# METHANE PERMEATION THROUGH ADVANCED HIGH-PRESSURE PLASTICS AND COMPOSITE PIPES

**Frans Scholten (frans.scholten@kiwa.nl) and**
**Mannes Wolters (mannes.wolters@kiwa.nl),**
**Kiwa Gas Technology, PO Box 137, 7300 AC Apeldoorn, Netherlands**

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**ABSTRACT**
There is a clear market wish to use plastic and composite pipes for natural gas pipelines at higher pressures than the traditional limit of 10 bars for PE100 pipes. Candidates are Polyamide 12, plasticized PA6.12, Polyamide 11, other long-chain Polyamide pipes and PE-based composite pipes (Multilayer M pipes).
However, at higher pressures permeation of natural gas through the wall of plastic or composite pipes increases, depending on materials composition and SDR.
An international testing programme was started to measure the permeation rate and permeability coefficient of 14 different 110mm plastic and composite pipes. Sponsors are pipe and resin manufacturers and GERG (European Gas Research Group).
Included in the investigation were 5 different brands of Polyamide pipe, a pipe produced from a PE100 resin containing 10% of a special anti-permeation additive and a RTP Light pipe. Two PE100 pipes were measured for reference.
Using the permeation curves, the permeability coefficient PC (in ml.mm/m2/bara/day), diffusion coefficient D (in $cm^2$/sec.) and solubility coefficient S (in $kbara^{-1}$) for methane have been calculated for all measured pipes.
The PA pipes show only a few percent of the permeability coefficient of PE100 pipe. The PE100 pipe containing 10 % of a special anti-permeation additive possesses a 5.2 times lower permeability coefficient than regular PE100 pipe. Therefore, this modified PE100 pipe shows a permeation rate in between the values for PE100 and PA pipes.

## INTRODUCTION

Any plastic material will show some permeation of methane or other gases, although the permeability coefficient (permeation rate under standard conditions) can be very different for different polymers. Because the pipe systems investigated in this project are intended for natural gas pressures higher than 10 bars, the permeation rate is more important than for pipes only used at lower pressures.

There could be three reasons to assess permeation losses through the wall of plastic pipes in gas distribution systems:

1. The economic value of lost natural gas
2. Contribution to global warming and climate change caused by these permeation losses.
3. Safety issues, because permeated gases may accumulate in unwanted and unexpected locations.

It is clear that reasons 1 and 2 are not important enough. Natural gas leakages at pipeline connections and joints are much more important than permeation losses, both from an economical and from a "climate change" point of view.

This leaves safety as most important reason to investigate permeation losses. Permeated gas may flow several meters away from a pipeline and accumulate elsewhere. In rare occasions this may lead to flammable or explosive mixtures with air at unexpected locations. Accumulation may occur under the following conditions:

- in impermeable soil
- under impermeable pavements
- near impermeable foundations of buildings
- inside protective jacket pipes.

Still, permeation does not imply any loss of mechanical integrity of the pipeline.

Plastic pipes intended for pressures above 10 bars can be made of different types of PA resins, like PA12, PA11, plasticized PA6.12 or other long-chain PA. RTP (Reinforced Thermoplastic Pipes, containing aramid or other fibres [1]) and multilayer PE100 pipe strengthened by highly oriented PE100 foil [2] are also possible. Most of these pipe materials have been investigated in this work.

The goal of the work is to determine the permeability coefficient of the different pipe materials. The measurements have been performed on whole pipe segments and not on foils.

## EXPERIMENTAL METHODS

### Materials

All investigated pipes had a nominal diameter of 110 mm, except pipe 11 (Table 1).

Investigated were 3 types of PA12 pipe, all 110mm and SDR11 (pipes 1, 2 and 3). A fourth PA material, a plasticized PA6.12 grade was also investigated (pipe 7). Pipe 6 is still under test.

