	ppm
Carbon dioxide (CO <sub>2</sub> ) in dry gas	103 000	n.a.	8 900	ppm
Aromatic hydrocarbons (including BTX)	10 000	10 000	500	ppm
BTX (benzene, toluene, xylene)	500	500	2	ppm
Oxygen (O <sub>2</sub> ) in dry gas	5 000	5 000	< 100	ppm
Hydrogen (H <sub>2</sub> )	120 000	n.a.	< 100	ppm
Methane number (CH <sub>4</sub> )	> 80	> 80		-
Dust	technically free	technically free		-
Siloxanes	5	n.a.	< 0.1	mg/m <sup>3</sup> (n)
Smellability	sufficient	sufficient		-
Phosphine	technically free	technically free		-
Pathogen / corrosive micro-organism	technically free	technically free		-

*n.a.* = not applicable

*blank cell* = not measured

narrow band gas as well. Nevertheless in some cases the odour of narrow band gas is overwhelming the odour of THT. Therefore also the smellability has been added to the criteria.

Another important difference in requirements is the water dew point for respectively G-gas and narrow band gas. G-gas is cooled to -12 °C at 40 bar pressure to remove moisture and other components that can condensate. If the gas is cooled to lower temperatures or if the pressure is increased, more moisture and other components in the gas will condensate and the gas will therefore be 'drier'.

However, the required water dew point for narrow band gas is -10 °C at 8 bar pressure. Due to this difference with G-gas the risk of condensation of not only water, but all components that can condensate, in narrow band gas may be higher than that of G-gas.

## 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).

### 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 4 the length of each material in the distribution network in 2010 can be found.

Table 4. Length and MOP of distribution mains in 2010 for different types of materials [5].

Material	(Sub)total length (km)	Length (km)	MOP* (bar)	Material-standard
Polyvinyl chloride (PVC)	75 062			
<i>High Impact PVC (PVC-HI)</i>		53 996	0.1	[6]
<i>Unplasticized PVC (PVC-U) †</i>		21 066	0.1	-
Steel	27 484			
<i>Carbon steel</i>		19 228	16	[7,8]
<i>Grey cast iron †</i>		6 241	1	[9]
<i>Nodular cast iron</i>		2 015	8	[10]
Polyethylene (PE)	19 529			
<i>2<sup>nd</sup> and 3<sup>rd</sup> generation PE</i>		14 422	8 §	[11]
<i>1<sup>st</sup> generation PE †</i>		5 107	4 §	-
Other	1 918			
<i>Asbestos cement (AC) †</i>		1 719	0.1	[12]
<i>Unknown</i>		199	-	-
<b>Total</b>	<b>123 993</b>			

\* 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 5). Based on an average length of approximately ten meter of the service line, the total length of the service lines in the Netherlands is about 70 000 km.

Table 5. The materials used in service lines. [13]

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 an elastomeric membrane, which is used as diaphragm [14]. The typical elastomeric material used as diaphragm in gas pressure regulators is nitrile butadiene rubber (NBR i.e. Perbunan®, Buna-N®) [14].

### 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 [15] 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. 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 chapter 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 [16]. However, to date still many old PVC-U gas pipes are in operation in the Netherlands (see Table 4). [17-19]

### 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 [18-26] 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.

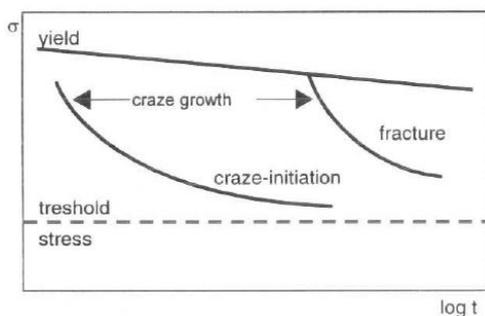


Figure 1. Craze initiation, craze growth, yield and fracture in PVC [22]

Crazes initiate on local stress concentrations, such as small imperfections. They 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 [18,20], 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 [27], 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 [19,28]. 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 Narrow Band Gases on PVC*

#### 4.1.2.1 *Effects of Hydrocarbons*

Natural gas contains many different aromatics and aliphatics. Appendix I gives the composition of natural gas condensate. However, sustainable 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.

Craze initiation is accelerated considerably at high aromatic concentrations. It was found that an r.s. of aromatics of 4 % is not high enough to result in any effect on craze initiation [22]. 4 % r.s. is about 5000 ppm (at 20 °C and 100 mbar), which is much higher than the tentative limits for narrow band gases (500 ppm, see Table 3).

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 2) [22].

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 [18].

Aliphatics have a much lower effect on craze initiation than aromatics at the same concentration (see Figure 3), 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. [18]

Aromatics and aliphatics in the liquid phase (condensate) have the same effect on craze initiation and failure behaviour as saturated vapour (100 % r.s.) [22].

It is also known from other literature sources [29] 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 [22]:

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.

