

Estimation of hydrocarbon fluid
permeation through a Polyethylene
based re-inforced thermoplastic pipe

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Estimation of hydrocarbon fluid permeation through
a Polyethylene based re-inforced thermoplastic pipe

by

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Keywords: Pipeline flowline, non metallic, permeation, environment, aromatic hydrocarbons, barrier, venting

Summary

BSP is considering the use of a trenched 4-6" Aramid Fibre reinforced High Density Polyethylene pipe, generally denoted as Reinforced Thermoplastic Pipes (RTP) for the transport of a hydrocarbon fluid in the range of C5-C16. On request of BSP the permeation of a test medium, representative for the intended hydrocarbon service, through an RTP, as considered by BSP, was calculated using experimental data.

The calculations show that, without any further measures there will be significant permeation of hydrocarbons (including aromatic hydrocarbons) into the environment, particularly soil and groundwater.

The resulting concentrations in soil and groundwater cause a risk of adverse effects on human beings and ecosystems. When permeating into ground water "intervention levels" will be reached within a few days, were "intervention levels" are defined as concentration in the ground water above which the risk of adverse effects on human beings and ecosystems is unacceptable. Any mitigating effects by dilution by groundwater flows was not taken into account since dilution as "cleaning principle" has been sworn off a long time ago and is for most countries an (legally) unacceptable solution.

It is therefore strongly recommended to trench the RTP using further means of preventing the emission of the hydrocarbon fluid into the soil and groundwater, such as the use of permeation barriers. Venting as an alternative option was discarded by BSP.

A supplier of RTP has proposed an external permeation barrier based on an aluminium foil similar to geomembranes used for secondary containment for crude oil storage tanks. Preliminary test results indicate that this barrier reduces permeation by at least a factor 150, however a further reduction is required to stay below the "intervention levels" within the design life of the line. Area for improvement of the suggested barrier is the joining method (axial seam), which is currently based on a permeable thermoplastic weld.

Amsterdam, February 2005

Contents

	Page
1. Introduction	1
2. Theory	1
2.1 Permeation calculations	1
2.2 Assessment of permeation levels	2
3. Experimental	2
4. Results	2
4.1 Permeation levels	2
4.2 Assessment by the HSE experts	2
5. Discussion of results	3
6. Conclusion	4
Table 1 ULLG test media permeability coefficient of HDPE (density 0.960 gr/cm ³)	5
Table 2 Calculated LLG test media emission 5" RTP dimension	5
Appendix 1 Guideline for a preliminary assessment of permeation levels	6
Appendix 2 ULLG fluid and simulated medium	8
Appendix 3 Determination of the permeation coefficient	9
Appendix 4 Estimation of hydrocarbon fluid permeation through a Polyethylene based re-inforced thermoplastic pipes	13
Appendix 5 Scouting studies on an external permeation barrier foil, interim results	17
References	

1. Introduction

BSP considers installing 17 kilometres of 4-6" Aramid Fibre reinforced High Density Polyethylene pipes, generally denoted as Reinforced Thermoplastic Pipes (RTP), for the transport of a hydrocarbon fluid in the range of C5-C16. This onshore pipeline, denoted as the LLG pipeline, runs from BLNG to SCOT through a jungle prone to bush fire. The line will be trenched.

Currently the level of hydrocarbons emission into the environment due to permeation though the RTP pipe wall is unknown.

Data on this level is required by BSP to confirm that the level is not above the levels allowed by the local authorities or causes any other HSE issues.

Shell Global Solutions had been contacted to reach the following objectives.

- (a) Measure the permeation of a hydrocarbon mixture, similar to the transported fluid, through polyethylene membranes at two different temperatures;
- (b) Estimate the level of permeation of the hydrocarbon mixture through a PE based pipe on the basis of the experimental results.

2. Theory

2.1 Permeation calculations

All polymeric materials permit to a larger or smaller extend the permeation of fluids. Permeation is the transmission of fluids (gas and liquid) right through the polymer. The transmission is driven by the surface concentration difference between the inside and the outside of the pipe. For liquids the surface concentration is essentially **pressure independent** until very high pressures (typical several hundreds of bar) are reached. The amount of liquid permeating trough a polymer pipe can be calculated using the following equation:

$$Q = P \cdot \frac{\pi \cdot d_i \cdot L \cdot t}{x} \quad (1)$$

in which ;

- Q: quantity of permeating liquid [gr];
- P: permeability coefficient [gr mm/m² day];
- d_i: inside diameter of the pipe [m];
- L: length of the pipe [m];
- t: duration [day];
- x: wall thickness of the pipe [mm].

Previous investigations indicated that in the current RTP designs the reinforcement fibres are do not have a significantly influence on the permeation rates [1]. For permeation calculations the sum of the liner thickness and the outer cover thickness is therefore used as the "effective" wall thickness of the pipe.

2.2 Assessment of permeation levels

In Appendix 1 a Guideline for a preliminary assessment of permeation levels is given based on Dutch legislation. This was used as a benchmark until the requirements from the local authorities have been identified.

At a later stage of this study the results were send two Shell HSE experts for assessment following detailed questions from BSP. Outcome of this assessment is given in Section 4.2.

3. Experimental

Permeability and Diffusion coefficients of HDPE

Weight change measurements of specimens, immersed in simulated ULLG transport fluid, were used to determine the permeability and diffusion coefficients of HDPE. The HDPE was taken from the liner material of an RTP pipe. An analysis of the ULLG Fluid and the composition of the simulated fluid are given in Appendix 2. The weight change due to fluid uptake of the HDPE was measured as a function of time. The experiment was performed at four different temperatures i.e. 31 °C, 55 °C, 62 °C and 80 °C. In Table 1 the ULLG test media permeability of HDPE is given as a function of temperature.

Further details on the experimental work are given in Appendix 3.

4. Results

4.1 Permeation levels

The ULLG test media emission of a 5" RTP were calculated using the experimentally obtained data. The results are given in Table 2.

At 65 °C a 5" RTP will loose approx. 12 gr/(m_{run} day) of hydrocarbon fluid.

At 25 °C, the envisaged operating temperature, a 5" RTP will loose approx. 0.45 gr/(m day) of hydrocarbon fluid. The aromatic hydrocarbon content by weight is 7.2 % (0.6 % Benzene, 4.0 % Toluene and 2.6 % Xylene).

4.2 Assessment by the HSE experts

The results of the permeation study were send to Shell HSE experts for an assessment based on questions received from BSP. The outcome of the assessment is given in Appendix 4. Following is a summary

- (a) Shell EP 95-0000 Series contains documents with Environmental Quality Standards (EQS), with EP 95-380 for water.
- (b) It follows the principles of the E&P Minimum Environmental Standards, that is manage HSE risks down to an As Low As Reasonably Possible level.
- (c) EQS shall be used as screening criteria for further action in case of contaminated soil and groundwater.
- (d) Risk assessment for the RTP shall demonstrate that the total amount of fluids permeating through the Pipe would be such that no damage is to be expected to the environment.

i The RTP was provided by Pipelife, Enhuizen The Netherlands

- (e) The "intervention levels" of the Dutch EQS refer to concentrations in the soil and groundwater above which the risk of adverse effects on human beings and ecosystems is unacceptable.
- (f) The permeation levels of the RTP into ground water will reach these "intervention levels" within a few days, and therefore may damage the environment.
- (g) Dispersion and dilution of permeated hydrocarbons is the only process that will reduce significantly the concentration around the RTP. Dilution however as "cleaning principle" has been sworn off a long time ago and is for most countries an (legally) unacceptable solution. Legally has been placed between brackets because although there is an almost endless series of publications about this subject, there are no official references in legislation to the principle of "dilution is not the solution to pollution". This principle was a result of developments a few decades ago that can be summarised as follows.

