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Hydrogen permeation of PVC-O pipe and coupler at different temperatures

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Colophon

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1 Hydrogen permeation of PVC-O is comparable to PVC-U and PVC-HI however between couplers and temperatures permeation rates vary

PVC4pipes, the value chain platform of the European Council of Vinyl Manufacturers dedicated to PVC pipes and fitting systems, is interested to know the resistance to hydrogen permeation of an oriented PVC (PVC-O) pipe and a solvent cement coupler (M-110). In particular, PVC4Pipes is interested to know the performance of the PVC-O pipe compared to rigid PVC (PVC-U) and impact modified PVC (PVC-HI) pipes. Furthermore, they are interested to gain understanding of the influence of temperature on the permeation rate. Permeation is a characteristic which is well expressed by the permeability coefficient (P_c) for monolayer pipes and by the permeation rate (Q) for couplers.

The hydrogen permeability coefficients for PVC-U and PVC-HI pipes and permeation rate of PVC socket sliding couplers have been determined in previous research ([1], [2]). However, the hydrogen permeability coefficients at different temperatures for the specific PVC-O pipes supplied by Molecor, a PVC4pipes partner, have not been established before. This is also the case for the permeation rates of the M-110 (solvent cement coupler).

Therefore, the hydrogen permeability coefficients at ~8 ˚C and ~23 ˚C and at pressures of 200 mbar(g) are determined for a monolayer PVC-O pipe. The results show that the permeability coefficient of PVC-O is higher at higher temperatures (Chapter 2). Furthermore, the permeability coefficient of PVC-O is comparable to the permeability coefficient of PVC-U, PVC-HI and PE pipes at 23 ˚C (Chapter 2). Also, the permeation rates of the M-110 (solvent cement coupler) at ~8 ˚C and ~23 ˚C and pressures of 200 mbar(g) are determined. The results show that the resistance to permeation of hydrogen of the M-110 (solvent cement coupler) is higher at lower temperatures (Chapter 3). Also, the permeation rate of the M-110 (solvent cement coupler) is comparable to the permeation rate of a PVC-O pipe with equal length, as well as the permeation rate of PVC-U and PVC-HI socketed sliding couplers from the Dutch gas grid (Chapter 3). The sample details including their assigned Kiwa identification numbers are described in appendix I. Appendix II elaborates on the test method and a brief overview on the theory of the process of permeation is given in appendix III.

2 Permeability coefficient for PVC-O is comparable to the permeability coefficient of PVC-U and PVC-HI

The hydrogen permeability coefficients for PVC-U and impact modified PVC (PVC-HI) pipes have been determined in previous research ([1], [2]). However, the hydrogen permeability coefficient for the specific PVC-O pipe has not yet been determined. Therefore, the permeation rate of the PVC-O pipe is measured and described in §2.1. As temperature influences the resistance to permeation, two measurements were carried out, one at 8 °C and the other at 23 °C. The permeation rates are converted to permeability coefficients in §2.2 and the influence of temperature discussed. In §2.3 the permeability coefficients of the different types of PVC are compared.

2.1 Determining the permeation rate of the PVC-O pipe

The permeation rate is determined from the part of the hydrogen accumulation curve (figure 1) where steady state permeation is reached (recognizable by its linearity). This curve is experimentally acquired as explained below and results in a permeation rate of 3,47 ml/day at 8 °C and 5,81 ml/day at 23 °C.