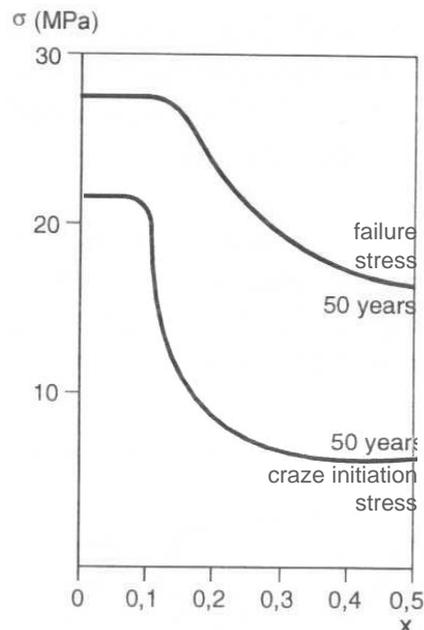


Figure 2. 50-year craze initiation stress and failure stress as a function of relative degree of aromatic concentration.  
 $x = 0,1$  equals 10 000 ppm. [22]

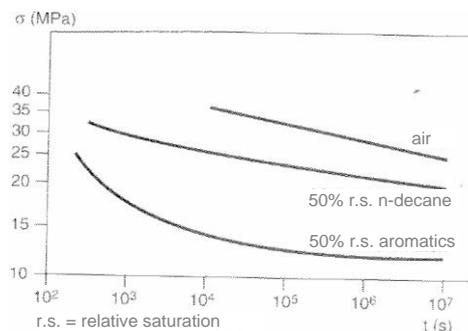


Figure 3. Craze initiation in different gas environments.[18]

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 ( $T_g$ ).  $\text{CO}_2$  is considerably more soluble than methane or inert gases like He,  $\text{N}_2$  and Ar. Exposure of small samples to 20 bars  $\text{CO}_2$  up to equilibrium resulted in a decrease of  $T_g$  of 18 °C, while the low soluble gases resulted in no noticeable reduction in  $T_g$  [30]. Similar to the effect of aromatic components to PVC, the plasticizing effect of  $\text{CO}_2$  may cause a faster formation of crazes which may influence the impact strength, although this is still to be confirmed.

#### 4.1.2.3 *Effects of Hydrogen Sulphide*

In experiments with 1000 ppm hydrogen sulphide ( $\text{H}_2\text{S}$ ) 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 [31]. The maximum concentration of  $\text{H}_2\text{S}$  in narrow band gas is 5 mg/m<sup>3</sup>(n) (see chapter 2), which corresponds to 3.6 ppm. Any effect on the long-term failure of PVC is therefore unlikely.

$\text{H}_2\text{S}$  causes a colour change (dark brown to black) at the surface of lead stabilised PVC pipes, caused by the formation of PbS. Such a colour change can occur already after exposure to less than 500 ppb  $\text{H}_2\text{S}$  [32]. However, only a very small layer at the surface is discoloured. There is no significant embrittlement found in impact tests when exposed and non-exposed PVC-U samples were compared [33].

#### 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 [34]. ISO/TR 10358 [35] 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 narrow band gases the limiting concentration for chlorine containing components is 50 mg/m<sup>3</sup> and for fluorine containing components 25 mg/m<sup>3</sup>. This is much higher than currently measured in G-gas (see Table 3). It is unknown if these concentrations are high enough to negatively affect the long-term and impact resistance properties of PVC.

#### 4.1.2.5 *Effects of Other Components*

Practically no literature about the effect of other components present in narrow band gases was found. Because the concentration limits for narrow band gas are low (see Table 3) a deleterious effect is expected to be unlikely, although the concentrations are higher compared to the current average concentrations in G-gas. Only the concentration of CO and  $\text{H}_2$  can be much higher than in G-gas. The consequences of high  $\text{H}_2$  concentrations will be researched on pipeline material from regions where upgraded biogas is already used.

### 4.1.3 Conclusions

The concentrations of aromatic and aliphatic components in narrow 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 narrow band gases.

Long-term effects on strength or effects on impact resistance are not expected from the presence of H<sub>2</sub>S. On the other hand CO<sub>2</sub> may have some effect on long-term strength as well as on impact resistance.

The consequences of other components in narrow band gases are unknown. A deleterious effect of chlorine and fluorine containing components, CO and H<sub>2</sub> cannot be excluded, because the concentrations of these components in narrow band gases are relatively high.

These conclusions are summarised in the table below.

Table 6. The effect of components present in narrow 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 <sub>2</sub> S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydro-carbons	Aromatic hydro-carbons	O <sub>2</sub>	H <sub>2</sub>
probably none	none	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 4). 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 [36]. 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.