Pollution can take two major forms: local pollution and global pollution. In the very past, only local pollution was thought to be a problem. For example, coal burning produces smoke, which in sufficient concentrations can be a health hazard. One slogan, taught in schools, was "The solution to pollution is dilution". The theory was that sufficiently diluted pollution could cause no damage. In recent decades, awareness has been rising that some forms of pollution pose a regional/global problem. For example, human activity (primarily by nuclear testing) has significantly raised the levels of background radiation all over the world, which may lead to human health problems. Other types of pollution and specifically some persistent organic compounds can be carcinogenic and do pose a risk to people and the environment even at molecular level. Awareness of these kinds of pollution, among other things, has led to the environmentalism movement, which seeks to limit the human impact on the environment in a pro-active manner.

This movement focussed also on "dilution is not the solution to pollution" and has led to a mindset with legislators - first in the US but later all over the world - which has find its way into new legislation, where discharge limits apply to the end-of-pipe status, i.e. undiluted conditionsⁱⁱ.

5. Discussion of results

The permeation rate of low molecular weight hydrocarbons through Polyethylene is high.

The composition of the ULLG fluid consists mainly out of low molecular weight hydrocarbons hence the permeation rate of this fluid trough a Polyethylene RTP pipe will be high.

From a HSE point of view the present of aromatic hydrocarbons is the major concern.

Based on the assessment of the HSE experts the use of a trenched RTP for the envisaged application is only allowable when further means of preventing the emission of the hydrocarbon fluid into the soil and ground water are taken.

It is therefore strongly recommended only to use a trenched RTP for the envisaged service when further means of preventing the emission of the hydrocarbon fluid into the soil and groundwater, such as venting or the use of permeation barriers, are taken. BSP discarded the option of venting for following reasons:

ⁱⁱ Input for Bullet point (g) of Section 4.2 provided by Jacobs, Rene PWM GSNL-GSCH/1 on 03.02.2005 by E-mail

"We have looked at venting option, which poses higher risks due to concentrated HC at one location and also there is possibility of through wall permeation along the pipeline. This option also has around 51 buried flanges which is not a preferred designⁱⁱⁱ."

The use of a barrier remains the only option.

Within Shell (NAM) on a previous occasion the use of RTP for water condensate transport was prevented due to the anticipated levels of aromatic hydrocarbon permeation. Emission rates in this case were 1.5 times higher than those for the ULLG line. Since the NAM still considers the reelable RTP as an attractive pipe system a program for the development of a permeation barrier for RTP's was initiated. RTP with integrated permeation barrier suitable for hydrocarbon service is still under development.

A supplier of RTP has proposed an external permeation barrier based on an aluminium foil. Similar to geomembranes used for secondary containment for crude oil storage tanks. Preliminary test results see Appendix 5 indicate that this barrier reduces permeation by at least a factor 150. However a further reduction is required to stay below the "intervention levels".

Area for improvement of the suggested barrier is the joining method (axial seam), which is currently based on a permeable thermoplastic (Polyethylene) weld.

6. Conclusion

The envisaged use of RTP by BSP, without any further measures, will result in a permeation of hydrocarbons (including aromatic hydrocarbons) into the environment, particularly soil and groundwater.

The resulting concentrations in soil and groundwater will be such that there is a risk of adverse effects on human beings and ecosystems.

Any mitigating effects by dilution by groundwater flows was not taken into account since dilution as "cleaning principle" has been sworn off a long time ago and is for most countries an (legally) unacceptable solution.

It is therefore strongly recommended only to use a trenched RTP for the envisaged service when further means of preventing the emission of the hydrocarbon fluid into the soil and groundwater, such as venting or the use of permeation barriers are taken. Since BSP has discarded the option of venting, the use of a barrier remains the only option.

Preliminary test results on a external barrier based on an aluminium foil proposed by a RTP suppliers results in a significant reduction in permeation by at least a factor 150, however a further reduction is required to stay below the "intervention levels" within the design life of the line. Area for improvement of the suggested barrier is the joining method (axial seam), which is currently based on a permeable thermoplastic bond.

Amsterdam, February 2005,

mv

Table 1 ULLG test media **permeability coefficient** of HDPE (density 0.960 gr/cm³)

Temperature °C	Permeability coefficient $\frac{gr \cdot mm}{m^2 \cdot day}$
25	8
65	192

Table 2 Calculated LLG test media **emission** 5" RTP dimension:

Inside diameter 125 mm

Effective wall thickness 7 mm*

Temperature °C	Fluid emission $\frac{gr}{m_{run} \cdot day}$
25	0.45
65	12

*liner thickness plus protective cover thickness

Example

5" RTP at 25 °C

P: permeability coefficient [gr mm / m² day] = 8d_i: inside diameter of the pipe [m] = 0.125

L: length of the pipe [m] = 1

t: duration [day] = 1

x: wall thickness of the pipe [mm] = 7

$$Q = 8 \cdot \frac{\pi \cdot 0.125 \cdot 1 \cdot 1}{7} = 0.45 \text{ gram, per day, per meter length of pipe}$$

Appendix 1

Guideline for a preliminary assessment of permeation levels

This assessment is based on the Intervention levels for soil and groundwater pollution in the Netherlands. Target and intervention levels for soil and ground water pollution are provided by the Dutch Government in a document called "Circulaire Interventiewaarden Bodemsanering d.d. 4 februari 2000".

Target levels are the maximum levels of concentration of a specific chemical in soil or ground water under ideal circumstances. Below these levels the soil and groundwater are considered healthy and not polluted. **Intervention levels** are the levels of concentration of a specific chemical in soil or ground water at which the owner of the land has to take action to clean the soil, the soil is considered polluted.

It is **not allowed to anticipate on these intervention levels, every emission of hazardous chemicals into the environment must be prevented**. The following calculation is therefore only intended to benchmark the aromatic hydrocarbon permeation rate of RTP.

The target value and the intervention levels of the most common aromatic hydrocarbons i.e. Benzene, Toluene and Xylene are given in Table 1-1. This table shows that the intervention level for, for example, Benzene pollution in the Netherlands is 1 mg/kg soil.

