

Guidance on the use of plastic membranes as VOC vapour barriers

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Summary

Buildings are often constructed on sites where volatile organic compounds (VOC) are present in the ground. This publication provides guidance on the use of plastic membranes to reduce vapour migration into buildings. It discusses vapour transport mechanisms that occur in membranes, factors that influence this and the test methods available for determining the rate of vapour permeation. It then explains how to use the results in a risk assessment. Durability and resistance to damage when plastic membranes are exposed to VOCs is a concern and the guide considers the potential for degradation and which tests methods are suitable to assess performance. Physical damage during and after installation can also occur and the guide identifies the key performance properties that should be specified to minimise the risk of defects. This guide should allow readers to make a robust evaluation of the contribution to membranes to reducing indoor inhalation risk from VOCs in the ground and to specify the most appropriate type of membrane for any given site.

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Glossary

Challenge chemical	Any chemical used to assess the durability or permeation rate of a membrane when exposed to that chemical.
Hydrocarbon resistant	The ability of a membrane to remain serviceable when exposed to a hydrocarbon challenge chemical, especially VOCs (ie to continue to prevent gas or VOC ingress). This does not give any indication of the membranes ability to prevent or reduce the migration of VOC vapours through it. Testing to determine resistance to damage from VOCs is discussed in Section 4.2.
Mass flux	Mass of gas that passes through a membrane per unit area per unit time (Welburn <i>et al</i> , 2012). This is the property that is required for use in risk assessments. Note this should be quoted in mg/m ² /h. If the manufacturer's literature does not quote the permeation rate in mg/m ² /h ask them to provide a conversion. It is not possible to compare the performance of different membranes without using test data obtained using the same test method and presented in the same units. The mass flux is calculated from permeation rate tests and is the primary transport mechanism for VOCs diffusion.
VOCs	In this publication, VOCs are considered to comprise organic compounds that are volatile under 'normal' environmental/atmospheric condition. They may be found in the ground in the solid, liquid and dissolved phase form as well as in gaseous phase.
VOC barrier	<p>A membrane is considered a barrier to a specific challenge VOC if its steady state diffusive mass flux, when tested in accordance with ISO 15105-2:2003, is less than that required to reduce the risk associated with VOC ingress to an acceptable level.</p> <p>The required level of mass flux will be site specific and depend on a number of factors such as the concentration gradient across the membrane and the ventilation provided in the building. For this reason a generic minimum value of mass flux cannot be specified for VOC barriers. In this guide the term VOC barrier is used, rather than hydrocarbon barrier (which implies the membrane will be a barrier to more than just VOCs). The supplier of a VOC barrier should provide all the necessary test data referred to in this guide to allow risk assessors to determine its suitability for a given site.</p>
VOC permeation rate	The rate at which a VOC challenge chemical (liquid or vapour) will pass through a unit thickness of the membrane per unit area per unit time (Welburn <i>et al</i> , 2012). Units are mg/m ² /h. Testing to determine the permeation rate is discussed in Section 2.3. The permeation rate will be dependent on the source concentration and concentration gradient across the membrane (Scheirs, 2009).
VOC vapours	VOCs in gaseous phase when present in an air space.

Abbreviations and acronyms

BBA	British Board of Agrément
BTEX	Benzene, toluene, ethyl benzene, xylene
CSPE	Chlorosulfonate-polyethylene
DPM	Damp proof membrane
EIA	Ethylene Interpolymer Alloy
EPDM	Ethylene-Propylene-Diene-Monomer
EVOH	Ethylene vinyl alcohol
fPP	Flexible polypropylene
HDPE	High Density Polyethylene
HSP	Hansen Solubility Parameters
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
PCE	Tetrachloroethene
SSPR	Steady state permeation rate
TCE	Trichloroethene
USEPA	US Environmental Protection Agency
VLDPE	Very low density polyethylene
VOC	Volatile organic compounds

1 Introduction

1.1 BACKGROUND

Buildings are often constructed on sites where volatile organic compounds (VOCs) such as benzene, toluene, chlorinated solvents, ethers etc are in the ground. The usual remedial solution is to provide a gas membrane under or over the floor slab, of the same type as used to prevent methane and carbon dioxide migration into buildings. The membranes are often made from polymeric materials and are assumed to break the contaminant pathway by preventing vapour transmission. It is well known that VOCs will migrate through polymeric materials (Welburn *et al*, 2012, ITRC, 2007, Massey, 2003 and Scheirs, 2009). In some cases the permeation rate of contaminants through the membrane is so great that it may not reduce the predicted level of indoor air contamination to acceptable levels, although this will depend on the concentration of vapour in the ground and the nature of the membrane.