A steel jacket pipe was placed around the PVC-O pipe and the pipe ends were sealed using multi-joint end fittings (see appendix II for a schematic representation). Subsequently the PVC-O pipe was filled with 200 mbar hydrogen (1,2 bar absolute pressure) and the jacket pipe with nitrogen and left at a small overpressure. Due to permeation, the hydrogen passes through the pipe wall into the steel jacket pipe. The accumulation of hydrogen in the jacket pipe over time at 8 ˚C and 23 ˚C is followed using gas chromatography (figure 1). The first measurement at 23 ˚C, taken a couple of hours after installation, shows no accumulation of hydrogen (black data point in figure 1). The next measurement, after about three days, shows the first hydrogen accumulation in the steel jacket pipe. The first measurement at 8 ˚C already shows some hydrogen has accumulated in the jacket pipe. At least five additional measurements per temperature were performed over the course of three weeks. For each temperature a linear regression line was fitted through the datapoints. The coefficient of determination of the regression lines (R^2) are very close to 1, which indicates that the regression line describes the relationship between the time passed and accumulated hydrogen in the jacket pipes very well. A value of ‘1’ would indicate a perfect correlation between the regression line and the datapoints.
The PVC-O pipe shows an accumulation of 3,47 ml/day and R^2 of 0,999 at 8 ˚C and 5,81 ml/day and R^2 of 0,997 at 23 ˚C (figure 1).

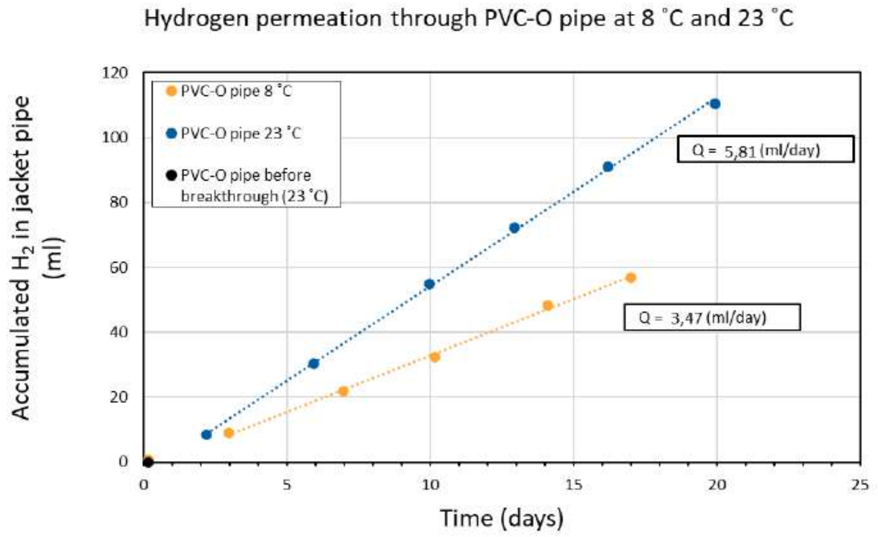

Figure 1: accumulated hydrogen in jacket pipe with the pipe specimen at 8 ˚C and 23 ˚C in ml

2.2 The resistance to permeation is higher at lower temperatures (8 ˚C) compared to higher temperatures (23 ˚C)

The permeation rates of the pipe from figure 1 are converted to permeability coefficients, a material property, by correcting for the pipe's dimensions and the measured partial pressure during testing. The corrected accumulation is shown in figure 2. The slope of the steady state permeation phase represents the permeability coefficient in (ml·mm)/(m^2·bar·day). The permeability coefficient of PVC-O at 8 ˚C is 47,6 (ml·mm)/(m^2·bar·day) and at 23 ˚C 79,7 (ml·mm)/(m^2·bar·day) (figure 2). The correction improved the coefficient of determination (R^2) to respectively 1,000 and 9,998.

