EVAL

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Introduction of EVAL® EVOH for Geosynthetics 2011

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Outline

- **Kuraray Company Limited**
  - Introduction of Kuraray Company
- **EVAL® EVOH resin**
  - Properties and Applications
- **Application Development**
  - Examples of non-food application development

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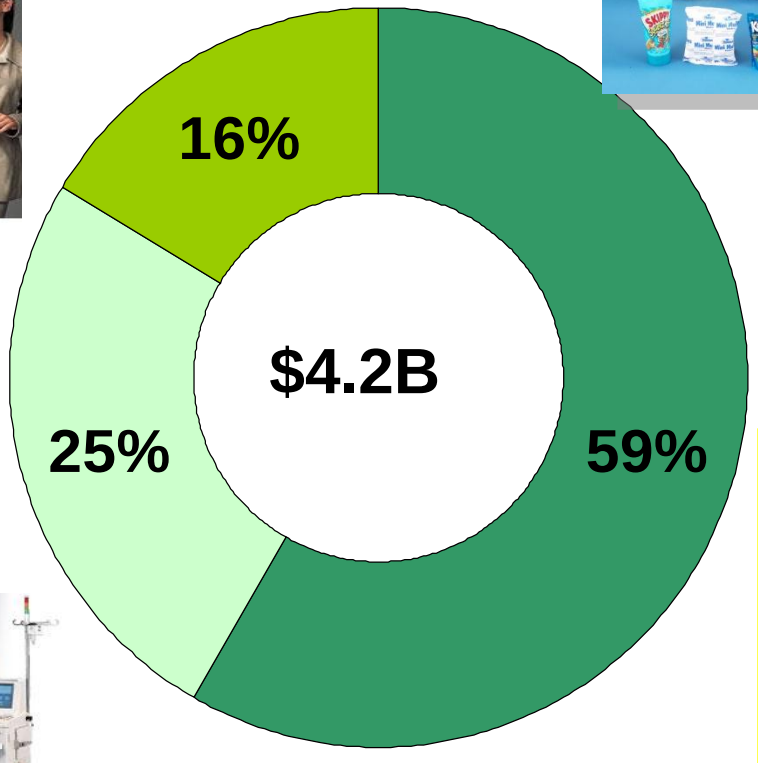
Kuraray Company Limited

Fibers & Textiles



Chemicals & Resins

High Performance & Medical Products

Founded in 1926, Kuraray is headquartered in Tokyo and Osaka

A specialty chemical company conducting business in 40 countries with 6800 employees

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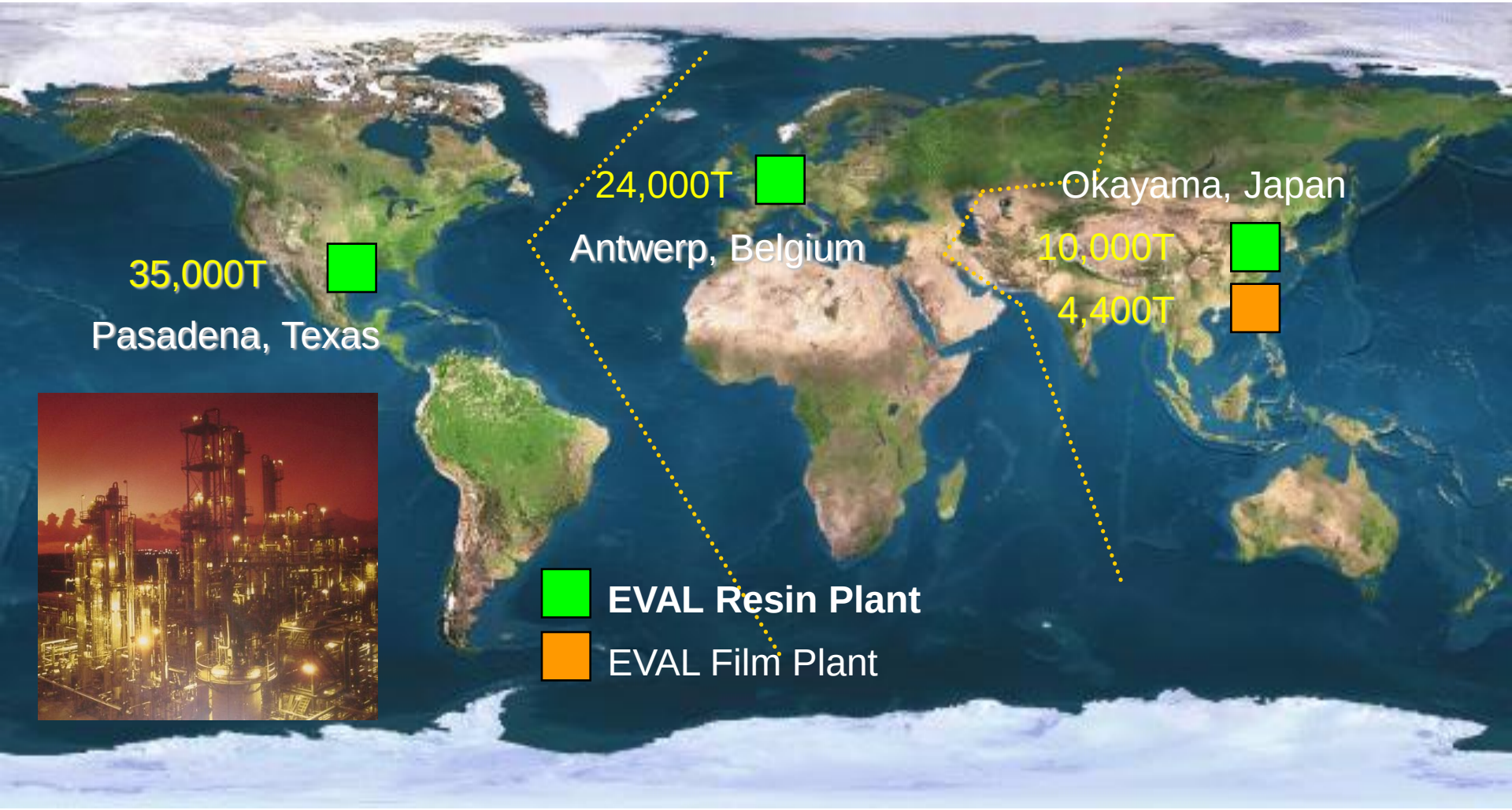
Global EVAL® EVOH Production



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EVAL® EVOH production in the USA

Pasadena, Texas

Manufacturing 35,000 MT of EVAL resins in America

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Global EVAL R&D Group Capabilities

- 80 people devoted to development and support of EVAL and barrier technologies
  - Core competency polymer chemistry and polymer processing

EVAL Capabilities

- Analytical support
  - Permeation – Gases and hydrocarbons
  - Analytical Chemistry & Microscopy
  - Physical Characterization of polymers
- Pilot facilities
  - Coextrusion Cast Film & Sheet, Co-Injection, Blowmolding and Sheet manufacturing
  - Downstream converting, forming, sealing
- Training & Support
  - Timely support and troubleshooting of process/product issues
  - Training for manufacturing or development teams

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What is EVOH?