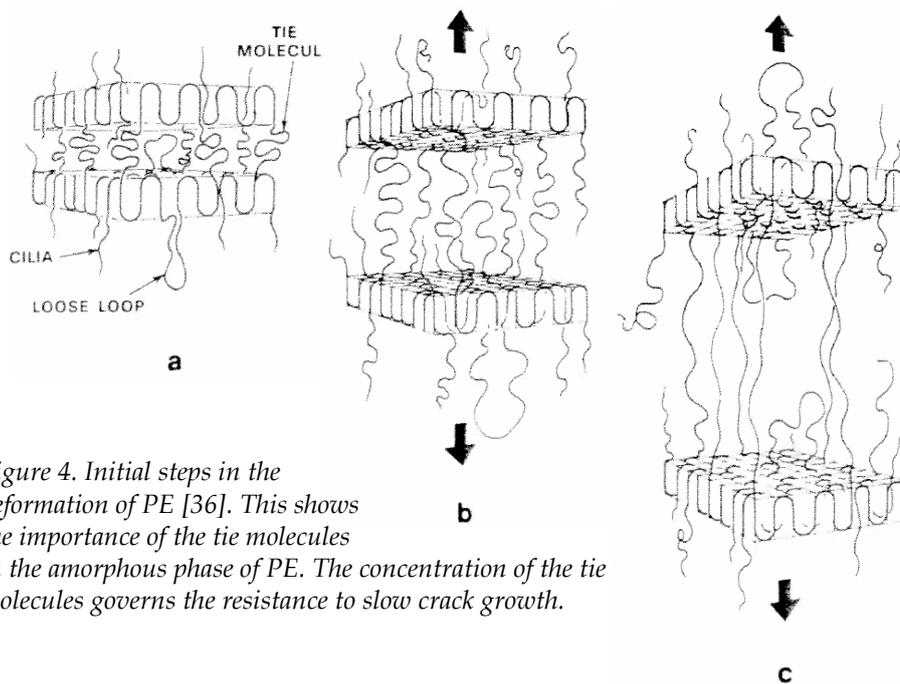


Figure 4. Initial steps in the deformation of PE [36]. This shows the importance of the tie molecules in the amorphous phase of PE. The concentration of the tie molecules governs the resistance to slow crack growth.

At high localised stress, for instance point loading, SCG is enhanced which causes premature failure. This is the experience of Kiwa Gas Technology and established in various researches (e.g. [37]).

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 [37,38].

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. [37,38]

Because tie molecules are very important to the resistance to SCG, any effect of components in narrow 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 [39]. 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 narrow band gas on the SCG behaviour of PE is reviewed.

#### 4.2.1.2 Impact Loadings

Although third party damage is the most important 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 narrow band gases on the impact resistance of PE pipelines.

## 4.2.2 *The Influence of Narrow 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 [17,20]. As far as hydrocarbons are concerned, narrow band gas has a similar chemical composition as G-gas (see chapter 2). 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 narrow 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 [40,41]. PE can absorb about 7 wt.% of natural gas condensate [21] (the composition is given in Appendix I). This lowers the yield strength of a MDPE from about 19 MPa to 15 MPa [20,21] and it drastically reduces the long-term strength measured by internal water pressure testing [17,20]. If the condensate can desorb, the original strength will return, unless additives are leached from the PE [20,21].

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 [17,42].

The concentrations for BTX and aromatic hydrocarbons are in the current specifications for narrow band gas similar to the limits given for G-gas (see Table 3). However, the average concentration of aromatic hydrocarbons and BTX in G-gas is much lower than the limits. This means that practically the concentration of these components may increase, although the limits are similar. Nevertheless, the concentration of BTX and aromatic hydrocarbons in various sustainable gases is lower than the concentration in natural gas [43]. A high concentration of BTX and aromatic hydrocarbons in narrow band gas is therefore not expected.

On the other hand, the required water dew point for narrow band gas is different than that for G-gas (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 narrow 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) [20,21].

### 4.2.2.2 *Effects of Oxygen, Carbon Dioxide and Nitrogen*

Gases like oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) 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 lose its influence [44]. This critical temperature increases as the gas pressure increases. Since O<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> have an effect only at very low temperatures, these gases are not an important factor in influencing the lifetime of a PE gas pipeline [45].

### 4.2.2.3 *Effects of Hydrogen*

No macroscopic differences were found between unexposed PE and PE exposed to H<sub>2</sub> 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 [46]. More recent experiments with H<sub>2</sub> diffusion at pressures up to 100 bar for 12 months,

revealed no influence on the tensile strength [47]. Any effect of hydrogen on PE is therefore not expected.

#### 4.2.2.4 Effects of Hydrogen Sulphide

The same experiments with H<sub>2</sub>S in sewer systems for PVC (see section 4.1.2.2) have been performed on PE. Similar results were obtained: after 8 months of testing (1000 ppm H<sub>2</sub>S), no (mechanical) failures whatsoever were reported [31]. The maximum concentration of H<sub>2</sub>S in narrow band gas is 5 mg/m<sup>3</sup>(n) (chapter 2), which corresponds to 3.6 ppm. Any effect on the lifetime of PE caused by this low concentration is unlikely.

#### 4.2.2.5 Effects of Chlorine and Fluorine Containing Components

ISO/TR 10358 [35] 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 narrow band gases the limiting concentration for chlorine containing components is 50 mg/m<sup>3</sup> and for fluorine containing components 25 mg/m<sup>3</sup>. This is much higher than currently measured in G-gas (see Table 3). It is unknown if these concentrations 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 narrow band gases, such as sulphur, mercaptanes, ammonia, HCl, HCN and CO on PE is still unknown. Because the concentration limits for narrow band gas are low a deleterious effect is unlikely. Only the concentration of CO can be much higher than in G-gas.

### 4.2.3 Conclusions

A deleterious effect of most components in narrow band gases on PE is not expected. There is an exception for the effect of liquid aromatic hydrocarbons (including BTX) and/or liquid higher hydrocarbons, because this will soften PE. The effect of chlorine and fluorine containing components and the effect of CO is also unknown.

These conclusions are summarised in the table below.

Table 7. The effect of components present in narrow 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 <sub>2</sub> S	Mercaptans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydrocarbons	Aromatic hydrocarbons	O <sub>2</sub>	H <sub>2</sub>
probably none	none	probably none	none	probably none	unknown	unknown	probably none	unknown	unknown	none	none, unless liquid	none	none	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 narrow 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 Narrow Band Gases on Rubber*

#### 4.3.2.1 *Effects of Hydrocarbons*

In several studies, it has been shown that NBR will swell in contact with aromatic hydrocarbons [20,48-50]. 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) [49,50]. 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 [51]. 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 narrow band gas (see Table 3) it is not expected that these components in narrow 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 [51] states that there is little or no adverse effect on NBR expected by CO, CO<sub>2</sub> and H<sub>2</sub>. This is confirmed by NBR producers [52-54].