*Table 1. Investigated pipe materials. All pipes 110 mm, except pipe 11 (125 mm). Most are SDR11, except 4, 5 and 11.*

| Pipe nr. | Pipe | Resin manufacturer | Grade name | SDR |
|---|---|---|---|---|
| 1 | PA12 | Evonik Degussa | Vestamid ® LX9030 | 11 |
| 2 | PA12 | EMS-GRIVORY | Grilamid ® FE 8566 | 11 |
| 3 | PA12 | Ube | Ubesta ® 3035 UF | 11 |
| 4 | PE100 + 10 % UB39 | DuPont | Pipelon ® UB39 | 15.8 |
| 5 | PE100 | | | 15.8 |
| 6 | Long chain PA | DuPont | Pipelon ® HT | 11 |
| 7 | plasticized PA6.12 | DuPont | Pipelon ® 401 | 11 |
| 11 | PE100 multilayer | Pipelife | RTP "Light" | 8.9 |
| 15 | PE100 | - | - | 11 |

Three pipes were investigated produced by Pipelife (Netherland), pipes 4, 5 and 15. Pipe 5 is a modified PE100 pipe with an usual SDR of 15.8 (7 mm wall thickness). The composition was this pipe is PE100 resin containing 10% of a special anti-permeation additive. Pipe 4 is a normal PE100 pipe with the same wall thickness and SDR, to allow comparison with pipe 4 at the same pipe dimensions.
Pipe 15 is a SDR11 110mm PE100 pipe, used as reference in this publication.

Finally, a fourth pipe from Pipelife in Netherland was investigated, a Reinforced Thermoplastic Pipe (pipe 11). This pipe was denoted "RTP Light", with a diameter of 125 mm and wall thickness of 14 mm.

**Methods**

The typical shape of a permeation curve is (Figure 2 and Figure 3):

- At first no there is no permeation, followed by:
- Slow increase of the permeation rate (the slope) and finally:
- Steady state permeation with constant slope.

The permeation rate is linearly related to the slope of the curve in the final, linear part. From this slope the permeability coefficient PC can be calculated, by taking into account the wall thickness, pipe diameter, volume of the jacket pipe used for accumulation of permeated gas and the pressure difference (in bar(a), with respect to vacuum). The formula is given in equation (1):

$$PC = Q \cdot e / ( A \cdot \Delta P) \qquad (1)$$

In which:

PC is in ml.mm/m$^2$/day/bara
Q is in ml/day
e = wall thickness in mm
A = surface area of the pipe in m$^2$
$\Delta P$ = pressure difference for methane in bara (with respect to vacuum)

*Permeation and the Median Pipe Diameter*

The pipe diameter that is used for the calculations needs consideration. This is illustrated in Figure 1.

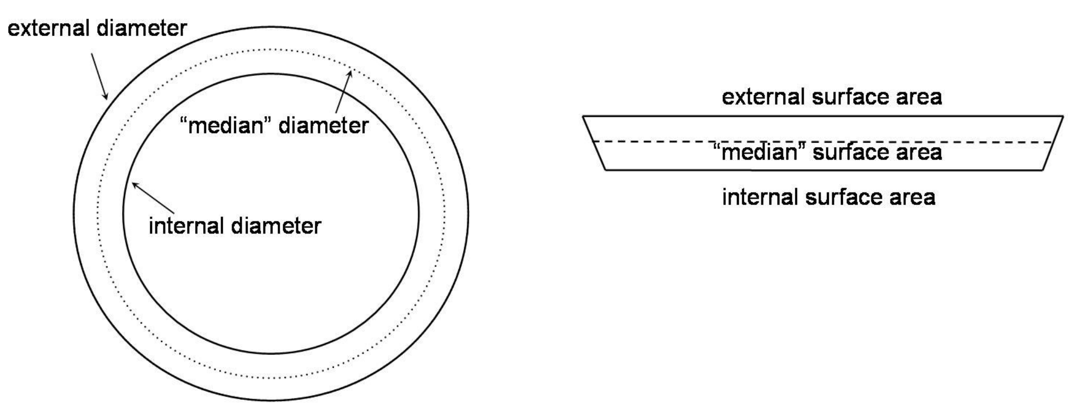


*Figure 1. The external diameter $D_e$, the internal diameter $D_i$ and the "median" pipe diameter $D_m$. At right: "flattened pipe".*

The median pipe diameter ($D_m$) is the diameter halfway between external diameter ($D_e$) and internal diameter ($D_i$). In formula:

$$D_m = (D_e + D_i)/2 \qquad (2)$$

The right-hand part of Figure 1 illustrates that the median surface area A (in $m^2$) through which permeation takes place is the correct choice. The external surface area is too large and the internal surface area is too small. The median surface area A is defined in equation (3):

$$A = \pi \cdot D_m \cdot L \qquad (3)$$

In which:
L = the length of the jacket pipe (m).
$D_m$ is in meters as well.