A random co-polymer of …

Polyethylene (PE)

Extrudes and orients easily

$$—(CH_2 - CH_2)_m —$$

Polyvinyl Alcohol (PVA)

Provides Gas Barrier

$$—(CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}})_n—$$

$$—(CH_2 – CH_2)_m - (CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}})_n—$$

Ethylene Vinyl Alcohol

Key properties of EVOH

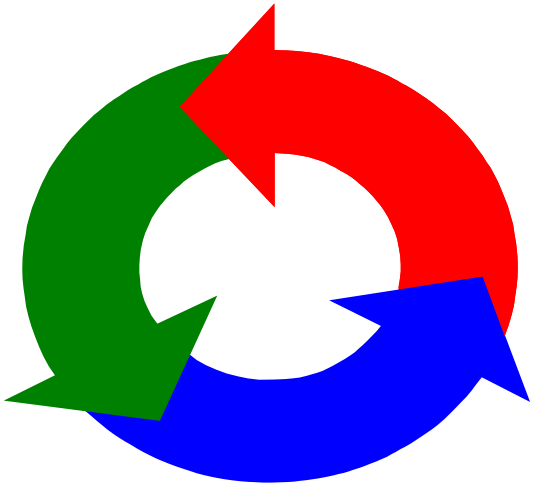
Gas Barrier (O_2, CO_2, etc)

Abuse resistance

Oil resistance

Extrudable

Solvent Barrier



Recyclability

Hydrocarbon Barrier

Odor Barrier

EVOH PROPERTIES

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Effect of mol% on properties of EVOH

27
32
35
38
44
48

Ethylene Molar Percent

- Better O_2 barrier
- Better solvent barrier

Better:

- Water vapour barrier
- Flexibility

EVOH is a random copolymer of

Ethylene and **V**inyl **AL**cohol

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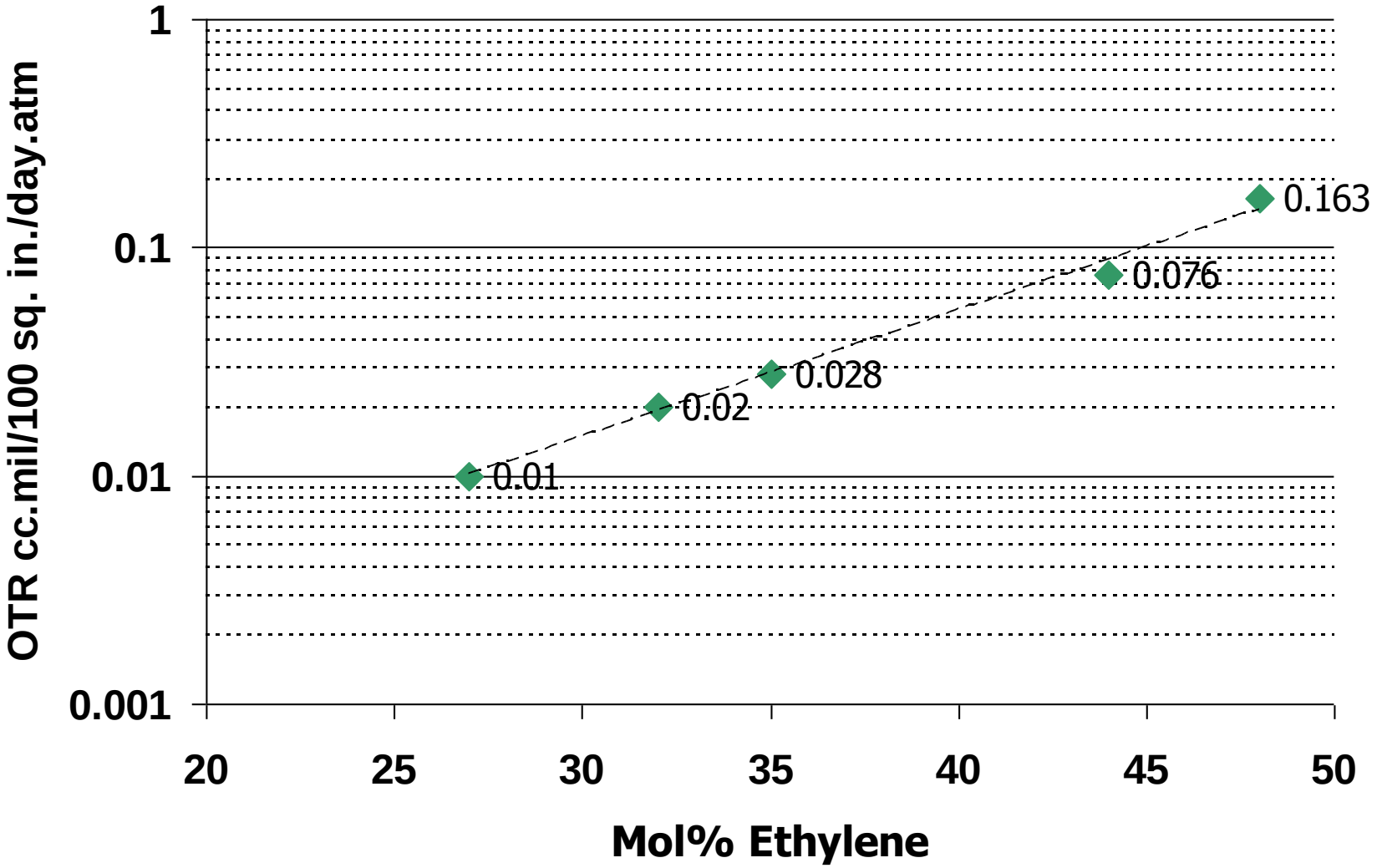
Effect of mol% on oxygen barrier



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Gas Barrier Property

Oxygen Transmission Rate of Films

Polyolefin	Oxygen Transmission at 20C, 65%RH
EVOH - 32 mol%	0.4
EVOH – 44 mol%	0.8
PVDC copolymer (Extrusion Grade)	2.6
Nylon	38.0
PET	54.0
HDPE	2300.0
C-PP	3000.0
PC	5000.0
LDPE	10000.0
EVA	18000.0