Also in research by the former VEG-Gasinstituut it was concluded that no deleterious effect would be expected for CO, CO<sub>2</sub> and H<sub>2</sub> [55]. 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 [55].

#### 4.3.2.3 *Effects of Oxygen*

Although O<sub>2</sub> has a low solubility in NBR as well, oxidation can cause a degradation of the rubber [55]. O<sub>2</sub> 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 [51] and NBR producers [52-54] no negative effect by O<sub>2</sub> is to be expected.

#### 4.3.2.4 *Effects of Sulphur Containing Components (H<sub>2</sub>S, S and THT)*

According to ISO DTR 7620 [51] a severe deleterious effect of H<sub>2</sub>S (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<sub>2</sub>S [52-54]. This was also concluded after a research led by the former VEG-Gasinstituut [55], due to the low concentrations ( $\leq 5 \text{ mg/m}^3$ ) in the gases considered. THT was investigated in this research as well and no negative effects were found at nominal THT levels.

#### 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 [51]. Also NBR producers [52-54] warn their customers to be careful using NBR products with halogen containing components.

Deleterious effects on NBR by halogen containing components in narrow band gases therefore cannot be excluded. Only HCl will probably have no effect because the concentration limit of 1 ppm (see Table 3) is probably not high enough.

#### 4.3.2.6 *Effects of Other Components*

NBR has a moderate resistance when fully submerged in HCN according to ISO DTR 7620 [51]. Because the concentration limit of HCN in narrow band gas is only 10 ppm (see Table 3), the negative effects are expected to be very low.

According to ISO DTR 7620 [51] NBR has an outstanding resistance against refrigerant ammonia. This combined with the low concentration limit for narrow band gas (see Table 3), leads to the conclusion that no deleterious effect is expected.

### 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 the literature, no deleterious effect of ammonia, CO, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> present in narrow band gases is expected. Because the concentration limits for narrow band gas are low for sulphur containing components and HCN a deleterious effect is unlikely. Also (aromatic) hydrocarbons are not expected to have a negative effect on the mechanical and physical properties. However, liquid aromatic hydrocarbons and BTX will decrease the mechanical properties of elastomeric diaphragms, made of NBRs.

The effect of halogen containing components is unknown.

These conclusions are summarised in the table below.

Table 8. The effect of components present in narrow 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 <sub>2</sub> S	Mer-captans	Odorant	Ammono- nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydro-carbons	Aromatic hydro-carbons	O <sub>2</sub>	H <sub>2</sub>
probably none				none	unknown		probably none		none		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 Narrow 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 [56], however some literature is available in which corrosion problems are described at a relative humidity of 60 – 70 % [57,58]. A relative humidity of 70% is considered critical, as above this relative humidity corrosion becomes rapid [59]. 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.

As the specified water dew point in the distribution of narrow band gas at 8 bar pressure is -10 °C, condensation of water in the natural gas infrastructure is not likely for narrow band gas, although the required water dew point for G-gas is more stringent (see Table 3). 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 [57]. The gas constituents with a known influence on the corrosion of steel are oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) and hydrogen sulphide (H<sub>2</sub>S), 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<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>S.

#### 5.1.2.2 Effects of Carbon Dioxide

The natural gas distributed in the Netherlands to date is considered non corrosive [56]. The average concentration of CO<sub>2</sub> in G-gas is 0.89 mol%, while the specified maximum concentration of CO<sub>2</sub> in narrow band gas in dry gas distribution systems is 10.3 mol%.

The effect of CO<sub>2</sub> on the corrosion rate of steel in the natural gas infrastructure has been studied extensively. Generally, gases with a higher CO<sub>2</sub> partial pressure are increasingly corrosive [56-73]. This means that, with a given gas composition, the gas becomes more corrosive at higher pressures due to the increased partial pressure of the corrosive components at higher pressure.

The corrosivity of gases containing CO<sub>2</sub> is based on the easy dissolution of CO<sub>2</sub> 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<sub>2</sub> 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) [57].

Various models have been proposed to predict the corrosion rate, dependent on the concentration of CO<sub>2</sub> and the temperature, of which the model by De Waard and Milliams, as shown in Figure 5, is the most well known [66]. For narrow band gas, with a maximum concentration of CO<sub>2</sub> of 10.3 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 0.4 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 [57].

