PURAFLEX®

Hydrocarbon & Chemical Resistant Environmental Protection Barrier Membrane

TECHNICAL BRIEFING

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Permeation of Hydrocarbons through Geosynthetic Membranes

Geosynthetic membranes are widely used for containment, separation, secondary containment and environmental and groundwater protection applications. Though considered chemical resistant, HDPE and other common homogeneous geosynthetic membrane materials are susceptible to Hydrocarbon permeation. This briefing reviews the limitations of current industry standards and test methods for chemical resistance and highlights the importance of permeation data for environmental protection Risk Assessments.

Environmental Risk Assessments

Environmental Risk Assessments are conducted to ensure that unacceptable risk is removed and to make a site suitable for its intended use and to protect the wider environment, notably surface water and groundwater.

If links between Contaminants, Pathways and Receptors constitute a risk, the Risk Assessment determines the degree of risk and whether the risk is acceptable or not. On any individual site, contaminants can migrate to a receptor via more than one pathway and receptors maybe at risk from more than one source of contamination.

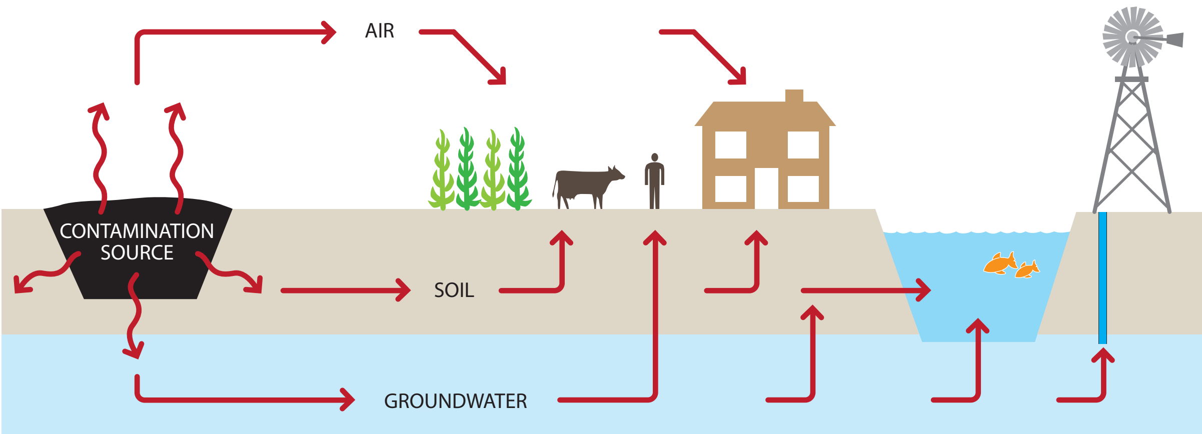

Fig.1 *Typical conceptual model of Pathways from a Contamination Source to Receptors.*

The UK Environment Agency's Contaminated Land Exposure Assessment (CLEA) model provides assumptions about the movement of chemicals and contaminants in the environment and thus human exposure to soil contaminants.

Soil Guideline Values (SGVs) are derived using the CLEA model by comparing estimated exposure with Health Criteria Values (HCVs) that represent a tolerable or minimal risk to health from exposure to contaminants. SGVs represent trigger values above which soil concentrations may pose a risk to health.

Risk Assessments require soil analyses to identify concentrations of hydrocarbon and toxic chemical contaminants. The integrity of risk assessment models therefore relies on the permeation data of separating geosynthetic membranes so that accurate modelling predictions can be made of the migration of contaminants from the source, through the membrane and into pathways to receptors.

