

HyDelta

WP 1C Pipes and indoor installations (components)

D1C.3 question 135 – The influence of existing natural gas distribution grid on the quality of hydrogen

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Executive summary

As part of the national HyDelta research programme, a study was conducted into the influence that the use of the existing natural gas distribution grid could have on hydrogen quality. For this purpose, the contaminants that occur when using natural gas distribution grid have been mapped out and measured. The focus of this study is on the release of the natural gas components from the pipe materials and the contaminants from the environment that reduce the purity of hydrogen gas.

The hydrogen gas picks up absorbed natural gas components, such as THT, aromatics and alkanes, from the pipe material.¹

Desorption of THT and other natural gas components decreases as the amount of hydrogen flowing through the gas grid increases. The quantities of these substances that can be absorbed by the hydrogen per time unit depend on the equilibrium concentration and the time that the gas is stagnant and therefore also on the extent of flushing. The desorption rate also depends on the amount of THT, alkanes or aromatics in the pipe material and attached to the wall, which clearly decreases over time. Based on the results obtained, desorption rates were determined for the various pipe materials. These desorption rates are used to calculate desorption coefficients for each of the pipe materials investigated, which could then be used to calculate the concentrations of THT, aromatics and alkanes that could be expected after a certain period of time.

After approximately 50 days and approximately 50 flushings with the inner pipe volume, the THT content was below the minimum THT content for odourisation (10 mg/m³) in most cases.

The permissible concentrations of natural gas components in the hydrogen gas depend on the application.

Contamination from the environment reduces the purity of hydrogen gas in plastic pipes. This is caused by an unavoidable natural process called permeation. Permeation does (practically) not occur in steel pipes. Permeation occurs regardless of the type of gas transported, meaning that even the natural gas of today is contaminated with components from the environment such as oxygen, nitrogen and water. The results of this study can be used to estimate the speed at which the hydrogen gas is contaminated. The basis for the prognosis for the pipe material PVC (rigid as well as impact-modified PVC) and PE (1st, 2nd and 3rd generation PE) has been established using the results shown in the table below. The estimate also depends on the pipe dimensions, the temperature, and the length of time the hydrogen gas remains in the pipe. For the study, a temperature of ~23°C was taken into account as the worst-case scenario. Ultimately, whether the degree of contamination is acceptable for the intended application will have to be assessed in consultation with the end user.

As an indication, an estimate has been provided for two practical circumstances with deliberately selected conditions that will result in a high relative oxygen increase as a result of permeation. This concerns two thin-walled pipes with a small diameter and a low hydrogen content (low gas pressure). It is assumed that the pipe will be completely disconnected from the distribution grid so that no diffusion of oxygen through the pipe grid can occur. For a DN 16 PE pipe with 20 mbar pure hydrogen gas, the oxygen content in the hydrogen will increase from 0% to 0.296% in the first 24 hours. For a DN 16 PVC pipeline with 20 mbar pure hydrogen gas, the oxygen content in the

¹ In this report, THT is referred to as a natural gas component because, although it is not naturally present in natural gas, it is inherently associated with natural gas in the distribution grid and is included as such in ISO 6976.

hydrogen will increase by 0.077% in the first 24 hours. For pipes with a larger diameter, larger wall thickness or higher hydrogen pressure, the relative oxygen increase will be (much) lower.

Table 1. Conservatively chosen permeation coefficient for the various materials.

Component	PVC	PE	Unit
Oxygen	19.1	77.7	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Nitrogen	19.1	23.3	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Water	3.06	0.17	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day})]$

Contents

Document summary	2
Executive summary	3
Contents	5
1 Reason	8
1.1 General	8
1.2 Problem definition.....	8
1.3 Research question 135 and objective	9
1.4 Procedure	9
1.5 Reader's guide	9
1.6 List of symbols	10
2 Theoretical background.....	11
2.1 Literature review on THT desorption	11
2.2 Modelling the desorption rate of THT.....	11
2.3 Permeation	12
2.3.1 Permeation coefficient of atmospheric gases and water	13
2.3.2 Permeation rate for pipe systems	14
2.3.3 Time lag	16
2.3.4 Temperature.....	17
2.3.5 Solubility	18
3 Method.....	19
3.1 THT.....	19
3.1.1 Materials.....	19
3.1.2 Sampling and gas analyses	20
3.2 Atmospheric gases	22
3.2.1 Materials.....	22
3.2.2 Setup.....	22
3.2.3 Permeation measurements.....	23
3.3 Water.....	24
3.3.1 Materials.....	24
3.3.2 Setup.....	24
3.3.3 Permeation measurements.....	25
4 Measurement results	26
4.1 Desorption of THT	26
4.1.1 Desorption of THT from the pipe wall to H ₂	26

4.1.2	Desorption of alkanes from the pipe wall to H ₂	28
4.1.3	Desorption of aromatics from the pipe wall to H ₂	29
4.1.4	Desorption of THT from the pipe wall to the jacket pipe.....	30
4.1.5	Desorption of alkanes from the pipe wall to the jacket pipe	31
4.1.6	Desorption of aromatics from the pipe wall to the jacket pipe	32
4.1.7	Speed of desorption of THT from the pipe wall to H ₂ by surface.....	33
4.1.8	Kinetic model for desorption rate	34
4.2	Permeation of atmospheric gases.....	35
4.3	Permeation of water	39
5	Consideration of results	41
5.1	Duration of desorption of THT, aromatics and alkanes	41
5.1.1	Desorption of THT	41
5.1.2	Desorption of aromatics and alkanes.....	41
5.1.3	Desorption rate	41
5.1.4	Contamination of steel pipes	41
5.2	Influence of end caps permeation experiments	42
5.3	Reference measurement of water permeation is not suitable	42
5.4	Difference between oxygen and nitrogen permeation measurements.....	42
5.5	Water permeation of PE not in equilibrium.....	43
5.6	Comparison to the literature review on permeation.....	43
5.7	Calculation for scenarios	44
5.7.1	Scenario 1 – 2km PE50 pipe above groundwater level	44
5.7.2	Scenario 2 – 2km PE50 pipe below groundwater level	45
5.7.3	Scenario 3 – 5km PVC-A pipe under groundwater level	46
5.7.4	Scenario 4 – 5km PVC-A pipe under groundwater level	46
5.7.5	Scenario 5 – Increase in oxygen content 1m PE pipe and PVC pipe (ø16mm).....	47
6	Conclusions and answers to the research question and recommendations	49
6.1	Desorption from pipe material.....	49
6.2	Permeation from the environment.....	49
6.3	Recommendations for desorption of THT and other components.....	50
6.4	Recommendations for permeation water.....	51
7	References.....	52
	References literature study THT.....	53
I	List of questions HyDelta WP1C	55
II	List of participants Expert- and Assessment Group (EAG) question 135	56

III	Measurement data for THT desorption	57
IV	Permeation and diffusion coefficient from literature.....	60
V	Derivation for calculating the permeation	62
VI	Results of the permeation measurements for atmospheric gases and water	64
VI.1	Permeation of nitrogen	64
VI.2	Permeation of oxygen	65
VI.3	Water permeation	66
VII	Measuring equipment used	68

1 Reason

1.1 General

This study has been carried out within the framework of the national HyDelta research programme. The programme focuses on the safe integration of hydrogen into the existing gas transport and distribution infrastructure and aims to remove barriers that hamper innovative hydrogen projects. The complete research programme is divided into work packages. For an explanation of the various work packages, please visit hydelta.nl.

1.2 Problem definition

During the process of distributing hydrogen through the gas grid, it is possible for various contaminants to affect the quality of the hydrogen. The contaminants fall into two different categories: contaminants already present in the natural gas grid and contaminants coming from the environment. There are five different mechanisms that influence hydrogen gas quality:

1. Used as an odorant for natural gas, THT has been passing through the natural gas grid for several decades². Throughout this period, THT has been absorbed in the pipe wall. When switching to a THT-free gas, the THT will leach over time and contaminate the hydrogen gas. According to information obtained from Stedin, this effect has also been observed in the Rozenburg and Uithoorn projects.
2. In addition, THT can easily attach to a surface. In this case, the THT does not penetrate the pipe wall but adsorbs to the surface. When switching to a THT-free gas, the THT will then detach from the inner surface and contaminate the hydrogen gas.
3. The atmosphere consists of various gases such as oxygen and nitrogen. These gases permeate through the pipe wall to the inside of the pipe, which will contaminate the transported hydrogen gas.
4. The pipe system may come into contact with groundwater, for example³. Permeation causes water from the environment to enter the pipe system, which will contaminate the transported hydrogen gas.
5. Due to the transition from natural gas to hydrogen gas, the gas flow rate and possibly also the flow direction of the gas will change, for example during work carried out prior to the transition. As a result of these differences in gas flow, solid contaminants present in the gas grid could possibly rise up and contaminate different systems. This could occur in both the existing natural gas distribution grid and the future hydrogen distribution grid. This problem has a very large overlap with research question 173 (Hydelta, Work Package 1B) and will be taken into account in the latter.

² This research includes the natural gas distribution grid of the Regional Distribution System Operators. This does not include the high-pressure transport pipelines (HTL), regional transport pipelines (RTL) and indoor installations. HTL and RTL are currently made of steel.

³ The ingress of water through a leak is a different process than water permeation. With a leak there is no physical barrier. The ingress of water through a leak falls outside the scope of this study.

1.3 Research question 135 and objective

This report answers research question 135 from Work Package 1C: *Pipes and Indoor Installations*⁴.

The research question is as follows:

How does the use of the existing natural gas grid affect the quality of hydrogen?

The objective is as follows:

To identify and measure the contaminants that result from using natural gas distribution grids to distribute hydrogen.

1.4 Procedure

The execution of this study was coordinated together with an Expert and Assessment Group (EAG), consisting of participants from the grid operators (see Annex II).

1.5 Reader's guide

Sources of literature were first consulted in order to gain insight into the available information on permeation mechanisms and contamination of transported gas. The results of the literature review are presented in Chapter 2. The literature review revealed a number of uncertainties that were then investigated in more detail. The research methodology is described in Chapter 3. The results of the conducted research are presented in Chapter 4 and discussed in Chapter 5. The conclusion and recommendations are described in Chapter 6. The following chapters in the report are each subdivided into two main categories:

- I. The experiments for determining the desorption of THT and the detachment of THT and other natural gas components have been performed in one experimental setup, resulting in a lot of overlap between the two methodologies. For the other natural gas components, the alkanes and aromatics present in natural gas were chosen as they are also able to desorb from the pipe wall. The literature review, measurement setup, results and findings are therefore discussed in the same sections.
- II. The permeation mechanisms for atmospheric components and (ground)water are very similar. For this reason, there is a lot of overlap in the literature review and they are also discussed in one section (§2.3). In the other chapters, however, atmospheric gases and water are addressed in separate sections.

⁴ The other questions from this work package are included in Appendix I.

1.6 List of symbols

Symbol	Description	Unit
A	Surface	m ²
bar(a)	bar absolute	-
bar(g)	bar gauge pressure	-
CO ₂	Chemical symbol for carbon dioxide	
D _c	Diffusion coefficient	cm ² /s
D _e	Outer diameter of the pipe	mm
D _i	Inner diameter of the pipe	mm
D _m	Diameter of the median of the pipe	mm
e	Wall thickness	mm
HDPE	high-density polyethylene	-
k_0, k_1	time-dependent desorption indicators	-
L	Length of the pipe	m
LLDPE	Linear low-density polyethylene	
N ₂	Chemical symbol for nitrogen	
O ₂	Chemical symbol for oxygen	
P _c	Permeation coefficient, the unit varies according to the situation	(ml·mm)/(m ² ·day·bar) or (ml·mm)/(m ² ·day)
PE100	Third generation HDPE	-
PE50	First generation HDPE	
PE80	Second generation PE (this could be either HDPE or MDPE) or third generation MDPE	
PVC	polyvinyl chloride	-
PVC-A	Impact modified PVC with acrylate as a modifier	
PVC-CPE	Impact modified PVC with chlorinated PE as a modifier	
PVC-HI	High impact PVC, PVC with a impact modifier	
PVC-U	Rigid PVC (unplasticized)	
Q	The permeation rate, the unit varies according to the situation	ml/day or g/day
Q _t	desorbed component quantity	μg
Γ _{THT}	desorption rate of THT	μg/(m ² ·day)
SDR	Standard dimension ratio of the pipe, the ratio between the diameter and the wall thickness	-
THT	tetrahydrothiophene, odorant	-
T _{lag}	Time lag	hours
α, β	quantity-dependent desorption indicators	-
ΔP	Pressure difference of the permeate on both sides of the barrier	bar
Δt	time difference	day

2 Theoretical background

2.1 Literature review on THT desorption

A literature review on the desorption of THT by searching ScienceDirect did not yield any articles that are related to question 135 of HyDelta Work Package 1C. References [20] to [31] are the articles that could have some overlap with this question. These ultimately did not contain any information on THT absorption by hydrogen from existing natural gas pipelines.

2.2 Modelling the desorption rate of THT

Desorption is a phenomenon in which a substance is released from or over a surface. This process is the opposite of adsorption and absorption. It occurs when a system is in the state of sorption equilibrium between the free phase or gas phase and the adsorbing or absorbing surface; this is the equilibrium concentration of THT in the gas in question. When the concentration or pressure of a substance in the free phase is lowered, part of the adsorbed/absorbed substance will be released.

Adsorption is the process in which a component from the environment attaches itself to a surface of the solid. Where the component adheres to the surface.
In the case of absorption, the component is able to penetrate into the solid after adsorption.
Desorption is the release of the component from the solid into the environment. This is the reverse process of adsorption.

Changing the free phase of the mixture from natural gas to simple and pure hydrogen changes the equilibrium so that natural gas components will desorb from the wall and pipe material to the hydrogen. Depending on the quantity of components adhering to the wall and the level of binding of these components to the material, this will initially result in fast equilibrium. After that, the rate of release of the component will be limited by the rate of permeation from the material. Depending on the type of material used for the gas pipe, natural gas components will be released mainly from the wall (e.g. steel gas pipes), from a (shallow) part of the pipe wall or will permeate from along the entire pipe wall.

The quantity of THT (or other natural gas components) desorbed from the pipe wall per unit of time is calculated according to the equation below:

$$r_{THT} = \frac{m_{THT,t}}{A_{buis} \cdot \Delta t_{bemonstering}}$$

equation 1

Where:

r_{THT} is the THT desorption rate ($\mu\text{g}/\text{m}^2 \cdot \text{day}$)

$m_{THT,t}$ is the THT quantity for the pipe volume of the current sampling (μg); concentration times volume

A_{pipe} is the internal surface of pipe (m^2)

$\Delta t_{\text{sampling}}$ is the time difference between current and previous sampling or flushing (day)

The Elovich equation has been used to model the desorption rate of THT (and the other natural gas components) [1].

$$\frac{dQ_t}{dt} = \alpha \cdot e^{\beta \cdot Q_t}$$

equation 2

Where:

Q_t is the desorbed quantity of THT (μg)

α and β is the material and quantity of dependent desorption indicators (-)

Since the experiments concern an equilibrium state (for sampling), this equation has been combined with the linearised (integrated) form:

$$Q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln(t)$$

equation 3

To a simplified first order model:

$$r_{THT} = e^{k_0 + k_1 \cdot \ln(t)}$$

equation 4

Where:

k_0 and k_1 are the material and time-dependent desorption indicators (-)

For the measurements performed by Kiwa, it is assumed that the pipe material is completely saturated with THT, as it has been in use for several years as a regular distribution grid with a nominal THT value in the distributed gas of 18 mg/m^3 . The fact that there is a quantity of hydrogen that is stagnant and that measurements could be carried out at a constant temperature and pressure means that the rate at which THT is released from a specific pipe material into hydrogen can be accurately determined. Based on these results, an estimate can be made of how long it takes before a pipeline can be assumed to be clean.

In addition to the release of THT, this study also monitored other common natural gas components that can potentially contaminate hydrogen. These are subdivided into (the total sum of) aromatics and alkanes. General texts will therefore often mention 'natural gas components' instead of mentioning THT specifically.⁵

2.3 Permeation

Permeation is a natural process in which a liquid, gas or vapour travels through a solid. The driving force for this process is a difference in concentration. For example, in the gas distribution grid, the concentration of oxygen is higher outside of the gas grid than inside. This causes oxygen to permeate from outside the gas grid to the inside. Conversely, the transported gas (for example hydrogen gas or biomethane) permeates from the gas grid to the outside (not part of this research programme). The speed of permeation is determined by the resistance of the material to permeation. For example, metals have a (much) higher resistance to permeation than plastics. The resistance of a material to permeation is expressed in the permeation coefficient (P_c). The P_c is a material property that is not dependent on the dimensions of the object, but is strongly influenced by the type of permeate

⁵ In this report, THT is referred to as a natural gas component because, although it is not naturally present in natural gas, it is inherently associated with natural gas in the distribution grid and is included as such in ISO 6976.

(liquid, gas or vapour), the concentration difference (for gases this is equal to the partial pressure difference) and the temperature. The influence of temperature is discussed separately in §2.3.4.

Permeation is a different process to leakage. With leakage, there is no physical barrier separating the pipe medium from the environment. This occurs, for example, due to the presence of a hole. With permeation, there is always a physical barrier present through which the permeate has to penetrate, such as the pipe wall.

2.3.1 Permeation coefficient of atmospheric gases and water

The P_c of different pipe materials can be estimated based on available literature and previous studies. For the present study, it was decided to focus on the PE and PVC pipe materials, because:

1. the Dutch gas distribution grid consists for 83% of the plastics PE and PVC (both rigid and impact modified PVC), against 14% of steel [2]. Therefore, the majority of pipelines are made of plastics.
2. metals have a higher resistance to permeation than plastics [3]. By considering only plastics, the material most susceptible to permeation is being considered.

During the literature review, a variety of permeation and diffusion coefficients for PVC and PE were found and compiled in Annex IV. The results are summarised in table 2. It is worth noting that the permeation coefficient from one literature source clearly differs from the other sources. This has therefore been listed separately in the table.

Table 2. Permeation coefficients as identified through the literature review. The complete list is provided in Annex IV.

Component	PVC	PE	Unit
Oxygen	1.93-10.0 (and one source 774)	38.9-77.7	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Nitrogen	0.84 (one source)	15.3-23.3	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Carbon dioxide	7.74-38.7 (and one source 1161)	134.2-272	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Water	1.20-36.8 (and one source 4900)	0.10-7.30	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day})]$

However, there are some limitations to the permeation coefficients found in the literature review:

- The literature describes the permeation behaviour of mainly newly produced as well as unused materials. However, older materials are also present in the distribution grid.
- The exact type of materials is often not adequately specified. For example, materials are referred to as 'PVC'. But it is not stated whether an impact modifier of the type CPE or A has been added. Also, for PE, no distinction is made between different generations (see box below). That is why the results in table 2 have been grouped together under PVC and PE.
- The permeation coefficients vary significantly. For instance, for oxygen permeation through PVC, the lowest value is 1.93 $[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$ and the highest value is 774 $[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$. This is a difference of a factor of 400.
- Some of the materials reviewed in the literature are intended for packaging food and/or medicines ([4], [5] and [6]). Although PE and PVC are also used, it is not a given that the materials are the same as the PE and PVC used for pipe systems. For example, the density or

the composition may differ because other additives have been used, meaning that the permeation behaviour may also differ.