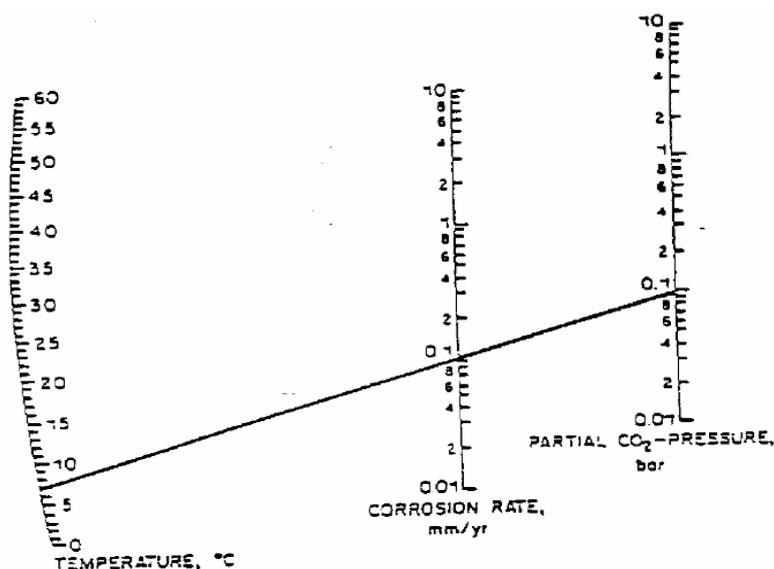


Figure 5. The 'De Waard and Milliams Nomogram' gives the relation between the CO<sub>2</sub> concentration, the temperature and the corrosion rate [66]

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<sub>2</sub> in narrow 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<sub>2</sub> 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<sub>2</sub>SO<sub>4</sub>) [58-61,64,74]. This means that the corrosion rate increases with the concentration of O<sub>2</sub>. Other literature sources report little effect of the presence of O<sub>2</sub> concentrations below 100 ppm [67,73], while also an improvement of the resistance to carbon dioxide corrosion is sometimes reported at an oxygen concentration of 2 ppm [63] and 0.5 - 2.5 mol% [57]. This is explained by an improved protectivity of the scales formed due to the presence of low oxygen concentrations [57,63].

With liquid water present in gas distribution systems the maximum concentration of O<sub>2</sub> in narrow band gas is not expected to result in a corrosion rate limiting the service life of steel components. Low oxygen concentrations may in fact 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<sub>2</sub>S in an aqueous environment results in a corrosive medium. The presence of H<sub>2</sub>S can result in various corrosion mechanisms. H<sub>2</sub>S can increase the general corrosion rate. Due to the dissociation of H<sub>2</sub>S dissolved in water, H<sup>+</sup> ions are formed. The electrons formed during dissolution of steel, can be consumed in the formation of molecular hydrogen (H<sub>2</sub>) from the hydrogen ions. In general corrosion due to the presence of H<sub>2</sub>S, 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 [75]

The major risk of the presence of H<sub>2</sub>S 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<sub>2</sub>) or can penetrate into the metal as adsorbed hydrogen. In the presence of H<sub>2</sub>S the equilibrium between recombination and adsorption shifts strongly towards adsorption. Typical hydrogen embrittlement mechanisms are environmentally induced corrosion mechanisms like Hydrogen Induced Cracking (HIC) and stress corrosion mechanisms like Sulphide Stress Corrosion Cracking (SSCC) [72]. 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<sub>2</sub>S 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 6. For an 8 bar gas distribution system at a partial pressure of H<sub>2</sub>S 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<sub>2</sub>S concentration of 333 ppm. [76, 77] At lower gas pressures the transition shifts towards higher concentrations of H<sub>2</sub>S, because the partial pressure of H<sub>2</sub>S required forms an increasing part of the gas pressure. For high pressure gas transport the transition shifts towards lower concentrations.

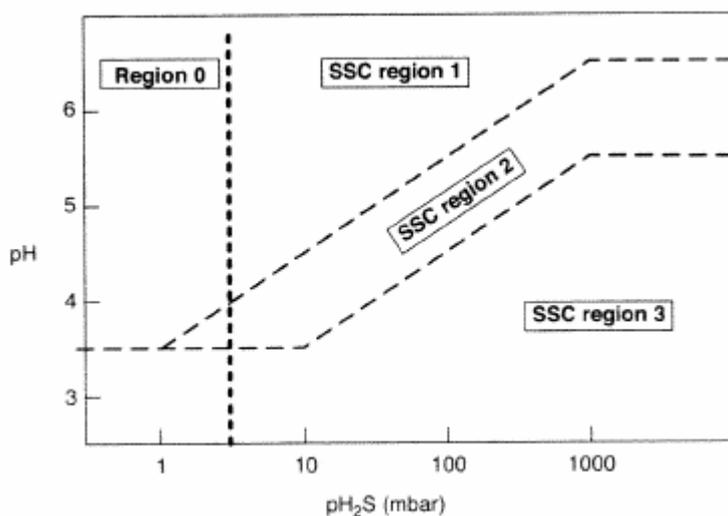


Figure 6. Regimes for stress corrosion cracking mechanisms in sour service [77]

With the maximum concentration of H<sub>2</sub>S in narrow band gas the risk of stress corrosion cracking is low (region 0). For narrow 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 5 ppm H<sub>2</sub>S in narrow band gases only a limited influence on general corrosion is to be expected. Interactions with other gas components may affect the corrosion rate to a great extent as is described in section 5.1.2.5 and 5.1.2.7.

#### 5.1.2.5 Effects of Interactions between CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>S

At temperatures below 60 °C, as in the natural gas infrastructure, the presence of H<sub>2</sub>S in combination with CO<sub>2</sub> can increase the corrosion rate because the H<sub>2</sub>S prevents the formation of protective iron carbonate (FeCO<sub>3</sub>) scales [69].

The presence of both H<sub>2</sub>S and O<sub>2</sub> 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 [78,79]. Operational

problems with pressure regulators may occur for example by clogging of restrictions by the precipitating sulphur [80].