Further:

$$D_m = D_e \cdot (SDR\text{-}1) / SDR \qquad (4)$$

This leads to the general permeation equation for pipes:

$$PC = 1000 \cdot Q / (\pi \cdot (SDR\text{-}1) \cdot L \cdot \Delta P) \qquad (5)$$

It is emphasised again that L is in meters.
This formula means that the permeability coefficient is not directly dependent on the pipe diameter and wall thickness separately, but only on the ratio between both, the SDR, via the factor (SDR-1). At constant SDR, a larger pipe diameter is exactly compensated by the increase in wall thickness.

*Diffusion coefficient and solubility*
There is more information to be derived from the permeation curves. When the straight line in the final linear part of the curve is extrapolated back to the x- axis, a breakthrough time (BT) is found (in days). From BT the diffusion coefficient D can be calculated [3, 5] by equation (6):

$$BT = (e)^2 / (6 \cdot D) \qquad (6)$$

in which D is the diffusion coefficient in $mm^2$/day, which value is converted to $cm^2$/sec.
Finally, the solubility (S) of the methane gas in the polymer materials can be calculated by equation (7) [3, 4]:

$$PC = D \cdot S \qquad (7)$$

The unit of S is $bara^{-1}$ or $kbara^{-1}$. This means that the solubility of methane in the polymer is linearly dependent on the methane partial pressure (in bara). This is in agreement with Henry's Law [6].

*Comparison with Other Laboratories*
One reference PE100 pipe (pipe 15, see Table 1) was used for an inter-laboratory comparison of permeation results. The participating labs are mentioned in Table 2.

*Table 2. The 3 labs that have performed permeation measurement on the same PE100 pipe nr. 15.*

| Lab code | Laboratory | Country |
|---|---|---|
| A | Gaz de France/Degaz | Hungary |
| B | DBI | Leipzig, Germany |
| C | Kiwa Gas Technology | Apeldoorn, Netherland |

## RESULTS

All measurements described in the Results section have been performed by lab C (Table 2). Additional data measured by other labs are presented under Discussion in Table 5.

The results of permeation experiments on 110mm SDR11 PA pipes are presented in Figure 2. The results of PE100 reference pipe 15 are included.