In short, there is room for improvement when it comes to applying the literature to practical situations, especially for older pipe materials. For this reason, permeation measurements on (old) gas pipes were carried out for this study.

The designations for the polyethylene materials differ. In the literature, the material is categorised based on the density of the PE. In other words, LDPE is low density PE (of which there is also a variant LLDPE), MDPE is medium density PE, and HDPE is high density PE. The materials in the gas distribution grid are categorised according to the stress that the material is able to withstand or the generation of the material. For the sake of clarity, the relationship between the literature designation and the gas distribution grid designation is shown below.

- PE 50 (as called PE 63), 1st generation PE, made of HDPE.
- PE 80, 2nd generation PE, made of MDPE as well as HDPE, or 3rd generation MDPE.
- PE 100 and PE 100-RC, 3rd generation PE, made of HDPE.

Note that this relationship is not exact, as the terms can still be used interchangeably and there is some overlap depending on the exact definitions.

2.3.2 Permeation rate for pipe systems

The speed at which a gaseous medium permeates through a pipe wall in equilibrium is calculated using equation 5 [7]:

$$Q = \frac{P_C \cdot A \cdot \Delta P}{e}$$

Equation 5

Where:

- Q is the permeation rate in ml/day;
- P_C is the permeation coefficient in (ml·mm)/(m²·day·bar(a));
- A is the surface in m²;
- ΔP is the pressure difference of the permeate on both sides of the pipe wall in bar(a) (absolute pressure); this is also called the partial pressure difference;
- e is the wall thickness in mm.

The system has been in use in practice for several decades. This has given the system sufficient time to reach an equilibrium with the environment.

Equation 5 can be re-written for a pipe into equation 6. The derivation is shown in Annex V:

$$Q = \frac{P_C \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000}$$

Equation 6

Where:

- *SDR* is the standard dimensional ratio of the pipe, or the ratio between the diameter and the wall thickness of the pipe;
- *L* is the length of the pipe in m.

The concentration of the components present in the atmosphere amounts to:

- 78.08% nitrogen (N₂)
- 20.95% oxygen (O₂)
- 0.93% argon (Ar)
- 0.038% carbon dioxide (CO₂)
- 0.002% trace gases

Therefore, the pressure difference for the permeate on either side of the pipe wall differs for each component. These components are not present inside the gas pipe filled with hydrogen, so the absolute pressure is 0 bar(a). In the environment, the atmospheric pressure prevails (about 1 bar(a)). Therefore, for nitrogen the pressure difference (ΔP) is about 0.78 bar and for oxygen it is about 0.21 bar. The pressure difference for carbon dioxide is several times smaller than the pressure difference for nitrogen and oxygen. The net contribution of carbon dioxide to the contamination of the gas grid will therefore be limited. For this reason, it was decided, in consultation with the Expert and Assessment Group and the guidance group for sub question 135 WP1C, not to include the influence of carbon dioxide in this study.

For the same reason, trace gases also have not been included in this study. Argon is not considered a contaminant, so only the permeation of nitrogen and oxygen have been considered further.

Kiwa Technology delivered two reports in 2020 and 2021, commissioned by the grid operators Coteq Netbeheer, Enduris, Enexis, Liander, RENDO Netwerken, Stedin and Westland Infra, in which the permeation of water through a PE100 pipe was investigated ([8], [9]). This study shows that no correlation was found between the influence of the water pressure and the permeation rate of the water through the HDPE pipe wall. Water pressures up to 10 bar(g) were investigated. However, the strong influence of temperature was in fact demonstrated, with higher temperatures resulting in higher permeation rates. The influence of temperature is described in §2.3.4.

Because water pressure has no influence on the permeation rate, this component has not been included in the calculation. The speed of permeation of water through a pipe wall has been calculated using equation 7 and equation 8:

$$Q = \frac{P_c \cdot A}{e}$$

Equation 7

$$Q = \frac{P_c \cdot (\pi \cdot (SDR - 1) \cdot L)}{1000}$$

Equation 8

For the same reason, the unit for the permeation coefficient of water is different from the unit for the gases. Here, a pressure dependent component (bar) is missing.

When the permeation coefficient (P_c) of a material is known for a certain circumstance, the permeation rate can be calculated using equation 6 and equation 8 for different pipe systems. Some scenarios are given as examples in §5.7.

2.3.3 Time lag

At the start of the permeation experiment, the decrease or increase of the contamination will not be immediately noticeable. This is because the contamination must first diffuse through the material. The time it takes for it to pass through the pipe wall is called *time lag*. In practice this has little effect on the system. The gas pipes are in use for several decades and this is many times more than the expected time lag. Therefore, over most of the operating life, an equilibrium will occur and the pipe wall will be saturated with the components. However, for the experiments it is important to consider time lag. This can significantly affect the testing time. Based on the diffusion coefficient, the time lag (t_{lag}) is determined using equation 9 [10]:

$$t_{lag} = \frac{e^2}{6 \cdot D_c} \cdot \frac{1}{10^2 \cdot 60 \cdot 60}$$

Equation 9

With:

- e is the thickness of the test sample (= wall thickness of the pipe) in mm;
- D_c is the diffusion coefficient in cm^2/s ;
- t_{lag} is the time lag in hours.

As a rule of thumb, it is assumed that the permeation experiment should last three times the time lag. This is the time needed to reach equilibrium.

The time lag depends only on the diffusion coefficient and the thickness of the material. The experiment cannot be accelerated by increasing the pressure of the test gas. However, the process can be accelerated by increasing the temperature, which in turn increases the diffusion coefficient.

Four diffusion coefficients obtained from the literature review are given in Annex IV and figure 1. These were used to determine the time lag for two different systems:

- For PE an SDR 11 DN 110 pipe ($e = 10$ mm);
- For PVC an SDR 41 DN 110 pipe ($e = 2.7$ mm).

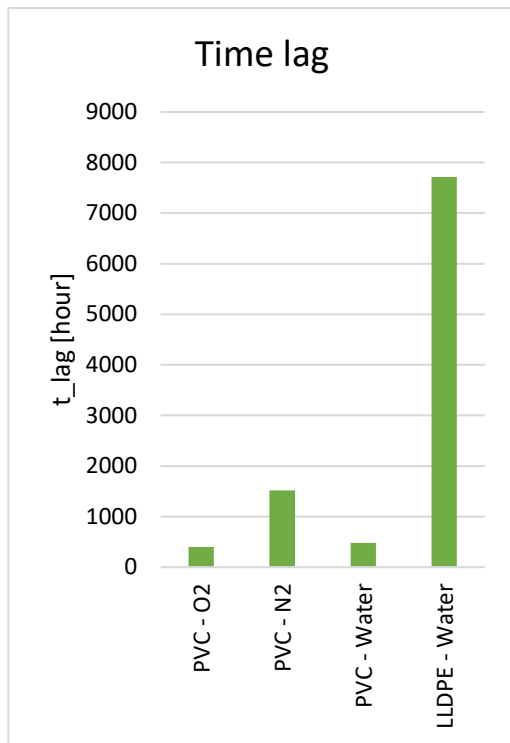


Figure 1. The calculated lead time for the intended experiment based on diffusion coefficients obtained from literature, see Annex IV.

The lead time for PVC is short enough to complete the experiments within the lead time set by the HyDelta programme. The lead time for the experiments of PE with water is too long. However, this estimate is based on one source and concerns a different type of PE (LLDPE instead of HDPE as used for gas pipes). Therefore, the water permeation measurements for the PE pipes were used anyway.

2.3.4 Temperature

The permeation rate of the various components through the pipe material is strongly dependent on the movement of the molecules. This concerns both the movement of the polymer chains and the movement of the permeate. The movement of molecules is again strongly dependent on the temperature. A high temperature means a lot of energy and consequently a high degree of movement of the molecules. That means that the permeation rate is higher at higher temperatures. Therefore, the diffusion rate of water [11], for example as well as the permeation rate of water through various materials [8], [9], [11] increase with an increase in temperature. The same will be the case for the permeation rate of atmospheric gases.

In practice, the pipes mainly take on the temperature of the soil. In the Netherlands, the soil temperature at a depth of 100 cm is between the 5°C and 18°C, and is on average about 11°C [12]. The experiments were conducted at room temperature, which may therefore be regarded as the worst-case scenario.

2.3.5 Solubility

During the permeation process, some of the permeate dissolves into the material. When the permeate is dissolved, it is able to diffuse (read: move) through the material, which eventually results in the permeation of the component. The degree to which the permeate can dissolve in the material is called the solubility coefficient. The literature shows that the permeation rate of water is dependent on time. This is due to the interaction of the material with the water during the permeation process. The permeation rate of water through a dry material is different from the permeation rate of water through a wet material. It follows from [4] that the permeation rate of water through wet PVC is higher than through dry PVC. Conversely, [5] shows that the permeation rate of water through LDPE is lower for wet PE than for dry PE. This has also been observed for a PE100 gas pipe, as described in [8] and [9]. [13] describes that the change in permeation rate is caused by cluster formation of the water within the polymer structure. The difference between PE and PVC is that PE is primarily an apolar material and therefore has little affinity for polar water. As a result, the water clusters have a high affinity for each other and it is more difficult for a water molecule to separate from the cluster and diffuse further through the material. PVC is a polar material. It has a higher affinity for water and therefore the formation of clusters will slow down the permeation process less.

The system has been in use in practice for several decades. This has given the system sufficient time to reach an equilibrium with the environment. The expectation is therefore that the permeation rate through a wet system is the most relevant for the practical situation. It is important that the experiments are run for a long enough period to be able to determine the permeation through the wet material. The assumption is that the environment will remain stable with respect to the pipe. For a pipe, which is for instance located in ground with a heavily fluctuating groundwater level, the estimation can therefore differ from the practical situation.

3 Method

3.1 THT

Before the tests were started, a literature review was carried out and there was consultation with Stedin. This is because Stedin also conducts experiments at the Rozenburg test site that are related to THT absorption. Stedin measures on larger systems under practical conditions. Kiwa measures on smaller systems (lengths up to about 1 metre) under laboratory conditions. The measurements from Kiwa result in calculation parameters that can also be used to assess other systems.

3.1.1 Materials

In order to investigate the desorption of THT from pipe materials, the following pipe materials were requested from the distribution system operators.

- High Impact PVC (PVC-HI)
- Unplasticised PVC (PVC-U)
- PE 80
- PE 100
- Steel

The pipe sections had to be at least 10 years old and had to have a maximum diameter of DN 250. The distribution system operators were asked to cap pipes as soon as possible and send them to Kiwa. This process was not supervised. The pipes delivered to Kiwa were flushed as soon as possible and for a long period with THT-containing natural gas (from GOS N084 Kiwa Gastec) in order to disturb the balance of the THT and other natural gas components in the pipe material as little as possible. This was done until enough samples had been received. All pipe materials were adequately flushed with THT-containing natural gas for the test.

For a reproduction of the test setup see figure 2 and figure 3.

table 3 contains an overview of the pipes received for the study. The material PE100 was not available; PE50 was examined instead. Jacket pipes were used in 5 of the 12 samples; they were installed before flushing with natural gas. When a jacket pipe was applied, a distinction can be made between THT (and aromatics and alkanes) adhering to the inside of the pipe wall and the natural gas components included in the pipe material. The natural gas components will 'vaporize' out of the pipe materials. For permeable materials this happens both on the inside and the outside. The attached natural gas components are only on the inside of the pipe. The concentration measured in the jacket pipe is therefore only the THT contained in the pipe material. This does not apply for steel, because with this material the natural gas components can only adhere to the pipe wall and are hardly absorbed, if at all.

Table 3. Test materials used

Material	Diameter (DN) [mm]	Installation year	Jacket pipe	Kiwa reference
PVC-HI	110	2003	yes	PVC 2021-091
PVC-HI	110	2000	no	PVC 2021-092
PVC HI	160	1979	no	PVC 2021-114
PVC HI	32	1984	yes	PVC 2021-120
PVC-U	160	1971	no	PVC 2021-122
PVC-U	110	1968	yes	PVC 2021-123
PE 50 ⁶	50	Unknown	yes	PE 2021-417
PE 80	32	1987	yes	PE 2021-416
PE 80	50	1973	no	PE 2021-418
Steel	150	1973	n/a	OV 2021-124
Steel	60	1987	n/a	OV 2021-121
Steel	100	1993	n/a	OV 2021-122

3.1.2 Sampling and gas analyses

Before the 1st sampling, the pipes were flushed with H₂ (5.0 - 99.999% pure hydrogen gas) about 10 times the internal volume in order to remove as much as possible of the natural gas present in the pipe sections. After this initial flushing, there was a waiting period of at least one day before the first sampling.

Immediately after the first sampling and each subsequent sampling, the pipes were flushed with H₂ with at least 5 times their internal volume, after which the gas supply to the pipe sections and jacket pipes was cut off (i.e. stagnant gas). This was done to avoid the saturation concentration from being reached and to stop the desorption process.

In order to minimise dilution of the gas sample with the flushing gas, the pipes with a diameter of 32 mm were sampled with a 3 litre Tedlar bag; the other pipes and the jacket pipes were sampled with a 5 litre Tedlar bag. The contents of the pipes and jacket pipes were pressed into the Tedlar bag sample bags with a light positive pressure of hydrogen. The same procedure and Tedlar bag volume was maintained for each pipe for each subsequent sampling.

Gas samples were taken from the inner pipes after day 1, 4, 8, 14, 21, 28 and 50. The gas samples were analysed for THT, aromatics C6-C11 and alkanes C5-C15.

The jacket pipes were flushed and filled with nitrogen (5.0 - 99.999% pure). They were sampled on days 14, 21, 28 and 50.

The gas samples obtained were analysed using a GC analysis method for higher (natural) hydrocarbons; using an FID detector for THT, alkanes and aromatics.

⁶ Although the terms PE50 and PE63 were used for similar materials in the past, only PE50 has been used in this report.

The left and right sides of the pipe sections with end caps and five pipes with jacket pipes are shown below.



Figure 2. Filling side



Figure 3. Sampling side

Both the gas pipes and the jacket pipes were sealed at two ends with a ball valve, and after flushing were sealed under approximately 100 mbar positive pressure. The gas meter, shown in figure 2, was used to read the flushing volume. The temperature during the measuring period was $21^{\circ}\text{C} \pm 3^{\circ}\text{C}$.

3.2 Atmospheric gases

3.2.1 Materials

The plastic pipe sections were partly supplied by the participants of the Expert and Assessment Group and partly from the materials collection from 'Kenniscentrum Gasnetbeheer'. Each pipe has been allocated a unique internal reference number by Kiwa, see table 4. The pipes made of PE 50, PVC-CPE and PVC-U have been used in the gas distribution grid. The PVC-A, PE 100 and PE 100-RC pipes are new.

Table 4. Pipes used for the permeation measurements on atmospheric gases.

Pipe type	Diameter (DN) [mm]	Wall thickness (e) [mm]	Length (L) [m]	Installation year	Kiwa reference
PE 50	110	11.1	0.99	Unknown	PE 2019-229
PE 100-RC	110	10.6	1.69	(new)	PE 2021-349
PE 100	110	11.1	1.40	(new)	PE 2021-350#03
PE 100	110	11.6	1.24	(new)	PE 2021-350#04
PVC-A	110	2.9	0.92	(new)	PVC 2021-019
PVC-CPE	110	2.7	1.02	1991	PVC 2019-003
PVC-U	110	3.2	1.43	1970	PVC 2016-066
PVC-U	110	3.2	0.72	1970	PVC 2018-005

3.2.2 Setup

The PE pipe sections were closed on both sides with an electrofusion end cap (type: CapSet E+ PE 100). Every end cap was placed over the pipe along a length of 0.165 m. The PVC pipe sections were closed on both sides by a metal end cap (type: Multijoint 3207+ with NBR sealing ring). Every end cap was placed over the pipe along a length of 0.105 m. Connections were provided on both types of end caps so that the content of the pipe could be flushed with a gas and so that gas samples could be taken. The setup is depicted in figure 4. The influence that the end caps (could) have on the measurement results is assessed and described in §5.2.



Figure 4. Four PE pipes where 500 mbar(g) of hydrogen gas has been applied.

3.2.3 Permeation measurements

The pipes were filled with hydrogen gas (5.0 H₂, 99.999% pure) at a positive pressure of 500 mbar. During the experiment, the pressure slightly decreased due to permeation of the hydrogen to the environment. Care was taken to ensure that the hydrogen pressure always remained at a positive pressure by refilling the pipes with pure hydrogen gas where necessary. The results were corrected for the change in pressure by using the actual partial pressure difference in the calculation. Corrections were also made for the intermittent refilling of pure hydrogen gas by determining the decrease in oxygen and nitrogen content as a result of the refilling, and adding the decrease to the subsequent results. It was also ensured that the oxygen and nitrogen content in the pipes remained sufficiently low so that the partial pressure difference remained sufficiently high. This prevented the permeation rate from decreasing as equilibrium with the environment was slowly reached.

Over a period of 96 days, the content of the oxygen and nitrogen components in the hydrogen gas was determined at ten different times using gas chromatography. A 5 ml sample was taken from the system using a gas syringe, placed in the gas chromatograph and analysed. The gas chromatograph is capable of satisfactorily distinguishing and detecting the oxygen and nitrogen components. Therefore, the content of the oxygen and nitrogen components has been determined for each measurement with one gas analysis. The loss of hydrogen due to sampling has a negligible influence on the measurement. The internal volume of the system was at least 6.0 litres. A sample of 5.0 ml therefore amounts to ~0.1% of the total internal volume of the pipe.

The oxygen and nitrogen components are present in the atmosphere. During the sampling process and the application of the gas sample to the gas chromatograph, a measurement inaccuracy was obtained as a result of atmospheric contamination of the gas sample. This measurement inaccuracy has been made transparent by using the same measurement procedure for a 99.999% pure hydrogen gas as a reference. Here, the oxygen and nitrogen components have been detected in a content of 0.02% and 0.04% respectively. This is the value for the measurement accuracy. The results have been corrected accordingly.

Prior to each series of gas measurements, at least three reference measurements were performed with one or more reference gases. Then the gas samples from the pipes were analysed. Finally, at least one more reference measurement was analysed. The three reference gases used had oxygen contents of 0.027%, 0.246% and 2.30% and nitrogen contents of 0.093%, 0.911%, and 8.54%. The results of the gas analyses of the pipes were corrected with the reference measurements.