At least 25 m³ of soil should have this level on average to be legally considered as soil pollution. Knowing the specific weight of sand is 1400 kg/m³ the maximum legally allowed amount of a polluting chemical in 25 m³ can be calculated:

$$Q = V \cdot \rho \cdot \frac{conc_i}{1000} \quad (2)$$

Q: quantity of chemical [g]

V: Volume of soil [m³]

ρ : Density of soil [kg/m³]

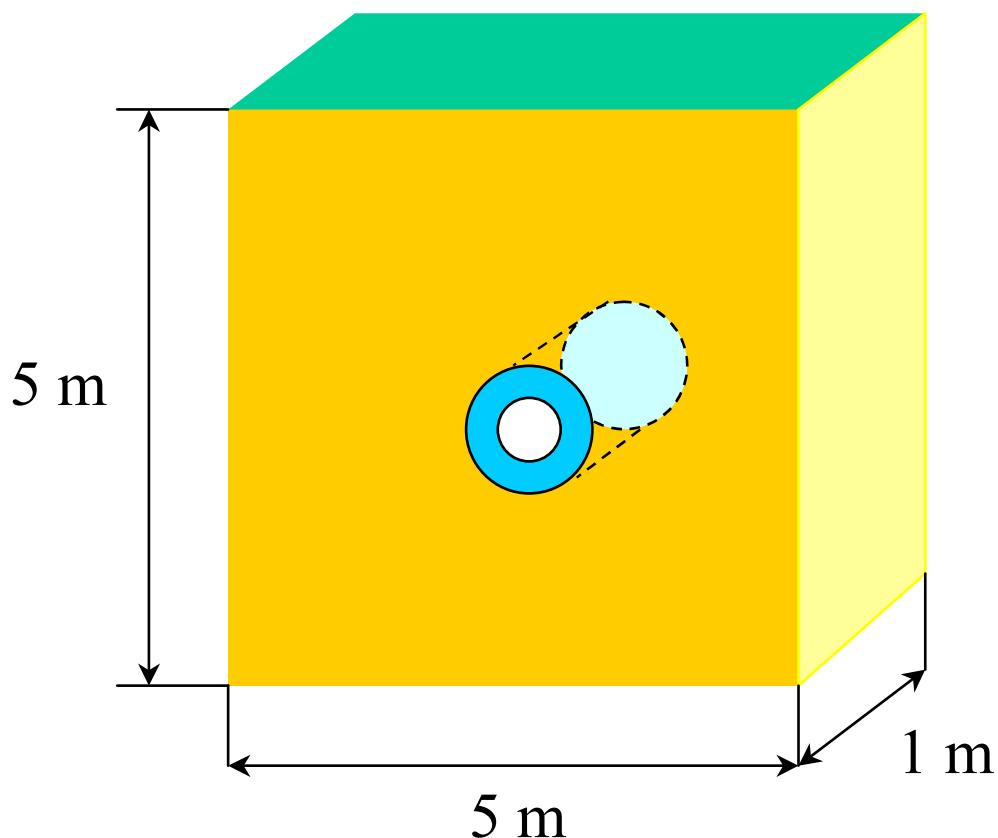
conc_i: Intervention level [mg/kg]

For Benzene with a conc_i of 1 this gives a quantity of:

$$Q = 25 \cdot 1400 \cdot \frac{1}{1000} = 35g$$

For an area of 5 by 5 meters in radial direction around the pipe, see Figure 1-1, a pipe length of 1 meter may therefore not loose more than 35g of Benzene per meter length of pipe during its total service live.

Target values from an environmental case point of view are much lower respectively 0.01, 0.01 and 0.1 mg/kg.

**Figure 1-1**

Based Dutch regulation, in an area of 5 by 5 meters in radial direction around the pipe, a pipe length of 1 meter may not loose more than 35g of Benzene per meter length of pipe during its total service live.

Table 1-1 The target value and the intervention levels of Benzene, Toluene and Xylene

Chemical	Target value [mg/kg dry soil]	Intervention level [mg/kg dry soil]
Benzene	0.01	1
Toluene	0.01	130
Xylene	0.1	25

Appendix 2

ULLG fluid and simulated medium

Table 2-1 ULLG Medium

Carbon number	ULLG composition 23-06-2004			total WT%
	Wt % Naphthenes	Wt % Paraffins	Wt % Aromats	
3	0	1.92	0	1.92
4	0	5.72	0	5.72
5	0.97	9.82	0	10.79
6	9.85	11.64	0.6	22.09
7	17	8.83	2.37	28.2
8	10.16	5.99	2.53	18.68
9	3.12	3.14	1.16	7.42
10	1.07	1.45	0.19	2.71
11	0.21	0.42	0	0.63
12+	1.69	0	0	1.69
Total			6.85	
Tolerance	0.38	0.45	0.2	99.85

Table 2-2 Simulated medium

solvent	gram	Mol	Mol Frac	%W	type	Molfraction	weight %
CYCLOPENTANE	10	0.14	0.014	1.1			
CYCLOHEXANE	280	3.33	0.317	30.3			
CYCLOHEPTANE	76	0.77	0.074	8.2	naphtenes	0.40	40
pentane	175	2.43	0.231	18.9			
hexane	116	1.35	0.129	12.6			
heptane	88	0.88	0.084	9.6			
octane	60	0.53	0.050	6.5			
nonane	31	0.25	0.023	3.4			
decane	15	0.10	0.010	1.6			
undecane	4	0.03	0.003	0.5	alkanes	0.53	53
benzene	6	0.08	0.007	0.6			
toluene	24	0.26	0.024	2.6			
Xylene	37	0.35	0.033	4.0			
cymene	2	0.01	0.001	0.2	aromatics	0.066	7
totaal	924	10.51	1.000	100.0			
Mol weight	88.0						
volume	500	cc					
weight	358.4	gram					
density	0.717	gram/cc					
volume	1289	ltr					

Appendix 3

Determination of the permeation coefficient

1. Weight change measurements

Small plate specimens of HDPE^{iv} with a dimension of 25.9 x 8.3 x 5.0 [mm] were machined from an actual liner of a Reinforced Thermoplastic Pipes^v. The specimens were used to determine the weight change as a result of exposure to the test media. The experiments were continued until saturation was reached.

The weight of the specimens was determined before starting the exposure using an analytical balance^{vi}. After a specified exposure period, specimens were removed from the autoclave and transported to the testing facilities. At the testing facilities the specimens were dried with a paper tissue. After drying the weight of the specimens were determined. The percentage change in weight ΔW_{100} was calculated as follows:

$$\Delta W_{100} = \frac{W_e - W_o}{W_o} \cdot 100 \quad (1)$$

where

W_o is the initial weight of the specimen

W_e is the weight of the specimen after exposure

Following exposure temperatures 80, 62, 55, 32 °C were applied in order to be able to interpolate and extrapolate to envisaged operating conditions.

The weight changes of the specimens as function of time for the different temperatures in given in Figure 3-1.

2. Calculation of the permeation coefficient

The permeation of fluids through a polymer occurs in steps of dissolution of a fluid in the polymer and diffusion of the dissolved fluid. The best definition for permeability is

$$P = \frac{\text{(quantity_of_permeant)} \times \text{(film_thickness)}}{\text{(area)} \times \text{(time)}} \quad (2)$$

For the calculation of permeation through polymer pipe the following unit is considered the most practical: [gr mm / m² day], since its thickness is often given in [mm] and the area in [m²].

Permeation from a pipe will most likely be a matter of days or even years therefore days are preferred as unit time over seconds.

The product of the diffusion coefficient D and the solubility coefficient S is referred to as the permeability coefficient.

$$P = D \cdot S \quad (3)$$

^{iv} TUB172 HDPE

^v Supplier Pipelife, product name Soluforce

^{vi} Satorius analytical balance type 1872, serial nr. 3503192

Typical unit for D is [mm²/s], for S [gr/mm³].