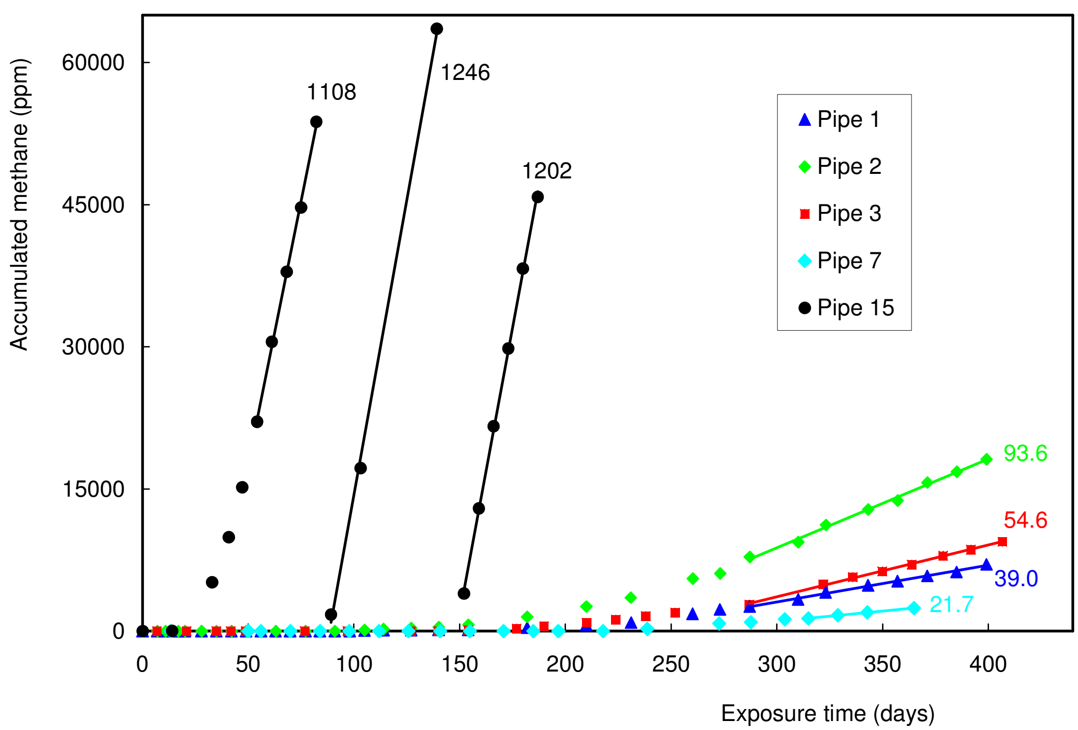


*Figure 2. Accumulation of methane in a jacket pipe after permeation through the wall of 4 PA pipes and a PE100 pipe. All pipes SDR11 and diameter 110mm. Please note PA7 was measured at 16 bar(g), whilst the other pipes were all measured at 10 bar(g). The numbers near the straight lines are the permeation rates in ppm/day.*

The results of the measurements are summarized in Table 3.

*Table 3. Permeability coefficient (PC), Diffusion coefficient (D) and Solubility of methane (S) of 4 PA pipes, 2 PE100 pipes and a pipe containing a PA/PE100 mixture.*

| Pipe nr. | Pipe | PC (ml.mm/m$^2$/bara/day) | D (cm$^2$/sec) | S (kbara$^{-1}$) |
|---|---|---|---|---|
| 1 | PA12 | 0.92 | 8.95 $10^{-9}$ | 11.8 |
| 2 | PA12 | 2.20 | 9.62 $10^{-9}$ | 26.4 |
| 3 | PA12 | 1.28 | 8.26 $10^{-9}$ | 17.9 |
| 4 | PE100 + UB39 | 7.0 | 1.8 $10^{-9}$ | 46.0 |
| 5 | PE100 | 36.6 | 5.57 $10^{-8}$ | 76.0 |
| 6 | Long chain PA | Under investigation | | |
| 7 | Plasticized PA6.12 | 0.40 * | 7.65 $10^{-9}$ * | 6.0 * |
| 11 | RTP | Under investigation | | |
| 15 | PE100 | 34.1 | 6.42 $10^{-8}$ | 61.5 |

** preliminary value, based on 4 data points in the linear range in Figure 2*
*PE100 pipe 5: 110mm PE100 pipe with a wall thickness of 7mm (SDR 15.8)*