The combined presence of O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>S in an aqueous environment results in a highly corrosive medium [81]. The combined effect of O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>S on the corrosion rate has been modelled, using gas compositions in the range of narrow band gases [73]. 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<sub>2</sub> 1 %, O<sub>2</sub> 100 ppm, H<sub>2</sub>S 3.8 ppm, T = 15 °C) [73]. In recent experiments [82] 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<sub>2</sub>S) 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<sub>2</sub> and H<sub>2</sub>S on the corrosion rate has to be performed.

#### 5.1.2.6 *Effects of Interactions between O<sub>2</sub>, CO and CO<sub>2</sub>*

The combined presence of CO and CO<sub>2</sub> in an aqueous environment may result in the occurrence of stress corrosion [76,83,84]. The presence of oxygen is reported to mitigate the stress corrosion process [76], while another study reports a promotion of the stress corrosion process by the presence of oxygen [84]. In some experiments stress corrosion was observed at a partial pressure of 0.07 bar for CO as well as CO<sub>2</sub>. In another study stress corrosion cracking was observed at a partial pressure of CO<sub>2</sub> above 2.4 bar and a CO partial pressure above 0.3 bar [84]. For the distribution of G-gas no failures due to CO stress corrosion are known.

Given the expected partial pressures of CO and CO<sub>2</sub> for narrow band gases, based on the above mentioned experimental results, the occurrence of stress corrosion due to the presence of CO is deemed unlikely for gas distribution networks. The acceptable concentration of CO in narrow 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 narrow band gas. 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<sub>2</sub> or a combination of O<sub>2</sub> and CO<sub>2</sub> 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 [76]. Because the concentration limit for ammonia in narrow band gas is low (see Table 3), an adverse effect on steel is not expected.

#### 5.1.2.8 *Effects of Hydrogen*

Hydrogen Stress Cracking (HSC) can occur if steel is exposed to H<sub>2</sub>, but this only occurs at high stresses in other 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<sub>2</sub> 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. [20].

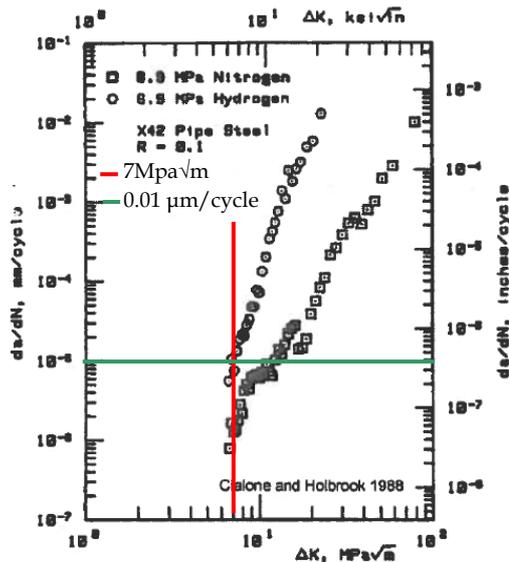


Figure 7. Fatigue crack growth rate ( $da/dN$ ) as a function of the stress intensity factor ( $\Delta K$ ) for hydrogen and nitrogen for API X42 steel [85]

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 [85]. Compared to the crack growth rates in air, the largest effect of hydrogen is found for high values for the stress intensity factor ( $\Delta K$ ) as is illustrated in Figure 7 [86].

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 [86]. An analysis of the stress situation for gas distribution infrastructure showed that the  $\Delta K$  values are relatively low ( $7 \text{ MPa}\sqrt{\text{m}}$ ). The results and assumptions of this analysis are summarised in Appendix II. This means that for loads as applicable to the gas distribution infrastructure the effect of hydrogen on the fatigue crack growth is negligible ( $0.01 \text{ }\mu\text{m/cycle}$ ), irrespective of the concentration of hydrogen. Therefore the acceptable concentrations of  $H_2$  in narrow band gas are not expected to have deleterious effects 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 [84], but this effect is only expected for components which dissociate into ions in aqueous solutions, resulting in chloride and fluoride. Because the concentration limit for chlorine and fluorine containing components in narrow band gas is low (see Table 3), and the expected components are stable, no adverse effect on the integrity of steel gas distribution materials is expected.

The maximum concentration of HCl in narrow band gas is limited (max 1 ppm). Because of the limited concentration the presence of traces of HCl are not expected to limit the service life of steel gas distribution materials.

The concentration of chloride salts in the ground water is rather limited (max ca  $300 \text{ mg/l}$  at a depth of 1 m) and is in the same order of magnitude as for potable drinking water (max  $150 \text{ mg/l}$ ). 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 [87]. 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) [88].

#### 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 concentration limits for other components in narrow band gas are low, deleterious effects by these components seem unlikely.

### 5.1.3 *Conclusions*

Generally the maximum acceptable concentrations of the gas constituents for narrow band gases are lower than the concentrations resulting in unacceptable corrosion in corrosion experiments [57].

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 these constituents in narrow band gases are limited and given the current chemical specification for narrow band gas no detrimental corrosion of steel gas pipes is expected from the individual constituents.

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 concentration limits for other components in narrow band gas are low, a deleterious effect is unlikely.

These conclusions are summarised in the table below.

Table 9. The effect of components present in narrow 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 <sub>2</sub> S	Mer-captans	Odorant	Ammonia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydrocarbons	Aromatic hydrocarbons	O <sub>2</sub>	H <sub>2</sub>
with water: possibly	probably none						with H <sub>2</sub> S 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 10) which have different mechanical properties.