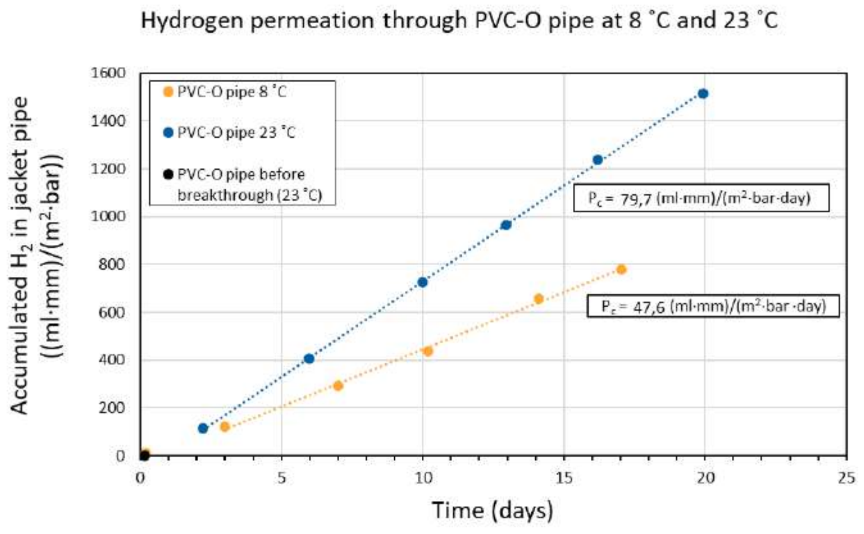

Figure 2: the accumulated hydrogen in the jacket pipe corrected for pipe dimensions and pressure variations in (ml·mm)/(m^2·bar)

The hydrogen permeability coefficient of PVC-O at approximately 8 ˚C is 1,7 times smaller compared to the PVC-O permeability coefficient at 23 ˚C. The resistance to permeation is thus higher at lower temperatures and lower at high temperatures. The explanation for this difference can be found in the energy that the gas molecules possess. The mobility of molecules increases when the energy of the system increases. Increasing temperature is a way to increase the energy of the system and subsequently increase mobility of the molecules and the rate of permeation.
The coefficient of determination for all measurements is close to ‘1’ indicating a near perfect relationship.

2.3 PVC-O permeability coefficient is comparable to PVC-U, PVC-HI and PE permeability coefficient

Ultimately the permeability coefficient of PVC-O is compared to the permeability coefficients of other types of PVC and PE. Table 1 lists the permeability coefficient of PVC-O and the range of permeability coefficients of PVC-U and PVC-HI determined in previous projects ([1], [2]) and the range of permeability coefficients of PE as listed in [3]. The range of permeability coefficients of both PVC-U and PVC-HI were determined using 8 pipes excavated from the Dutch natural gas distribution grid (table 7 in [2] provides a list of all pipes tested). For the 3 PVC-U pipes the year of construction ranged between 1965 and 2005. The PVC-HI pipes included 3 PVC-A specimen with the year of construction between 1975 and 2009, and 2 PVC-CPE pipes with the year of construction in 1990 and 1991.

Table 1: permeability coefficients of PVC-O, PVC-U, PVC-HI and PE.

	Permeability coefficient at 20-25 ˚C (ml·mm)/(m²·bar·day)	Reference
PVC-O	79,7	Current study
PVC-U	87,3-115,3	[1], [2]
PVC-HI	113,3-181,3*	[1], [2]
PE80, PE100, 100RC	108-193	[3]

** The dataset of PVC-HI in* [2] *consists of four specimens with a permeability coefficient between 113,3-119,5 (ml·mm)/(m²·bar·day) and one with a permeability coefficient of 181,3 (ml·mm)/(m²·bar·day). No causes were found to exclude the sample with the higher permeability coefficient from the dataset (a PVC-A pipe with construction year 2009* [2]*). An explanation for this difference can most likely be found in the type of resin and/or manufacturing method used. All other parameters that varied (e.g. slight variations in wall thickness and gas pressure in the pipes) have been corrected for. Also, temperature has been kept as stable as possible thus excluding it as an environmental influence.*