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Chemical Resistance – Geosynthetic Membranes

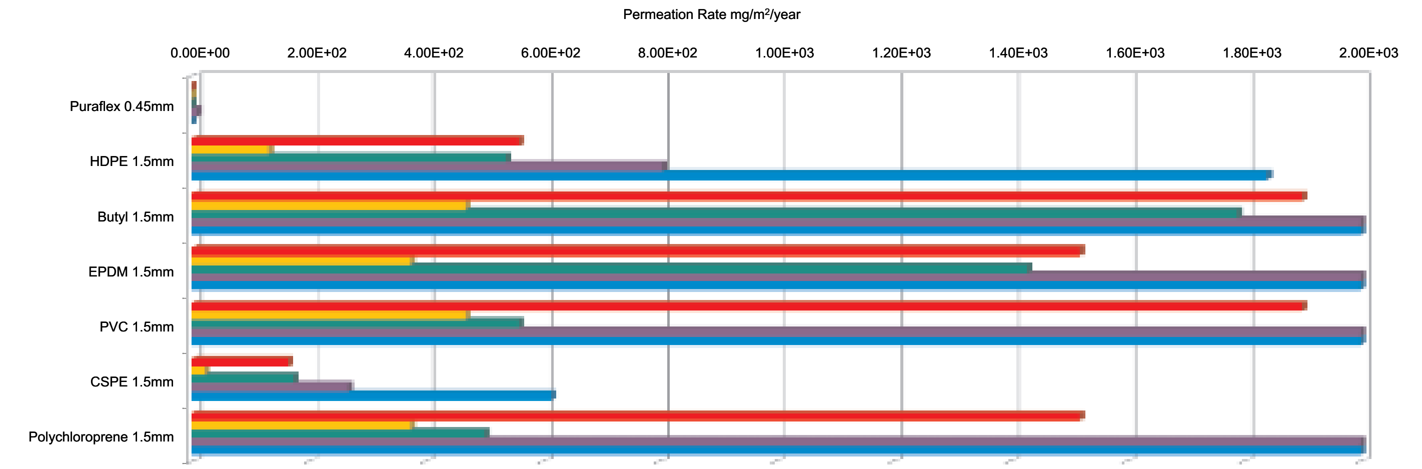
Current geosynthetic membranes are available in a range of polymer materials, including Butyl, CSPE, Polychloroprene, EPDM, HDPE, LLDPE, fPP and EIAs. These are homogeneous constructions whereby the membrane is made of the same polymer throughout.

A membrane's Chemical Resistance is determined by the polymer's molecular properties. In particular, Polarity is a key characteristic in determining chemical resistance; it defines the material's solubility and it follows that the higher the solubility, the higher the permeation rate.

It is important to make the distinction between a membrane being resilient to a hydrocarbon and a membrane being effective as a barrier to permeation. HDPE is widely regarded as chemical resistant but it is not a particularly effective barrier against hydrocarbons. HDPE is a hydrocarbon and since "like is soluble in like", hydrocarbons permeate relatively easily through HDPE.

Contaminated soil risk assessments commonly report on over 60 contaminant hydrocarbons. Some of the more significant are illustrated in Fig. 2 which compares permeation rates between common homogeneous geomembrane polymer materials and a new patented barrier membrane, Puraflex, specifically developed for resistance to hydrocarbons.

Limited chemical resistance data is generally available and material selection is often made on a 'best fit' basis, relying on industry standard chemical resistance test results (discussed below) and basic chemical resistance charts which usually provide a traffic light opinion i.e. Resistant (Green), Limited Resistance (Amber) and Unsuitable (Red). Thereafter, permeation rates can only be reduced by increasing a membrane's thickness; a membrane's thickness has to be doubled to halve the permeation rate.