3.3 Water

3.3.1 Materials

A similar series of pipes as described in §3.2.1 has been used for this study, see table 5. In this case as well, a PVC-A pipe and the PE 100 and PE 100-RC pipes are new and the other pipes have been used in the gas distribution grid.

Table 5. Pipes used for permeation measurements with water.

Pipe type	Diameter (DN) [mm]	Wall thickness (e) [mm]	Length (L) [m]	Installation year	Kiwa reference
PE 50	110	2.9	1.14	1992	PE 2017-307
PE 50	110	6.4	1.36	1970	PE 2018-184
PE 100-RC	110	7.1	1.31	(new)	PE 2021-338
PE 100	110	11.1	1.40	(new)	PE 2021-350#01
PE 100	110	11.1	0.99	(new)	PE 2021-350#02
PVC-A	110	3.2	1.03	(new)	PVC 2020-001
PVC-A	110	2.7	1.04	1991	PVC 2018-070
PVC-CPE	110	2.9	0.87	Unknown	PVC 2019-149
PVC-CPE	110	3.2	1.15	1990	PVC 2017-108
PVC-U	110	3.7	0.87	1972	PVC 2018-086
PVC-U	110	3.0	1.16	1964	PVC 2020-013

3.3.2 Setup

The PE pipe sections were closed on both sides with an electrofusion end cap (type: CapSet E+ PE100). Every end cap was placed over the pipe along a length of 0.165 m. The PVC pipe sections were closed on both sides with a glued end cap (type: Cap PVC-U PN16 d110). Every end cap was placed over the pipe along a length of 0.075 m. Both types of end caps have connections so that the contents of the pipe could be flushed with a gas or liquid. The pipes were placed in a closed space with a desiccant to minimise the influence of the local air humidity. There is also no moisture in pure hydrogen gas. The setup is depicted in figure 5. The influence that the end caps have on the measurement results has been assessed and described in §5.2.



Figure 5. A section of the PVC and PE pipes in which water was applied.

3.3.3 Permeation measurements

The pipes were filled with water at the atmospheric pressure and then closed with a Swagelok plug. As a result of permeation, the water passes outwards through the pipe wall, where it is collected by the desiccant beads⁷. This leads to a decrease in mass over time. Over a period of 120 days, the mass of the pipes was measured at sixteen different times.

In order to validate the mass calculations, a PVC pipe (Kiwa reference PVC 2016-116) with glued end caps was not filled with water and was included during the series of measurements. This mass was expected to remain constant over time. It was found that the mass decreased slightly. This is presumably because some water was present in the pipe wall that was permeating to the ambient environment due to the low humidity. The validation measurement was therefore not suitable. This is discussed in §5.3.

⁷ The permeation behaviour of water from inside the pipe to the outside is equal to the permeation behaviour of water from outside the pipe to the inside. Permeation is a concentration driven process and in both cases the concentration difference is equal.

4 Measurement results

4.1 Desorption of THT

The THT, alkanes and aromatics that desorb from the pipe wall are presented in graphs in the following paragraphs for each pipe, both for the desorption to the hydrogen in the pipes (the first three sections) and to the nitrogen outside in the jacket pipes (the three sections thereafter).

4.1.1 Desorption of THT from the pipe wall to H_2

The desorption of THT from the wall of the pipe for the different materials has been shown in figure 6 by plotting the analytical results of each sampling with respect to time. Please note that after each sampling, the content was flushed; the measuring points are concentrations at the end of the measuring period.

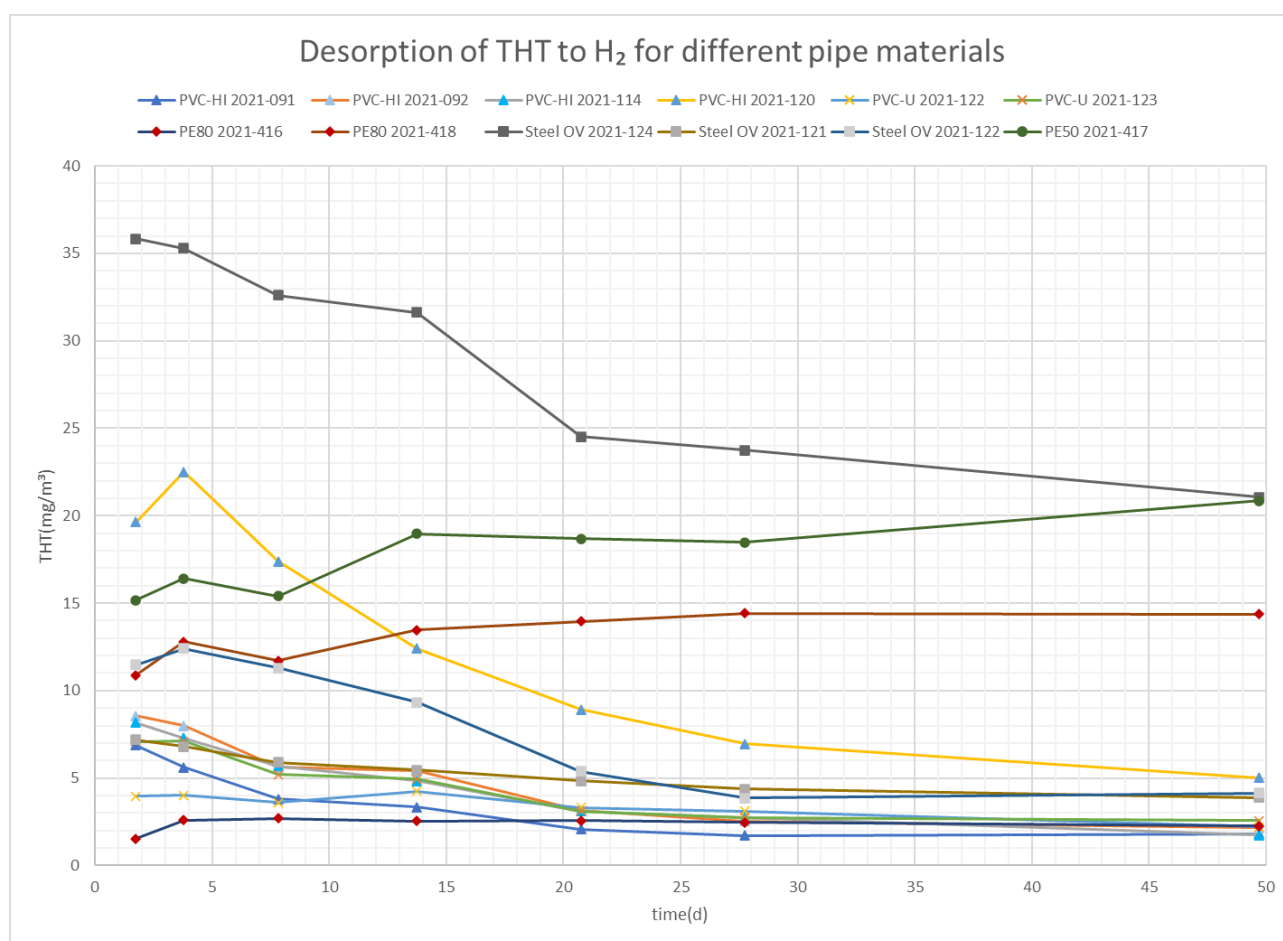


Figure 6. THT desorption in H_2 flushed gas pipes.

Except for PE50 and PE80, the content of THT in the gas pipe constantly decreased. Relatively speaking, the steel gas pipe “OV 2021-124” deteriorated less rapidly than the other materials. In the process, concentrations were reached that are higher than the value of 18 mg/m^3 THT, such as the nominal content in natural gas (it is assumed that this involves the equilibrium concentration in natural gas). The application of the pure hydrogen as free phase therefore lead to a higher equilibrium concentration for THT in PE and steel.

Note: after each measurement, the gas pipe was flushed with pure hydrogen gas (5.0 H_2 , 99.999% pure). This hydrogen gas then remained in the gas pipe until the next measurement. As the measurement interval increases, the hydrogen gas has more time to absorb THT from the pipe (and

thus reach the equilibrium concentration). However, if the concentration remains the same in the next measurement, or even decreases, it can be concluded that less and less THT is effectively coming out of the pipe wall; see §4.1.7.

Furthermore, a fatty deposit (on the inside of the pipe) was observed in the three steel pipes; this could possibly explain the relatively high release of THT.

The results for desorption of the THT to H_2 are presented in table 15 in Annex III.

4.1.2 Desorption of alkanes from the pipe wall to H_2

The desorption of the alkanes present in natural gas from the pipe wall for the different materials is shown in figure 7 below. This concerns the sum of the alkanes C5 (pentane isomers) up to and including C15 (pentadecane isomers).

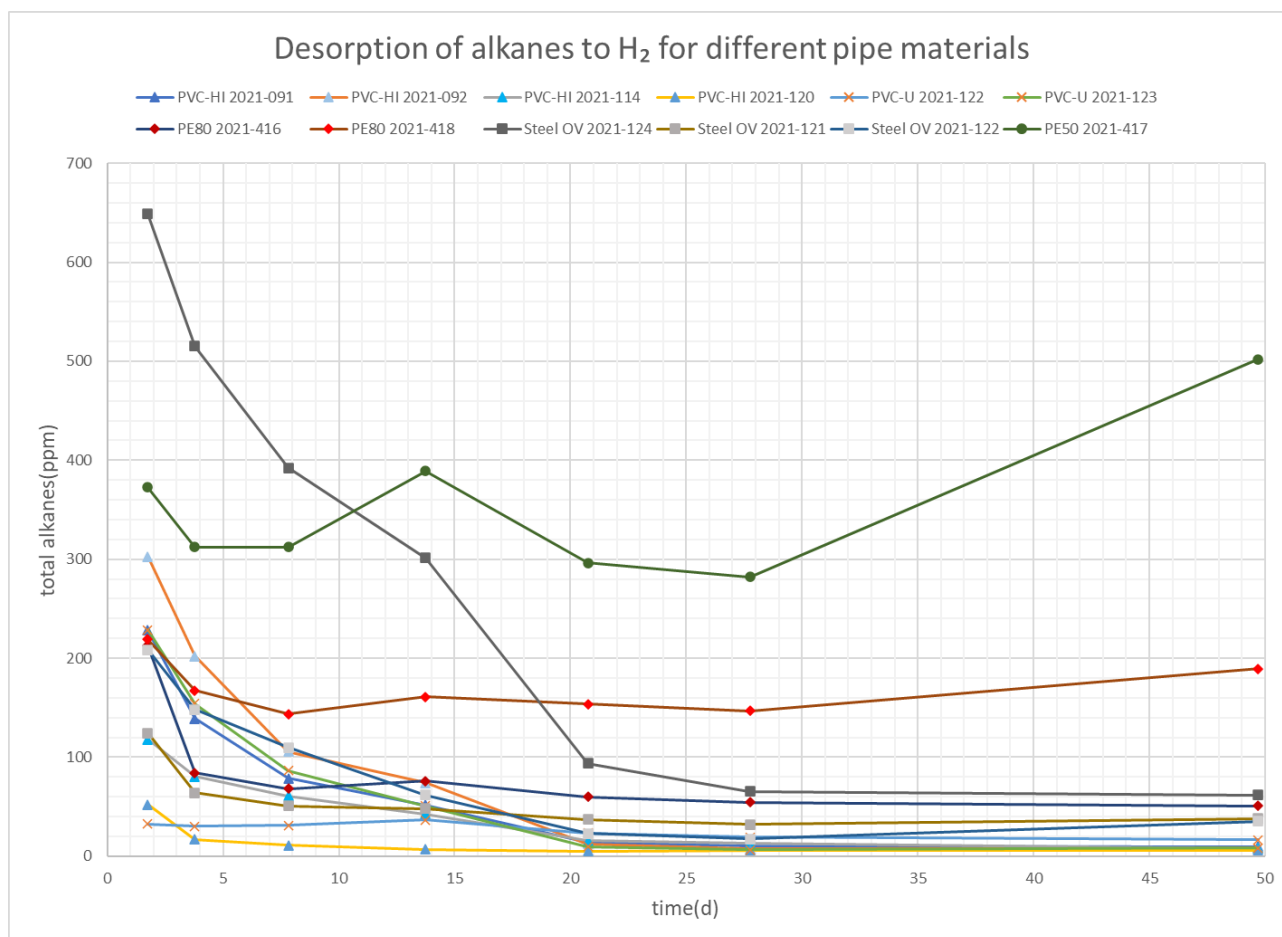


Figure 7. Desorption of alkanes in H_2 flushed gas pipes.

The desorption of the alkanes in natural gas in the gas pipes largely shows the same picture as the results for THT; except for PE50 and PE80 all the contents decrease over the course of the given time (in these two cases the desorption rate is higher than the replenishing frequency). 'Steel OV 2021-124' also shows this decreasing trend for the desorption of alkanes from the pipe wall. A 'competition effect' with THT may possibly have caused PE50 and PE80 to have a higher equilibrium value with the last measurement (50 days) than with the previous measurement (28 days).

The results for desorption of the alkanes to H_2 are provided in table 16 in Annex III.

4.1.3 Desorption of aromatics from the pipe wall to H₂

The desorption of the aromatics present in natural gas from the wall of the pipe for the different materials is shown in figure 8 below. This concerns the sum of the aromatics C6 (benzene) up to and including C11 (PAHs).

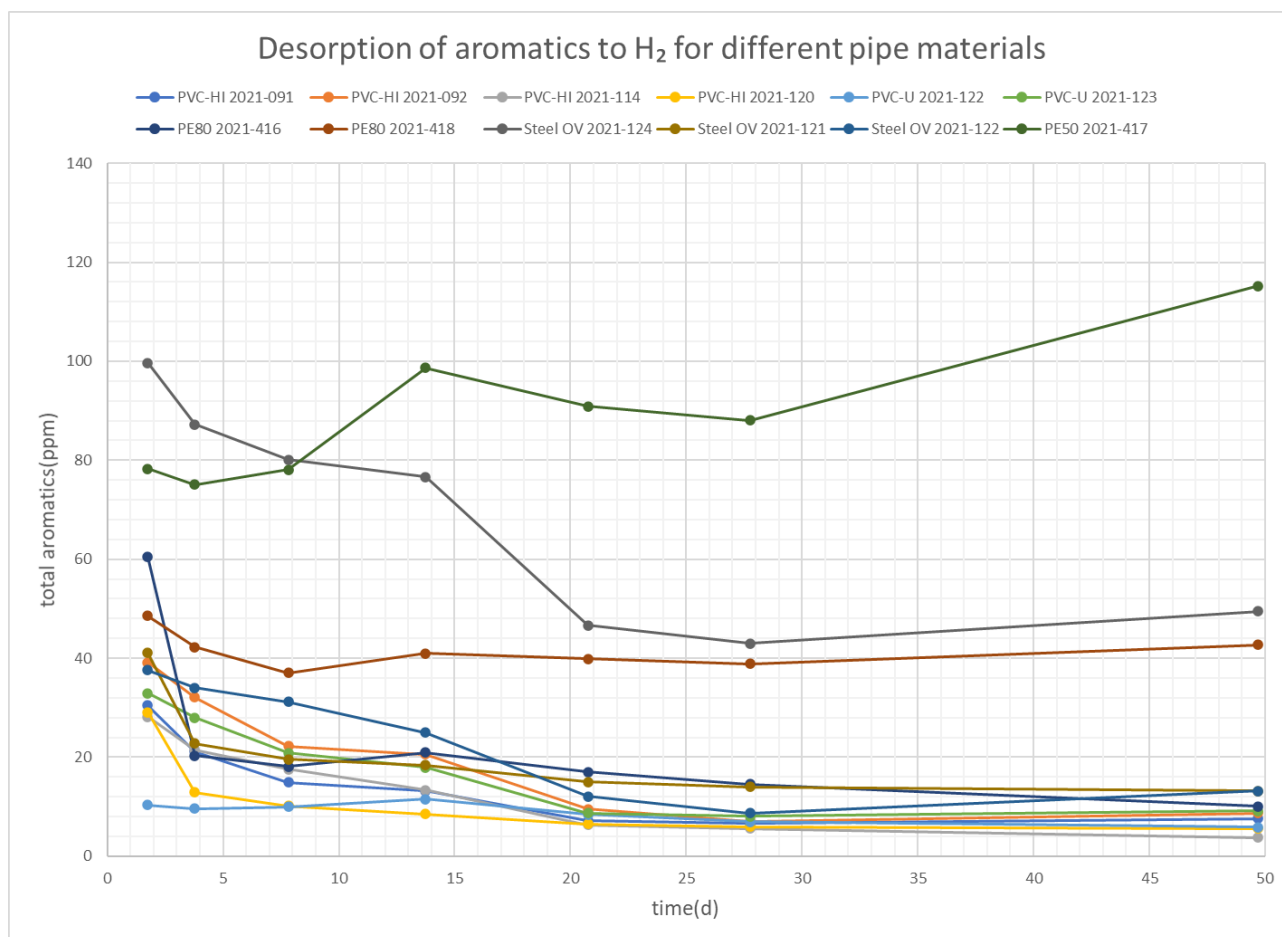


Figure 8. Desorption of aromatics in H₂ flushed gas pipes.

The desorption of the aromatics in natural gas in the gas pipes largely shows the same picture as the results for THT and the alkanes. As with the alkanes, it is possible that a 'competition effect' with THT has caused PE50 and PE80 to have a higher equilibrium value with the last measurement than with the previous one.

table 17 in Annex III

4.1.4 Desorption of THT from the pipe wall to the jacket pipe

The desorption of THT from the wall of the pipe to the jacket pipe for the different materials is presented in figure 9 below.