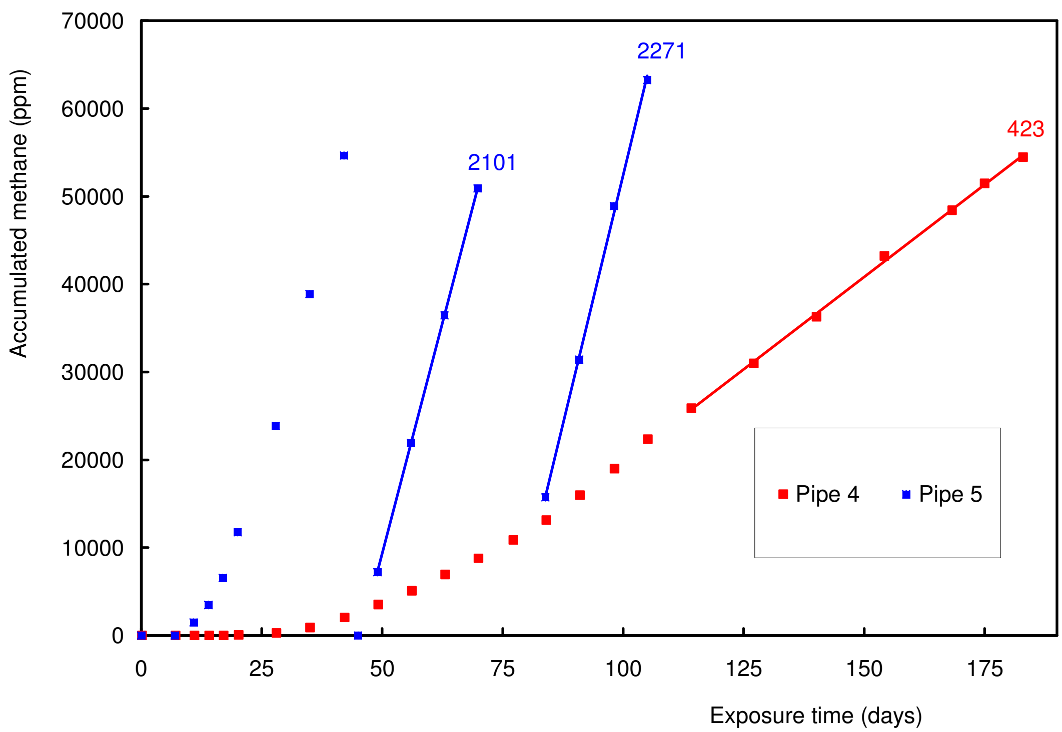


*Figure 3. Accumulation data of a PE100 pipe with special anti-permeation additive and a PE100 reference pipe.*

**DISCUSSION**
The diffusion coefficient of PE (density 964 kg/m$^3$) was reported earlier by Stannett as 5.7 $10^{-8}$ cm$^2$/sec [7]. The values for pipe 5 and 15, PE100 materials with a similar density, compare favourably with this value.

Pipe 1 and pipe 3 are both produced from PA12 resins and therefore show similar results. Pipe 2 is also produced from PA12 resin, but the value is higher. The reason is not known. Initial results obtained at 16 bars methane pressure (see Future work) confirm these differences.

The permeability coefficients of the 4 PA pipes are much lower than the permeability coefficient of PE100 pipe. Even when PA pipes will be used at higher pressures than PE100 pipes, the permeation rate will be much less. From a permeation point of view, this makes PA an attractive plastic pipe material for gas transport.

Table 4 shows the factor by which the permeability coefficient is reduced with respect to PE100 pipe. The average of the values of the 2 PE100 pipes in Table 3 (5 and 15) was taken as reference, except for pipe 4.

*Table 4. Permeability coefficient of PA pipes with respect to the permeability coefficient of PE100 pipes.*

| Pipe | Reduction in Permeability coefficient in comparison to PE100 pipe | Remark |
|---|---|---|
| 1 | 39 | |
| 2 | 16 | |
| 3 | 28 | |
| 4 | 5.2 | Compared to pipe 5 |
| 7 | 87 | |

It appears that addition of an anti-permeation component to PE100 pipe is an interesting option. Adding 10% of Pipelon ® UB39 reduces the permeability coefficient PC of this modified PE100 pipe by a factor of 5.2.

It appears that pipe 4, with 10% of an anti-permeation component added to PE100 resin, takes an intermediate position between PE100 pipe on the one hand and PA12 and plasticized PA6.12 pipes on the other hand.

**Measurements by Other Laboratories**
Two other labs (Table 2) have also made permeation measurements on the PE100 reference pipe (nr. 15). The results are presented in Table 5. The column PL is explained in a next section.
The values obtained by the 3 labs compare relatively well.