	Polychloroprene 1.5mm	CSPE 1.5mm	PVC 1.5mm	EPDM 1.5mm	Butyl 1.5mm	HDPE 1.5mm	Puraflex 0.45mm
Benzene	1.52E+03	1.65E+02	1.90E+03	1.52E+03	1.90E+03	5.60E+02	3.52E-04
Fluorene	3.75E+02	2.17E+01	4.69E+02	3.75E+02	4.69E+02	1.32E+02	3.23E-06
Hexane	5.01E+02	1.74E+02	5.59E+02	1.43E+03	1.79E+03	5.37E+02	1.56E-06
Methyl Isopropyl Ketone	2.15E+03	2.67E+02	2.68E+03	2.15E+03	2.68E+03	8.05E+02	9.43E+00
Vinyl Chloride	4.92E+03	6.14E+02	6.15E+03	4.92E+03	6.15E+03	1.84E+03	1.67E-01

Fig.2 *Permeation rate comparisons of some key environmental contaminants.*

'Hydrocarbon Resistant'

The term 'Hydrocarbon Resistant' may simply mean that a membrane has passed a chemical resistance test which has no obvious relationship to the membrane's ability to block a challenge hydrocarbon to a level that ensures adequate protection over time. Furthermore the vagueness of the word "hydrocarbon" can lead to false claims that a barrier good for one hydrocarbon (e.g. methane) is automatically good for a very different type of hydrocarbon (e.g. benzene).

Most materials offered as 'Hydrocarbon Resistant' are no more than HDPE membranes. Aluminium laminates are sometimes specified but these materials, originally developed as methane gas barriers, are not recommended as a barrier to hydrocarbons or for use in moist or acidic soil environments.

The Aluminium layer is susceptible to oxidation which negates any barrier properties. Since the aluminium layer itself is thin and vulnerable, it has to be sandwiched in between two layers of polyethylene and reinforced to prevent any tearing by ground movements.

Chemical Resistance – Current test methods

Current industry standards for chemical resistance measure the physical changes to a membrane after exposure to a challenge chemical.

The American ASTM D5322 is a widely recognised test method for chemical resistance and it is incorporated within the EPA Method 9090 and ASTM D5747. The European test method procedures for EN BS 14414 & EN BS 14415 are virtually identical to ASTM D5322, the main difference being that the EN Standards define a fixed test period of 56 days, whilst the ASTM Standard allows the manufacturer to determine the duration of the test period.

The test procedure involves immersing a sample of membrane in the challenge chemical at an elevated temperature of 50 °C for the test period after which it is inspected. Thickness, weight, tensile strength and elongation are then compared with a control sample and providing variations are within 25% of the control sample test results, the membrane is considered chemical resistant.

EN BS 14414 Method C is the relevant immersion test for hydrocarbons. This single immersion test comprises a challenge solution cocktail of 35% diesel fuel, 35% paraffin and 30% lubricating oil. The value of such a test to a design engineer is limited since the test does not report on individual constituent hydrocarbons, of which the cocktail comprises many - in different and variable ratios.

Therefore, immersion tests are indicative of the membrane's resilience to chemical attack. They are essentially gatekeepers in terms of material selection. The test results do not provide any quantitative measure of a membrane's effectiveness as a barrier.

Aluminium laminates fail the EN 14414 Method A (chemical resistance to acids for geosynthetics) and are also vulnerable to delamination with hydrocarbon vapours.

Fig.3
EN14414 Method A 20% Sulphuric acid Oxidation within 14 days immersion

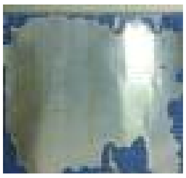


Fig.4
EN14414 Method A 2% Sulphuric acid Oxidation within 16 weeks immersion

Fig.5
Migration of vapour in reinforcement scrim of aluminium foil membranes. Delamination within 25 days exposure to diesel vapours at 50^{o}C

Permeation data – Measuring barrier performance

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.

There is a common misconception that HDPE is hydrocarbon resistant. Resilient it may be to some hydrocarbons, but hydrocarbons permeate readily through homogeneous HDPE membranes, mainly because the two are of the same species, i.e. HDPE is a hydrocarbon.

A membrane's chemical resistance is determined by its molecular structure and polarity, the latter characterised by a balanced or imbalanced molecular electrical field. The rule of "like is soluble in like" means that two Polar chemicals will be soluble, as will be two Non-Polar chemicals. Conversely, a Non-Polar and a Polar chemical will be insoluble. Since both hydrocarbons and HDPE are Non-Polar molecules, solubility is higher and therefore Permeability is greater.