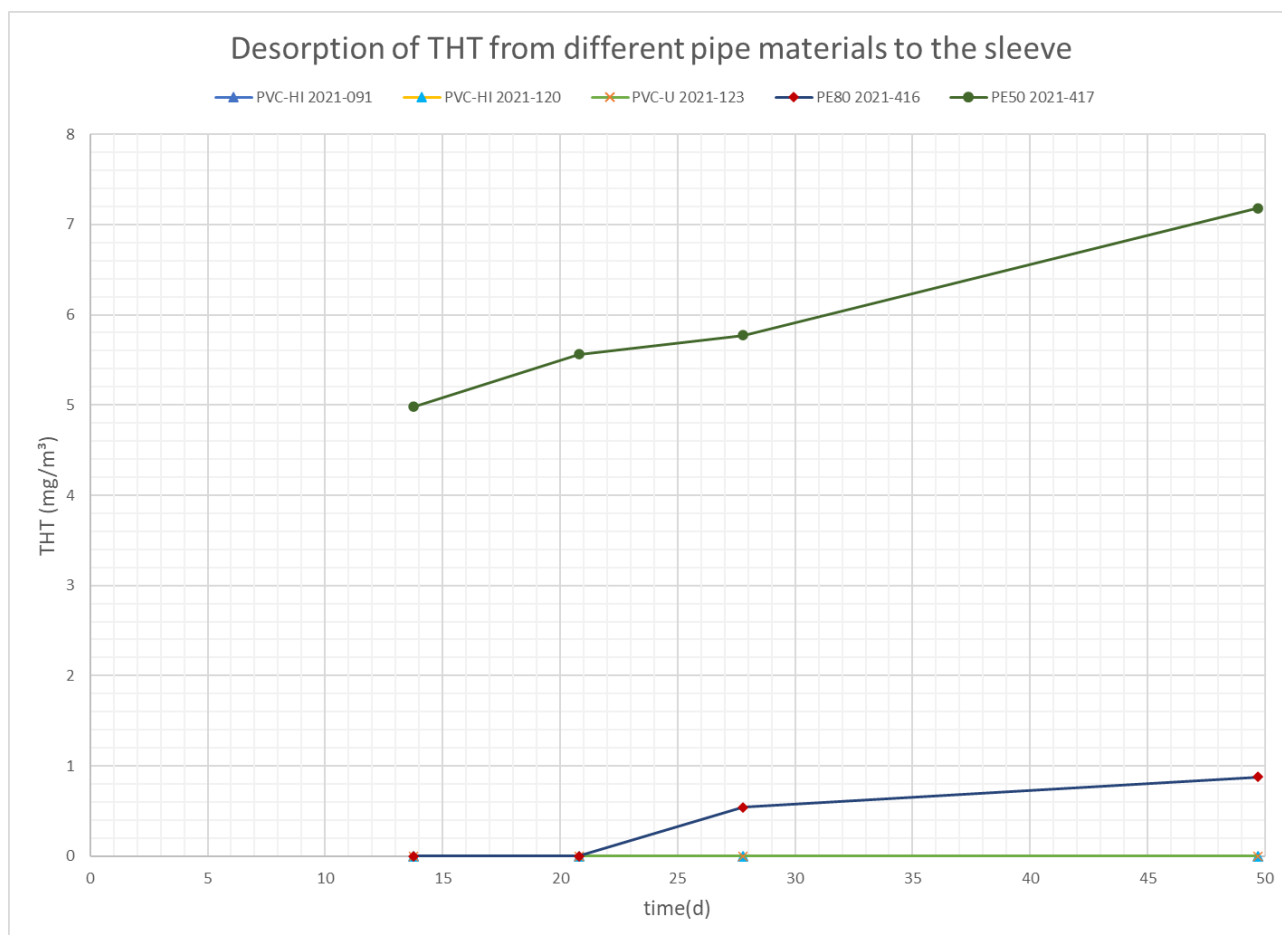


Figure 9. Desorption of THT to the jacket pipe.

Only PE50 and PE80 show desorption of THT on the outside of the pipe (from the pipe wall). The PVC samples do not show any desorption of THT during the measurement period.

The results for desorption of the THT to the jacket pipe are presented in

Table 18 in Annex III.

4.1.5 Desorption of alkanes from the pipe wall to the jacket pipe

The desorption of the alkanes present in natural gas from the pipe wall to the jacket pipe for the different materials are presented in figure 10 below. This concerns the sum of the alkanes C5 (pentane isomers) up to and including C15 (pentadecane isomers).

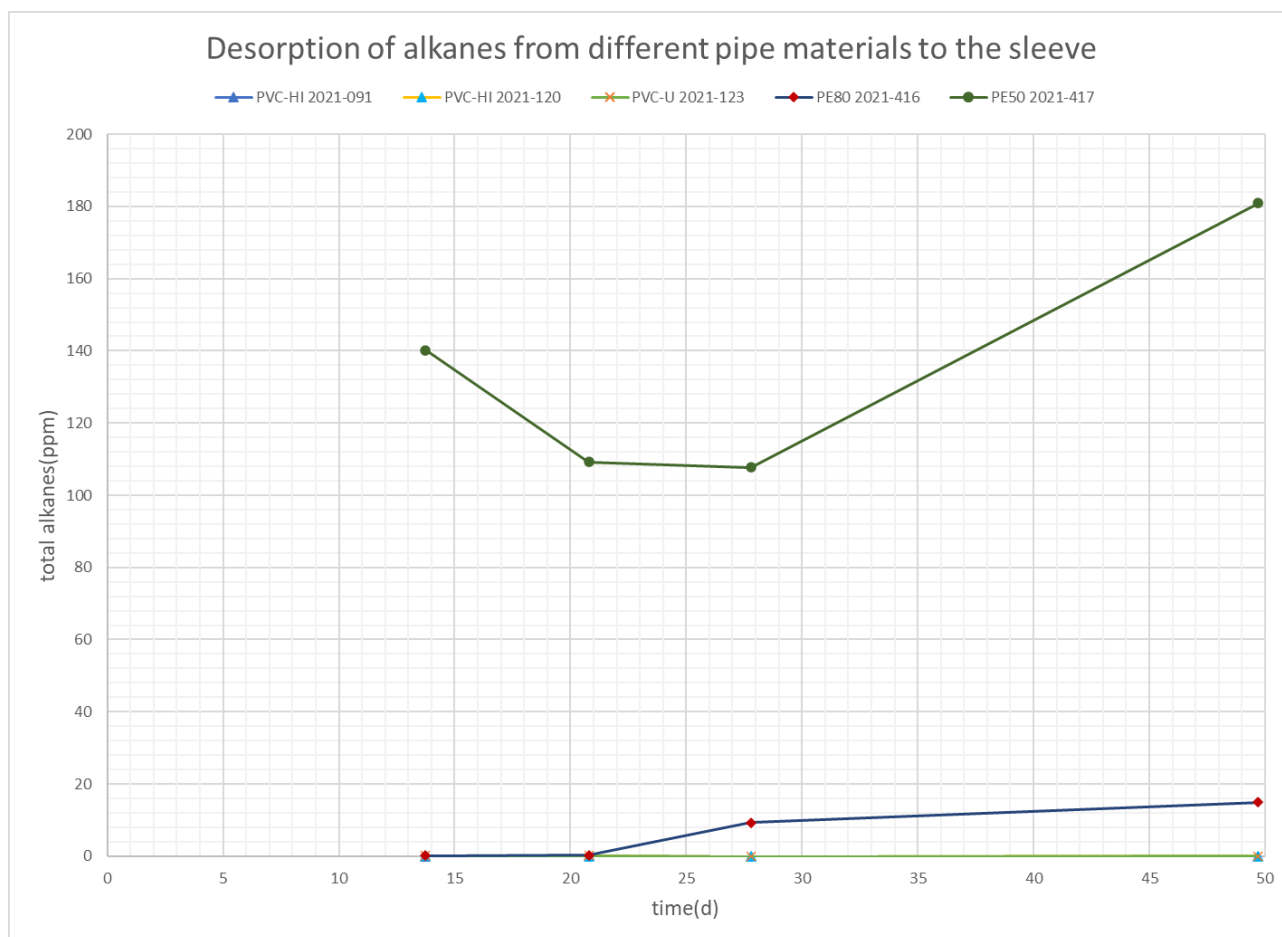


Figure 10. Desorption of alkanes to jacket pipe.

Only PE50 and PE80 show desorption of alkanes on the outside of the pipe (from the pipe wall). The PVC samples do not show any desorption of alkanes during the measurement period.

The results for desorption of the alkanes to the jacket pipe are presented in table 19 in Annex III.

4.1.6 Desorption of aromatics from the pipe wall to the jacket pipe

The desorption of the aromatics present in natural gas from the pipe wall to the outside for the different materials is presented in figure 11 below. This concerns the sum of the aromatics C6 (benzene) up to and including C11 (PAHs).

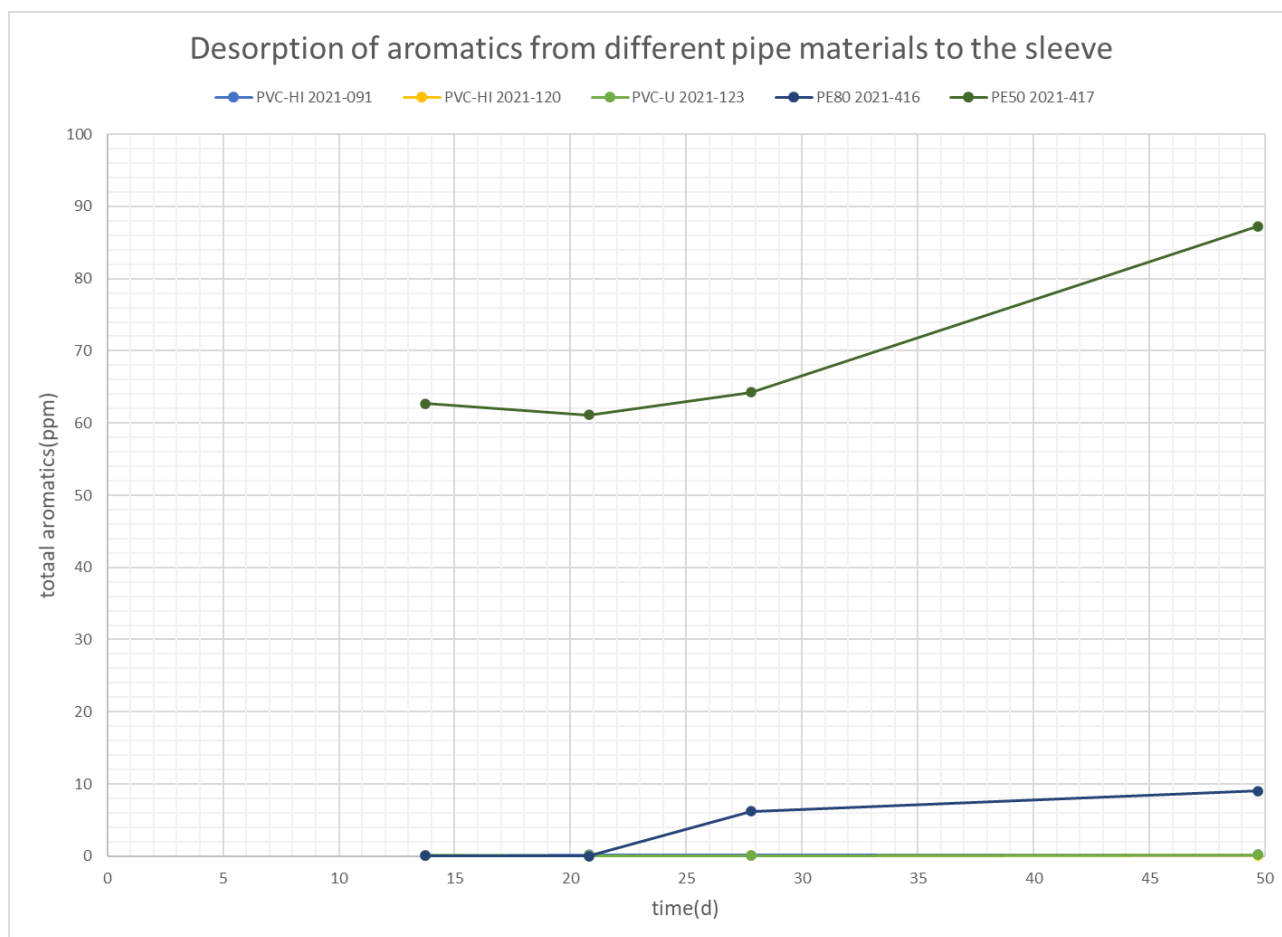


Figure 11. Desorption of aromatics to jacket pipe

Only PE50 and PE80 show desorption of aromatics on the outside of the pipe (from the pipe wall). The PVC samples do not show desorption of aromatics during the measurement period.

The results for desorption of the aromatics to the jacket pipe are presented in table 20 in Annex III.

4.1.7 Speed of desorption of THT from the pipe wall to H₂ by surface

The speed of desorption of THT of the pipe wall is calculated according to equation 1; here the amount of THT is calculated for each surface of the inner wall of the pipe in the time between the sampling or H₂ flushing for the different materials. This equation is similar to that of equation 7 (§2.3.2), where the amount of THT is calculated using the volume of the inner pipe and the concentration found.

The results for the desorption rate of THT are presented figure 12 below.

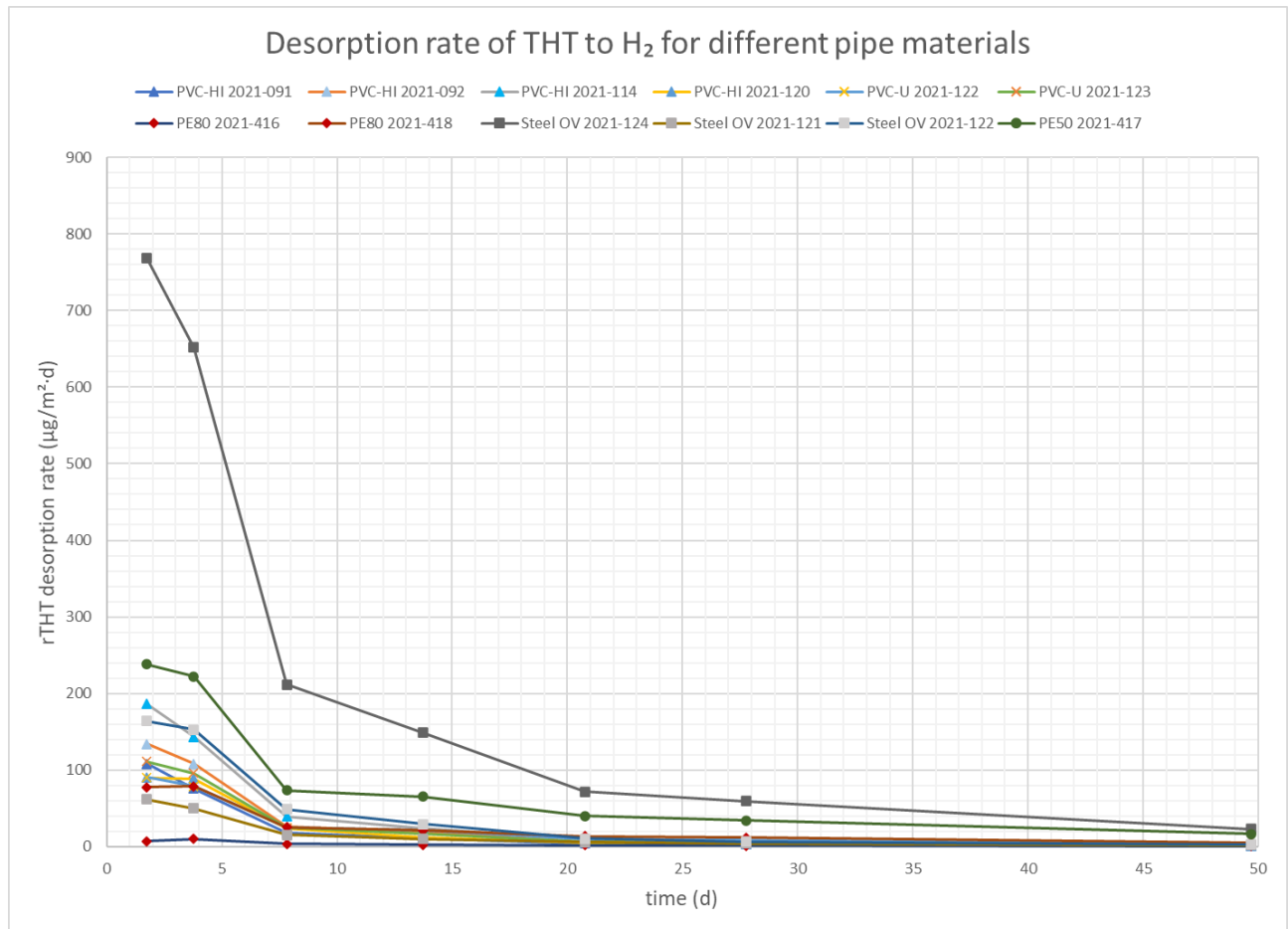


Figure 12. Desorption rate of THT in H₂ flushed gas pipes.

The speed at which THT is desorbed from the (inner) pipe wall decreased for all materials to below 25 µg/(m²·d) after 50 days.

4.1.8 Kinetic model for desorption rate

In the graph below (figure 13), the dependent quantities for the desorption of THT have been compared (speed of desorption versus time), in order to determine the desorption indicators as described in equation 4. In this regression, the results of the first sampling have been omitted, because this lead to an improvement of the correlation coefficient for all materials. The graphical representation has only been included for THT. For higher alkanes and aromatics, the desorption indicators (k_0 and k_1) have been determined in a similar way.

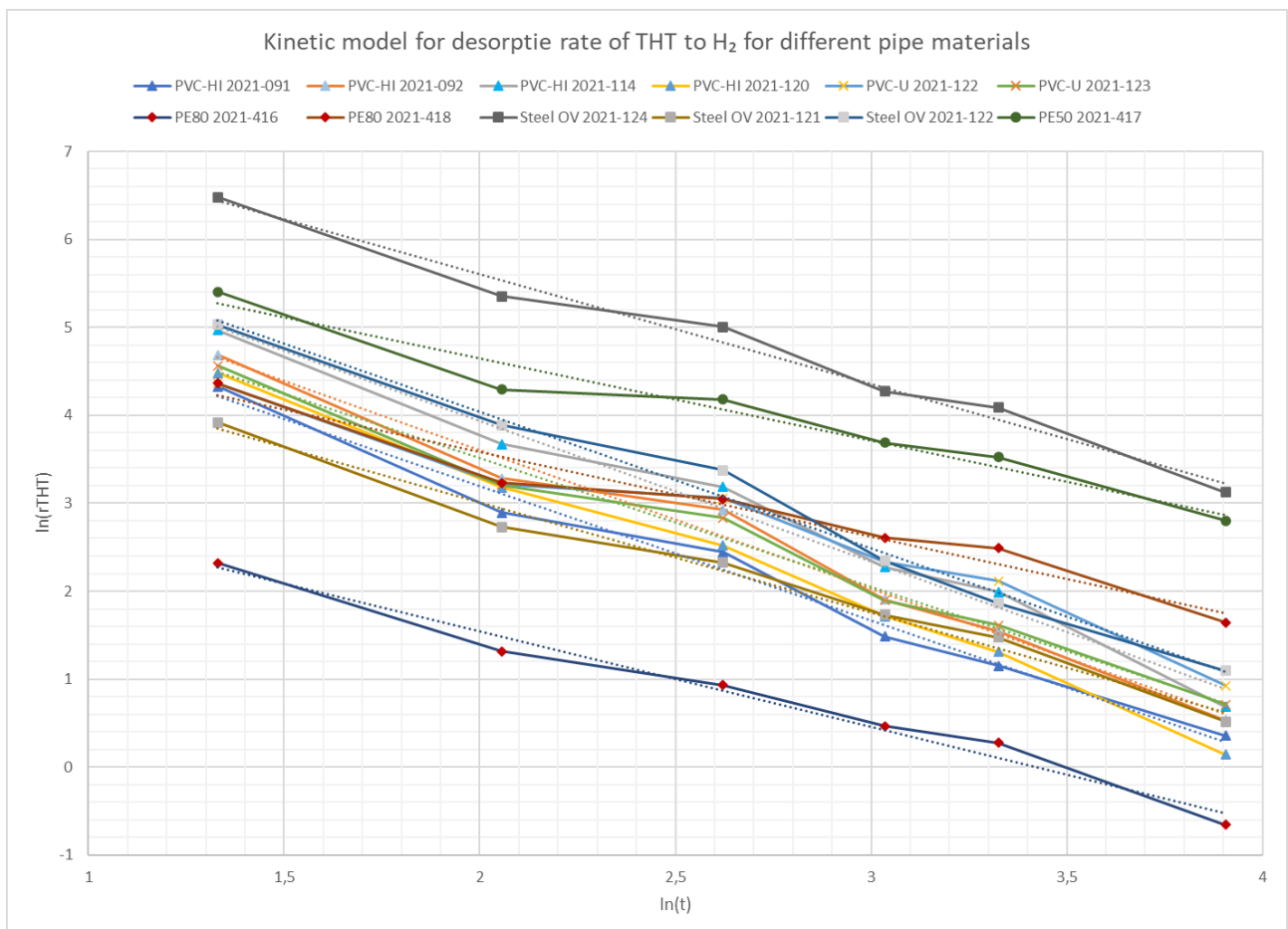


Figure 13. Representation of kinetic model for the desorption rate of THT

For these results, the desorption indicators have been calculated and are presented for THT in table 6 below, together with the correlation coefficient found for the chosen model. Using these indicators and equation 4 it is possible to calculate the quantity of THT desorbed per unit of time from one of the materials listed below.