Using equation (3) this gives

$$P = \frac{mm^2}{s} \cdot \frac{gr}{mm^3} = \frac{gr \cdot mm^2}{mm^3 \cdot s} = \frac{gr \cdot mm}{s \cdot mm^2}$$

Both D and S can be determined from the weight change measurements. The solubility coefficient S can directly determined from the weight change of the saturated specimen.

The diffusion coefficient D can be calculated using the following procedure generally denoted as the ("Slope Method").

The diffusion coefficient of the test media in the HDPE can be calculated using the following equation [2]:

$$D = \pi \cdot \left(\frac{wt}{4 \cdot M_e} \right)^2 \cdot \left(\frac{M_1 - M_2}{\sqrt{t_1} - \sqrt{t_2}} \right)^2 \quad (4)$$

In which:

- D is the overall diffusion coefficient,
- M₁ and M₂ are the percentage of fluid uptake at times t₁ and t₂ respectively
- wt is the wall thickness of strip specimen and,
M_e is the fluid equilibrium/saturation level.

The term:

$$\left(\frac{M_1 - M_2}{\sqrt{t_1} - \sqrt{t_2}} \right)$$

Is the slope of the linear portion of the plot of M against the square root of time, see Figure 3-1.

Equation 4 provides the one-directional diffusion coefficients D_x in the case of isotropic thin sample strips (wt << l and wt << b) where the fluids entering the parallelepiped specimen though the edges can be neglected.

The dimension of the strips specimens applied in this investigation did not fulfil this requirement and therefore a correction denoted as an edge correction or size factor must be introduced [4]. In that case the one-directional diffusion coefficients D_x is related to the sample dimensions thickness (wt), length (l), width (b) and D as:

$$D_x = D * \left(1 + \frac{wt}{l} + \frac{wt}{b} \right)^{-2} \quad (5)$$

The temperature dependence of P, D and S.

The temperature dependence of the permeability coefficient P, the diffusion coefficient D, and the solubility coefficient S can be expressed by:

$$P = P_0 * e^{\frac{-E_p}{RT}} \quad (6)$$

$$D = D_0 * e^{\frac{-E_d}{RT}} \quad (7)$$

$$S = S_0 * e^{\frac{-E_s}{RT}} \quad (8)$$

Consequently

$$E_p = E_d + E_s \quad (9)$$

In which:

E_p is the activation energy of permeation,

E_d is the activation energy for diffusion,

E_s is the heat of solution.

Values of E_p , E_d and E_s are typically given in [kJ/mol].

R is the gas constant [8.3144x10-3 kJ/K mol]

T is the temperature in [K].

Sometimes equations 7, 8 and 9 are simplified. As an example for equation (7)

$$D_x = A * e^{-k \cdot \frac{1}{T}} \quad (10)$$

By linear fitting of the natural logarithm of the values of the one directional diffusion coefficient (D_x) with the reciprocal value of the corresponding absolute temperature ($1/T$) the parameters A and K of Eq. (10) can be calculated.

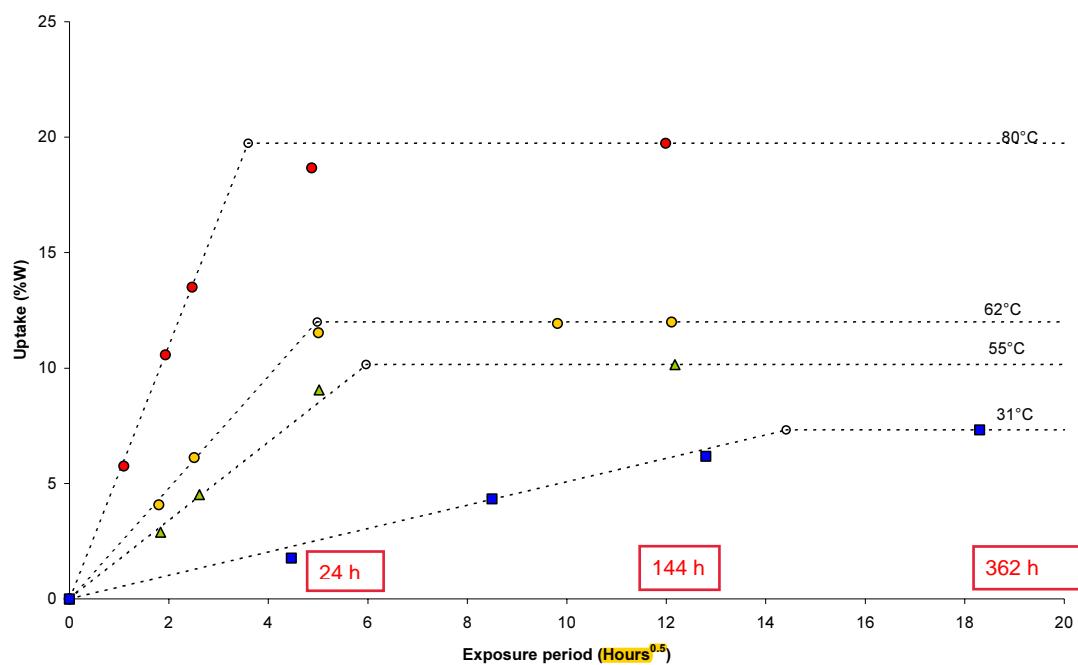


Figure 3-1

Weight change of HDPE specimens as a function of time due to the exposure to the simulated gas condensate at 31, 55, 62 and 80 °C.

Appendix 4

Estimation of hydrocarbon fluid permeation through a Polyethylene based re-inforced thermoplastic pipes

Questions posed by Naren Ramaiah (email dated 23.09.2004)

Answers in red by René Jacobs and William Veerkamp

- 1] Is there any reference to allowable HC content levels in soil and ground water in EP 95-0370 Environmental Impact Assessment?

[Janssen, Frans FAH OGNL-OGEI/2]

I do not know, I will ask advice from our HSE people in The Hague.

The Shell Group and specifically E&P have issued a lot of guidance documents on aspects related to environmental management. However, only the EP 95-0000 series contains documents with environmental quality standards (EQS), for air (0375), water (0380) and soil and ground/water (0385). The last document was issued in 1995 and could well be outdated. It gives, however, a nice overview of the leading regulatory systems in the US, Canada and The Netherlands.

General guidance in EP 95-0380 on usage of the EQSs follows the overall approach of the E&P MES (Minimum Environmental Standards): manage the HSE risks down to an ALARP level.

In that context the EQSs shall be used for contaminated sites as screening criteria for further action, e.g. more detailed site investigations or clean-up.

The EQSs are not meant to be the upper limits for soil quality, i.e. the levels to which soil can be contaminated without breaching the law.

Risk assessment for the RTP shall be carried out and is meant to demonstrate that the total amount of material permeating through the polyethylene would be such that no damage is to be expected to the environment. In other words: the soil cannot be used as a buffer with self-purification.

- 2] I think in BSP we do not have a specific value of allowable HC content in soil or ground water; However we have an HSE document for contaminated site management guideline [attached] which only indicates on management but not specific values; I still need to engage our HSE to get their views but before that I need to understand fully well on the contamination due to permeation.