Unit : cc・20μm / m²・day・atm

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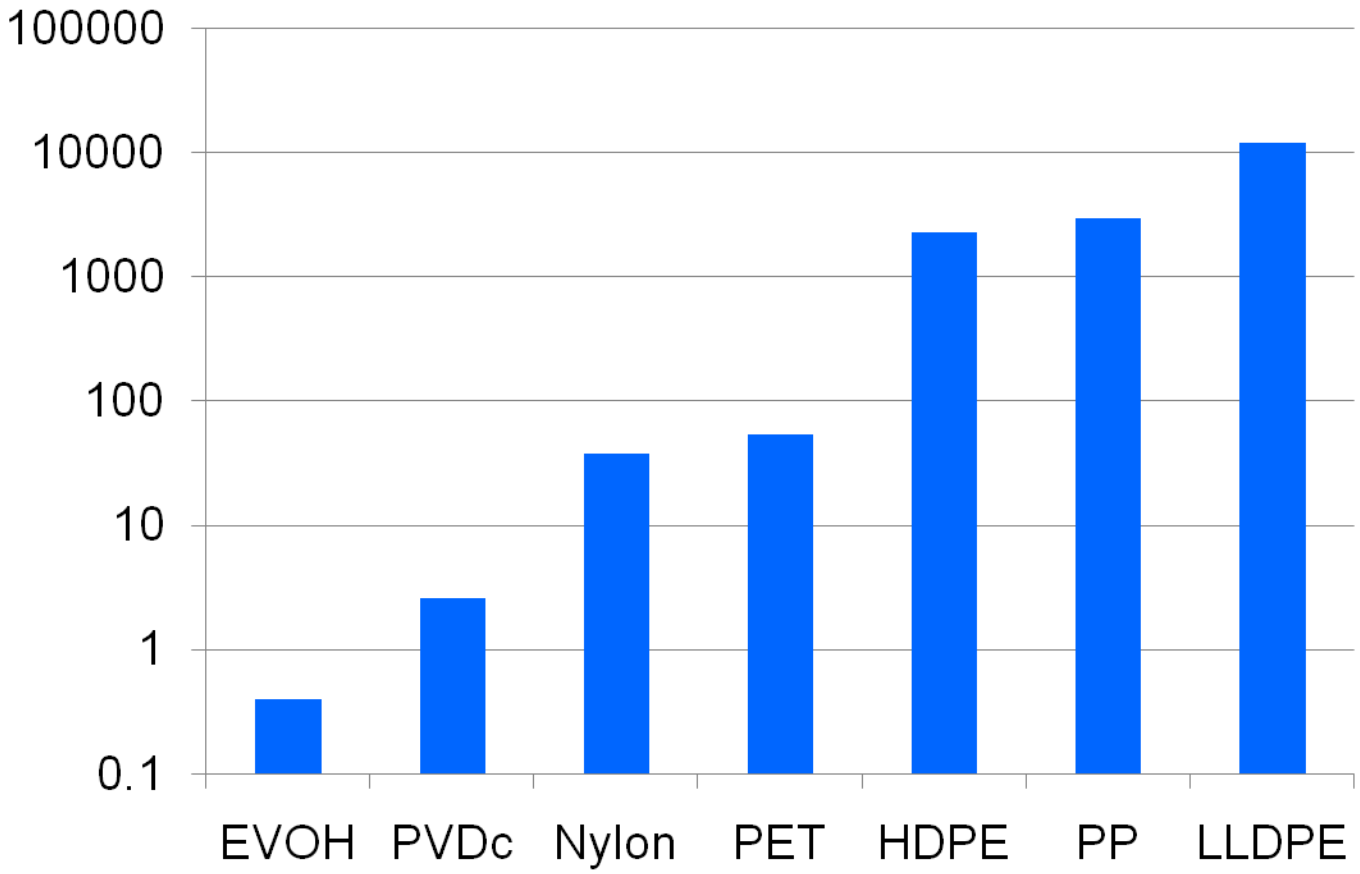
EVOH oxygen barrier

Oxygen Transmission Rate of Films



Unit : cc・20μm / m^2・day・atm

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EVOH vs. HDPE Gas Barrier Properties

Gas	EVOH*	HDPE**
Nitrogen	0.019	190
Oxygen	0.25	2300
Carbon Dioxide	0.6	17526
Sulfur Dioxide	0.3	21844
Methane	0.4	2845

Volumetric permeation rate in (cc.20μ/m^2.day.atm)
Conditions: 23° C – 0% RH (ASTM D1434T)
* ASTM D1434 at Kuraray lab – 32mol% EVOH
**Permeability Properties of Plastics and Elastomers, Massey, 2nd Edition

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EVOH solvent barrier

- A common measure of solubility is the solubility parameter (a numerical value)
  - It is derived from the cohesive energy density of the solvent which is in turn derived from the heat of vaporization

- One of the simplest and most convenient relative measures of solubility is the Hildebrand solubility parameter.

- The solubility parameter of a polymer is more difficult to predict but in many cases the combined Hildebrand parameter is used with success to predict the interaction of solvent and solute

The basic concept of solubility parameters is "like dissolves like" and that a comparison of solubility parameters can be used as a predictor of chemical resistance and barrier properties.

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Solubility parameters – solvents vs polymers

Solvent	Solubility Parameter δ(SI) [MPa]
dichloromethane	20.3
1,2 dichlorethane	20.0
trichloroethylene	19.0
benzene	18.7
toluene	18.2
ethyl benzene	18.0
m-xylene	18.0
water	47.9

Polymer	Solubility Parameter δ(SI) [MPa]
Polypropylene	16.2
Polyethylene	16.4
Polyvinylchloride	19.6
Polyurethane	20.5
Nylon 6	26.0
Nylon 66	27.8
EVOH (32mol%)	38.9

Solubility parameters predict that EVOH will have excellent resistance to majority of hydrocarbons and VOC solvents

Moisture barrier of EVOH is lower than polyethylene due to affinity to water

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EVOH vs HDPE – solvent resistance

Diffusion coefficient Dg of solvents in EVOH and HDPE

Solvent	EVOH *	HDPE**
trichloroethyelene	$3.1x10^{-17}$	$4.0x10^{-13}$
toluene	$3.1x10^{-17}$	$3.0x10^{-13}$

Diffusion coefficient D_g in m^2/s
*Kiwa NV report April 2008 for EVAL Europe N.V
** Sangam and Rowe, Migration of dilute aqueous organic pollutants through a HDPE geomembrane, Geotextiles and Geomembranes 19 (2001) 329-357

Wide ranging studies of solvent resistance (weight gain, retention of physical properties etc) established excellent performance of EVOH for automotive and ag-chemical applications

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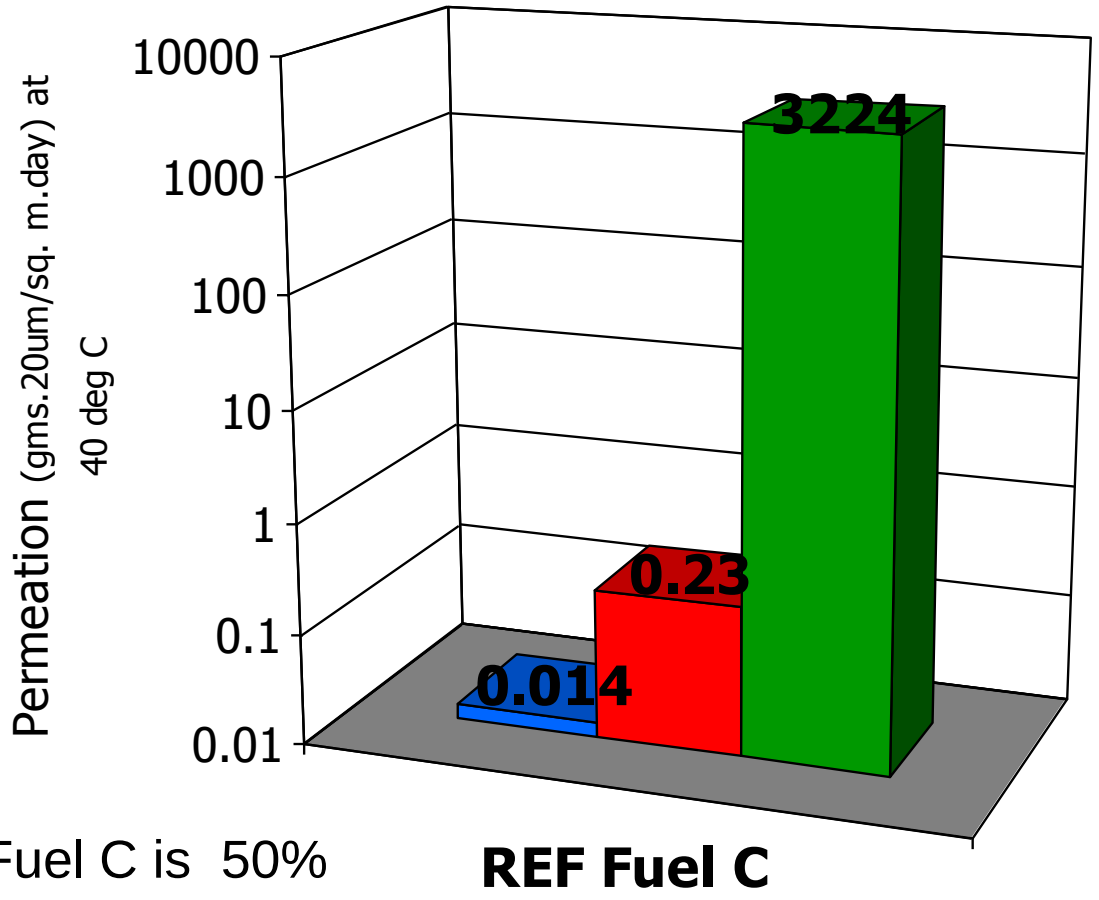
Example of EVOH solvent barrier…