Table 6. THT desorption indicators

Kiwa reference	Pipe#	k_0^{THT}	k_1^{THT}	correlation
PVC-HI 2021-091	7	6.247	-1.526	99.4%
PVC-HI 2021-092	8	6.750	-1.575	99.3%
PVC-HI 2021-114	11	7.127	-1.597	99.3%
PVC-HI 2021-120	3	6.680	-1.642	99.7%
PVC-U 2021-122	9	6.026	-1.237	98.0%
PVC-U 2021-123	6	6.439	-1.463	99.3%
PE80 2021-416	1	3.720	-1.086	99.2%
PE80 2021-418	4	5.515	-0.965	98.1%
Steel OV 2021-124	10	8.106	-1.249	99.3%
Steel OV 2021-121	2	5.517	-1.254	99.4%
Steel OV 2021-122	12	7.142	-1.552	99.4%
PE50 2021-417	5	6.512	-0.932	98.2%

Example calculation for PE50 (2021-417) after 100 days:

$$r_{\text{THT}} = e^{6.512 - 0.932 \cdot \ln(100)} = 9.2 \mu\text{g}/\text{m}^2 \cdot \text{d}$$

equation 10

Therefore, after 100 days, a maximum of 9.2 μg THT per square metre of internal surface area will be desorbed from this pipe material in one day with stagnant gas. One metre of this PE50 pipe has an internal surface area of 0.138 m^2 and an internal volume of 1520 mm^3 . This means that in one day, with stagnant gas, 1.3 μg of THT will be desorbed per metre of pipe. The increase of the concentration in the gas is dependent on the amount of gas flowing through the pipe. No flow will cause the concentration of THT to increase.

The calculated indicators are based on approximately 50 flushes of the entire pipe volume over a period of 50 days with a maximum downtime of two days. Depending on the flow rate through the pipeline, the level of THT (and other natural gas components) in the hydrogen can then be calculated. A fairly constant flow of hydrogen gas will prevent the equilibrium concentration from being reached and will therefore lower the actual values.

For the alkanes and aromatics occurring in natural gas, the desorption indicators have been calculated in the same way; these can be found in

table 21 and table 22 in Annex III.

Based on the results obtained, no significant distinction can be made for the desorption indicators for the examined materials of steel, PE and PVC.

4.2 Permeation of atmospheric gases

Two examples of the results of the oxygen permeation are presented in figure 14 and the results of the nitrogen permeation are presented in figure 15. A full overview of the results is provided in Annex VI. The bars in the graph represent the measurement inaccuracies caused by the presence of the components in the atmosphere at the time the sample was taken and at the time the sample was

injected into the gas chromatograph. For the setup of PVC 2021-019, a latent leak was observed during the measurement. The pipe was then re-installed after 40 days. The results have been corrected for the system pressure and the intermediate addition of pure hydrogen gas to keep the setup at a positive pressure.

The slope in figure 14 and figure 15 is a measure for the permeation rate, see dotted lines. Not all of the measurement points have been used to determine the permeation rate. Three criteria have been used for this:

- To be able to estimate the reliability of the slope, at least five consecutive measurement points are required. An exception to this was with PVC 2021-019, as the measurement was repeated after 40 days.
- The system needed time to stabilise and reach equilibrium. The last measurement points were used for this reason.
- In selecting the measurement points, an attempt was made to include as many measurement points as possible in the slope determination without compromising the accuracy of the regression line (dotted line). The accuracy is represented by the Pearson correlation coefficient (R^2), see table 7 and table 8.

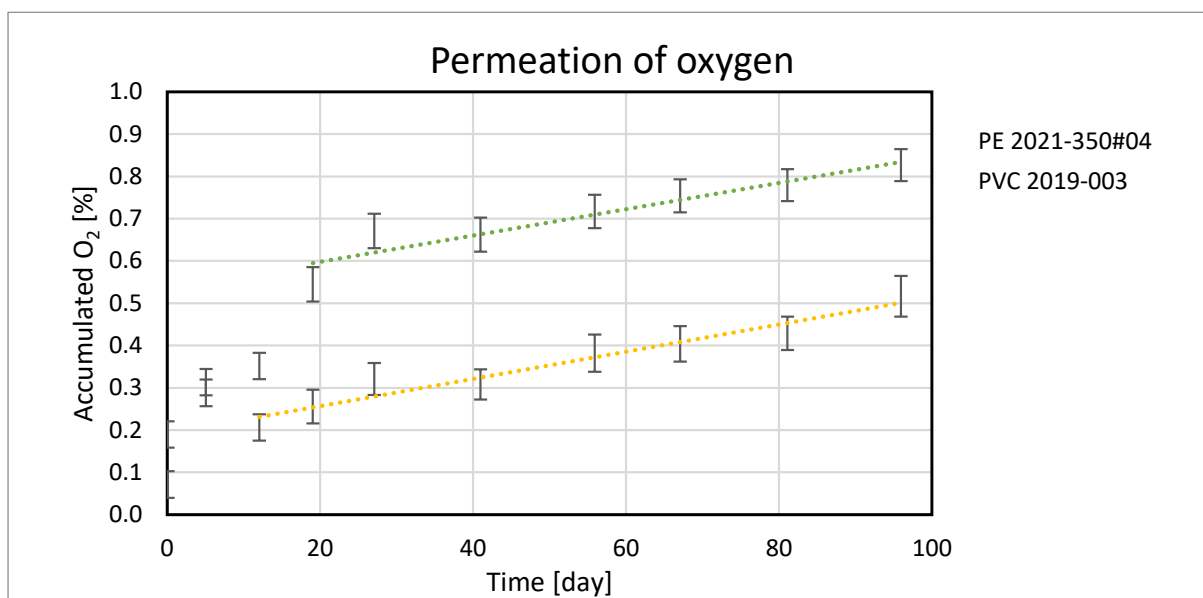


Figure 14. The progression of accumulated oxygen on the inside of the different pipes over time.

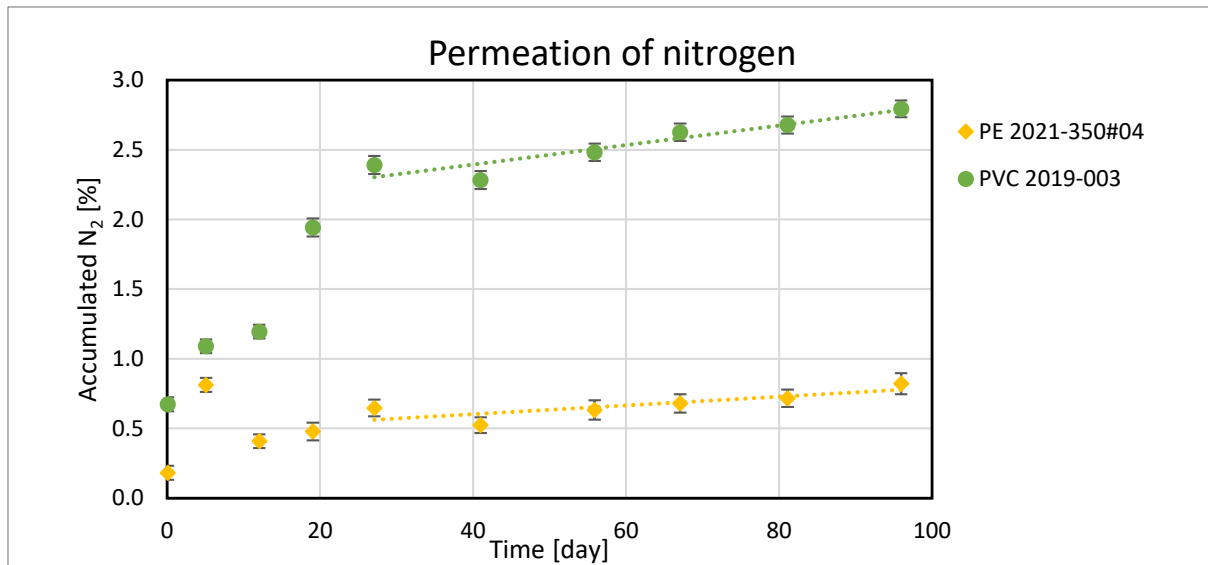


Figure 15. The progress of accumulated nitrogen on the inside of the different pipes during the time.

The slope obtained from figure 14 and figure 15 and Annex VI was used to determine the permeation rate of the oxygen/nitrogen through the pipe wall and the permeation coefficient of the material. Using equation 5 corrections were made for the dimensions of the pipe, including the partial covering of the pipe by the end caps, and the gas pressure of the atmospheric components. The results are provided in table 7 and table 8. It is worth noting that the accuracy of the oxygen measurements is different from that of the nitrogen measurements. This is discussed in §5.2.

The closer the correlation coefficient is to the value of 1, the better the regression line (dotted line in figure 14 and figure 15) matches the raw data. For the nitrogen measurements for PE 2021-349 and PVC 2018-005, the correlation coefficient leaves much to be desired. The correlation coefficient is so far away from the value 1 that these results cannot be used for determining the permeation rate and the permeation coefficient indicated (shown in red in the tables). The correlation coefficient above the 0.8 is considered accurate (shown in green in the tables). The correlation coefficients below 0.8 should be interpreted with caution.

Table 7. The permeation rate and correlation coefficient of the different measurements have been calculated into the permeation coefficient for the oxygen measurements.

Permeation of oxygen O ₂						
Kiwa reference	Pipe type	Number of measurement points	Slope [% (STP)/day]	Correlation coefficient (R ²) [-]	Permeation rate [ml/(m·day)]	Permeation coefficient [(ml·mm)/(m ² ·day·bar)]
PE 2019-229	PE50	8	4.88E-03	0.897	0.394	70.6
PE 2021-349	PE100RC	5	3.75E-03	0.591	0.289	46.8
PE 2021-350#03	PE100	5	3.09E-03	0.965	0.245	41.7
PE 2021-350#04	PE100	8	3.22E-03	0.949	0.292	49.9
PVC 2021-019	PVC-A	4	2.09E-03	0.946	0.207	9.4
PVC 2019-003	PVC-CPE	7	3.11E-03	0.895	0.337	12.9
PVC 2016-066	PVC-U	7	4.19E-03	0.993	0.463	19.1
PVC 2018-005	PVC-U	5	8.44E-04	0.577	0.100	4.6

Table 8. The permeation rate and correlation coefficient of the different measurements have been calculated into the permeation coefficient for the nitrogen measurements.

Permeation of nitrogen N ₂						
Kiwa reference	Pipe type	Number of measurement points	Slope [% (STP)/day]	Correlation coefficient (R ²) [-]	Permeation rate [ml/(m·day)]	Permeation coefficient [(ml·mm)/(m ² ·day·bar)]
PE 2019-229	PE50	7	4.62E-03	0.796	0.373	17.9
PE 2021-349	PE100RC	5	6.01E-03	0.169	n.b.*	n.b.*
PE 2021-350#03	PE100	5	2.75E-03	0.493	0.218	10.0
PE 2021-350#04	PE100	6	3.13E-03	0.659	0.284	13.0
PVC 2021-019	PVC-A	4	6.05E-03	0.978	0.598	7.3
PVC 2019-003	PVC-CPE	7	9.31E-03	0.841	1.009	10.3
PVC 2016-066	PVC-U	7	1.56E-02	0.995	1.728	19.1
PVC 2018-005	PVC-U	5	4.34E-05	0.000	n.b.*	n.b.*

n.b.*, the correlation coefficient is so far away from the value of 1 that the regression line is a poor indicator of the measured data. Consequently, the subsequent calculations were imprecise and therefore not carried out.

4.3 Permeation of water

Three results of the water permeation are provided in figure 16 as examples. A full overview of the results is provided in Annex VI. The bars in the graphs show the measurement accuracy of 0.1 grams, caused by the accuracy of the mass balance.

The slope in figure 16 and Annex VI shows the permeation rate, see the dotted lines. Not all of the measurement points have been used to determine the permeation rate. The same three criteria have been used as the criteria for the atmospheric gases (see §4.2).

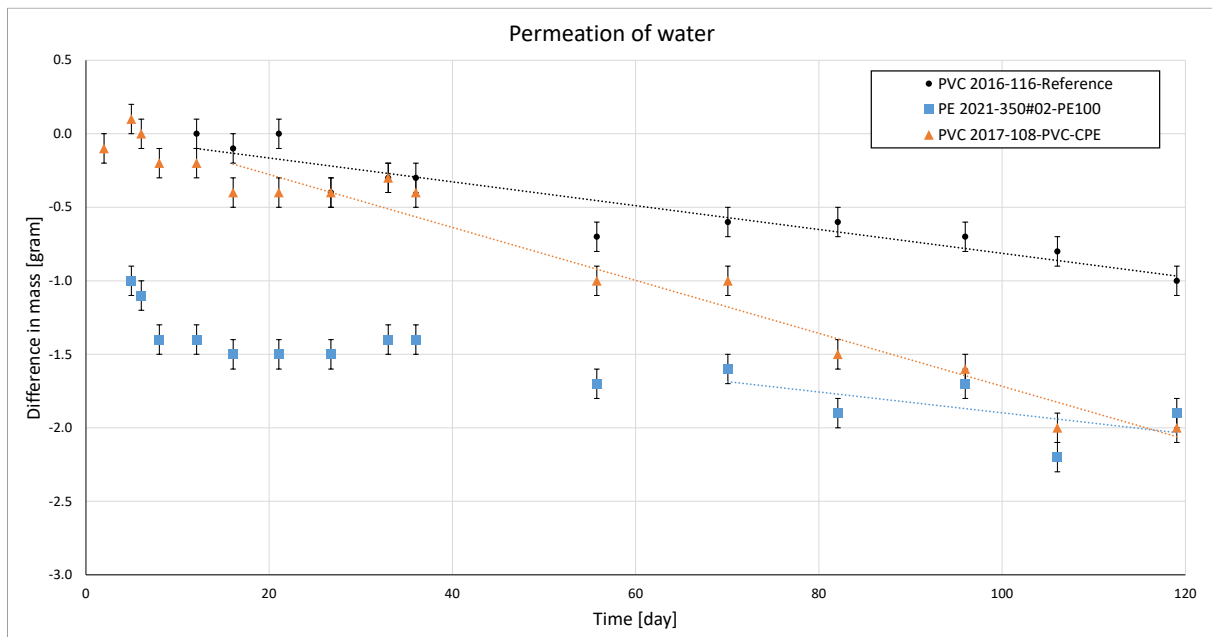


Figure 16. The progress of water loss for the various pipes during the time.

The slope obtained from figure 16 and Annex VI has been used to determine the permeation rate of water through the pipe wall and the permeation coefficient of the material. Corrections were made for the dimensions of the pipe including the end caps. The results are presented in table 9.

The closer the correlation coefficient is to the value of 1, the better the regression line (dotted line in figure 16) matches the raw data. For the PE measurements, the correlation coefficient leaves much to be desired. The correlation coefficient is so far away from the value 1 that these results cannot be used for determining the permeation rate and the permeation coefficient indicated (shown in red in the tables). This is further discussed in §5.5. The correlation coefficient above the 0.8 is considered accurate (shown in green in the tables). The correlation coefficient of less than 0.8 should be interpreted with caution.

The permeation coefficient of PVC 2018-086 is higher than that of other PVC pipes. No explanation has been found for this.

Table 9. The permeation rate and correlation coefficient of the different measurements have been calculated into the permeation coefficient for the water measurements.

Water permeation						
Kiwa reference	Pipe type	Number of measurement points	Slope [g/day]	Correlation coefficient (R ²) [-]	Permeation rate [g/(m·day)]	Permeation coefficient [(g·mm)/(m ² ·day)]
PVC 2016-116	Reference	12	-8.12E-03	0.87	n.b.*	n.b.*
PE 2017-307	PE50	5	-6.21E-03	0.31	n.b.**	n.b.**
PE 2018-184	PE50	8	-8.98E-03	0.77	0.01	0.17
PE 2021-348	PE100RC	5	-3.03E-03	0.15	n.b.**	n.b.**
PE 2021-350#01	PE100	5	-4.64E-03	0.29	n.b.**	n.b.**
PE 2021-350#02	PE100	5	-7.06E-03	0.35	n.b.**	n.b.**
PVC 2020-001	PVC-A	11	-2.85E-03	0.22	n.b.**	n.b.**
PVC 2018-070	PVC-A	11	-3.32E-02	0.99	0.04	0.30
PVC 2019-149	PVC-CPE	11	-1.36E-02	0.94	0.02	0.16
PVC 2017-108	PVC-CPE	11	-1.80E-02	0.95	0.02	0.17
PVC 2018-086	PVC-U	11	-1.97E-01	0.96	0.28	3.06
PVC 2020-013	PVC-U	11	-2.11E-02	0.97	0.02	0.19

*n.b.**, this concerned the reference measurement with no water in the pipe.

*n.b.***, the correlation coefficient is so far away from the value of 1 that the regression line is a poor indicator of the measurement data. Consequently, the subsequent calculations were imprecise and therefore not carried out.

5 Consideration of results

5.1 Duration of desorption of THT, aromatics and alkanes

It is visible in the results for the desorption of all measured natural gas components that, although decreasing, the components still continue to desorb from the pipe material after 50 days. When looking at the desorption rate, it can be observed that it is very low after about 50 days. Based on this, any further sampling, or a continuation of the experiment, will not provide additional information.