Polarity (actually a composite of two factors, Polar and Hydrogen Bonding) is measurable and therefore can be illustrated graphically by plotting Hansen Solubility Parameters.

The sphere in Fig. 6 represents the solubility parameters of HDPE and those for typical industrial contaminants are represented by the satellites. The closer a red hydrocarbon satellite is to the green HDPE sphere, the more "like" it is and therefore the more soluble it is and therefore the more permeable the chemical will be through HDPE.

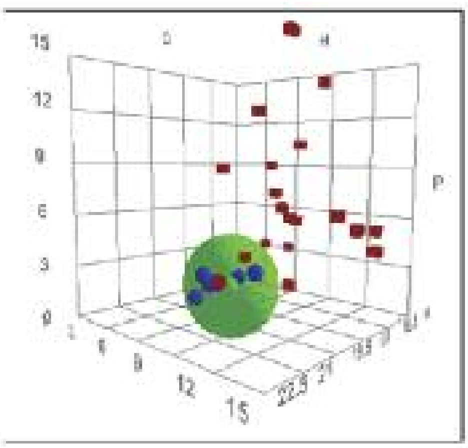


Fig.6
HSPs of generic HDPE and hydrocarbons.
Typical compatible hydrocarbons such as Benzene and Toluene (in blue) are shown as being inside the green sphere that represents HDPE.

Thus Benzene has a higher Solubility in HDPE and will therefore have a higher permeation rate.

Other chemicals (e.g. Alcohols, Ketones) are outside the sphere (in red) and therefore are not so soluble in HDPE.

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New Barrier Membrane Technology

Puraflex is a new chemical resistant barrier membrane material specifically developed for its resistance to hydrocarbons and toxic industrial chemicals. Developed by Industrial Textiles & Plastics Ltd, a manufacturer of chemical protective clothing materials and membranes resistant to chemical and biological warfare agents, its patented technology incorporates a multilayer structure incorporating both Polar and Non-Polar polymers.

The outer surfaces of the barrier membrane comprise Non-Polar polyolefinic polymers - insoluble to Polar chemicals but soluble to Non-Polar chemicals and Hydrocarbons. The Polar core sandwiched in the middle of the membrane is the effective barrier to Hydrocarbons and other Non-Polar chemicals as illustrated in Fig.8.

HDPE Membrane (homogeneous)

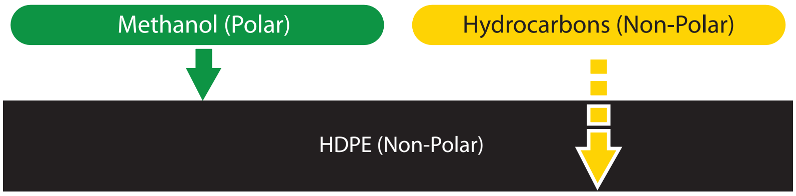

Fig.7
Since both HDPE and Hydrocarbons are Non-Polar, hydrocarbons will permeate more readily through the membrane

Puraflex Barrier (composite)

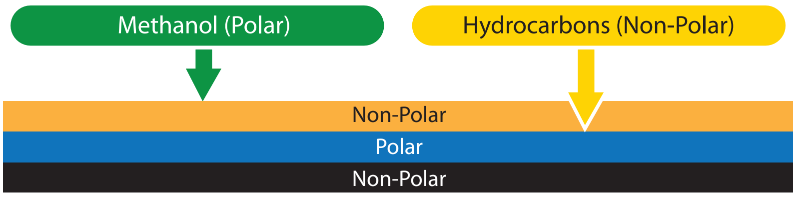

Fig.8
Puraflex incorporates a Polar core which provides the barrier to hydrocarbons

This multilayer composite construction provides enhanced barrier performance against a wider chemical spectrum for Polar and Non-Polar challenge chemicals. The benefit can be illustrated by comparing the concentration gradients for a typical non-Polar hydrocarbon (Benzene) across a homogeneous HDPE membrane and Puraflex.