*Table 5. Permeability coefficient (PC), Diffusion coefficient (D) and Solubility of methane (S) of reference pipe 15, a 110 mm SDR11 PE100 pipe, measured by 3 laboratories. One additional value for pipe 5 and a measurement at 8 °C on pipe 15 were added for comparison.*

| Pipe | Lab | Temperature (°C) | PC (ml.mm/m²/bara/day) | D (cm²/sec) | S (kbara⁻¹) | PL (10 barg) (m³/km/year) |
|---|---|---|---|---|---|---|
| 15 | A | 21 | 26.2 | $5.22\ 10^{-8}$ | 58 | 3.3 |
| 15 | B | 21 | 27.1 | - | - | 3.4 |
| 15 | B | 21 | 36.8 | $5.37\ 10^{-8}$ | 79 | 4.6 |
| 15 | C | 21 | 34.1 | $6.42\ 10^{-8}$ | 61 | 4.3 |
| 5 | C | 21 | 36.6 | $5.57\ 10^{-8}$ | 76 | 4.6 |
| 15 | A | 8 | 8.7 | $2.64\ 10^{-8}$ | 38 | 1.1 |

**The Influence of Temperature**

Gas pipelines are installed underground. Typical soil temperatures often vary between 8 and 14 °C. Therefore it is important to know the permeability coefficient of the investigated pipes in this temperature range. For one pipe, the PE100 SDR11 reference pipe nr. 15, a measurement was performed at 8 °C by lab A. The value is given in Table 5 as well.

It appears that the influence of temperature on the permeability coefficient is relatively large. At 8 °C the permeation rate of PE100 pipe is about 3 times as low as at 21 °C.

**Practical Permeation Losses**

The last column in Table 5 illustrates what the permeation loss under practical circumstances of the investigated pipes is. All calculations were made for 10 bar(g) methane pressure and SDR11. This Permeation Loss (PL) is given in cubic meters of methane per kilometre pipeline length per year. Equation (5), the general permeation equation for pipes was used, because PL is actually Q / L in that equation, at a known permeability coefficient.

It is emphasized that these values are only valid for PE100 pipes. Based on other permeation results at the lab of the authors, it may be expected that PE80 MDPE pipes will have a PL about 1.5 times as high.

It is possible to calculate the permeation rate for pipes with another SDR value, also by using equation (5). The conversion to a pipe with another SDR value is based on the factor (SDR-1) in that equation.

## CONCLUSIONS

- The permeability coefficients measured by 3 laboratories on a PE100 reference pipe are similar. There also is a good correlation between the diffusion coefficient for PE100 and a literature value.
- Polyamide pipes (PA12 and plasticized PA6.12) possess a permeability coefficient which is 16 to 87 times lower than the permeability coefficient of

PE100 pipes. Hence, from a permeation point of view these long-chain PA pipe materials are attractive for natural gas transport and/or distribution.
- The investigated pipe which consists of a mixture of 10% of a special PA-based anti-permeation additive with PE100 resin shows a reduction in permeability coefficient by a factor of 5.2.

## FUTURE WORK

The project is continued with:

- Completing permeation measurements on the PA12 pipes, the plasticized PA6.12 pipe and another long-chain PA pipe at 16 bars methane pressure.
- Completing permeation measurements on the RTP Light pipe.
- Measuring permeation of hydrogen gas at 10 bars of the 3 PA12 pipes.

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## REFERENCES

1. Wolters M, Wessing W., Dalmolen B., Eckert R. and Wuest J., "Reinforced Thermoplastics Pipeline (RTP) Systems for Gas Distribution", 23rd World Gas Conference, IUG, Amsterdam, 2006.
2. Wessing W., "Plastic Pipes in the High-Pressure Gas Area – an Evaluation from the Perspective of a Pipeline Operator" (in German), Presentation 10 at the Wiesbadener Kunststoffrohrtage, 23-24 April 2008, Brömstrup Intern. Ingenieurberatung, Wiesbaden, Germany.
3. Curry J.E. and McKinley M.D., J. Polym. Sci., Polym. Phys. Ed., 11 (1973), 2209.
4. Singh A., Freeman B.D. and Pinnau I., J. Polym. Sci., Part B: Polym. Phys., 36 (1998), 289.
5. Lin Y. and Yasuda H., J. Appl. Polym. Sci., 60 (1996), 2227.
6. Moore W.J., "Physical chemistry", Prentice Hall, 5th ed., 1972, ISBN 0 582 44234 6.
7. Stannett V., Chapter 2 in: "Diffusion in Polymers" by J. Crank and G. S. Park, Academic Press, London and New York, 1968.