A wide variety of gas membranes are available with very different properties and performance characteristics. Limited practical guidance currently exists, which enables a robust evaluation of suitable membranes to enable their specification for use to act as barriers to VOC migration into buildings, however some examples include Welburn *et al* (2012) and ITRC (2007).

This guide does not deal with the issues of chemical attack on plastic materials used as buried, in ground barriers, water pipes, soil reinforcement or similar.

On the basis of current research/evidence (CIEH, 2008) it is very clear that standard damp proof membrane (DPM) material is not suitable to act as a barrier to VOC migration into buildings in any circumstances.

This guide provides additional information on VOC permeation through membranes and complements the information provided by Welburn *et al* (2012). In preparation of the guide due regard has been given to the wealth of experience in studying chemical permeation through plastic materials that is available in the food packaging, protective clothing and other industries.

1.2 PURPOSE OF THIS GUIDE

The purpose of this guide is to provide a summary of the functions of a vapour membrane and the factors that may affect the performance of the membrane in a protection system for a building on land contaminated by VOCs. It goes on to explain how to allow for the presence of the membrane in an indoor inhalation risk assessment. Examples of how to do this are also explained in Welburn *et al* (2012). The results of the risk assessment can help determine the necessary performance characteristics of a membrane for use in a specification.

1.3 RISK-BASED APPROACH

The guide will explain how to take a risk-based approach to the specification of membranes to prevent VOC migration into new buildings. The approach is consistent with CLR 11 (Environment Agency, 2004), and NHBC guidance (NHBC and Environment Agency, 2008a and b) and Welburn *et al* (2012).

Wilson (2008) showed that in the UK the Johnson & Ettinger (J&E) model is not suitable for the most common types of new buildings that do not have basements. It was also suggested that a modular approach allows the properties of a vapour resistant membrane to be incorporated into the risk assessment, provided the barrier properties of the membrane can be adequately modelled.

Membranes should not be the only consideration in VOC vapour risk assessment. Assessment and mitigation of the pathway or link between the source of the VOCs and the building requires consideration of more than just the membrane. So, the risk model should include the membrane (if required), floor slab construction and any underfloor ventilation. Effects in the ground that retard vapour migration should also be considered (eg biodegradation and other processes). With appropriate modelling it is possible to arrive at a rational, defensible protection system that gives a reasonable balance between risks and costs (Baker *et al*, 2009). The use of risk modelling should be fit for purpose, the input and output parameters should be transparent and their source/use justifiable as part of the process. The model should be easily understood and be able to be checked by regulators without access to proprietary software. This will provide regulators and other stakeholders with the necessary confidence in the data and demonstrate how the final design and specification of the vapour protection system has been derived and is suitable for use in the context of the land contamination risks on a site-specific basis.

Assessment of the permanent gases such as methane and carbon dioxide is more concerned with acute health effects or explosions and pressure driven flow. For this reason there is a much greater emphasis placed on redundancy within the protection system and providing multiple levels of protection.

The major issue with VOCs is normally long-term chronic health risks and there is less need for the same levels of redundancy used for permanent gases, although a precautionary approach should still be adopted. The level of redundancy in the protection system will depend on how effective in ground processes (such as biodegradation) and the floor slab construction will be in retarding vapour migration (Welburn *et al*, 2012). The potential for hazardous daughter/by-products from biodegradation processes should also be considered, eg vinyl chloride from chlorinated solvent breakdown.

2 Function of membranes in minimising VOC ingress to buildings

2.1 COMMON MISCONCEPTIONS ABOUT MEMBRANES

At present there are some common misconceptions about vapour transmission through membranes that are marketed as being 'hydrocarbon resistant'. This means that the protection provided could possibly be much less than expected. So, first ask what is meant by hydrocarbon resistant? Does this refer to vapour permeation rate through the membrane or to resistance to degradation when exposed to hydrocarbons and particularly VOCs? The two properties are different (see *Glossary*).

In contrast to how well a membrane withstands chemical attack, permeation measures the rate at which the challenge chemical moves through a membrane at molecular level. The polymer(s) forming the membrane will permeate contaminants depending on how similar the molecular structure is to the challenge contaminant.