Reference Fuel C is 50% toluene, 50% isooctane

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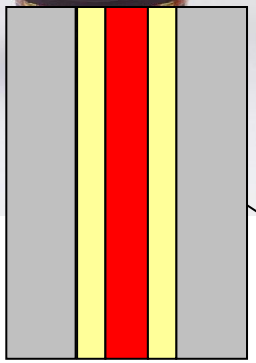
Applications



PP/Tie/EVOH/Tie/PP

EVOH is typically used as a discrete layer in a coextrusion or composite.

5~10% of total thickness will be EVOH

5 layer thermoplastic formed cup sidewall

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EVOH Application – Food Packaging

EVOH used in food packaging since 1986

Gas barrier properties of EVOH allow replacement of metal foil and glass with lightweight packaging, with shelf life of 30 days to 18 months

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EVOH Application – Nike Airsoles

Nike switched from SF6 to nitrogen in 2000

TPU/EVOH airsole was the only solution to meet barrier and physical performance requirements

Pressure retention of 20psi nitrogen for > 3 years

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EVOH Application Automotive Fuel Systems

- One of the major applications for EVOH is in auto-motive fuel systems to control emissions of hydro-carbons from fuel lines and tanks.
- The use of EVOH in a coextrusion blowmolded tank with high molecular weight HDPE (HMWPE) originated in the United States in response to mandates of VOC emission reductions by the US Environmental Protection Agency (EPA) and the California Air Resources Board (CARB)
- The EVOH barrier PFT has now been in widespread use for fifteen years in more than 100 million vehicles with zero failures
  - Following adoption in the US, the same coextrusion technology spread geographically to Europe, Latin America and is now entering China and India.

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EVOH Application Automotive Plastic Fuel Tanks

- Development started in 1989 in response to CARB and EPA mandates
- Emissions regulations have progressively becoming tighter each decade.
- EVOH became barrier of choice due to VOC barrier properties
  - emissions through tank shell are <10mg/24hrs

Regulation-Agency	Allowable Emissions*
Tier 1 - EPA	2000mg/test 3 day diurnal
LEV 1 - CARB	2000mg/test 3 day diurnal
LEV 2 - CARB	500mg/test 3 day diurnal
PZEV - CARB	350mg/test 3 day diurnal

Allowable emissions from entire vehicle over service life

(100,000 to 150,000 miles)

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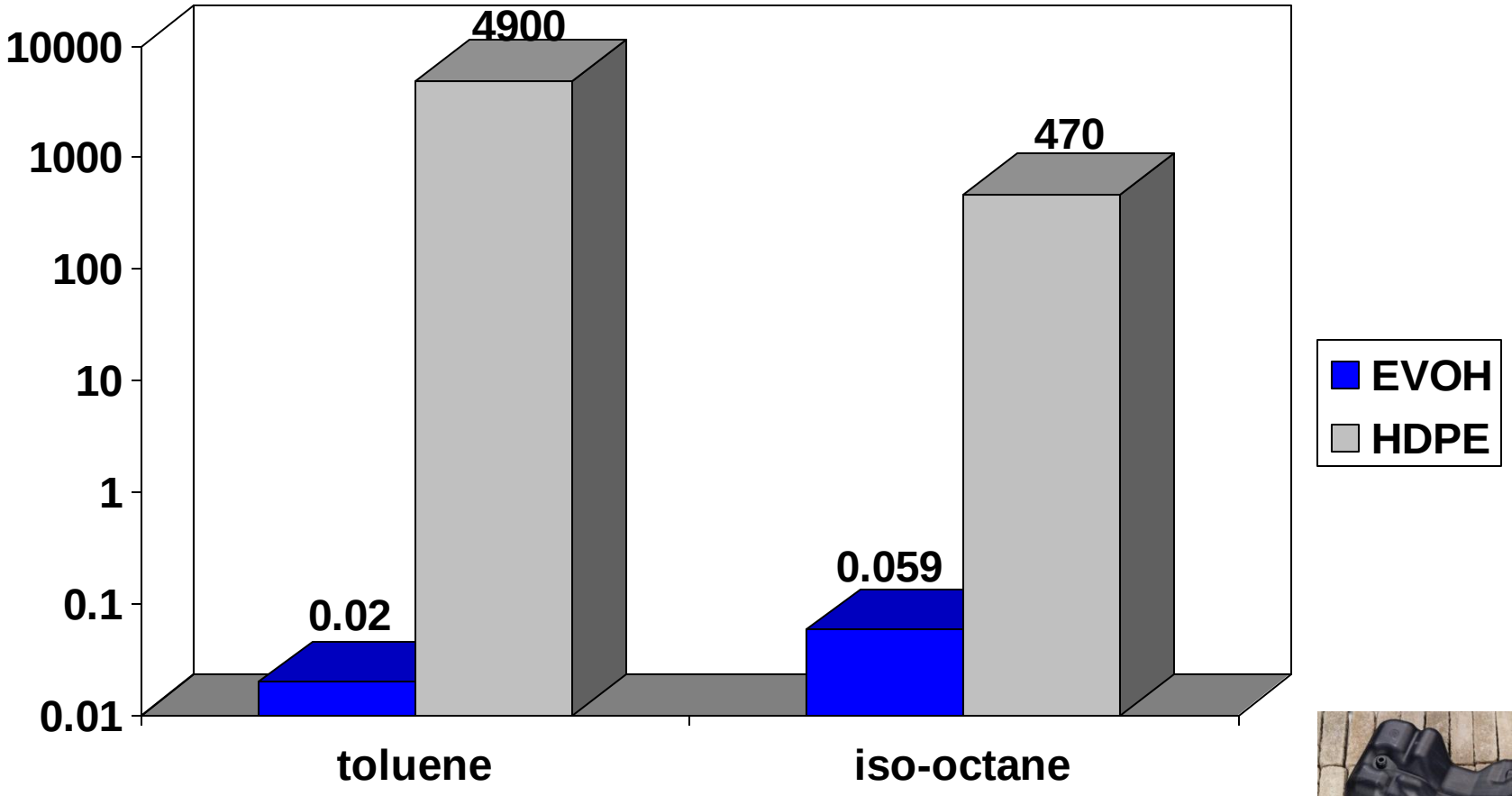
EVOH vs HDPE VOC barrier