The permeability coefficient of PVC-O and PVC-U lie in the same order of magnitude. The permeability coefficient of PVC-HI and PE is slightly higher. PVC-O has the smallest permeability coefficient for hydrogen gas (table 1), which corresponds with the highest resistance to permeation. An explanation for this difference can most likely be found in the type of material, resin and/or manufacturing method used. The oriented nature of the PVC-O material is one of the characteristics which could be of positive influence on the permeability coefficient. All other parameters that varied (e.g. slight variations in wall thickness and gas pressure in the PVC pipes) have been corrected for. Also, the test temperature has been kept as stable as possible thus excluding environmental influences.
Due to the limited sample size (only one PVC-O pipe has been tested, table 1) it cannot be experimentally substantiated that the PVC-O pipe scores statistically significantly better compared to PVC-U, PVC-HI, or PE pipes. PVC-O will also have a range of permeability coefficients coming forth from slight variations in resin or

manufacturing techniques. The permeability coefficients of PVC-O are however comparable to PVC-U, PVC-HI, and PE.
It is important to note that the actual loss of hydrogen due to permeation in practise is not determined solely by the permeability coefficient. The volume of hydrogen lost per time (permeation rate) is a combination of the permeability coefficient and the dimensions of the assessed pipe section, the temperature, and operating pressure (see equation 1 in appendix III). When considering equal temperatures, lengths and diameters, the operating pressure and wall thickness of the pipe section are critical factors. Doubling the wall thickness corresponds with dividing the permeation rate by two. Thus, even though a pipe has a higher permeability coefficient, the actual loss of hydrogen due to permeation can be smaller due to a greater wall thickness of the pipe with the higher permeability coefficient.

3 Permeation rates of the coupler are of the same order of magnitude as the PVC-O pipe

The resistance of the PVC-O pipe to the permeation of hydrogen is known. However, to fully understand the permeation behaviour of the pipe system, the connecting coupler need to be considered as well. Therefore, the hydrogen permeation rates of this coupler at different temperatures is measured and described in §3.1. Thereafter, the influence of temperature on the permeation rate is discussed in §3.2. Followed by a reflection of the performance of the coupler compared to the PVC-O pipe and PVC sliding couplers (both PVC-U and PVC-HI) with similar nominal diameter (DN) from the Dutch gas grid in §3.3. The coupler's resistance to permeation is of the same order of magnitude as a pipe segment of equal length and comparable to the couplers from the Dutch gas grid.

3.1 Hydrogen accumulation of coupler with pipe ends within the jacket pipe

The permeability coefficient of an installed component such as a coupler on two pipe ends cannot be determined as the different materials it is composed of have different permeability coefficients (see appendix II). To determine the permeability coefficient of an installed coupler, these materials should be tested separately. Also, the complex geometric shape makes it difficult to calculate the contribution of the individual components. And the performance of the solvent coupler cement needs to be quantified. Therefore, only the permeation rate of the installed component including pipe ends is determined.
The accumulated hydrogen in the jacket pipe over time at 8 ˚C and 23 ˚C is shown in figure 3. Over the course of three weeks 5 measurements per specimen were done. These were connected by regression lines with coefficients of determination (R^2) very close to '1' (0,996 at 8 ˚C and 0,998 at 23 ˚C). The permeation rate of the coupler including pipe sections inside the jacket pipe at 8 ˚C is 2,9 ml/day and 4,9 ml/day at 23 ˚C (figure 3).