<< File: Contaminated_Site_Management_Guidelines_(Rev._1).doc (Compressed) >>

[Janssen, Frans FAH OGNL-OGEI/2]

Briefly browsing the document, I noticed that there are several reference document that seems to have such values in it. As for comment 1 suggest to contact HSE experts.

See comments above. In addition, the guidance is on accidentally contaminated soil and groundwater and how to manage these situations in the case remediation is not possible (use of the site) or practicable (both technically and/or economically). As stated above the soil is different from surface water or air where we allow a certain emission/discharge and rely on self-purification.

- 3] As the liquids are coming from offshore pipelines, the temperature can never exceed the ambient temperature of 25deg C, so we should not make reference to permeation due to higher temperature which could mislead in the judgment of contamination.

[Janssen, Frans FAH OGNL-OGEI/2]

In the final version of my document I will make sure that TESTS have been performed at higher temperatures, but that operation takes place at 25 °C.

I will only mention the permeation of the RTP at 25 °C

For the permeation modeling and an assessment of risk for people and the environment, the most likely operational conditions (such as pipeline temperature and pressure, but also soil type (sand/peat/clay/etc.) and relative groundwater level) shall be taken into account.

- 4] Prorating the immediate permeation to time may not be correct. In terms of target and intervention levels on time basis, I believe we should consider the effect of soil and ground water permeation. This would further reduce the concentration of permeated HC in time. Also since it rains heavily in Brunei, ground water seepage is high. Also since the ground water table is high the soil density would be submerged density, which would be around 400kg/m³ i/o of 1400 kg/m³.

[Janssen, Frans FAH OGNI-OGEI/2]

As for comment 1 and 2 this is clearly an HSE expert issues.

Fate of the permeated hydrocarbons – let's limit this assessment to the most hazardous linear low molecular weight and monocyclic hydrocarbons – is determined by 5 processes, i.e. abiotic degradation, biodegradation, dispersion/ dilution, adsorption to the soil particles and evaporation from the soil to the air compartment.

With a continuing supply of permeating hydrocarbons (about 0.6 g/m.day according to Frans Janssen), the above-mentioned processes shall at least be equal or greater, otherwise a build-up of hydrocarbons around the RTP is to be expected.

Benzene is readily biodegradable. The biodegradation rate in soil is, however, very low as oxygen and nutrients are soon limiting. For instance, 10 mol of nitrate is required per mol of benzene degraded.

Abiotic degradation is insignificant under the local conditions.

Depending on the soil type, adsorption can be significant: clay and peat in particular have a high adsorption capacity. However, the capacity is limited once the clay is saturated.

If released to soil, benzene will normally evaporate very rapidly. However, due to the high groundwater level in the RTP trench, dissolution into groundwater (solubility benzene is 1800 mg/l) can be the dominating process.

From the above it can be concluded that dispersion / dilution of permeated hydrocarbons is the only process that will reduce significantly the concentrations around the RTP. This process will certainly be enhanced by the rainfall and local hydrology. One should realize that the solubility of these hydrocarbons is measured in mg/l and the toxicologically derived acceptable or action levels is in the order of ug/l (i.e. a thousand fold lower). In other words: dilution could become the solution for this pollution. However, this principle has been sworn off a long time ago and is for most countries a legally unacceptable solution.

5] Is there any limitation/governance on permeation in the DEPs?

[Janssen, Frans FAH OGNL-OGEI/2]

In principle yes, most DEP's include under HSE the following clause "All procedures should comply with the relevant national legislation".

Therefore any legislation regarding soil and ground water pollution must be respected.

6] Looking only at the Dutch law may be misleading since we cannot fully understand the underlying facts and basis, we also need to have other similar comparative document. Have you come across similar laws in other parts of the world? Earlier when we were trying use RTP for offshore riser, we almost disregarded RTP with the impression that RTP was totally banned in Holland, so we need to be careful in interpretation.

[Janssen, Frans FAH OGNL-OGEI/2]

Yes there are many similar laws, again an HSE expert issue.

RTP in the Netherlands are only banned when the level of Hydrocarbon permeation causes the soil to be polluted. The use of RTP for example for Pure Natural Gas transport or Water is allowed.

The Dutch law is certainly not the only relevant source; see references to EP 95-0380 above. However, since the EP document was issued in 1995, important Dutch documents on development of environmental quality standards were published and particularly the report entitled "Environmental Risk Limits in The Netherlands" (1999) is most valuable. This document provides also the scientific background information used for the derivation of the risk limits.

The soil quality standards Frans Jansen has presented in his Table 1-1, originally came from the Dutch 1999 report, where also the eco-toxicity and human toxicity data are presented. These EQSs refer to short-term exposure conditions and do not take (bio)degradation processes into account. However, as discussed above under 'comment [4]' these degradation processes are not relevant for the RTP environment.

The values for the "intervention level" in Frans' Table 1-1 actually refer to a concentration in the soil above which the risk of adverse effects (on human beings and ecosystems) is unacceptable.

Intervention values for groundwater

The "intervention values" for groundwater are, however, more relevant for the RTP environment:

Substance	Target value (µg/l)	Intervention value (µg/l)
Benzene	0.2	30
Toluene	7	1000
Xylene	?	?

Assessment of the risk of RTP usage for the BSP hydrocarbon fluids, leads to the following conclusions:

- Volume of permeated fluids is approximately $0.45 \text{ g/m}_{\text{run}} \cdot \text{day}$.
- 6.85 % of this fluid consists of monocyclic hydrocarbons (benzene, toluene and xylene), i.e. 0.031 g BTEX .
- As the RTP lays below the groundwater level, most of the substances will immediately dissolve and will be hydrologically dispersed.
- After 1 day diffusion in the groundwater to a distance of 0.5 m from the RTP (cube of $1 \times 1 \times 1 \text{ m} = 1000 \text{ liters of water}$), the average BTEX concentration will be approximately $31 \mu\text{g/l}$, of which 9 % (0.6 % of 6.85 %) ($2.7 \mu\text{g/l}$) benzene.
- without a strong groundwater flow the acceptable concentration of $30 \mu\text{g/l}$ will be exceeded within a few days

So, within a few days a concentration in the groundwater is reached that poses a serious risk of adverse effects. When the RTP lays in a trench with dry soil it will take longer before the applicable risk limits will be exceeded.

In addition US groundwater criteria for benzene would also be in the order of $0.1 - 1.0 \mu\text{g/l}$.

- 7] Our earlier understanding was that RTP is suitable with 10 % aromatics upto 65°C , how does this statement hold in view of the tests? does this contain some factors like in comment [4] above?

[Janssen, Frans FAH OGNL-OGEI/2]

The 10% aromatics up to 65°C , the suppliers are quoting is referring to the long term pressure containing performance of RTP, this has nothing to do with permeation. Hence there is also no link to comment [4].

g/l).

- 8] I think the term "intervention" should have definition of determining the actual levels of contamination due to permeation rather than soil cleaning, the determination levels will decide the mitigation as per the document in [2] above.

[Janssen, Frans FAH OGNL-OGEI/2]

Again HSE expert issues.

See explanation under 'comment [6]' above.

- 9] Does the fluid flow in the pipeline have any effect on the permeation levels? Since the pipeline will be operated intermittently, the fluid is pressured and depressurized, I would imagine the fluid would take the least resistant path, i.e., would permeate less when flowing and permeate more when stagnant. This would again affect the total volume of permeation in time.