5.1.1 Desorption of THT

THT adheres to the inner wall of the pipe and THT is absorbed by the plastic pipe material. When gas without THT flows through this type of pipe, the THT is released from the inner wall and from the pipe material. In the case of steel, only the THT that adheres to the inner wall is absorbed.

Based on the measurements with a jacket pipe (on two PE pipes) it can be observed that there is desorption of THT from the pipe material. However, in all instances, these concentrations are smaller than 10 mg/m³. The amount of THT released in hydrogen is primarily the THT that adheres to the wall.

In the case of PVC, no measurable quantity of THT was found in the jacket pipe. The PVC pipe material seems to contain only THT that adheres to the inner wall.

5.1.2 Desorption of aromatics and alkanes

Based on the measurements in the pipes, it can be observed that the concentrations of aromatics and alkanes continue to decrease after each series of flushes, except in the PE50 pipe. When looking at the measurements in the jacket pipe, a significant amount of alkanes and aromatics is measured, particularly in the PE50 pipe. The aromatics and alkanes appear to largely adhere to the inner wall of the pipe material. Whether or not the concentrations of aromatics and alkanes are harmful for hydrogen appliances will have to be examined further.

5.1.3 Desorption rate

Based on the results obtained, a desorption rate has been determined for the amount of THT, aromatics and alkanes per m² per day. The quantities of these substances that can be absorbed by the hydrogen depend on the equilibrium concentration (and therefore on the degree of flushing or gas consumption). During the measurements, it was not determined whether the actual equilibrium concentration had been reached. All pipes were sampled at fixed times. When an equilibrium concentration was reached before a sample was taken, the desorption rate for that time interval was actually too low. Because short periods were chosen for the sampling in the beginning, this effect is expected to be small. The desorption rate is also dependent on the amount of THT, alkanes or aromatics in the pipe material, which visibly decrease over time.

5.1.4 Contamination of steel pipes

In all of the three steel pipes received, a fatty deposit was observed to varying degrees. It is quite possible that this contamination caused a higher desorption of natural gas components, in addition to the desorption that is to be expected as a result of the adhesion of components to the pipe wall. Especially in sample OV 2021-124, the contamination seems to have a large influence on the measured concentrations of natural gas components. The difference between the quantities released from the pipe wall and the quantities from the fatty deposit has not been investigated

5.2 Influence of end caps permeation experiments

It is possible for the end caps to have an influence on the measurements during the permeation measurements of both the atmospheric gases and the water. The components being tested could also enter or exit through or along the end caps. This influence is expected to be limited because the wall thicknesses of the end caps are much higher than those of the pipes.

For example, the PVC-U end cap has a wall thickness of approximately 8 mm as compared to the wall thickness of the pipes with a maximum of 3.7 mm. The PE electrofusion cap has a wall thickness of 15 mm as compared to a maximum of 11.6 mm of the pipes. When the wall thickness doubles, the permeation rate decreases by half, see equation 6 and equation 8 in §2.3.2.

The end cap for measuring atmospheric gases through PVC is made of metal (which has a much higher resistance to permeation than plastics). However, some of the atmospheric gases may permeate through the NBR, but the total surface of the rubber seal is not in proportion to the surface of the pipe. Finally, the surface of the pipes is larger than the surface of the end caps. It follows from equation 6 and equation 8 in §2.3.2 that because of this, the contribution to the total permeation is also greater for the pipes when compared to the end caps.

5.3 Reference measurement of water permeation is not suitable

For the water permeation measurements, a pipe filled without water was weighed over time in the same way as the pipes examined. The purpose of this reference measurement was to be able to correct for a change in the mass determination as a result of fluctuations in the environment, such as the air pressure. In this case, the reference measurement did not fluctuate, but the mass of the reference pipe decreased for all subsequent measurement points, see figure 16. This is most likely caused by the desiccant in the closed space. The pipe was stored for a long time in the storage room of 'Kenniscentrum Gasnetbeheer'. It reached an equilibrium there with the moisture from the environment, (the air humidity normally fluctuates around the 40% RH to 60% RH). Because of the desiccant in the closed room, the humidity has been reduced considerably. This has caused some of the moisture to escape from the pipe wall, reducing the mass over time.

In addition, the pipe was not flushed with a drying gas and no desiccant was placed in the pipe. Therefore, moisture present in the pipe will migrate into the pipe wall and permeate outwards. This explains why the mass is constantly decreasing and does not seem to stabilise (which is expected when the pipe dries up more and more).

5.4 Difference between oxygen and nitrogen permeation measurements

As described in §3.2.3, the gas analysis technique is capable of separating oxygen and nitrogen sufficiently and detecting them separately. This allows the same gas sample to be used to determine the content of oxygen and nitrogen. The reference gases are also composed of a combination of oxygen and nitrogen. Therefore, the reference values are also taken from the same reference sample. Because of this, no difference in fluctuations between oxygen and nitrogen as a result of local circumstances, such as the sampling or the atmospheric pressure of the setup, is to be expected. However, different accuracies were obtained when the results for oxygen from table 7 are compared with the results for nitrogen from table 8. For example, the correlation coefficient of the same pipes is higher for virtually all oxygen measurements than for the nitrogen measurements.

This difference can be explained because the oxygen content is determined more accurately with gas chromatography than the nitrogen content. This can be seen in the dispersion between the reference measurements taken for each series of measurements (raw data not published). The dispersion for oxygen is less than 3% and therefore lower than the dispersion for nitrogen, less than 5%. In addition, the raw data from the gas chromatography for oxygen is more favourable than for nitrogen. For oxygen, the chromatogram results in a favourable high sharp peak while for nitrogen a broader lower peak is obtained.

5.5 Water permeation of PE not in equilibrium

The water permeation measurements for PVC resulted in a high accuracy in virtually all instances, see table 9. One exception was the measurement on PVC 2020-001, where there was a very large decrease in mass initially, but after 20 days no change was measured.

For the PE pipes, the water permeation measurements resulted in low accuracy in almost all instances. This was most likely caused by the time lag (see §2.3.3). Whereas the PVC pipes had already reached an equilibrium in the permeation process, this equilibrium had not yet been reached for the PE pipes. The pipe wall of the PE was not yet completely saturated with water on the inside. Without changing the setup, the only approach to correct for this was to measure the PE pipes longer. However, this did not fit within the schedule of HyDelta 1.0. In consultation with the Expert and Assessment Group and the supervisory group, the setup was nevertheless retained.

For the measurements on PE only one result was accurate enough to determine a permeation coefficient. The permeation coefficient obtained therefore cannot be compared with other results, which reduces the reliability of the results. However, the value can be compared with the results of the study commissioned by the grid operators Coteq Netbeheer, Enduris, Enexis, Liander, RENDO Netwerken, Stedin and Westland Infra and carried out by Kiwa Technology in 2020 and 2021 [8] [9]. The water permeation coefficient for a PE100 pipe was determined to be $0.081 \text{ [(g}\cdot\text{mm)} / (\text{m}^2\cdot\text{day})]$. This is relatively comparable with the found coefficient of $0.17 \text{ [(g}\cdot\text{mm)} / (\text{m}^2\cdot\text{day})]$.

5.6 Comparison to the literature review on permeation

The permeation coefficients obtained for PVC and for PE have been compared with the results of the literature review table 10 and table 11 respectively.

For PVC, the permeation coefficient of oxygen was higher than expected from the literature review. For nitrogen, the permeation coefficient was much higher than expected, but this expectation is also based on only one source. The water permeation coefficient varies greatly. In general, the measured values were lower than expected based on the literature, with the exception of the measurement on PVC 2018-086. The high permeation coefficients found in the literature for the permeation of oxygen ($774 \text{ [(ml}\cdot\text{mm)} / (\text{m}^2\cdot\text{day}\cdot\text{bar})]$) and water ($4900 \text{ [(g}\cdot\text{mm)} / (\text{m}^2\cdot\text{day})]$) are unrealistic for the gas distribution grid.

For PE, the permeation coefficient of oxygen is within the expectations as based on the literature. For nitrogen, the expectation from the literature slightly overlaps with the measured value, but in some cases the measured value is lower. The water permeation coefficient is only based on the pipe PE 2018-184, but is within the expectations from the literature review.

Table 10. Comparison of the permeation coefficients found in the literature with the measurement results for PVC.

Component	PVC literature	PVC measurement	Unit
Oxygen	1.93-10.0 (and one source 774)	4.6-19.1	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Nitrogen	0.84 (one source)	10.3-19.1	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Water	1.20-36.8 (and one source 4900)	0.16-0.30 (with 3.06 once)	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day})]$

Table 11. Comparison of the permeation coefficients found in the literature with the measurement results for PE.

Component	PE literature	PE measurement	Unit
Oxygen	38.9-77.7	41.7-70.6	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Nitrogen	15.3-23.3	10.0-17.9	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Water	0.10-7.30	0.17 (one measurement)	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day})]$

5.7 Calculation for scenarios

The permeation coefficients of different gas distribution materials have been determined through the different permeation measurements. These permeation coefficients can be used to determine the expected contamination due to the components of oxygen, nitrogen and water by permeation from the environment as a result of the distribution of hydrogen gas. The calculation has been performed for five scenarios as an example.

The results of the permeation measurements provide a tool for making a prediction of the expected degree of contamination as a result of the distribution of hydrogen gas. This estimate is based on permeation measurements on several types of materials. Please note that for the experiments, only a few metres of piping were examined. In practice, thousands of kilometres of pipelines are involved. We therefore urge caution in interpreting the results and ask that they not be considered representative of the entire distribution grid. The results should only be used as a guide.

For the scenarios, it is assumed that the pipe is entirely above or below groundwater level and therefore the exposure to the atmosphere or groundwater is unrestricted. The influence of the surrounding soil on, for example, the supply of fresh air or the (partial) covering of the pipe is beyond the scope of this study.

5.7.1 Scenario 1 – 2km PE50 pipe above groundwater level

In a first generation (PE50) pipe of two kilometres, 4 bar(g) of pure hydrogen gas is present. It is a pipe with an external diameter of 160 and an SDR class of 11 and a wall thickness of 14.5 mm. The pipe is located above groundwater level. Due to a limited gas release, the hydrogen gas in the pipeline is virtually stagnant during the weekend. The stagnant time is 48 hours. How much do the oxygen and nitrogen contents in the hydrogen gas increase?

Assume that the air pressure is exactly 1 standard atmosphere. Since air consists of 20.95% oxygen and 78.08% nitrogen, the partial pressure difference with the pure hydrogen gas is 0.21 bar(a) and 0.79 bar(a) respectively.

The measured permeation coefficient for oxygen by PE50 is 70.6 [(ml·mm)/(m²·day·bar)] and the measured permeation coefficient for nitrogen by PE50 is 17.9 [(ml·mm)/(m²·day·bar)]. For the calculation, equation 6 was used, see §2.3.2.

$$Q_{O_2} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000} =$$

$$\frac{70.6 \frac{ml \cdot mm}{m^2 \cdot dag \cdot bar} \cdot (\pi \cdot (11 - 1) \cdot 2000m \cdot 0.21bar)}{1000} = 941.6 ml/dag$$

The total oxygen increase in the pipe system over two days was 1883.3 ml.

$$Q_{N_2} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000} =$$

$$\frac{17.9 \frac{ml \cdot mm}{m^2 \cdot dag \cdot bar} \cdot (\pi \cdot (11 - 1) \cdot 2000m \cdot 0.79bar)}{1000} = 889.8 ml/dag$$

The total increase in nitrogen in the pipe system over two days was 1779.6 ml.

The pipe system has an internal volume of 26,919 litres. At a pressure of 4 bar(g), 134,595 litres (136 m³) of hydrogen gas is therefore present (STP). The relative increase in nitrogen and oxygen is therefore 13.99 ppmV and 13.22 ppmV respectively (0.001399% and 0.001322%).

5.7.2 Scenario 2 – 2km PE50 pipe below groundwater level

In a first generation (PE50) pipe of two kilometres, 4 bar(g) of pure hydrogen gas is present. This pipe has an external diameter of 160, an SDR class of 11 and a wall thickness of 14.5 mm (same as Scenario 1). The pipe is located below groundwater level. Due to a limited gas release, the hydrogen gas in the pipeline is virtually stagnant during the weekend. The stagnant time is 48 hours. How much moisture enters through the pipe wall?

The measured permeation coefficient for water through PE50 was 0.17 [(g·mm)/(m²·day)]. For the calculation, equation 8 was used, see §2.3.2.

$$Q_{H_2O} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L)}{1000} = \frac{0.17 \frac{g \cdot mm}{m^2 \cdot dag} \cdot (\pi \cdot (11 - 1) \cdot 2000m)}{1000} = 10.7 g/dag$$

The total increase in water in the pipe system over two days is 21.4 grams.

At a pressure of 4 bar(g), 134,595 litres (136 m³) of hydrogen gas is present in the pipe system (STP). The relative increase of water in hydrogen gas was 0.16 g/m³. (As an indication: for natural gas at 4

bar(g) with a dewpoint of -10°C and a temperature of 10°C the permeation of water would raise the dewpoint to -8.8°C, using the Arden Buck equation as described in [8])

5.7.3 Scenario 3 – 5km PVC-A pipe under groundwater level

In a impact modified PVC pipeline (PVC-A) of five kilometres, 100 mbar(g) of pure hydrogen gas is distributed. The pipe has an external diameter of 63 mm, an SDR class of 41 and a wall thickness of 1.5 mm. The pipe is located above groundwater level. The flow rate of the hydrogen gas is 5 m³_n/hour. How much do the oxygen and nitrogen contents in the hydrogen gas increase?

Assume that the air pressure is exactly 1 standard atmosphere. Since air consists of 78.08% nitrogen and 20.95% oxygen, the partial pressure difference with the pure hydrogen gas is 0.79 bar(a) and 0.21 bar(a) respectively.

The pipe system has an internal volume of 14,102 litres. At a pressure of 100 mbar(g) 15,513 litres of hydrogen gas are present (STP). The stagnant time for the hydrogen gas in the pipe amounts to 3.1 hours (hydrogen volume (STP)/flow rate).

The measured permeation coefficient for oxygen through PVC-A amounts to 9.4 [(ml·mm)/(m²·day·bar)] and the measured permeation coefficient for nitrogen through PVC-A amounts to 7.3 [(ml·mm)/(m²·day·bar)]. For the calculation, equation 6 was used, see §2.3.2.

$$Q_{O_2} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000} =$$

$$\frac{9.4 \frac{ml \cdot mm}{m^2 \cdot dag \cdot bar} \cdot (\pi \cdot (41 - 1) \cdot 5000m \cdot 0.21bar)}{1000} = 1253 ml/dag$$

The total oxygen increase in the pipe system over the stagnant time is 162 ml.

$$Q_{N_2} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000} =$$

$$\frac{7.3 \frac{ml \cdot mm}{m^2 \cdot dag \cdot bar} \cdot (\pi \cdot (41 - 1) \cdot 5000m \cdot 0.79bar)}{1000} = 3629 ml/dag$$

The total increase in nitrogen in the pipe system amounts to 469 ml over the stagnant time.

There are 15,513 litres of hydrogen gas (STP) in the pipe system. The relative increase of oxygen and nitrogen is thus 10.45 ppmV and 30.24 ppmV respectively (0.001045% and 0.003024%).

5.7.4 Scenario 4 – 5km PVC-A pipe under groundwater level

In a impact modified PVC pipeline (PVC-A) of five kilometres, 100 mbar(g) of pure hydrogen gas is distributed. This pipe has an external diameter of 63 mm, an SDR class of 41 and a wall thickness of 1.5 mm (same as Scenario 1). The pipe is located below groundwater level. The flow rate of the hydrogen gas is 5 m³_n/hour. How much moisture enters through the pipe wall?

The pipe system has an internal volume of 14,102 litres. At a pressure of 100 mbar(g) 15,513 litres of hydrogen gas are present (STP). The stagnant time for the hydrogen gas in the pipe amounts to 3.1 hours (hydrogen volume (STP)/flow rate).

The measured permeation coefficient for water through PVC-A is 0.30 [(g·mm)/(m²·day)]. For the calculation, equation 8 was used, see §2.3.2.

$$Q_{H_2O} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L)}{1000} = \frac{0.30 \frac{g \cdot mm}{m^2 \cdot dag} \cdot (\pi \cdot (41 - 1) \cdot 5000m)}{1000} = 188 g/dag$$

The total increase in water in the pipe system over the stagnant time of the gas is 24.4 grams.

There are 15,513 litres of hydrogen gas (STP) in the pipe system. The relative increase of water in hydrogen gas was 1.57 g/m³. (As an indication: for natural gas at 100 mbar(g) with a dew point of -10°C and a temperature of 10°C, the permeation of the water would raise the dew point to -8.3°C, using the Arden Buck equation as described in [8])

5.7.5 Scenario 5 – Increase in oxygen content 1m PE pipe and PVC pipe (ø16mm)

It follows from equation 6 that the permeation of oxygen through the pipe depends on the length of the pipe and the SDR class of the pipe, and therefore on the wall thickness and diameter of the pipe. Apart from the length and SDR class, no pipe dimensions are present in the equation. When the SDR class of different pipes are the same, the permeation rate of the oxygen per metre of pipe is also the same. In other words, the amount of oxygen per metre that permeates through a DN16 pipe is equal as that which permeates through a DN650 pipe, as long as the SDR class is the same. However, the relative increase in oxygen content for the DN16 pipe is greater since the internal pipe volume is smaller. In calculating Scenario 5, two situations were chosen in which the relative increase in oxygen content would be very high. In the first case, a thin-walled pipe with a small diameter and a low hydrogen content (low gas pressure). It is also assumed that the pipe is completely cut off from the distribution grid so that no diffusion of oxygen through the grid can occur. This is an approximation of the worst-case scenario that may occur in practice where the relative oxygen increase would be highest.

Scenario 5a. A one-metre PE pipe contains 20 mbar(g) of pure hydrogen gas. The pipe has an external diameter of 16 mm and a wall thickness of 2.3 mm (2.3 mm is the smallest wall thickness for PE based on EN 1555-2:2021 [14]; the actual SDR value is therefore 6.96). The pipe is located above groundwater level. Due to a limited gas release, the hydrogen gas in the pipeline has been stagnant for 24 hours. How much does the oxygen content of the hydrogen gas increase?

Scenario 5b. In a PVC pipe of one metre, there is 20 mbar(g) pure hydrogen gas present. The pipe has an external diameter of 16 mm and a wall thickness of 2.0 mm (2.0 mm is the smallest wall thickness for PVC based on NEN 7230:2019⁸ [15]; the actual SDR value is therefore 8). The pipe is located above groundwater level. Due to a limited gas release, the hydrogen gas in the pipeline has been stagnant for 24 hours. How much does the oxygen content of the hydrogen gas increase?