Assuming a soil concentration of 100 mg/kg of Benzene at a 20 ºC soil temperature without any soil moisture partition coefficient applied, at equilibrium, the concentration gradient for Benzene is linear across a HDPE membrane. However across Puraflex, there is an abrupt change as the Benzene reaches the Polar core region of the membrane. This results in a significantly lower Permeation Rate.

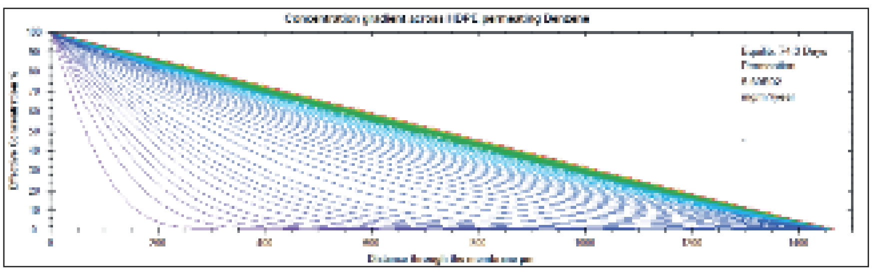

Fig.9
Concentration gradient of Benzene across a 1500 micron generic HDPE membrane
Permeation Rate:
5.69×10^{2} mg/m^2/year (569.0 mg/m^2/year)

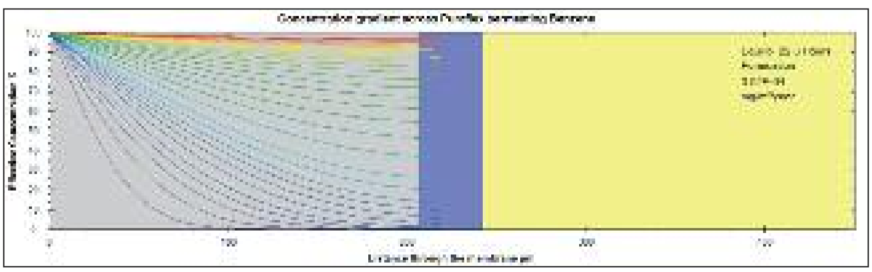

Fig.10
Concentration gradient of Benzene across a 450 micron Puraflex multi-layer membrane
Permeation Rate:
3.52×10^{-4} mg/m^2/year (0.000352 mg/m^2/year)

Risk assessments report on Total Petroleum Hydrocarbons (TPHs) comprising Aliphatic and Aromatic Hydrocarbons, as well as on Halogenated Hydrocarbons. Benzene, Toluene, Ethylbenzene and Xylene (BTEX) are well known Aromatic hydrocarbons and the permeation data for these compare as follows:

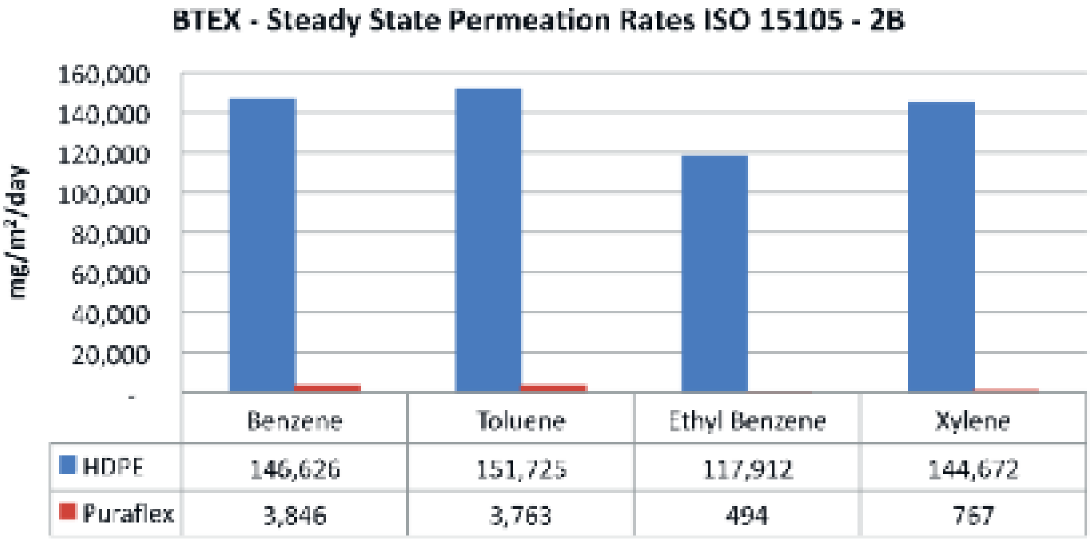

Fig.11 *BTEX Permeation rate comparisons between generic HDPE and Puraflex*

Puraflex has been subjected to an extensive chemical resistance test programme. In addition to the industry standard ASTM D5322, EN BS 14414 and EN BS 14415 immersion tests, individual Total Petroleum Hydrocarbons (TPH) and Halogenated Hydrocarbons have been tested to ASTM D5322 at 100% concentration.

Soil Moisture Partition Coefficient

Permeation data is therefore essential in determining the effectiveness of a geosynthetic membrane. However in order to make use of this data, a number of site-specific factors need to be taken in to consideration.

Permeation rates are particularly influenced by contaminant soil concentration, toxic additivity, soil temperature and soil moisture levels.

Soil moisture has the most significant influence on the effective concentration levels at the face of a geosynthetic membrane. As soil moisture increases, the more a hydrocarbon will partition away from the moisture-laden soil and congregate on the surface of the membrane, thus increasing its Effective Concentration.

	Soil Analysis mg/kg	Soil Moisture 10%	Soil Moisture 20%	Soil Moisture 30%
	No Partition Coefficient applied	Effective Concentration mg/kg Partition Coefficient applied		
Chlorophenol	100	170	170	180
Vinyl Chloride	100	890	1,100	1,360
Benzene	100	6,650	7,450	8,450

Fig.12
Soil Moisture content significantly influences Effective Concentration at the surface of the membrane

The Effective concentration depends upon the chemical's solubility and this can be seen by the different chemicals in Fig. 12.

With any geomembrane, a concentration level of 100mg/kg Benzene measured by soil analysis will have an Effective Concentration of over 6,000 mg/kg at the surface of the membrane in a 10% soil moisture environment. In Polarity terms, the non-polar hydrocarbon migrates away from the Polar water molecules.

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Permeation Modeller Software

Puraflex Permeation Modeller is a software program designed specifically to meet the needs of environmental consultants and design engineers, it is a powerful and effective program that calculates site-specific permeation rates for soil contaminants. The software uses Hansen Solubility Parameters for estimating permeation and has been calibrated via extensive absorption and permeation tests.

Following a contaminated soil test analysis, contaminant concentrations are uploaded into the program. Key variables directly influencing contaminant permeation rates (soil temperature, soil moisture content, soil density etc.) are entered and the software then calculates the project-specific permeation rates.

Using the appropriate soil densities, the Standard software also calculates the Permeated data in mg/kg/year for importing directly into environmental risk assessment modelling software programs such as the UK Environment Agency's CLEA Model.
The Professional software upgrade version calculates vapour migration in g/cc and $\mu m/m^3$.