[Janssen, Frans FAH OGNL-OGEI/2]

For gasses the pressure has an influence for liquids not, therefore in this case the intermittently fluid flow does not have an effect on the permeation rate.

- 10] Does the permeated HC develop any pressure during polymer permeation?

[Janssen, Frans FAH OGNL-OGEI/2]

I do not understand your question, please clarify.

Appendix 5

Scouting studies on an external permeation barrier foil, interim results

Pipelife supplier of Reinforced Thermoplastic Pipe suggested a Multilayer Foil that includes an Aluminium layer as external permeation barrier for hydrocarbon liquids.

1. Foil Details

Following details on the foil were provided^{vii}:

We have looked at some options for the permeation tight barrier film for Brunei. The selection criteria were:

1. Sufficiently thick metallic (aluminium) barrier layer, to ensure permeation tightness.
2. High tear strength and sturdiness.
3. Available on short notice.
4. Proven technology.

We have found a suitable film in the product range of WIPAK (www.wipak.com), Europe's nr1. supplier of multilayer films. This is a 5 layer film consisting of:

1. PET (thermoplastic polyester) support film, 12 micrometer, to ensure tensile and tear strength.
2. Bonding layer.
3. Aluminium, 9 micrometer, sufficiently thick to ensure 100% permeation tightness.
4. Bonding layer
5. PE film, 70 micrometer, for added strength and sturdiness, and to enable thermal bonding.

The total thickness is 100 micrometer.

This is a professional quality permeation tight packaging film, and comes on rolls of 1380 mm width. We think a multi-layer film is to be preferred over a thick aluminium sheet, as the latter have insufficient elongation at break and tear strength.

Note by Frans Janssen.

For future qualification of external permeation barrier the qualification criteria for geomembranes are recommended as a guideline, see Table 5-1.

2. Experimental

Shell Global Solutions measured the weight loss of a sealed bag made from this foil containing an open glass container with a simulated hydrocarbon product mixture. The size of the sealed area was approx. 0.5 m.

The bag was held at a temperature of approx. 23 °C.

Figure 5-1 shows the weight loss of the bag as function of time. After 50 days the bag lost 0.18 gram, which is expected to be caused by fluid permeating through either the foil or the seal or the foil and the seal.

^{vii} Dr. Bert Dalmolen, technical marketing manager, Soluforce, Pipelife Nederland BV via E-mail

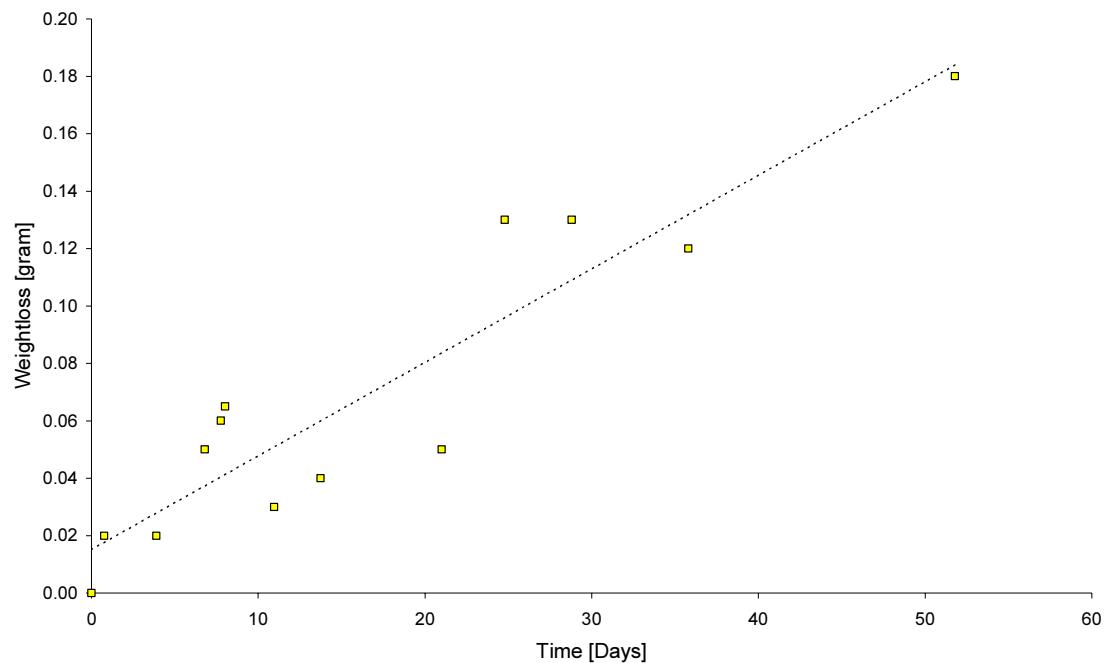
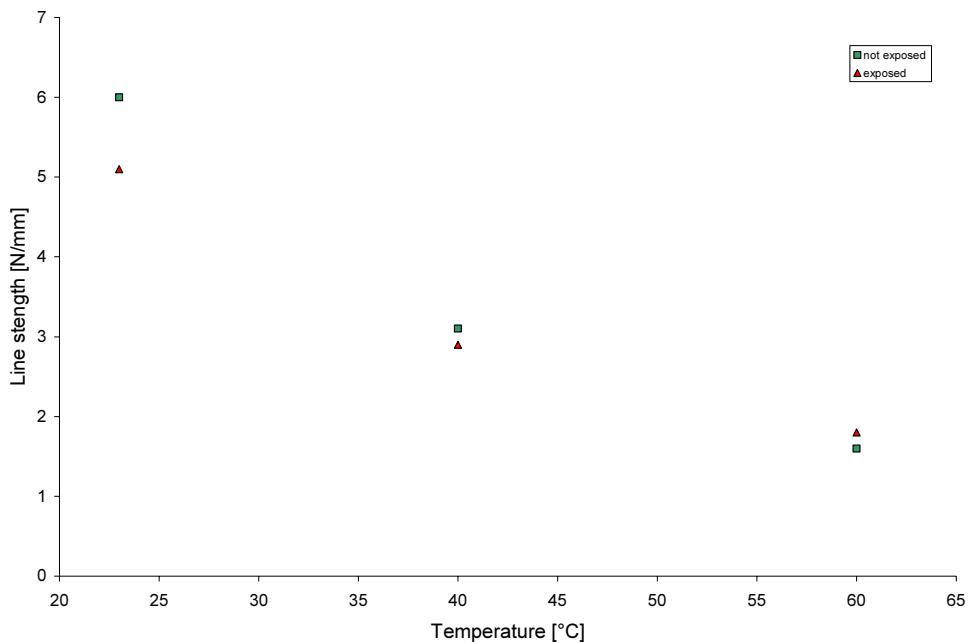


Figure 5-1 weight loss of the bag as function of time

The strength of the seal was determined on separate specimens of the foil as a function of temperature and fluid vapour exposure. Results are given in Figure 5-2.

The strength values are peel strength values.

**Figure 5-2**

The strength of the seal on separate specimens of the foil as a function of temperature and fluid vapour exposure

3. Discussion of the results.

3.1 Permeation

The weight loss results show that the foil is not an absolute barrier for the hydrocarbon fluid, however depending on the criteria of the application might be fit for purpose. The trend of the weight loss with time is linear. The average loss per meter per day is 0.003 gram.