There is a common misconception that High Density Polyethylene (HDPE) completely prevents VOC migration through it. VOCs and methane will permeate readily through homogeneous HDPE membranes mainly because the two are of the same species, ie both HDPE and many VOCs are hydrocarbons. However, in contrast to methane and carbon dioxide many VOCs can migrate through it at a rate that is quite high in comparison to the allowable concentrations of those vapours inside buildings. This is illustrated in Figure 2.1. Note the figure is illustrative only and the actual mass flux through the membrane will depend on the concentration gradient across the membrane.

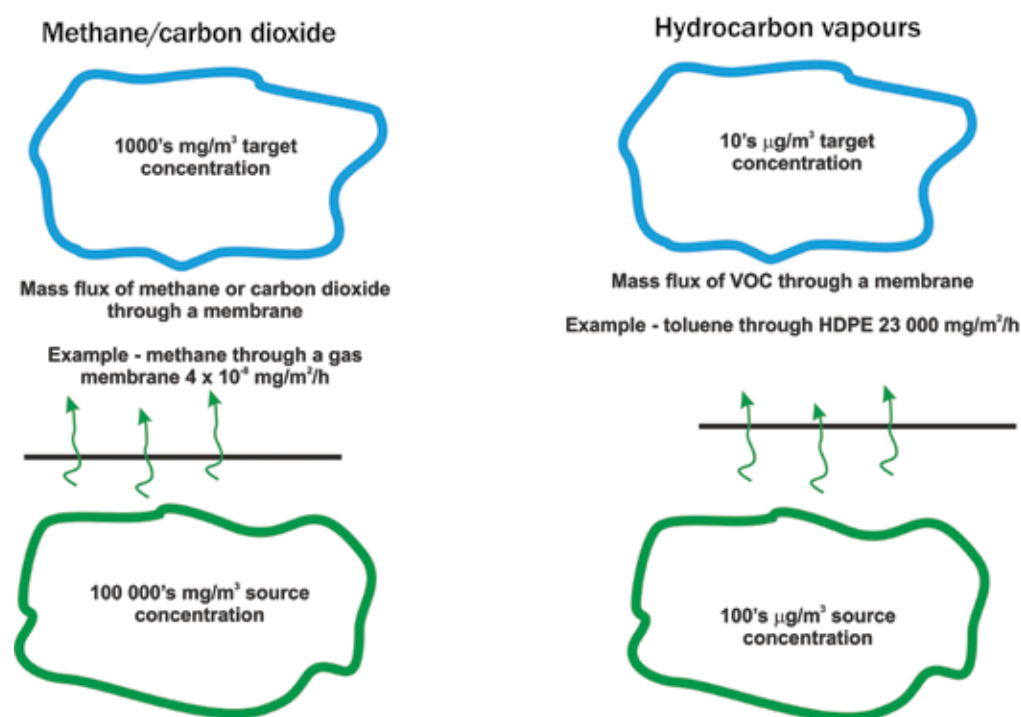


Figure 2.1 Illustration of membrane permeation rate to allowable concentrations inside a building

So, membranes used to reduce VOC migration into buildings will require very low mass flux through them in comparison with the internal allowable concentration of the VOC being considered. Reducing the permeation rate for VOCs by increasing the thickness is not particularly effective or practical in most cases. To halve the permeation rate, the thickness would need to be doubled.

Extensive experimental evidence (August and Tatzky, 1984) shows that benzene, toluene, ethyl benzene and xylenes (BTEX) can permeate rapidly through HDPE if it is exposed to high concentrations of the chemicals (reaching equilibrium concentrations in 10 to 20 days). In some cases they may not be that effective as barriers to these molecules. In light of this it should not be assumed that a membrane alone will block vapour migration of all VOC contaminants into a building and a site specific assessment of any membrane should be completed (see Chapter 6).