⁸ In NEN 7230:2019, the smallest diameter of the PVC pipe is 50 mm. This is larger than the diameter of 16 mm used for the calculation. In practice, old PVC pipes with this diameter may still be present.

Assume that the air pressure is exactly 1 standard atmosphere. Since air consists of 20.95% oxygen, the partial pressure difference with pure hydrogen gas is 0.21 bar(a).

The permeation coefficient for PE is 77.7 [(ml·mm)/(m²·day·bar)] and the measured permeation coefficient for oxygen through PVC is 19.1 [(ml·mm)/(m²·day·bar)]. For the calculation equation 6, see §2.3.2, and table 12.

$$Q_{PE,O_2} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000} =$$

$$\frac{77.7 \frac{ml \cdot mm}{m^2 \cdot dag \cdot bar} \cdot (\pi \cdot (6.96 - 1) \cdot 1m \cdot 0.21bar)}{1000} = 0.31 ml/dag$$

The total increase of oxygen over one day in the PE pipe is 0.31 ml.

$$Q_{PVC,O_2} = \frac{PC \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000} =$$

$$\frac{19.1 \frac{ml \cdot mm}{m^2 \cdot dag \cdot bar} \cdot (\pi \cdot (8 - 1) \cdot 1m \cdot 0.21bar)}{1000} = 0.09 ml/dag$$

The total increase of oxygen over one day in the PVC pipe is 0.09 ml.

The PE pipe system has an internal volume of 0.10 litres. At a pressure of 20 mbar(g) 0.10 litres of hydrogen gas are present (STP). The relative increase of the oxygen is therefore 2964.6 ppmV (0.29646%).

The PVC pipe system has an internal volume of 0.11 litres. At a pressure of 20 mbar(g) 0.12 litres of hydrogen gas are present (STP). The relative increase of the oxygen is therefore 772.9 ppmV (0.07729%).

6 Conclusions and answers to the research question and recommendations

6.1 Desorption from pipe material

When hydrogen gas is distributed through the current natural gas distribution grid, hydrogen gas absorbs the substances THT, aromatics and alkanes from the pipe material.

Desorption of THT and other natural gas components decreases as more hydrogen flows through the gas grid. The quantities of these substances that can be absorbed by the hydrogen per time unit depend on the equilibrium concentration and the time that the gas is stagnant and therefore also on the extent of flushing. The desorption rate also depends on the amount of THT, alkanes or aromatics in the pipe material and attached to it, which notably decreases over time.

Based on the results obtained, desorption rates were determined for the various pipe materials. These desorption rates were used to calculate desorption indicators for each pipe material investigated. The calculation of these indicators is based on approximately 50 flushes of the entire pipeline volume, spread over a period of 50 days, with a minimum downtime of two days. After approximately 50 days and approximately 50 flushings of the inner pipe volume, the THT content was below the minimum THT content for odourisation (10 mg/m^3) in most cases.

Depending on the flow rate through the pipe, the THT (and other natural gas components) content in the hydrogen after a certain time can be calculated. A more or less constant flow of hydrogen gas prevents the equilibrium concentration from being reached and therefore actual concentrations of THT, aromatics and alkanes may be much lower. A high flow rate of hydrogen gas limits the contamination.

The permissible concentrations of the natural gas components in the hydrogen gas depend on the application.

6.2 Permeation from the environment

Distributing hydrogen gas within the current natural gas distribution grid will lead to contaminants from the environment lowering the purity of the hydrogen gas. This is caused by an unavoidable natural process called permeation. Using the results of this research, an estimate can be made of the degree to which the hydrogen gas is contaminated. The basis for the prognosis is established with the results as shown in table 13 and table 14. As a conservatively selected fixed value, the permeation coefficients as given in table 12.

Table 12. Conservatively chosen permeation coefficient for the various materials.

Component	PVC	PE	Unit
Oxygen	19.1	77.7	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Nitrogen	19.1	23.3	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day}\cdot\text{bar})]$
Water	3.06	0.17	$[(\text{ml}\cdot\text{mm})/(\text{m}^2\cdot\text{day})]$

In addition to the permeation coefficient, the estimate for the degree of contamination depends on conditions such as pipe dimensions, temperature and the length of time the hydrogen gas remains. For the study, a temperature of $\sim 23^\circ\text{C}$ was taken into account as the worst-case scenario. Ultimately,

whether the degree of contamination is acceptable for the intended application will have to be determined in consultation with the end user and the end user market. A ministerial regulation, yet to be drafted, specifying the quality of the hydrogen to be supplied will make this harmonisation more feasible. This method of establishing the quality of the gas supplied will then be equivalent to the current method for natural gas [[wetten.nl – Regeling – Regeling gaskwaliteit – BWBR0035367](https://wetten.nl/Regeling-Regeling-gaskwaliteit-BWBR0035367) (overheid.nl)] [16]]

As an indication, an estimate has been provided for two practical circumstances with deliberately selected conditions that will result in a high relative oxygen increase as a result of permeation. It is assumed that the pipe will be completely cut off from the distribution grid so that no diffusion of oxygen through the pipe grid can occur. This concerns two thin-walled pipes with a small diameter and a low hydrogen content. For the DN 16 e 2.3 PE pipe with 20 mbar pure hydrogen gas, the oxygen content in the hydrogen will increase from 0% to 0.296% in the first 24 hours. For the DN 16 e 2.0 PVC pipe with 20 mbar pure hydrogen gas, the oxygen content in the hydrogen will increase by 0.077% in the first 24 hours. For pipes with a larger diameter, larger wall thickness or higher hydrogen pressure, the relative oxygen increase will be (much) lower.

Table 13. The permeation coefficients obtained from the literature review and the permeation measurements on PVC materials. These coefficients can be used to estimate the rate at which the purity of the hydrogen gas decreases over time.

Component	PVC literature	PVC measurement	Unit
Oxygen	1.93-10.0 (and one source 774)	4.6-19.1	[(ml·mm)/(m ² ·day·bar)]
Nitrogen	0.84 (one source)	10.3-19.1	[(ml·mm)/(m ² ·day·bar)]
Water	1.20-36.8 (and one source 4900)	0.16-0.30 (with 3.06 once)	[(ml·mm)/(m ² ·day)]

Table 14. The permeation coefficients obtained from the literature review and the permeation measurements on PE materials. These coefficients can be used to estimate the rate at which the purity of the hydrogen gas decreases over time.

Component	PE literature	PE measurement	Unit
Oxygen	38.9-77.7	41.7-70.6	[(ml·mm)/(m ² ·day·bar)]
Nitrogen	15.3-23.3	10.0-17.9	[(ml·mm)/(m ² ·day·bar)]
Water	0.10-7.30	0.17 (one measurement)	[(ml·mm)/(m ² ·day)]

6.3 Recommendations for desorption of THT and other components

In addition to the indicators determined in this research, it is useful to determine the indicators for other types of materials (e.g. PE100, as well as other pipe materials made of steel, PE and PVC with, for example, different construction years).

To improve the methodology, it is also advisable to determine the way in which the saturation concentration builds up for each material. This saturation concentration is dependent on the quantity of the substance to be tested in or on the pipe material (and this changes over time), the pressure and the temperature. This would provide more insight on the desorption behaviour in the case of more frequent flushing. After each sampling, the test sample is started at a concentration of zero. How fast a certain concentration is reached is currently unknown.

For the specific case of steel pipes, it would be helpful to examine 'pigging' in combination with a cleaning agent for removing contaminants. This is because the measurements show that for one pipe examined, a concentration of THT > 18 mg/m³ is desorbed.

6.4 Recommendations for permeation water

As stated in §5.5, based on the water permeation measurements on PE pipes, the permeation coefficient can only be determined accurately for one pipe. A longer measurement period is necessary to be able to do this for several PE pipes. The remaining lead time is difficult to estimate and may vary from 2 to 10 months. The measurement setup for the water permeation measurements with the six PE pipes are still intact at the time of writing.

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I List of questions HyDelta WP1C

The following questions are addressed in this work package.

- Question number HyDelta 187: Research into the safe commissioning and decommissioning of pipeline sections in hydrogen distribution during the conversion to a hydrogen grid and the associated costs.
- Question number HyDelta 124: Research into the performance of strength and density tests.
- Question number HyDelta 135: What is the effect of the existing gas grid on the quality of hydrogen in distribution and transport?
- Question number HyDelta 185: Home pressure regulator: What are the risks if it is not modified?
- Question number HyDelta 101: Investigation of risks related to existing gas installations (at the customers) when converting from natural gas to 100% hydrogen.
- Question number HyDelta 61: How is it ensured that the developments of all components suitable for 100% hydrogen are integrated - in the distribution grid (incl. connections), in the indoor installation and in the gas consumption appliances in homes and businesses - so that the entire chain is compatible?
- Question number HyDelta 55: What will a conversion to a hydrogen grid look

II List of participants Expert- and Assessment Group (EAG) question 135

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III Measurement data for THT desorption

The results of the gas analyses are presented in this Annex.

The results for desorption of the natural gas components to hydrogen are presented in table 15, table 16 and table 17.

The results for desorption of the natural gas components to the jacket pipes are presented in table 18, table 19 and table 20.

The results for indicators of the desorption rate of the natural gas components towards hydrogen are presented in table 21 and 22.

Table 15. THT in H₂ results in mg/m³

Kiwa reference	Pipe #	day of measurement						
		2	4	8	14	21	28	50
PVC-HI 2021-091	7	6.9	5.6	3.8	3.3	2.1	1.7	1.8
PVC-HI 2021-092	8	8.6	8.0	5.6	5.4	3.1	2.6	2.2
PVC-HI 2021-114	11	8.2	7.3	5.7	4.8	3.1	2.7	1.7
PVC-HI 2021-120	3	19.6	22.5	17.4	12.4	8.9	7.0	5.0
PVC-U-2021-122	9	4.0	4.0	3.6	4.3	3.3	3.1	2.2
PVC-U-2021-123	6	7.1	7.1	5.2	4.9	3.1	2.7	2.6
PE80 2021-416	1	1.5	2.6	2.7	2.5	2.6	2.5	2.3
PE80 2021-418	4	10.9	12.8	11.7	13.5	13.9	14.4	14.4
Steel OV 2021-124	10	35.8	35.3	32.6	31.6	24.5	23.7	21.1
Steel OV 2021-121	2	7.2	6.8	5.9	5.5	4.8	4.4	3.9
Steel OV 2021-122	12	11.5	12.4	11.3	9.3	5.4	3.9	4.2
PE50 2021-417	5	15.2	16.4	15.4	19.0	18.7	18.5	20.9

Table 16. Alkanes in H₂ results in ppm

Kiwa reference	Pipe #	day of measurement						
		2	4	8	14	21	28	50
PVC-HI 2021-091	7	228.3	138.8	78.8	51.7	13.8	9.9	9.6
PVC-HI 2021-092	8	302.5	201.9	105.6	73.9	12.6	7.6	8.4
PVC-HI 2021-114	11	118.1	80.4	60.8	42.4	15.6	13.4	7.9
PVC-HI 2021-120	3	52.2	16.9	11.2	6.9	5.2	5.8	6.0
PVC-U-2021-122	9	32.7	30.2	31.2	36.7	23.2	19.1	16.5
PVC-U-2021-123	6	228.7	154.3	86.6	51.0	9.7	6.4	8.4
PE80 2021-416	1	212.7	84.2	68.4	76.0	60.2	54.4	50.6
PE80 2021-418	4	219.0	167.2	143.7	160.8	153.8	146.7	189.3
Steel OV 2021-124	10	648.7	515.3	392.3	301.1	93.8	65.2	61.9
Steel OV 2021-121	2	124.5	63.9	50.8	48.3	37.0	32.2	37.9
Steel OV 2021-122	12	208.5	148.0	110.0	61.8	23.0	17.2	35.2
PE50 2021-417	5	372.6	312.3	312.4	388.9	296.4	282.2	501.8

Table 17. Aromatics in H₂ results in ppm

Kiwa reference	Pipe #	day of measurement						
		2	4	8	14	21	28	50
PVC-HI 2021-091	7	30.4	21.1	14.9	13.2	7.1	6.6	7.6
PVC-HI 2021-092	8	39.2	32.1	22.2	20.6	9.5	7.1	8.7
PVC-HI 2021-114	11	28.2	21.5	17.6	13.3	6.3	5.6	3.7
PVC-HI 2021-120	3	29.1	12.9	10.2	8.5	6.5	5.9	5.6
PVC-U-2021-122	9	10.4	9.6	10.0	11.5	8.4	6.9	5.9
PVC-U-2021-123	6	32.9	28.0	20.9	18.0	8.7	8.1	9.2
PE80 2021-416	1	60.4	20.3	18.1	21.0	17.0	14.6	10.0
PE80 2021-418	4	48.5	42.2	37.0	41.0	39.9	38.8	42.7
Steel OV 2021-124	10	99.7	87.2	80.1	76.6	46.6	43.0	49.5
Steel OV 2021-121	2	41.1	22.8	19.6	18.3	15.0	14.0	13.2
Steel OV 2021-122	12	37.6	34.1	31.2	25.0	12.1	8.7	13.1
PE50 2021-417	5	78.3	75.1	78.1	98.7	90.8	88.0	115.2

Table 18. THT in jacket pipe results in mg/m³

Kiwa reference	Pipe #	day of measurement						
		2	4	8	14	21	28	50
PVC-HI 2021-091	7				0.0	0.0	0.0	0.0
PVC-HI 2021-120	3				0.0	0.0	0.0	0.0
PVC-U-2021-123	6				0.0	0.0	0.0	0.0
PE80 2021-416	1				0.0	0.0	0.5	0.9
PE50 2021-417	5				5.0	5.6	5.8	7.2

Table 19. Alkanes in jacket pipe results in ppm

Kiwa reference	Pipe #	day of measurement						
		2	4	8	14	21	28	50
PVC-HI 2021-091	7				0.0	0.2	0.0	0.0
PVC-HI 2021-120	3				0.2	0.1	0.1	0.1
PVC-U-2021-123	6				0.1	0.1	0.0	0.0
PE80 2021-416	1				0.2	0.2	9.3	14.9
PE50 2021-417	5				140.1	109.2	107.7	181.0

Table 20. Aromatics in jacket pipe results in ppm

Kiwa reference	Pipe #	day of measurement						
		2	4	8	14	21	28	50
PVC-HI 2021-091	7				0.1	0.2	0.1	0.2
PVC-HI 2021-120	3				0.1	0.1	0.0	0.1
PVC-U-2021-123	6				0.1	0.1	0.1	0.2
PE80 2021-416	1				0.1	0.0	6.2	9.0
PE50 2021-417	5				62.7	61.1	64.2	87.3

Table 21. Desorption indicators for alkanes

Kiwa reference	Pipe#	k_0^{Alkanes}	k_1^{Alkanes}	correlation
PVC-HI 2021-091	7	10.542	-2.230	98.9%
PVC-HI 2021-092	8	11.327	-2.487	98.1%
PVC-HI 2021-114	11	10.192	-2.010	99.2%
PVC-HI 2021-120	3	5.950	-1.488	98.9%
PVC-U-2021-122	9	8.211	-1.299	98.4%
PVC-U-2021-123	6	10.895	-2.406	98.0%
PE80 2021-416	1	7.362	-1.231	98.9%
PE80 2021-418	4	8.086	-1.000	98.5%
Steel OV 2021-124	10	11.958	-2.002	98.7%
Steel OV 2021-121	2	7.733	-1.279	99.3%
Steel OV 2021-122	12	9.832	-1.823	97.4%
PE50 2021-417	5	9.430	-0.924	97.6%

Table 22. Desorption indicators for aromatics

Kiwa reference	Pipe#	$k_0^{\text{Aromatics}}$	$k_1^{\text{Aromatics}}$	correlation
PVC-HI 2021-091	7	7.546	-1.507	99.1%
PVC-HI 2021-092	8	8.211	-1.645	98.9%
PVC-HI 2021-114	11	8.502	-1.772	99.3%
PVC-HI 2021-120	3	5.683	-1.387	99.6%
PVC-U-2021-122	9	6.968	-1.240	98.4%
PVC-U-2021-123	6	7.941	-1.560	99.0%
PE80 2021-416	1	6.108	-1.275	98.0%
PE80 2021-418	4	6.779	-1.026	98.7%
Steel OV 2021-124	10	9.113	-1.326	99.2%
Steel OV 2021-121	2	6.728	-1.261	99.4%
Steel OV 2021-122	12	8.118	-1.556	98.7%
PE50 2021-417	5	7.999	-0.888	98.5%

IV Permeation and diffusion coefficient from literature

Material	Medium	P _c [ml·mm/(m ² ·day·bar)]	P _c [ml·mm/(m ² ·day)]	D _c [cm ² /s]	Source
PVC	O ₂	5,18		8,40E-09	[4]
PVC-plasticized	O ₂ - min	10,01			[17]
PVC-plasticized	O ₂ - max	773,75			[17]
PVC-Rigid	O ₂ - min	1,93			[17]
PVC-Rigid	O ₂ - max	7,74			[17]
PVC-250	O ₂ - min	1,97			[17]
PVC-250	O ₂ - max	7,80			[17]
PVC-63	O ₂	5,13			[17]
PVC-296	O ₂	3,16			[17]
PVC	CO ₂	18,15		1,60E-09	[4]
PVC-plasticized	CO ₂ - min	38,69			[17]
PVC-plasticized	CO ₂ - max	1160,62			[17]
PVC-Rigid	CO ₂ - min	7,74			[17]
PVC-Rigid	CO ₂ - max	19,34			[17]
PVC-250	CO ₂ - min	7,80			[17]
PVC-250	CO ₂ - max	19,44			[17]
PVC	N ₂	0,84		2,20E-09	[6]
PVC	Water	15488,48		7,00E-09	[4]
PVC	Water	17821,47			[18]
PVC-plasticized	Water - min		36,85		[17]
PVC-plasticized	Water - max		4900		[17]
PVC-Rigid	Water - min		36,85		[17]
PVC-Rigid	Water - max		2450		[17]
PVC-250	Water		1,20		[17]
PVC-264	Water – 40°C		1,20		[17]
PVC-296	Water - 37,8°C		1,70		[17]
LLDPE	Water	4406,76		6,00E-09	[5]
PE	Water	777,66			[18]
HDPE - Dow Chemical	O ₂ - min	38,86			[17]
HDPE - Dow Chemical	O ₂ - max	77,71			[17]
HDPE-264	O ₂	58,33			[17]
HDPE - Dupont Canada Sclair - 15A	O ₂	65,14			[17]
HDPE - Dupont Canada Sclair - 16A	O ₂	55,17			[17]
HDPE - Dupont Canada Sclair - 19A	O ₂	40,07			[17]
HDPE-138	O ₂	72,05			[17]
HDPE-306	O ₂	49,64			[17]
HDPE-293	O ₂	48,95			[17]
HDPE-101	O ₂	43,42			[17]
HDPE - Dow Chemical	CO ₂ - min	233,13			[17]

HDPE - Dow Chemical	CO ₂ - max	271,99	[17]
HDPE-138	CO ₂	225,02	[17]
HDPE-101	CO ₂	134,22	[17]
HDPE - Dow Chemical	N ₂ - min	15,54	[17]
HDPE - Dow Chemical	N ₂ - max	23,31	[17]
HDPE-138	N ₂	16,78	[17]
HDPE-306	N ₂	15,30	[17]
HDPE-101	N ₂	20,73	[17]
HDPE - Dow Chemical	Water	0,16	[17]
HDPE-264	Water	0,15	[17]
HDPE - Dupont Canada Sclair - 15A	Water-38°C	7,30	[17]
HDPE - Dupont Canada Sclair - 16A	Water-38°C	6,50	[17]
HDPE - Dupont Canada Sclair - 19A	Water-38°C	5,00	[17]
HDPE-296	Water- 37,8°C	0,10	[17]
HDPE-138	Water- 37,8°C	0,12	[17]
HDPE-101	Water- 37,8°C	0,12	[17]

V Derivation for calculating the permeation

The permeation rate at which a gaseous medium permeates through a pipe wall can be calculated using equation 11 [7]:

$$Q = \frac{P_C \cdot A \cdot \Delta P}{e}$$

equation 11

Where:

- Q is the permeation rate in ml/day;
- P_C is the permeation coefficient in (ml*mm)/(m²·day·bar(a));
- A is the surface in m²;
- ΔP is the pressure difference of the medium on either side of the pipe wall in bar(a) (absolute pressure);
- e is the wall thickness in mm.