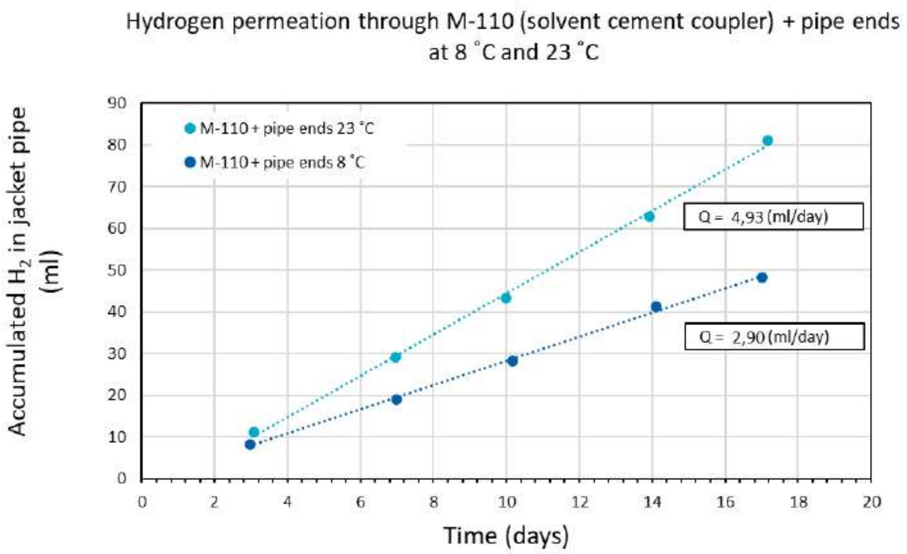

Figure 3: accumulated hydrogen of the M-110 (solvent cement coupler) including pipe ends extending in the jacket pipe at 8 ˚C and 23 ˚C in ml.

3.2 The resistance to permeation of the coupler is higher at lower temperatures

From equation 1 (appendix III) it follows that the partial pressure is proportional to the permeation rate for any component, pipe or coupler, tested. Doubling the pressure therefore results in a doubling of the permeation rate. This means that, similar to pipe segments, we can correct for test pressure for the coupler. In [2] this was also experimentally substantiated with hydrogen permeation tests on couplers including pipe ends at different pressures. The hydrogen permeation rates of the M-110 (solvent cement coupler) including the pipe ends and the PVC-O pipe corrected for test pressure and of even length (600 mm) are given in table 2.

The hydrogen permeation rate for both components (coupler and pipe) at 8 ˚C is 1,6-1,7 times smaller compared to the permeation rate at 23 ˚C. The resistance to permeation is thus higher at lower temperatures and lower at high temperatures. The explanation for this difference can be found in the energy that the gas molecules possess. The mobility of molecules increases when the energy of the system increases. Increasing temperature is a way to increase the energy of the system and subsequently increase mobility of the molecules and the rate of permeation.

Table 2: permeation rates of the M-110 (solvent cement coupler) including the pipe ends and the PVC-O pipe of equal lengths of 600 mm corrected for test pressure

	Permeation rate per 600 mm (ml/(bar·day))		Nominal diameter (mm)
	23 ˚C	8 ˚C	
M-110 (solvent cement coupler) including pipe ends	4,0	2,5	110
PVC-O pipe	5,0	3,0	110

3.3 Permeation rates of the M-110 (solvent cement coupler) coupler comparable to PVC-O pipe and PVC-U and PVC-HI couplers

The permeation rates of the coupler including pipe ends and PVC-O pipe of equal length lie in the same order of magnitude (table 2). The permeation rates of the M-110 (solvent cement coupler) are the smallest measured: 2,5 and 4,0 ml/(bar·day) at 8 ˚C and 23 ˚C respectively. A lower permeation rate corresponds with a higher resistance to permeation. Based on these single measurements the loss of permeation of a PVC-O pipe is 1,2 times larger compared to a M-110 (solvent cement coupler).

In [1] and [2] PVC sliding couplers (both PVC-U and PVC-HI), previously used for natural gas distribution, from the Dutch gas grid have been tested. The couplers came from different manufacturers and have similar nominal diameters (DN) which allows comparison to the coupler of this study. The selection included:

- one injection moulded PVC-U coupler (with unknown construction year),
- one hot moulded PVC-U coupler from 1960,
- one injection moulded PVC-HI coupler from 1988,
- and one PVC-HI coupler from 1976.

The permeation rates at 23 ˚C are listed in table 3 and were 5,4, 6,2, 6,1 and 6,1 ml/(bar·day) respectively [2]. Compared to the couplers from the Dutch gas grid, the M-110 (solvent cement coupler) scores 1,4-1,6 times better.