The loss of an RTP without barrier per meter per day is 0.45 gram, the barrier thus reduces the permeation with a factor of $0.45/0.003 = 150$.

In Appendix 4 the time to reach intervention levels for the RTP without barrier was estimated to be a few days. With the suggested foil this would be a factor 150 longer, therefore say one year. For a service life of 20 years a further reduction of the permeation by a factor of 20 would be required, that is a factor 3,000 (150×20) compared to the RTP without barrier.

3.2 Seal strength

In line with the typical characteristics of thermoplastic polymers the strength of the seal, a Polyethylene-Polyethylene thermal bond, reduced with increasing temperature.

Exposure to the fluid vapour only causes a limited additional reduction in strength. The strength of the seal appears fit for purpose for the expected vapour pressures inside the barrier foil.

Table 5-1

External Permeation Barrier compared with Geomembranes. Specifications. General test list for geomembranes^{viii} as found on the Internet

TEST	TEST DESIGNATION
Seam Peel Strength	ASTM D 4437
Seam Shear Strength	ASTM D 4437
Thickness	ASTM D 751
Density	ASTM D 1505
Melt Flow Index	ASTM D 1238, cond E
Carbon Black Content	ASTM D 1603, ASTM D 4218
Carbon Black Dispersion	ASTM D 3015, ASTM D 5596
Tensile Properties	ASTM D 638
Puncture Resistance	ASTM D 4833, FTMS 101C Method 2065
Tear Resistance	ASTM D 1004
Notched Constant Load SCR	ASTM D 5397
Environmental Stress Crack Resistance	ASTM D 1693
Volatile Component Compound	ASTM D 1203 (A)
Water Absorption	ASTM D 570
Tensile Modulus of Elasticity	ASTM D 638
Tensile Impact Strength	ASTM D 1822
Thermal Shrinkage	ASTM D 3417
Dimensional Stability	ASTM D 1204

viii <http://www.geospec.uk.com/geomembranes.htm>



Procedure application of permeation barrier

1. Dig trench ;
2. Apply sand bed of approx. 125 mm ;
3. Put permeation barrier foil (1100 mm width) on top of sand bed in trench;
4. Install and weld pipe(s) on surface next to trench ;
5. Lower pipe(s) in trench on the unfolded foil ;
6. Take foil edges together and thermo-seal the seam ;
7. Fold barrier foil neatly on pipe(s) and fix with adhesive tape ;
8. Back fill the trench with a layer of 125 mm of sand ;
9. Back fill remainder of trench with original soil ;

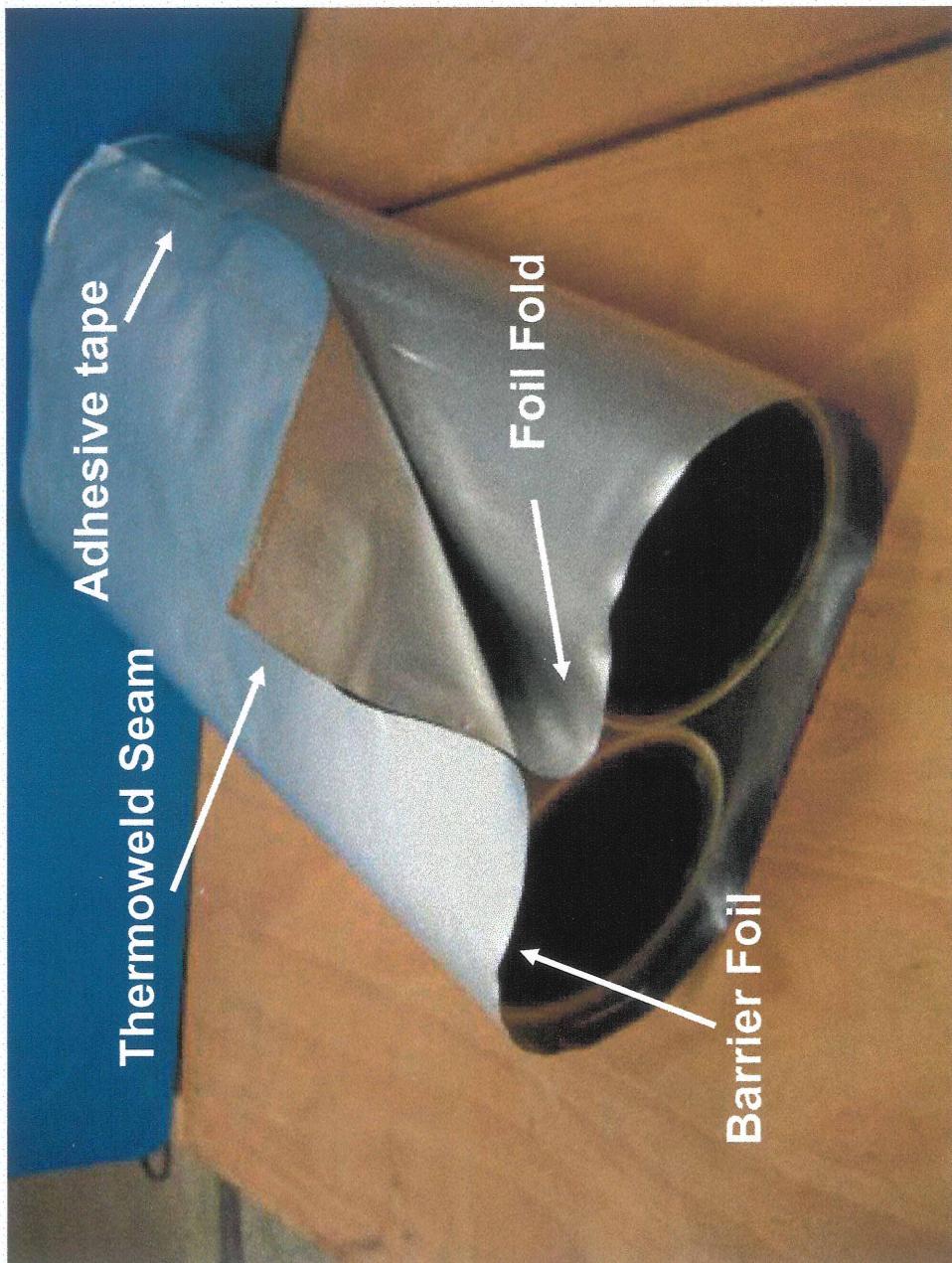
The logo for Soluforce, featuring the word "Soluforce" in a blue, bold, sans-serif font with a registered trademark symbol (®) at the top right.

Principles for road and river crossings

1. Directional drilling of a thick walled HDPE sleeve pipe (ID>200 mm), provided by Pipelife ;
2. Pull Soluforce pipe through sleeve pipe ;
3. Connect barrier foil to ends of sleeve pipe with self adhesive tape ;
4. Back fill trenches.