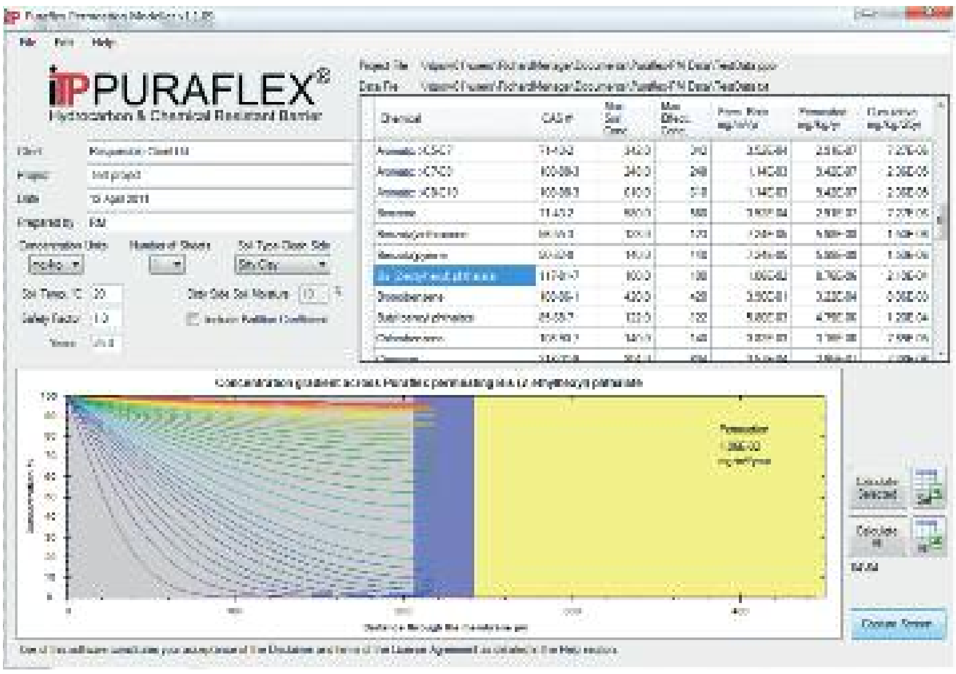

Fig.13
Puraflex Permeation Modeller uploads soil contaminant concentrations, provides for site-specific conditions and calculates permeation rates for Risk Assessment models

A software upgrade to the Professional version is also available to report on Vapour Phase migration.

The Standard Puraflex Permeation Software is available free of charge to qualified environmental consultants and design engineers. For your copy, available on disk or by email, please contact:
Puraflex Technical Support
Tel: +44 (0)1347 825221 or
Email: puraflex@itpltd.com.

Summary

Limited chemical resistance data is generally available and often charts provided by geosynthetic membrane manufacturer's list chemicals as simply Resistant, Limited Resistance or Unsuitable.

Current Industry Standards for Chemical Resistance are narrow in scope and value. Tests are limited to immersion tests which measure changes to the physical characteristics of the membrane to a challenge chemical. They therefore provide a measure of the membrane's resilience to a challenge chemical. Test results do not provide any quantitative measure of a membrane's performance.

It is important to make the distinction between a membrane being resilient to a hydrocarbon and a membrane being effective as a barrier to permeation.

Quantitative barrier performance is determined by the membrane's permeation rate. For Risk Assessment models, permeation data requires further interpretation since permeation is heavily influenced by site-specific variables. Soil moisture, temperature and density also need to be factored in to establish the appropriate site-specific permeation rates for each hydrocarbon before incorporating permeation rates in Risk Assessment models.

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DESIGN SOLUTIONS

Detailed CAD drawings are available. Puraflex can be supplied with or without adhesive backing to suit any design requirement and a DPC version provides a gas tight solution for cavity walls. We recommend that only Approved Installers and Approved Inspectors are commissioned to ensure that the barrier is correctly installed and independently inspected to verify that it will perform as intended.

1. PURAFLEX BARRIER

Puraflex BARRIER is an extruded membrane comprising protective polymeric layers on both sides of a chemical resistant inner core.

The outer polymeric layers protect the inner core barrier and are thermally-weldable to facilitate installation with conventional welding equipment.