Mass flux of solvent in gm.20 microns/m^2.day at 40° C and 65%RH

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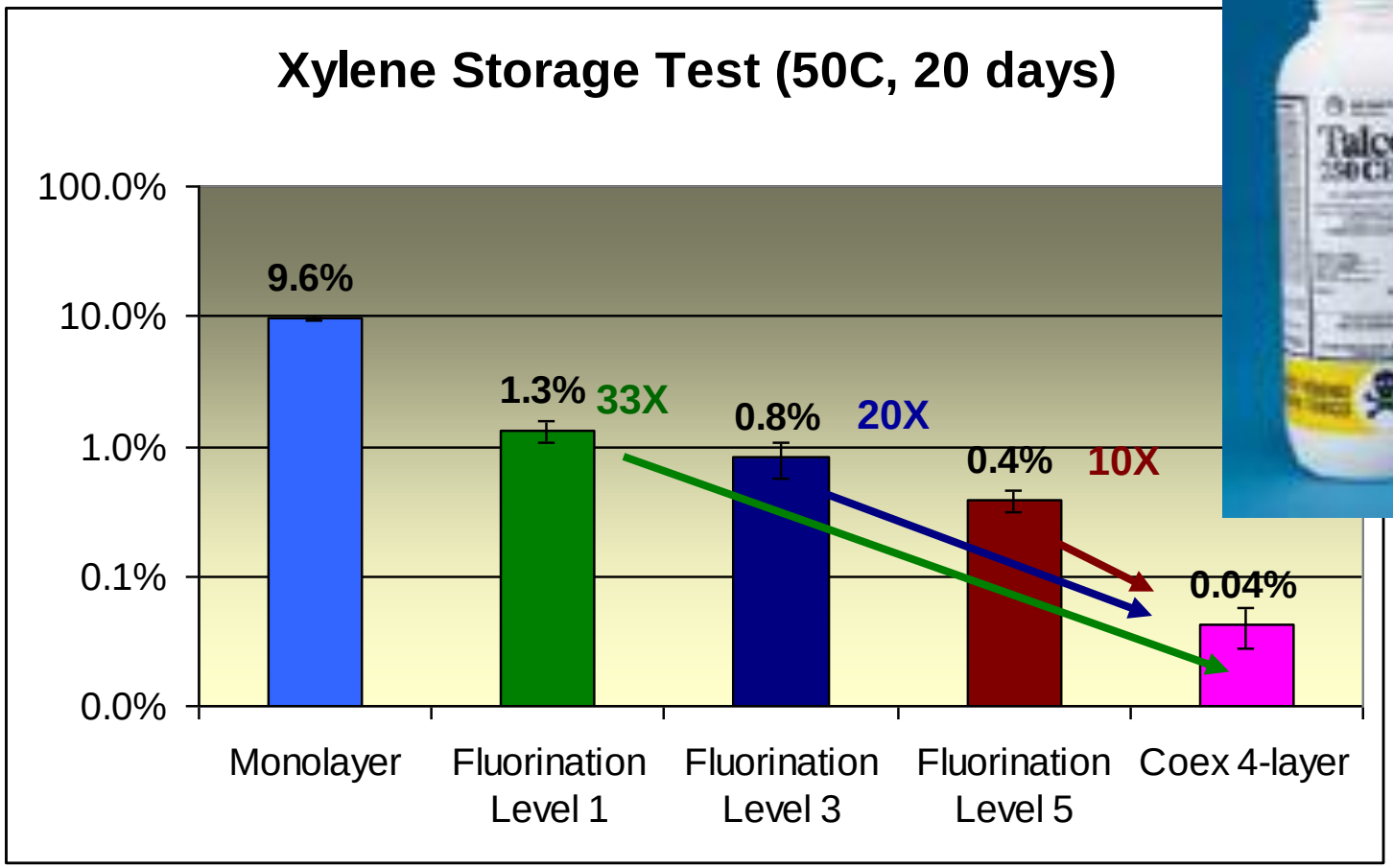
EVOH Application Ag-Chemical Bottle

Pesticides and herbicides with xylene or toluene solvents are packaged in ag-chem bottles with EVOH inner layer to prevent HDPE from dissolving



EVOH in use in this application since 1987

Conditions: CFR 49.173.24 Appendix B, 1L bottles, HDPE/Regrind/Tie/EVAL F101(in), 100% Xylene, 50° C, n = 3, 20 day, explosion proof oven storage test

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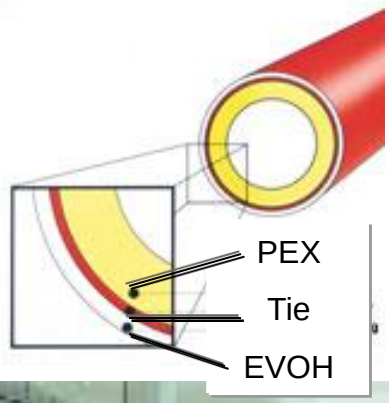
EVOH Application Underfloor heating pipe



EVOH in under floor and district heating pipe systems.

EVOH allows PEX pipe to comply with DIN4726 for <0.32mg/m^2 at 40C and replace metal piping

Physical tests of pipe include ageing for 2000hrs in 100° C water, 200hrs in air oven before tensile testing

EVAL EVOH certified for 50 year service life in EU at high temperature (up to 95° C water)

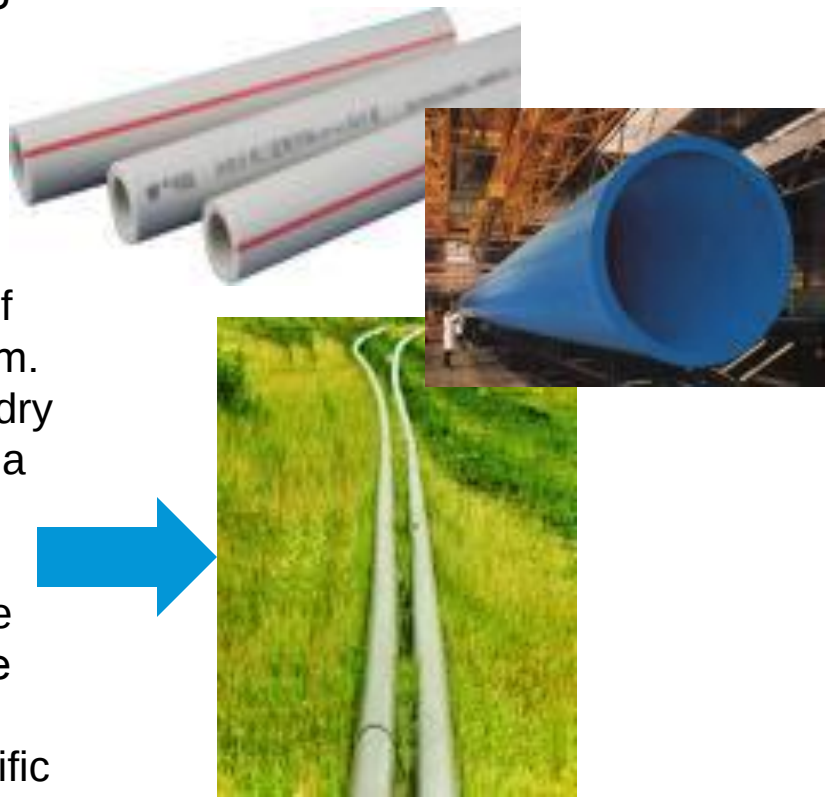
Water Pipe

Drinking Water Pipe

HDPE/EVAL™ coextrusion for piping through VOC contaminated soil

Since the early 1980's a growing number of permeation accidents have been reported in Europe.
These were mostly caused by the permeation of VOC's and organic solvents into the piping system.
In particular, plastic pipes near gasoline stations, dry cleaners and industrial areas have proved to be a potential threat to drinking water quality.

This contamination risk can be minimized by the incorporation of an EVAL™ barrier layer into the drinking water piping system.
Multilayer plastic drinking water pipes with a specific EVAL™ grade can be considered as CLASS I pipes for light polluted ground as validated by an accredited institute."