Table 3: permeation rates of the M-110 (solvent cement coupler) including the pipe ends and PVC-HI and PVC-U couplers from corrected for test pressure

	Permeation rate per 600 mm at 23 ˚C (ml/(bar·day))	Nominal diameter (mm)
M-110 (solvent cement coupler)	4,0	110
Injection moulded PVC-U	5,4	110
Hot moulded PVC-U	6,2	110
Injection moulded PVC-HI	6,1	110
Hot moulded PVC-HI	6,1	110

When installed properly, the loss of hydrogen gas of the M-110 (solvent cement coupler) including pipe ends is comparable to the loss of hydrogen through a pipe segment of equal length. The M-110 (solvent cement coupler) therefore has a neglectable influence on the loss of hydrogen of pipe system due to permeation.

Because the permeation measurements on the coupler have been corrected for pressure, these corrected permeation rates from table 2 can be used to calculate the permeation rate (ml/day) at different operating pressures. Please note that the acquired permeation rates of the coupler have not been corrected for dimensions. The corrected permeation rates can therefor only to be used for calculations of systems with corresponding nominal diameter of 110 mm, as listed in table 2.

4 References

[1] R. Hermkens, "Leak tightness of PVC fittings with hydrogen," Kiwa Technology, 2022.

[2] S. Jansma, "Permeatie van waterstof," Kiwa Technology in opdracht van Netbeheer Nederland, 2022.

[3] a. B. prEN 1555-1:2024.

[4] F. Scholten and M. Wolters, "Methane Permeation through Advanced High-Pressure Plastics and Composite Pipes," in *Plastic Pipes XIV*, Budapest, 2008.

[5] E. van der Stok, F. Scholten and L. Dalmolen, "Cover blow-off resistance of reinforced thermoplastic pipes for gas service," in *Plastics Pipes XV Conference*, Vancouver, 2010.

Links to the online reports:
[1], [2], [3], [4]

I Sample description

I.1 Pipe data

Supplied by	:	Molecor
Contact	:	Vincent Stone and Juan José Palma Guerrero
Type of material	:	10 PVC-O pipes and 2 M-110 (solvent cement couplers)
Date of registration at Kiwa laboratory	:	27-6-2023

I.2 Received materials

The received specimens consist of a total of ten PVC-O pipes (DN110), two M-110 (solvent cement couplers) and a can of Tangit PVC-U adhesive (figure 4). The wall thickness of the pipes was approximately 3 mm and the pipes have a length of about 1 m. The text “©Molecor TOM AENOR N 001/001014 PVC-0 500 110X2,0 PN 12,5 C1,4 02/05/23 11:22 111323043 UNE-EN 17176 ISO 16422 SANS 16422” was printed on one of the pipes. The other pipes contained partial prints of this text with sample specific timestamps.

Figure 4: the PVC-O pipes, M-110 (solvent cement couplers) a can of Tangit supplied by Molecor

Molecor did not assign specific identification numbers to the different pipes or sockets. For internal reference purposes of Kiwa Technology the pipes received the reference codes from PVC 2023-069 #1 up to PVC 2023-069#10 and sockets were referred to as M-110 (solvent cement couplers).

II Test method

Steel jacket pipes are placed around each tested pipe or coupler and pipe ends. A schematic representation of the test setup is depicted in figure 5. The jacket pipe is flushed with 99,999% pure nitrogen and subsequently filled with nitrogen and left at a small overpressure. The pipes are flushed with 99,999% pure hydrogen gas and pressurised to 200 mbar(g) (gauge pressure; 1,2 bar absolute pressure or *bar(a)*). To close off the pipe ends, end caps multi-joint connections of GF piping systems are used on both sides and fixed with lashing straps for safety reasons.

The pipes are then placed in the test chamber which has been set and kept at 8 °C (281 K) or 23 °C (296 K) during testing (figure 6). The temperature inside the chamber was monitored with an *Ahlborn Almemo 2590* and attached thermoelectrical thermometer.