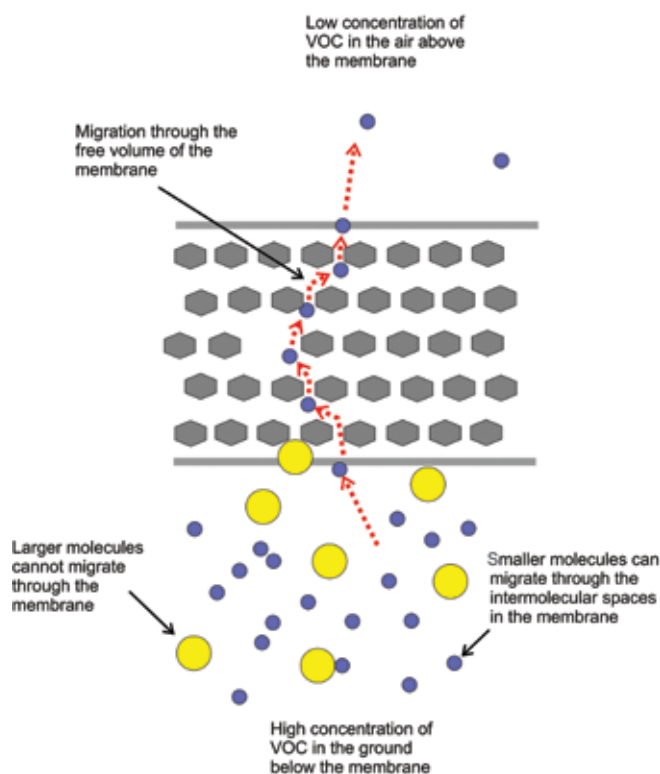
2.2 VAPOUR TRANSPORT MECHANISMS THROUGH MEMBRANES

2.2.1 Factors that affect permeation rate

Vapour permeability will vary greatly according to membrane material and the nature of the vapour. The correct specification for a membrane to act as a barrier to VOC ingress to buildings is critical. However the quality of the membrane is only one factor. If any membrane is poorly installed the main way in which vapours will pass through it will be via holes/punctures, poor joints and seals and/or other defects, rather than through the material itself. If the quality/specification of the membrane and integrity of the installation is adequate to minimise such defects the dominant mode of vapour transport will be via molecular diffusion through the membrane. This is in contrast to transport mechanisms for methane and carbon dioxide in soils, where the main driving force is often (but not always) the pressure head.

The key fact about the concentration gradient is that it depends both on the amount/concentration of contaminant in the soil or groundwater and the solubility of the contaminant in the polymer surface exposed to the contaminant. If it is insoluble (eg water exposed to the surface of polyethylene) then despite a high concentration of water in the soil and despite the fact that water is a very small molecule,

little water will permeate because it is insoluble. If it is soluble (eg benzene exposed to the surface of polyethylene) then the concentration gradient between one side of the membrane and the other can be large, so permeation will be large, and as a result the membrane will be ineffective as a vapour barrier.



Molecular diffusion is driven by a concentration gradient with molecules moving from zones of higher to lower concentration. Any given molecule may move through free spaces within the membrane. The speed at which it moves depends on the amount of free volume in the membrane structure. Typically membranes made of rubbers have large amounts of free volume and small molecules from the contaminant source, eg benzene, will readily move to fill this free space, ie an area of lower concentration (Figure 2.2).

Figure 2.2 Diffusion of VOCs through the free volume of a membrane

The regular, symmetrical structure of HDPE means it is highly crystalline with about 20 per cent that is amorphous. The free volume is low but benzene permeation will take place through the free volume of the amorphous areas. If one of the hydrogen atoms is substituted with a methyl group (flexible polypropylene) or chlorine (PVC) the crystallinity is reduced and the free volume increases. Smaller molecules (eg benzene) will move faster than larger molecules (eg paraffin). In summary, permeation depends on:

- ☐ the concentration gradient
- ☐ the nature of the membrane (free volume)
- ☐ thickness of the membrane
- ☐ the solubility of the contaminant in the polymer (which depends on molecular structure and polarity, see Section 2.4)
- ☐ the shape/size of the molecule and whether it is streamlined (Figure 2.3).