The surface can be determined according to equation 12⁹ [19]:

$$A = \frac{\pi \cdot D_m \cdot L}{1000}$$

equation 12

Where:

- D_m is the diameter of the median of the pipe in mm;
- L is the length of the pipe in m.

The diameter of the median can be determined according to equation 13:

$$D_m = \frac{(D_e + D_i)}{2} = D_e - e$$

equation 13

Where:

- D_e is the outer diameter of the pipe in mm;
- D_i is the inside diameter of the pipe in mm.

⁹ The use of the diameter of the median is a simplification for determining the surface of the pipe wall. A more accurate calculation would be to apply formulas for cylindrical bodies. However, it follows from [19] that the error made with this simplification is 0.33% for an SDR11 pipe. Therefore, the error is negligible and the simplified formula has been applied.

This formula can be converted using the SDR determination, equation 14:

$$SDR = \frac{D_e}{e}$$

equation 14

The combination of equation 13 and equation 14 results in equation 15:

$$\frac{D_m}{e} = (SDR - 1)$$

equation 15

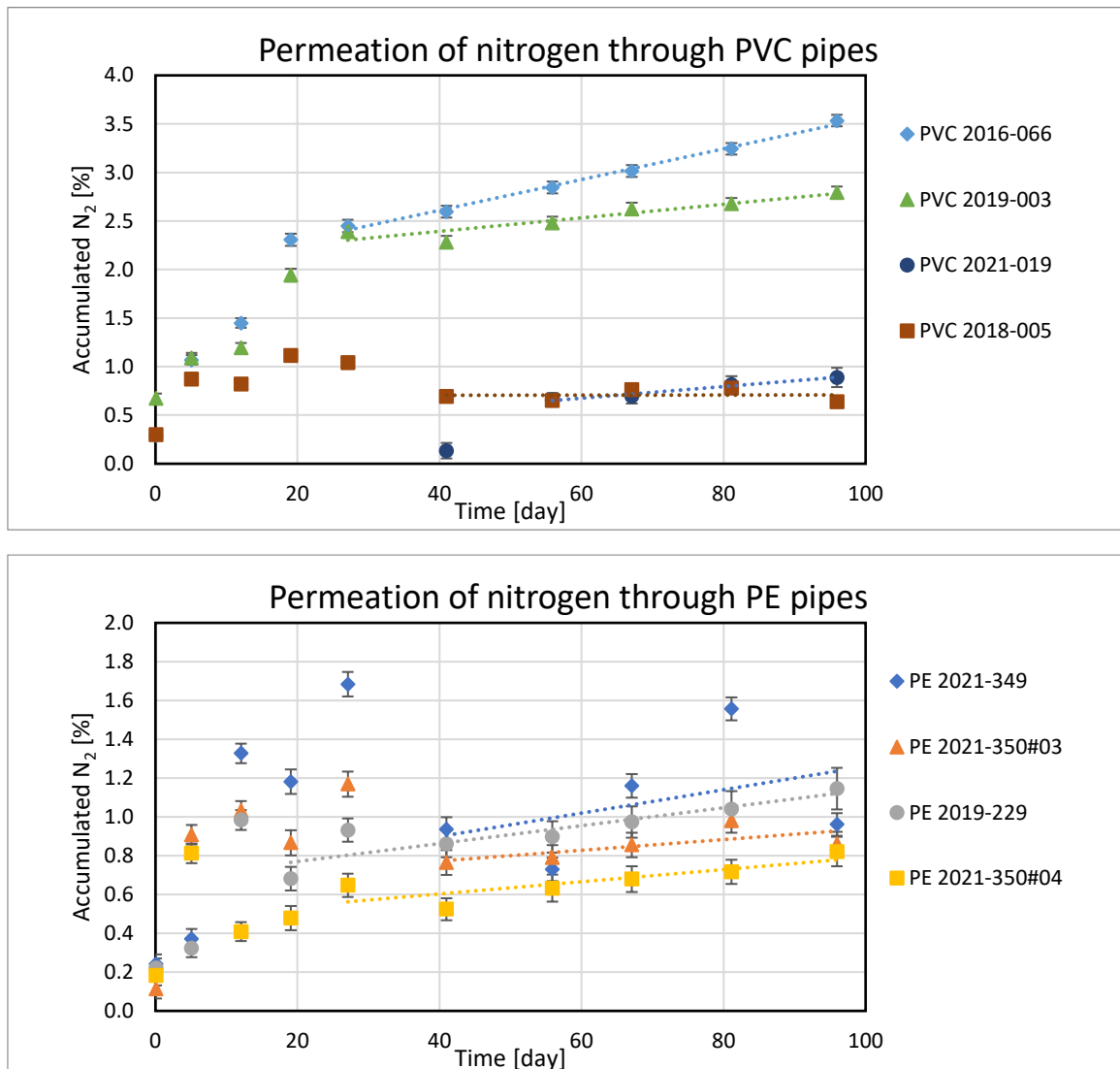
The combination of equation 11, equation 14, and equation 15 results in equation 16:

$$Q = \frac{P_c \cdot (\pi \cdot (SDR - 1) \cdot L \cdot \Delta P)}{1000}$$

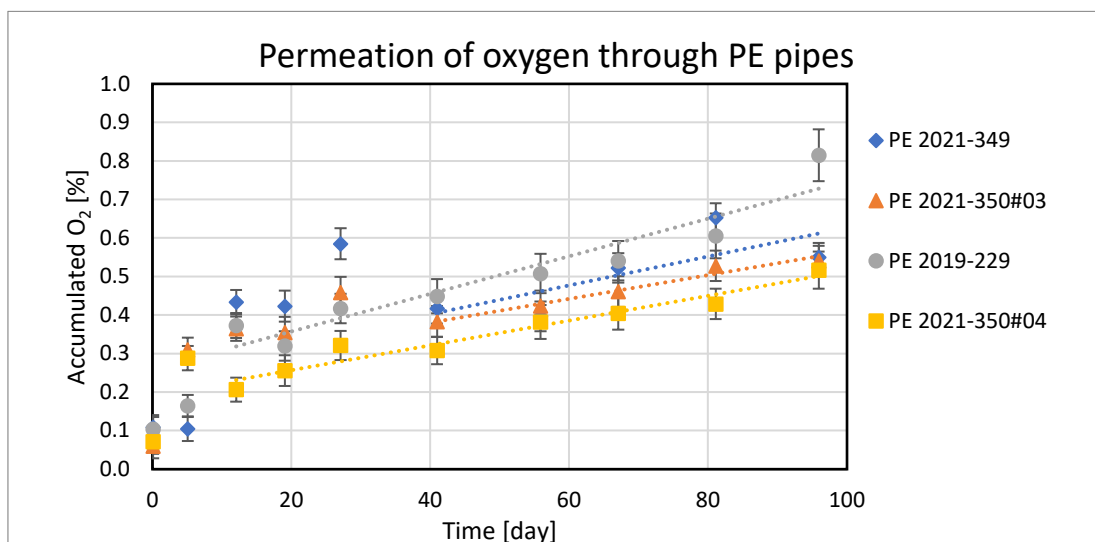
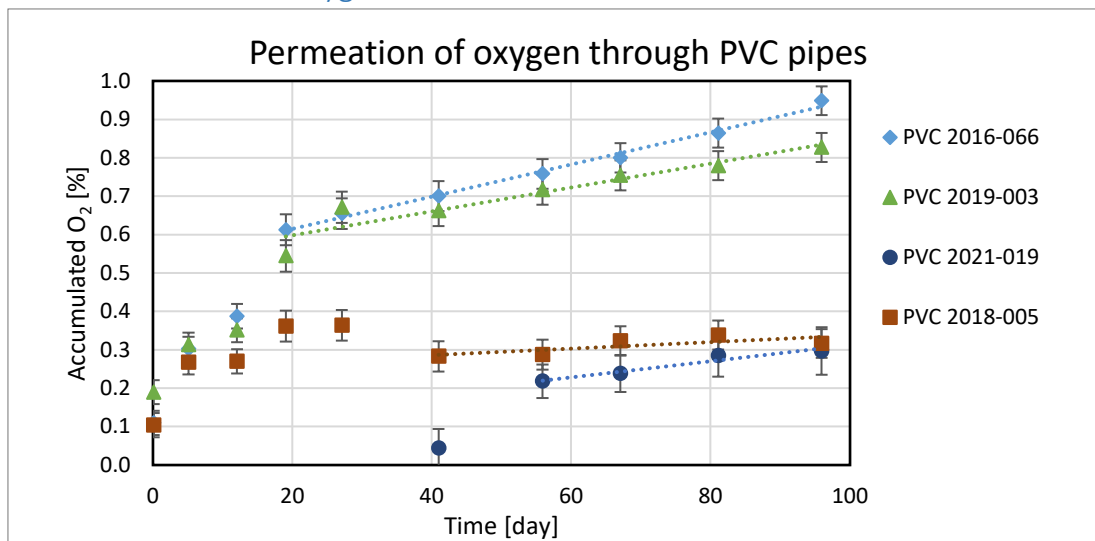
equation 16

VI Results of the permeation measurements for atmospheric gases and water

VI.1 Permeation of nitrogen

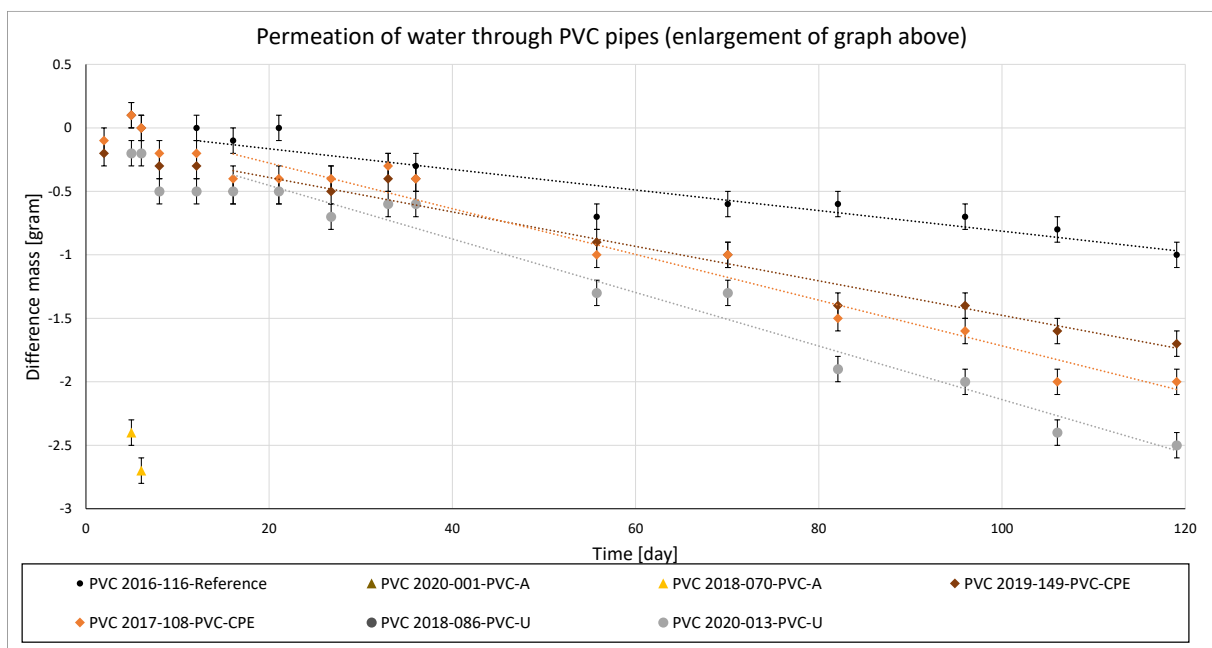
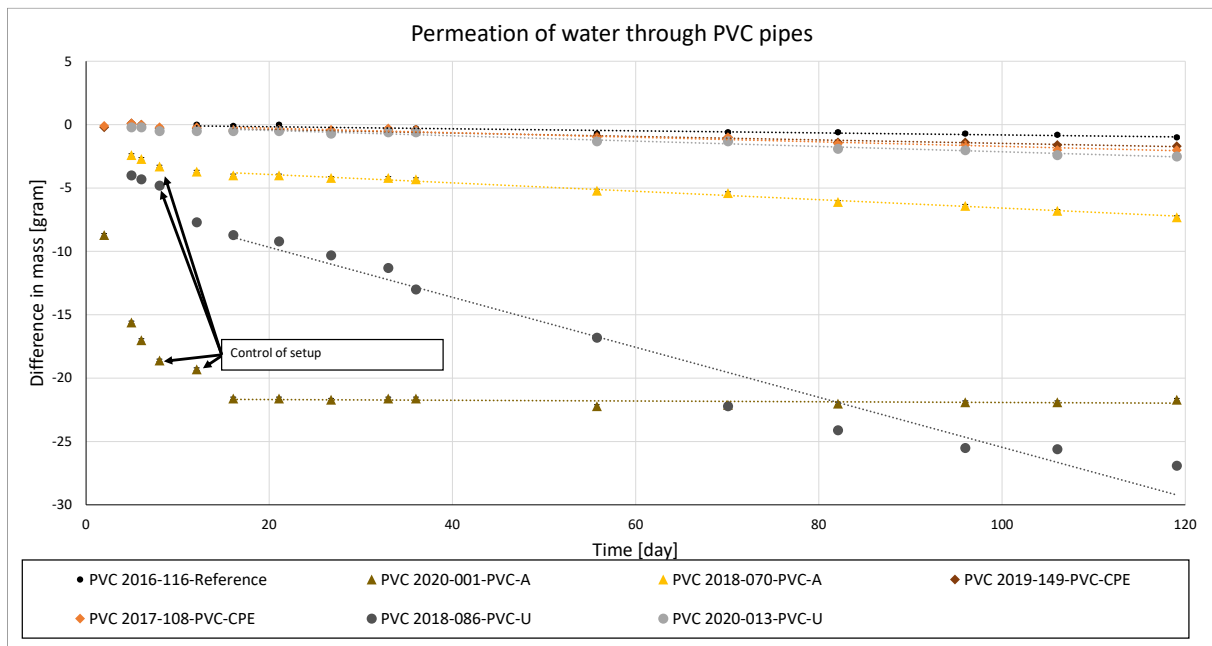


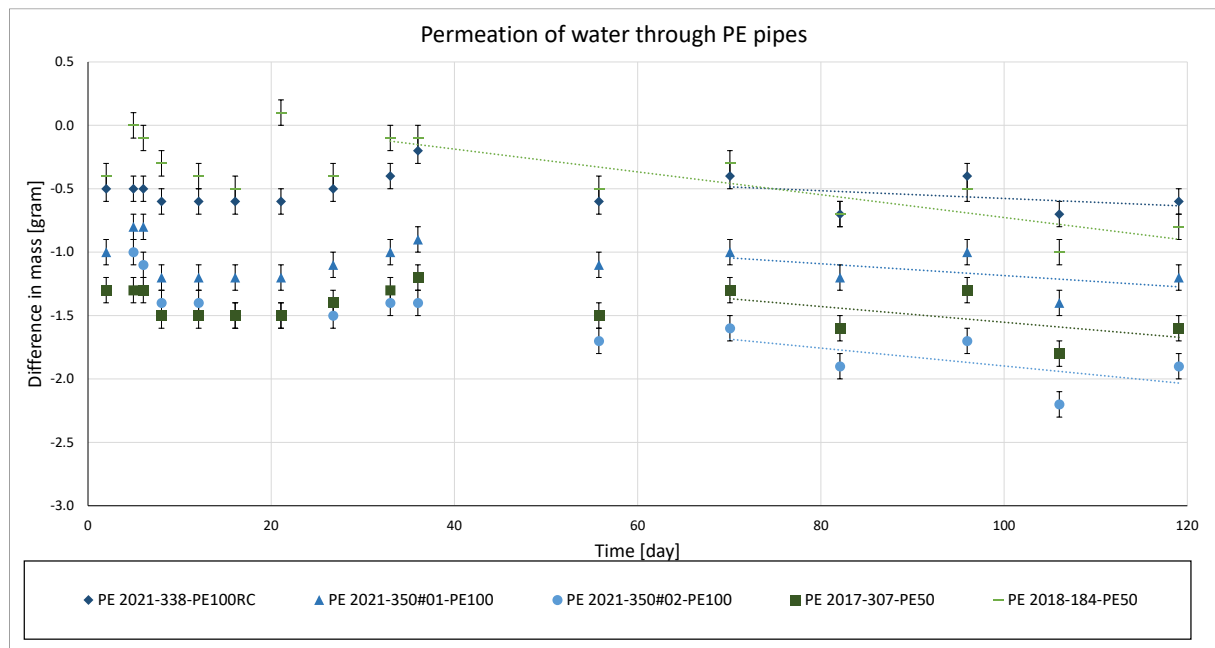
VI.2 Permeation of oxygen



VI.3 Water permeation

For the PVC 2020-001, PVC 2018-070, and PVC 2018-086 setups, the sealing of the Swagelok plug and PVC end cap was adjusted after 8 days, indicated by 'measurement setup check'.





VII Measuring equipment used

Description	Manufacturer and type	Kiwa no. / serial no.
GC for THT and natural gas - main components	Thermo Fischer GC-TCD/FID	ISQ 150647
Balance	Mettler Toledo – SR32001	Kiwa 111603
Micro-GC	Varian – CP-4900 Pro	GC907601