Due to the pressure difference, hydrogen gas will permeate through the sample and accumulate in the steel jacket pipe. Gas permeates through the available pathways in the sample. Hydrogen will permeate through the pipe wall ('1' in figure 5) in case of a pipe. In case of a sample with pipe and coupler, hydrogen also permeates through the pipe and coupler in places where an adhesive is absent ('2' in figure 5) and through the sealing solvent cement material ('3' in figure 5). The concentration of hydrogen in the jacket pipes is measured at specific times using a gas chromatograph (*Varian micro-GC CP-4900*). Before each measurement the system is calibrated using calibration gases with a known concentration of hydrogen. The calibration gas is selected to match the hydrogen concentration in the steel jacket pipe as closely as possible.

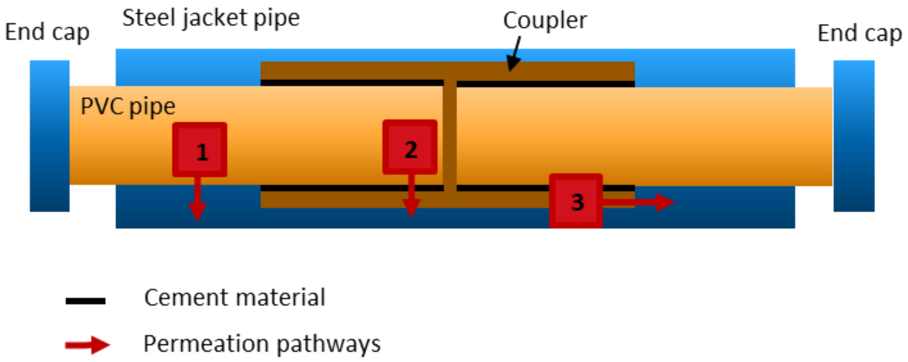

Figure 5: schematic of the test setup. The arrows indicate the hydrogen permeation pathways from the PVC-O pipe with solvent cement coupler into the jacket pipe.

Figure 6: the test setup showing the samples in the temperature controlled test chamber.

III Theory of permeation

Permeation is the phenomenon where a permeate, such as hydrogen gas, passes through a physical barrier (e.g. a PVC pipe wall). This process, although undesirable, is naturally occurring and inevitable. Any plastic material will show some permeation of gases [4], [5]. Please note that leakage is not the same as permeation. Leakage is a process where the barrier is punctured and locally not present as a result of which gas can flow out.

The permeation rate (Q_V) of a pipe expresses the volume of permeate lost over time. It depends on the material's permeability coefficient (P_C), the partial pressure difference of the permeate (ΔP), and the pipe's dimensions; the length (L) and median diameter (D_m) combine to form the surface area (A) and the wall thickness (e). The permeation rate (Q_V) is formulated as follows:

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

Equation 1

where:

- Q_V is the permeation rate in ml/day;
- P_C is the permeability coefficient in (ml·mm)/(m^2·bara·day) (a material property);
- A is the surface area using the length *(L)* median diameter *(D_m)* of the pipe in m^2 [5];
- ΔP is the difference in partial pressure of the permeate on either side of the pipe wall in bar;
- e is the wall thickness of the pipe in mm.

The permeability coefficient is a material characteristic. It is a measure for the resistance of a material against permeation and is highly temperature dependent, but only slightly pressure dependent. For monolayer pipes, the permeability coefficient can be calculated from the permeation rate if pipe dimensions are known. The permeation rate is determined from the accumulation curve when steady state permeation is reached [4]. This curve is acquired experimentally. The permeability coefficient of an installed component such as a coupler on two pipe ends cannot be determined as the different materials it is composed of have different permeability coefficients. To determine the permeability coefficient of an installed coupler, these materials should be tested separately. Therefore, only the permeation rate of the installed component the couplers and pipe ends within the jacket pipes are determined.