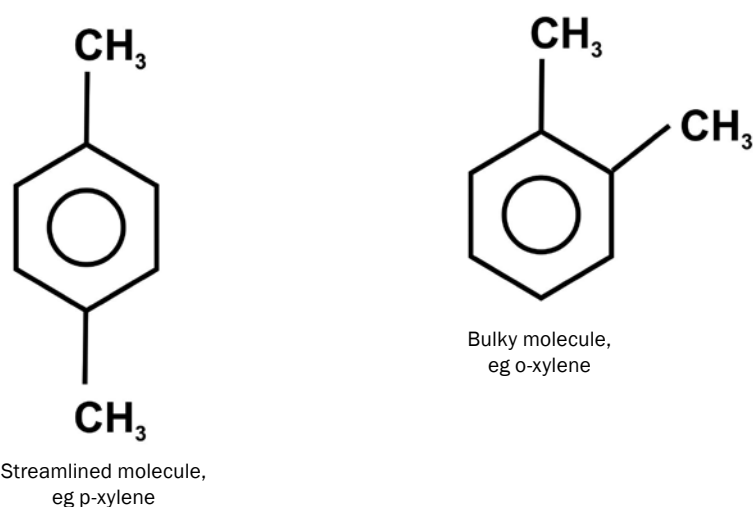


Figure 2.3 Structure of molecules affects permeation (after Scheirs, 2009)

The permeation of vapours through a membrane is summarised in Figure 2.4.

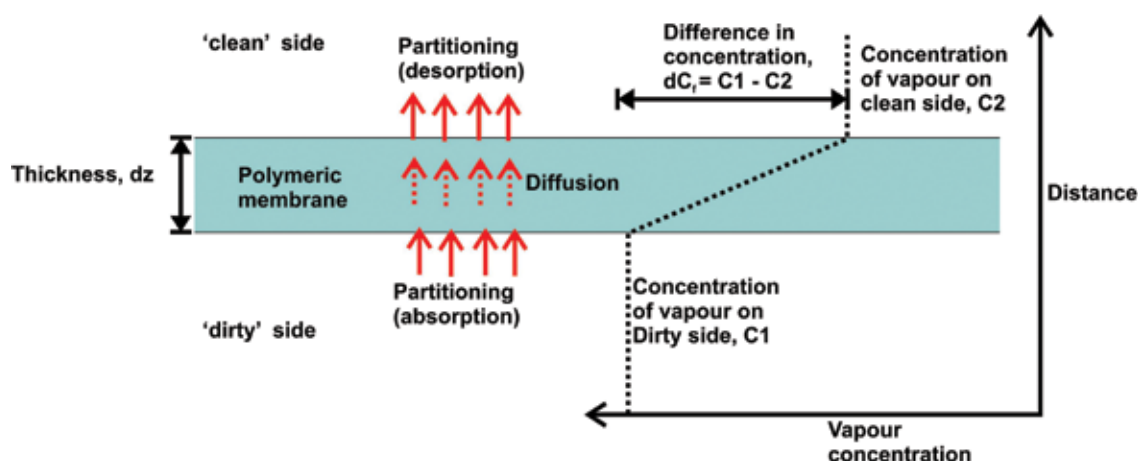


Figure 2.4 Permeation of vapours through a membrane

The permeation rate will also vary depending on whether the membrane is saturated with the challenge chemical (Wilson, 2008b). Over time VOCs can partition into the membrane until it is saturated (this will depend on the concentration of the VOC in the ground). This will cause the membrane to swell and the permeation rate will increase once the membrane is saturated.

When a membrane is exposed to a VOC the molecules first of all diffuse into the membrane. Eventually they will reach the other side of the membrane and breakthrough occurs. Before the breakthrough point there is essentially no permeation as the chemical is migrating into the membrane material but has not yet passed completely through it. The permeation rate is constant at zero. After breakthrough the permeation builds up to its steady state (ie constant equilibrium) value as the membrane becomes saturated with the VOC. The steady state value may be achieved within days in some cases (Chin *et al.*, 2013).

2.2.2 Available data on permeation rates

There is limited, readily available, peer reviewed data on the permeation rates through membranes used in building construction. One set of data for two particular VOCs (benzene and toluene) has been published in a series of papers by Islam and Rowe (2001), Sangam and Rowe (2009), McWatters and Rowe (2009), and McWatters and Rowe (2010). This is summarised in Table 2.1.

Table 2.1 Examples of permeation coefficients for VOCs through membranes (vapour phase)