EVOH piping is in test at Kiwa

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Agricultural Films

Fumigants are used for the commercial production of fruits, vegetables, trees and flowers

Methyl bromide (MB) is the most efficient fumigant – but MB is an ozone depleting substance and is being regulated out of use

MB alternatives pose both acute and chronic health effects on field workers and are also regulated

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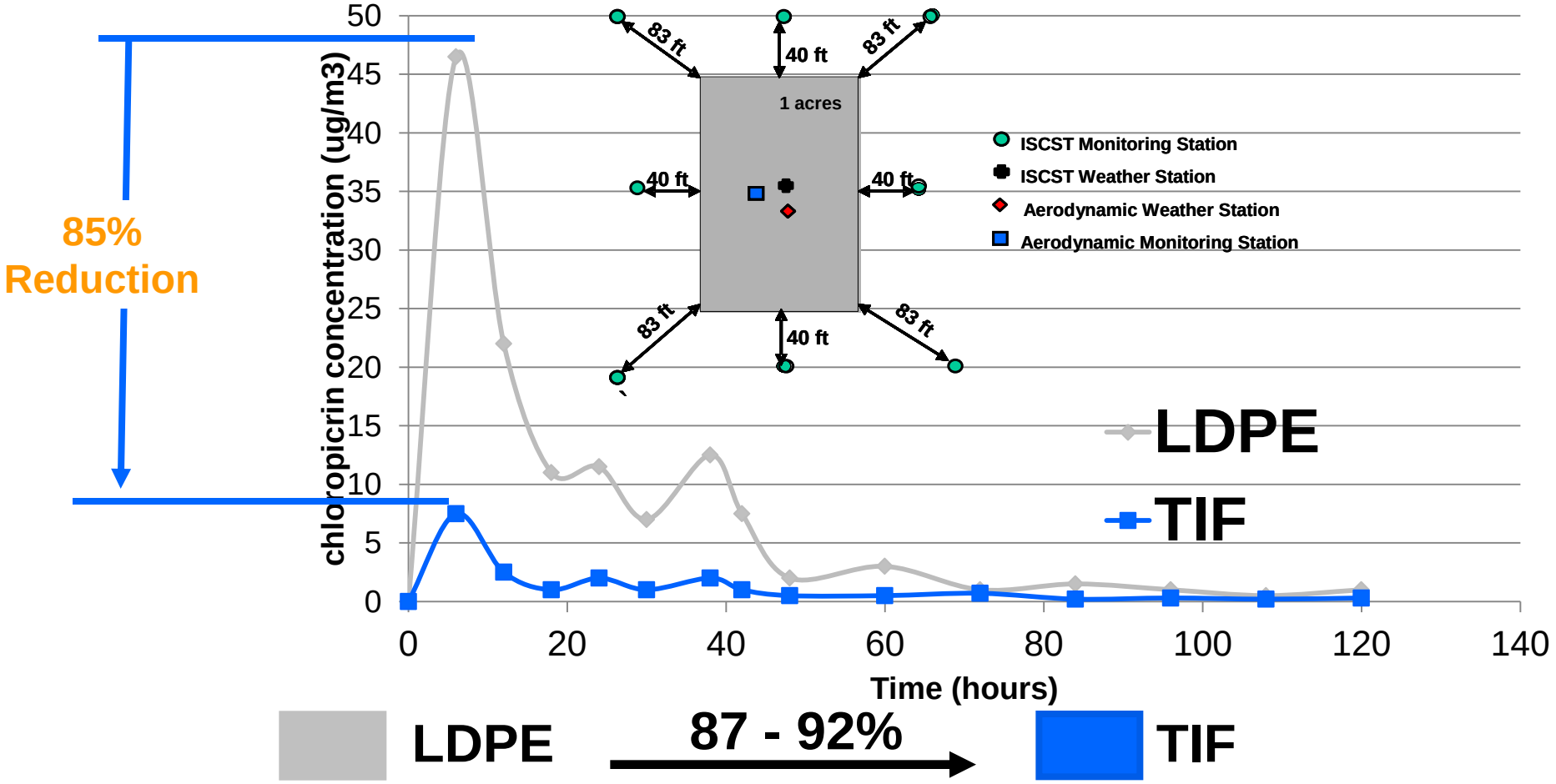
Benefit of EVAL in Fumigation Films

TIF = EVAL barrier film



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Target B&C Membrane applications

Heap leach mining liner

Land fill liners

Oil sand mining liner

Radon and vapor barrier and concrete liners

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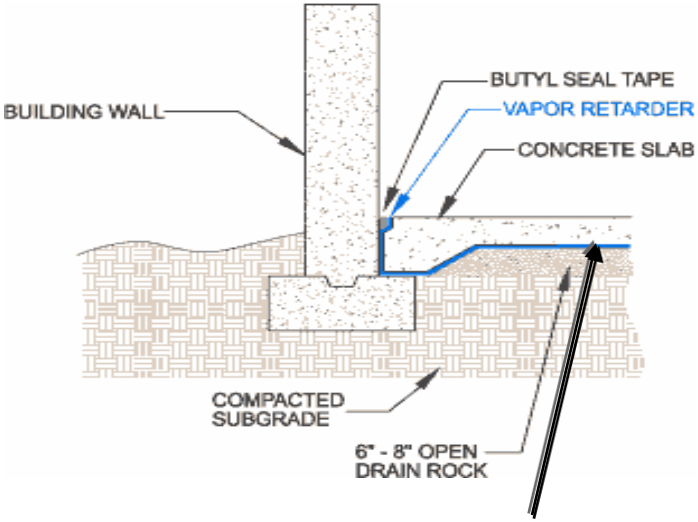
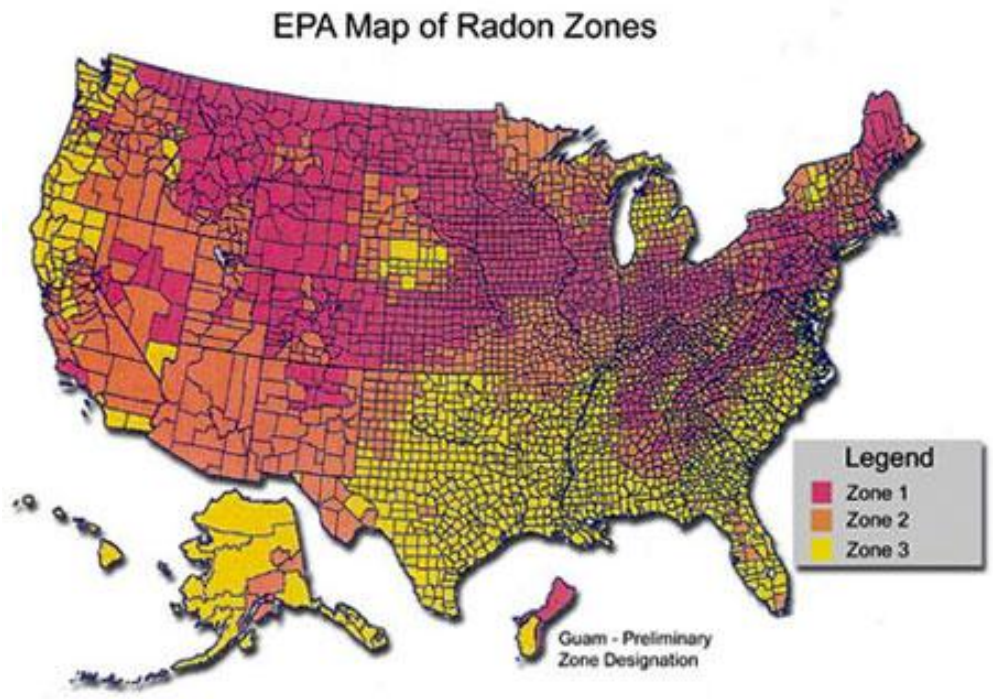
VaporBlock Plus is a trademark product of Raven Industries