Table 10. 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 [62]. Stress and environment must be present, from which stress is the most distinctive, for stress corrosion [89].

### 5.2.2 The Influence of Narrow 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. As the required water dew point in the distribution of natural gas at 8 bar pressure is -10 °C, condensation of water in the natural gas infrastructure is not likely for narrow band gas, although the required water dew point for G-gas is more stringent (see Table 3). 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 and the type of corrosion mechanism that takes place. Copper corrosion products and water containing minerals can form protective scales on the copper [90].

The gas constituents with a known influence on the corrosion of copper are oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen sulphide (H<sub>2</sub>S), sulphur (S) and ammonia (NH<sub>3</sub>), 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<sub>2</sub> 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 [62]. If no carbon dioxide is present, the oxygen will contribute to the formation of a protective scale on the copper. In the presence of water the combination of narrow band gases and water can possibly cause corrosion.

#### 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<sub>2</sub>S). In the presence of both H<sub>2</sub>S and S more corrosion is seen in comparison to the presence of the individual components [91]. A concentration of 0.35 ppm H<sub>2</sub>S 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<sub>2</sub>S and 0.5 ppm S. An increasing concentration of sulphur will further lower the threshold value for corrosion of copper by H<sub>2</sub>S even further.

The presence of ethyl mercaptan (CH<sub>3</sub>-CH<sub>2</sub>-SH) up to a concentration of 100 ppm does not lead to degradation. In the presence of both mercaptan and H<sub>2</sub>S it is observed that mercaptan has a protective effect on the degradation by H<sub>2</sub>S. 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. [91]

The presence of water accelerates the possible reactions. In order to prevent corrosion there has to be strived to have gas without H<sub>2</sub>S. If this is impossible the water content should be as low as possible [91].

As narrow gases can contain sulphur and hydrogen sulphide, the combination of narrow band gases with water can cause corrosion.

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 experience of negative influences of THT on copper 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 [89]. 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 [89]. 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. [89] Narrow band gases in combination with water and internal stress can cause corrosion.

#### 5.2.2.5 *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 concentration limit for chlorine and fluorine containing components in narrow band gas is low (see Table 3), 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 narrow band gas is limited (max 1 ppm). Because of the limited concentration the presence of traces of HCl are not expected to limit the service life of copper gas distribution materials.

#### 5.2.2.6 *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 [92]. Therefore it is unknown whether the effect can be contributed to the presence of the cyanides.

#### 5.2.2.7 *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.

#### 5.2.2.8 *Effects of Other Components*

In literature no record of effects of CO or H<sub>2</sub> 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 narrow band gases on the corrosion of copper can not be predicted. Therefore corrosion caused by narrow band gases can not be excluded. Additional experimental work is therefore needed.

These conclusions are summarised in the table on the next page.

Table 11. The effect of components present in narrow 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 <sub>2</sub> S	Mer-captans	Odorant	Ammono-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydro-carbons	Aromatic hydro-carbons	O <sub>2</sub>	H <sub>2</sub>
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 distribution network contains some aluminium used in gas pressure regulators and gas meters (see section 3.1.3).

#### 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 [72,93].

#### 5.3.2 The Influence of Narrow 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. As the required water dew point in the distribution of natural gas at 8 bar pressure is -10 °C, condensation of water in the natural gas infrastructure is not likely for narrow band gas, although the required water dew point for G-gas is more stringent (see Table 3). 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<sub>2</sub>). In combination with water the presence of CO<sub>2</sub> can lead to corrosion problems of aluminium by affecting the protective oxide layer [93].

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<sub>2</sub> will not lead to problems, although higher levels of CO<sub>2</sub> in combination with moisture can lead to corrosion problems of aluminium parts by lowering the pH [93].

In a CO<sub>2</sub>/H<sub>2</sub>O system at 25 °C a pH level of 4 will be reached at pCO<sub>2</sub> of 0.35 bar [61]. As the limiting value of CO<sub>2</sub> in narrow band gases lies below this partial pressure of 0.35 bar no effects are to be expected. However in the reference CO<sub>2</sub>/H<sub>2</sub>O system the effects of other acid constituents in the narrow band gases are not included. Therefore a negative effect of narrow band gases on aluminium is possible.

##### 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 [93].

This effect is only expected for chlorine containing components which dissociate into ions in aqueous solutions, resulting in chlorides. Because the concentration limit for chlorine and fluorine containing components in narrow band gas is low (see Table 3), and the expected components are stable, no adverse effect on the integrity of aluminium alloys applied in gas distribution systems is expected. The maximum concentration of HCl in Narrow band gas is limited (max 1 ppm). Because of the limited concentration the presence of traces of HCl are not expected to limit the service life of aluminium gas distribution materials

#### 5.3.2.4 Effects of Ammonia

Aluminium alloys have a good resistance against aqueous phases of amines and NH<sub>3</sub> [72].

#### 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. Any effects of THT on aluminium have not been observed.

In literature no record of effects of fluorine containing components, HCN, CO, or H<sub>2</sub>, 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. Aluminium alloys have a good resistance against ammonia.

Based on the literature the corrosion effects on aluminium caused by the constituents in narrow band gases cannot be predicted for all the constituents. Therefore corrosion caused by narrow band gases cannot be excluded.

Additional work is therefore recommended.

These conclusions are summarised in the table below.