Material	Chemical	Permeation coefficient (m ² /s)	Thickness of material (mm)	Source
Nylon VBP15 coextruded LLDPE:polyamide:LLDPE	Benzene	0.02×10^{-10}	0.38	McWatters and Rowe (2010)
	Toluene	0.02×10^{-10} to 0.03×10^{-10}		
EVOH coextruded LLDPE:EVOH:LLDPE	Benzene	0.009×10^{-12}	0.53	McWatters and Rowe (2010)
	Toluene	0.011×10^{-12} ⁽¹⁾		
LLDPE	Benzene	0.1×10^{-10}	0.53	McWatters and Rowe (2010)
	Toluene	0.2×10^{-10}		
LLDPE	Benzene	0.2×10^{-10}	0.76	McWatters and Rowe (2009)
	Toluene	0.4×10^{-10}		
PVC	Benzene	0.2×10^{-10}	0.76	McWatters and Rowe (2009)
	Toluene	0.8×10^{-10}		
HDPE	Benzene	2.29×10^{-12}	2.00	Sangam and Rowe (2001)
	Toluene	7.74×10^{-12}		
HDPE	Benzene	2.07×10^{-12} to 2.83×10^{-12}	1.50	Islam and Rowe (2001)
	Toluene	4.90×10^{-12} to 7.22×10^{-12}		

Note

- 1 The result quoted for LLDPE:EVOH:LLDPE is misleading. Other tests have not been able to detect anything passing through this type of membrane. The data point is likely to be simply the amount of benzene absorbed by the first layer of LLDPE. It is better to consider this value as $<0.009 \times 10^{-12}$.

The values in the table are permeation coefficients, not permeation rates. If the diffusive mass flux is not quoted for a material in mg/m²/hr for a standard concentration (eg pure liquid) it is difficult to make any reasonable comparison of membranes in a simple risk assessment. However an estimate of the likely diffusive mass flux of a chemical through a membrane can be estimated using the permeation rates in Table 2.1 using the following equation (Fick's Law of Diffusion):

$$\text{Diffusive mass flux of chemical [ML-2T-1]} = P_g (dC_l/dz)$$

Where:

P_g = Permeation coefficient [L²T⁻¹] that allows for partitioning and diffusion processes at each side and within the membrane, from Table 2.1. Values for other VOCs have not been found in a literature search and would have to be determined from specific testing.

dC_l = Difference in concentration of chemical from one side of membrane to other (Figure 2.4).

dz = thickness of membrane (Figure 2.4).

Care should be taken when using the permeation coefficients as they only relate to the thickness of material and concentration of the particular chemical used in the tests.

Data on diffusive mass flux through membranes may be presented in other forms from that in Table 1.1 and commonly, results from laboratory tests quote the values in terms of a mass per unit area per unit time (eg mg/m²/h). Values for the permeation of xylene and toluene through different thicknesses of HDPE membrane are provided in Table 2.2. The table also shows the variation that occurs due to changes in the concentration of the challenge chemical on the dirty side of the membrane.

Table 2.2 Diffusive mass flux for VOCs through membranes (vapour phase)

Material	Chemical	Diffusive mass flux (mg/m ² /h)	Thickness of material (mm)	Source
HDPE	Xylene	916	0.8	Schiers (2009)
HDPE		500	2.6	
LDPE		750	0.75	
HDPE	Xylene (10 mg/l)	0.71	0.76	Thomas and Koerner (1996)
	Xylene (50 mg/l)	3.21	0.76	
	Xylene (100 mg/l)	13.29	0.76	
	Xylene (100 mg/l)	1.79	1.52	
	Xylene (100 mg/l)	0.58	2.54	
HDPE	Toluene (10 mg/l)	0.79	0.76	Thomas and Koerner (1996)
	Toluene (50 mg/l)	4.42	0.76	
	Toluene (100 mg/l)	14.58	0.76	
	Toluene (100 mg/l)	2.92	1.52	
	Toluene (100 mg/l)	1.00	2.54	

Note

The tests are assumed to have used m,p and o xylenes as the isomer is not stated in the source references.

In practice, brownfield sites are contaminated by a wide spectrum of pollutants which vary from site to site. It is therefore important that the barrier membrane can demonstrate adequate barrier performance against each pollutant that is of concern on a particular site (a chemical may be present, but not at levels that constitute a risk to the occupiers).

2.2.3 Influence of polarity on permeation rate

The molecular structure and polarity of the membrane is one important factor in the rate of permeation of the challenge chemical. Polarity is an indication of a balanced or unbalanced molecular electric field and is determined by polar and hydrogen bonding.

A standard chemical rule is that 'like is soluble in like'. So if the membrane material and contaminant are either both polar or both non-polar the solubility will be high and the permeation rate will be high. If the membrane material is polar and the contaminant is non-polar (or vice versa) the contaminant will not be soluble and permeation will be low. Water is a common example of a polar material and grease, a non-polar material. Grease does not readily dissolve in water (although it can form an emulsion).