Radon & vapor barrier liners



Radon Barrier



- Radioactive gas formed from decay of Radium 86
- **Benefit of radon barrier**

  Health & safety
  - Reduce incidence of lung cancer (21,000 deaths per year)

  Economic
  - Eliminate expensive remediation costs of remodeling or venting

	Potential	Indoor detection
Zone 1	**high**	**> 4 pCi/L**
Zone 2	**moderate**	**2 - 4 pCi/L**
Zone 3	**low**	**< 2 pCi/L**

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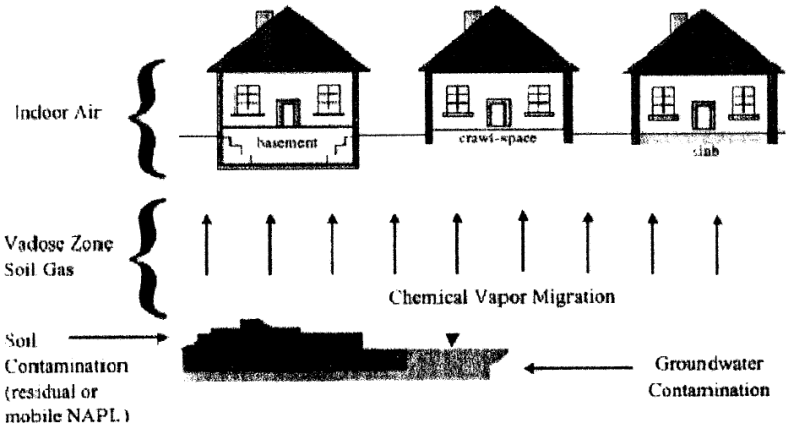
Radon and vapor intrusion



The ITRC is a coalition of state environmental regulators working with federal partners, industry, and stakeholders to advance innovative environmental decision making.

Vapor intrusion or VI is defined as the migration of volatile chemicals in building spaces from groundwater of soil. The chemicals of primary concern are benzene, ethyl benzene, toluene and xylene (BTEX) or chlorinated solvents such at trichloroethylene (TCE) or perchloroethylene (PERC).

Chronic effects of long term exposure to very low levels of these chemicals motivated the EPA to issue guidelines for limits on vapor intrusion in 2002 to 2005, which are now being acted upon by states, with California, Colorado, Wisconsin, New York and New Jersey being the most active.

Action level for remediation or mitigation based on VI is often very low, typically being the level of a volatile chemical with a one in a million chance of causing cancer over a 20 year period (translates to 1 µg/m3 for toluene in indoor air).

INTERSTATE TECHNOLOGY & REGULATORY COUNCIL
Advancing Environmental Solutions

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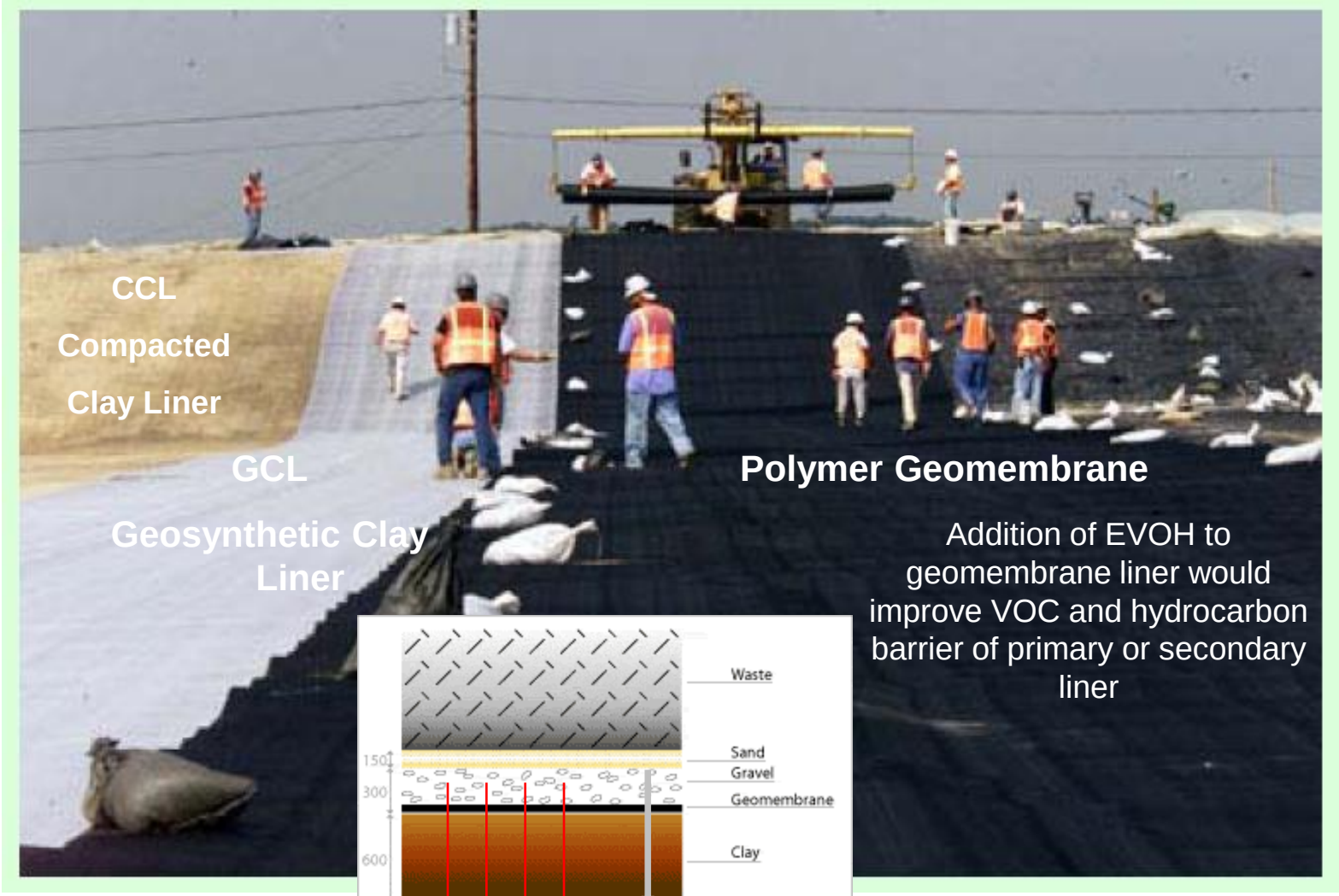
Geomembranes in landfill liner



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Canadian oil sands tailings pond