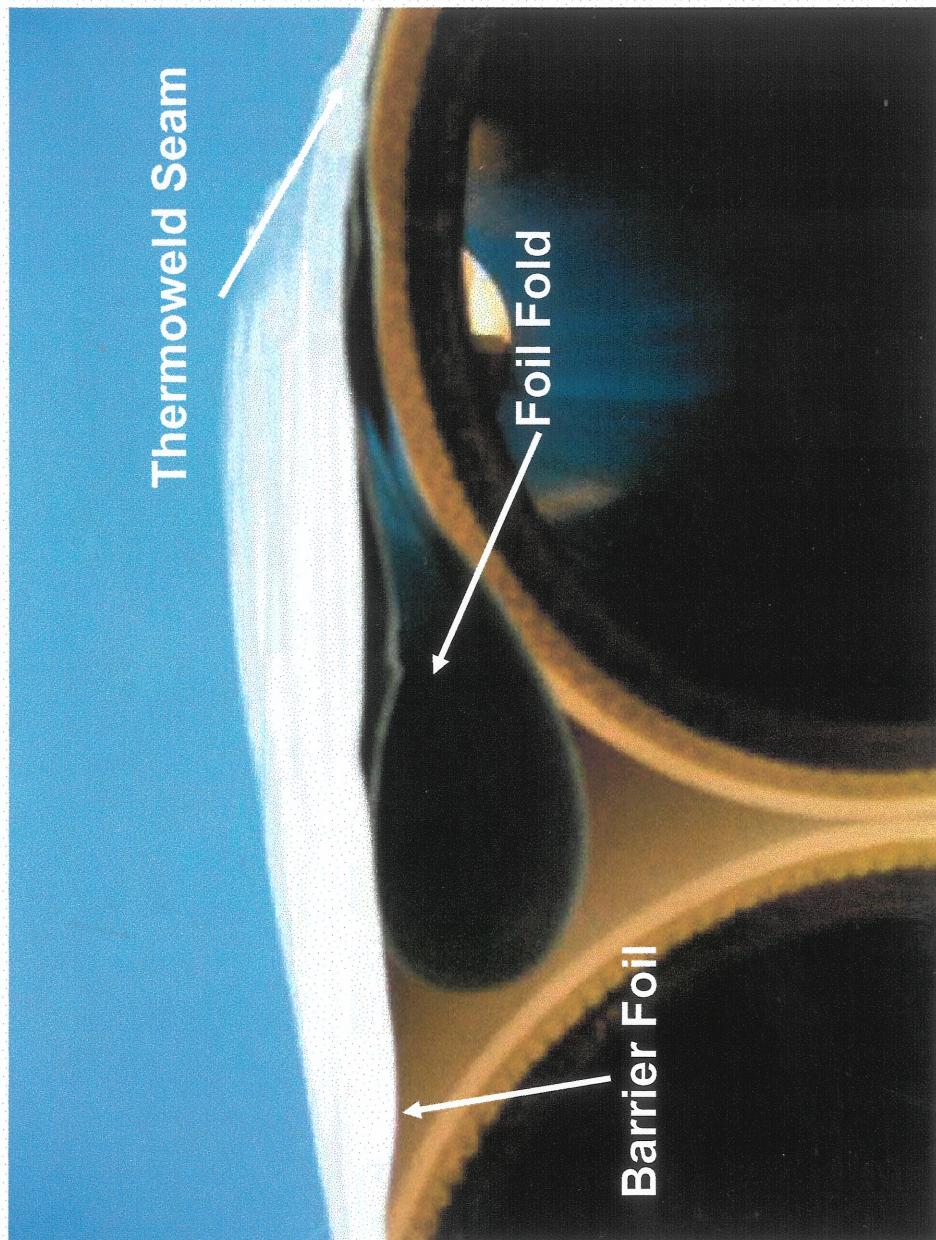
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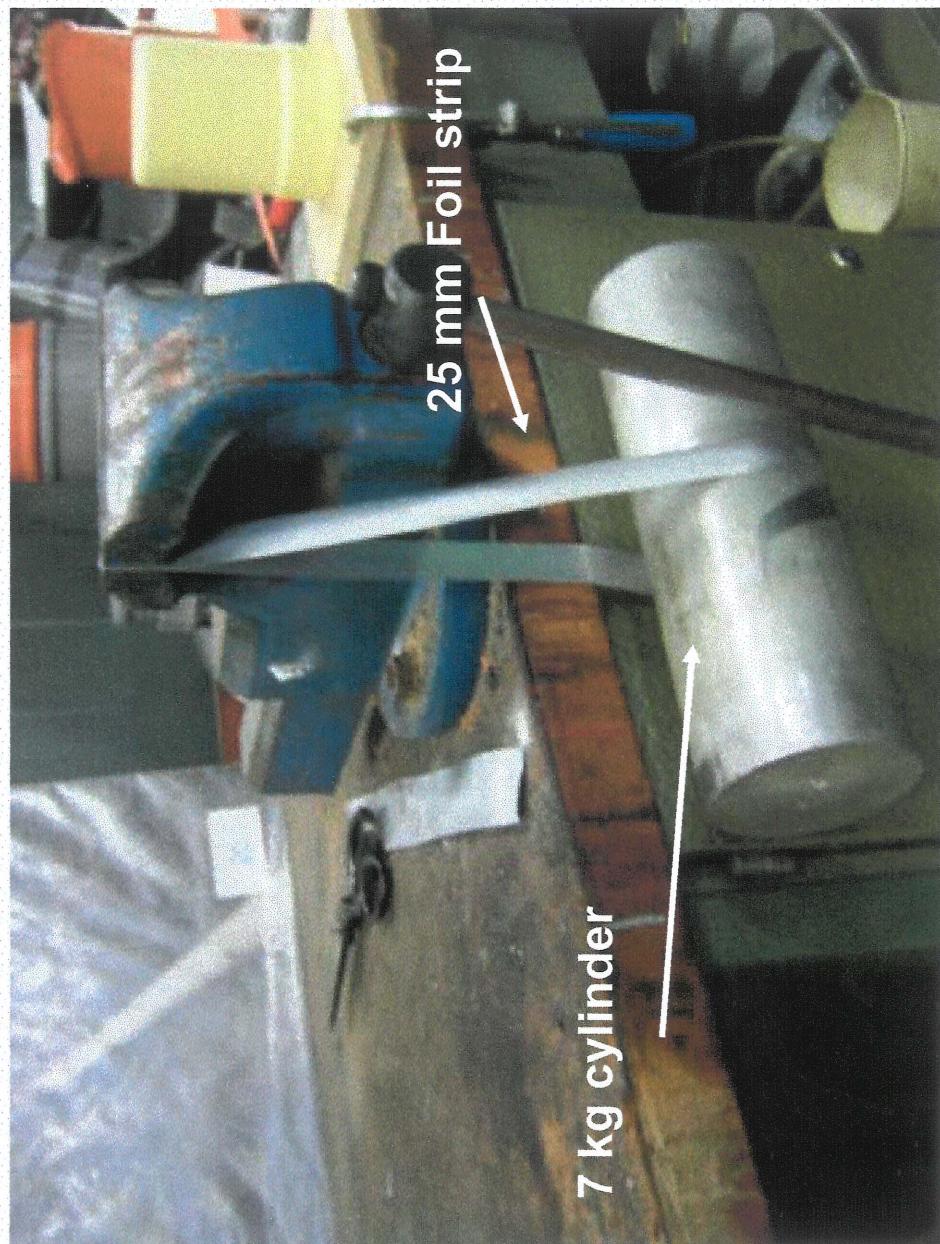
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Illustration of foil strength



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