Roll Size: 2.1 x 50m Weight: 48kg/roll

One-piece pre-fabricated panels with seams welded under factory controlled conditions are also available.

2. PURAFLEX TANK

Puraflex TANK incorporates a bituminous adhesive on one side for tanking applications.

The adhesive is protected by a removable silicone release paper.

Roll Size: 1.0 x 10m Weight: 20kg/roll

3. PURAFLEX DPC

Puraflex DPC incorporates an embossed surface finish for damp proof course installations.

Roll Size: 600mm x 30m Weight: 8.5kg/roll

4. INSTALLATION

Classed as a GBR-P polymeric geosynthetic barrier for covered installations, it is installed using conventional hot-air wedge welding equipment.

Seam welding speeds of up to 4m/min enable installers to complete installations quickly and efficiently. Best practice installation instructions provide detailed information on quality controls, site preparation, welding method and parameters, repair procedures and the sampling & testing of welded seams. Drawings are also included to provide the detail when connecting to concrete structures, pipe penetrations, flanges and drains.

5. QUALITY ASSURANCE

Puraflex Approved Distributor.

Design and technical advice is available from stockholding Puraflex Approved Distributors.

Puraflex Approved Installer.

Puraflex Approved Installers are experienced and certified installers of geosynthetic membranes and gas barriers accredited to BS EN 13067 Plastics Welding Personnel – Qualification testing of welders – thermoplastics welded assemblies.

Puraflex Approved Inspector.

Verification of barrier installation by independent Puraflex Approved Inspectors includes visual inspections of the entire barrier membrane surface, seam welds, penetration seals, Non-Destructive Testing of seam welds, porosity testing (to detect any holes in the installation) and photographs of all penetration seals and any repairs.

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KEYWORDS: Barrier membrane, brownfield development, chemical resistance, concentration, contaminated land, contamination, environmental protection, environmental risk assessment, geomembrane, geosynthetic, groundwater protection, hydrocarbon, membrane, partition coefficient, permeation, pollution, risk assessment, secondary containment, software model, soil analysis, soil moisture, solubility, toxic chemical.

GLOSSARY:

Butyl	polyisobutylene (PIB)	HDPE	high density polyethylene
CSPE	chlorosulphonated polyethylene	LDPE	low density polyethylene
CR	polychloroprene	PP	polypropylene
EDPM	ethylene propylene diene monomer	PVC	polyvinyl chloride

REFERENCES:

ASTM D5322 Laboratory Immersion Procedures for evaluating the Chemical Resistance of Geosynthetics to liquids.

ASTM D5747 Tests to Evaluate Chemical Resistance of Geomembranes to Liquids.

CLEA Model Environment Agency's Contaminated Land Exposure Assessment (CLEA)

EN BS 14414 Geosynthetics – Screening test method for determining chemical resistance for landfill applications (2004).

EN BS 14415 Geosynthetics barriers – Test methods for determining the resistance to leaching (2004).

EPA Method 9090 Test Methods for determining chemical waste compatibility of synthetic liners

PUBLICATIONS:

Puraflex Brochure Product information detailing relevant standards and test methods, our comprehensive chemical resistance testing programme, production and quality assurance

Puraflex Permeation Modelling (PPM) Software PPM is a unique software program which uploads soil analysis concentrations to report and provide permeation data of priority hydrocarbons and toxic industrial chemicals for incorporating in contaminated site risk assessment models (e.g. CLEA)

Puraflex Product Data Comprehensive test data for mechanical, hydraulic, thermal, durability and chemical resistance to BS, EN, ISO and ASTM test methods

Puraflex Design and Installation Details Design considerations and best practice installation instructions. Detailed CAD drawings are also available

Puraflex Model Specification Suggested specification to assist design engineers in the preparation of project documentation

Puraflex Safety Information Control of Substances Hazardous to Health (COSHH) & Material Safety Data Sheets (MSDS)

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