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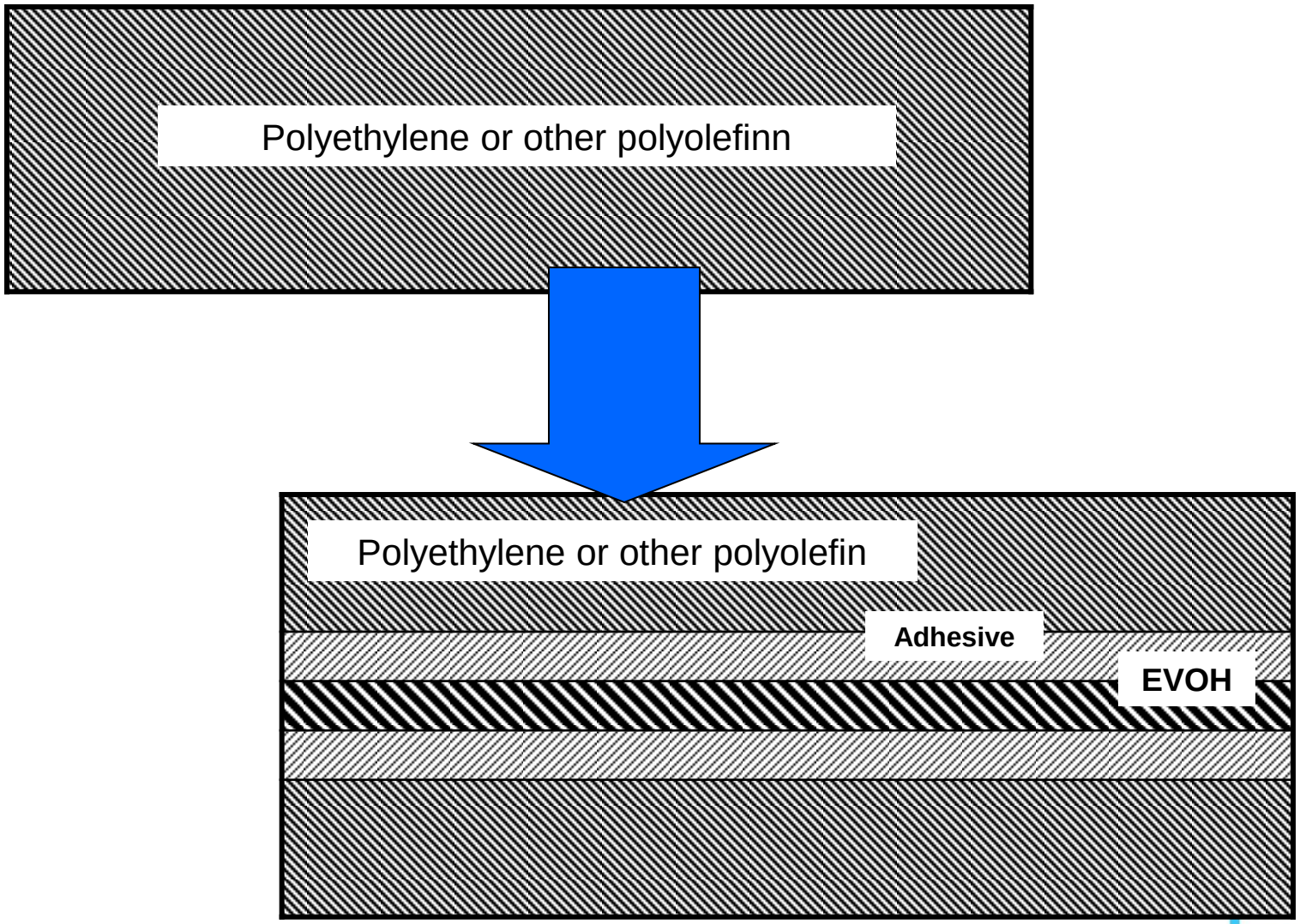
Concept for coextrusion for select geomembrane applications



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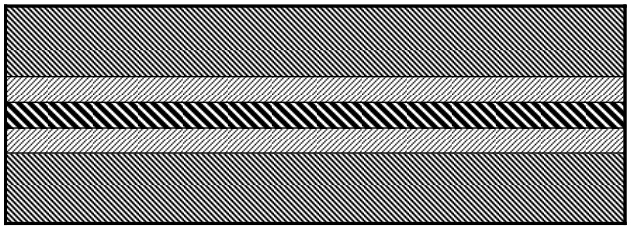
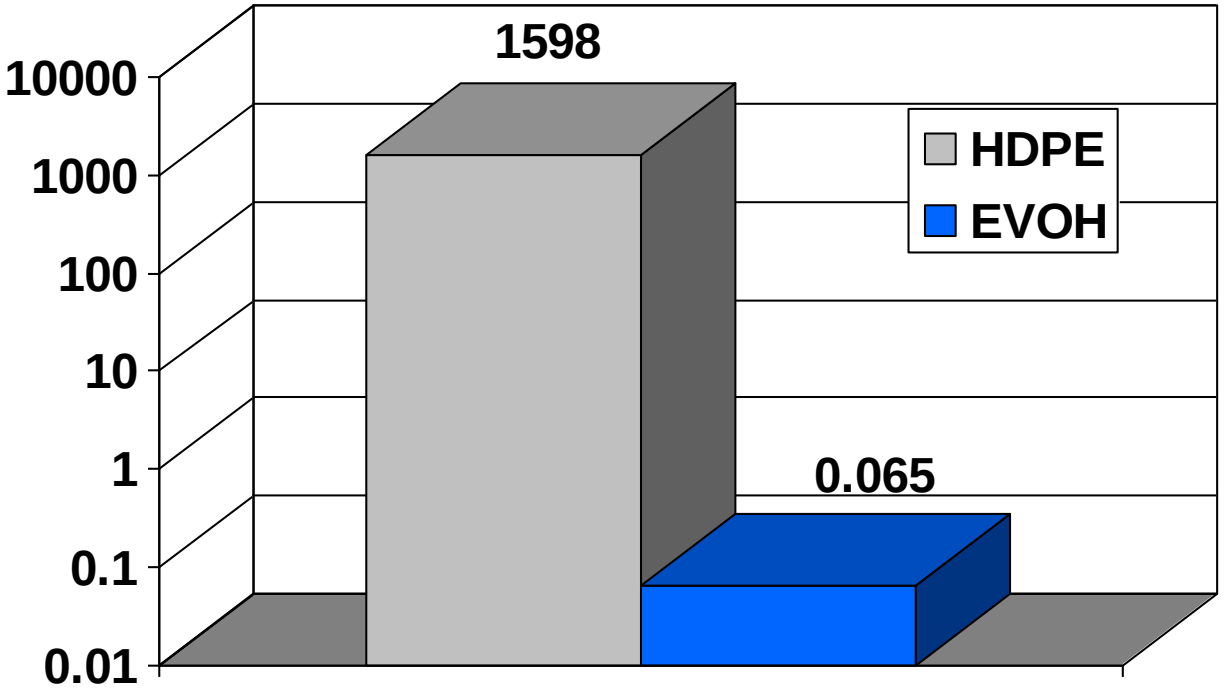
Potential for performance improvement



Model geomembrane
1500 µm (60 mil) with
3% EVOH(45 µm)

Addition of EVOH to HDPE liner..



Estimate of reduction in mass flux of toluene by including EVOH in geomembrane

Toluene concentration 2mg/L (2ppm). Service temperature 40° C

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Conclusion

- Existing monolithic geomembranes comprised of polypropylene, polyethylene and polyvinylchloride are excellent hydraulic and heavy metal barriers.
  - These materials are NOT good barriers for volatile organic compounds migrating by diffusion
- The inclusion of EVOH by coextrusion into select geomembrane designs would significantly minimize diffusive migration of VOC's
  - Offers a cost effective alternative to expensive remediation of contaminated sites
- A High Barrier Geomembrane (HBGM) with EVOH offers potential for significantly improved protection of soil and water quality.

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