Table 12. The effect of components present in narrow band gas on Aluminium. 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 <sub>2</sub> S	Mer-captans	Odorant	Ammono-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydro-carbons	Aromatic hydro-carbons	O <sub>2</sub>	H <sub>2</sub>
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 <sub>2</sub> S	Mer-captans	Odorant	Ammo-nia	Chlorine containing components	Fluorine containing components	HCl	HCN	CO	CO <sub>2</sub>	Hydro-carbons	Aromatic hydro-carbons	O <sub>2</sub>	H <sub>2</sub>
PVC	probably none	none	probably none			unknown		probably none		unknown	possibly	none, unless liquid (impact resistance)		probably none	unknown
PE	probably none	none	probably none	none	probably none	unknown		probably none		unknown	none	none, unless liquid		none	
NBR	probably none				none	unknown		probably none		none		probably none, unless liquid		none	
Steel	with water: possibly		probably none						with H <sub>2</sub> S and water: possibly	with water: possibly		probably none	with water: possibly	none	
Cu	with water: possibly, depending on their mutual influence			probably none	with water: possibly	probably none			unknown		with water: possibly	probably none	with water: possibly	unknown	
Al	unknown			probably none	none	probably none			unknown		with water: possibly	probably none	none	unknown	

	=	The effect is unknown, but is expected to be very small or non existent.
	=	This component 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 PVC is not expected due to the low concentrations in narrow band gas. Liquid aromatic hydrocarbons (including BTX) may have a negative effect on the impact resistance of PVC-HI.  
CO<sub>2</sub> may have an influence on the impact resistance of PVC, because CO<sub>2</sub> 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 effect of chlorine and fluorine containing components, CO and H<sub>2</sub> on PVC is unknown. Other components in narrow band gases are not expected to have any deleterious effect on PVC, because their concentration in narrow band gases is very low.
- The effect of chlorine and fluorine containing components and CO on PE is unknown. A deleterious effect of most other components in narrow band gases on PE is not expected. There is an exception for the effect of liquid aromatic hydrocarbons (including BTX) and/or liquid higher aliphatic hydrocarbons, because this will soften PE. Because the required water dew point for narrow band gas is different than that for G-gas, the risk of condensation of (aromatic) hydrocarbons in narrow band gas may be higher than that of G-gas.
- No deleterious effect of ammonia, CO, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> on NBR is expected. Because the concentration limits for narrow band gas are low a deleterious effect on NBR is unlikely for sulphur containing components, HCl, HCN and

(aromatic) hydrocarbons. However, liquid aromatic hydrocarbons and BTX will decrease the mechanical properties of elastomeric diaphragms, made of NBRs. The effect of halogen containing components on NBR is unknown.

- 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<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>S. 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 narrow 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 narrow band gases on aluminium is unknown.

It is too early, based on these conclusions, to conclude anything about the concentration limits given in the current tentative specification for narrow band gas. 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 within the Current Distribution Band for Natural Gas in the Netherlands".

# I Composition of a Natural Gas Condensate

Table 13. Composition of a G-gas natural gas condensate [20].

<b>Component</b>	<b>Quantity (%)</b>
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

## II 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 [94].

### 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 ( $\Delta K$ ) the following defect has been assumed, with:

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

(see Figure 8)

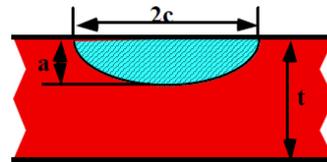


Figure 8. Assumed defect for calculation of the stress intensity factor.

The following loading frequencies have been assumed:

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

### Calculations

The stress intensity factor ( $\Delta K$ ) for different stress states has been calculated using the software program Signal as described in [94]. The above mentioned basic information and assumptions have been used.

### Results

Source of load	Stress Intensity Factor, $\Delta K$ [MPa $\sqrt{m}$ ]
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  $7 \text{ MPa}\sqrt{\text{m}}$ . At this stress intensity factor the fatigue crack growth rate for hydrogen loaded material reaches the threshold value of  $0.01 \text{ }\mu\text{m}/\text{cycle}$  as can be seen from Figure 9. This crack growth rate is considered acceptable to BS7910 [95]. Therefore it can be concluded that for the given conditions the fatigue crack growth is not influenced by hydrogen loading.

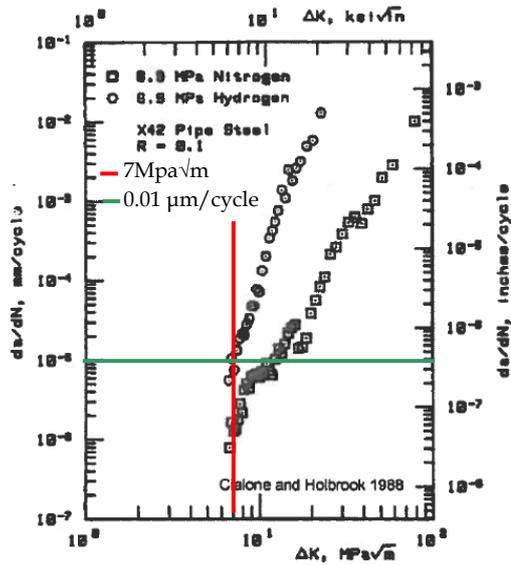


Figure 9. Fatigue crack growth rate ( $da/dN$ ) as a function of the stress intensity factor ( $\Delta K$ ) for hydrogen and nitrogen for API X42 steel [85]

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