Predicting Service Life of Geomembranes in Low-Level and Mixed-Waste Disposal Facilities

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University of Virginia Engineering

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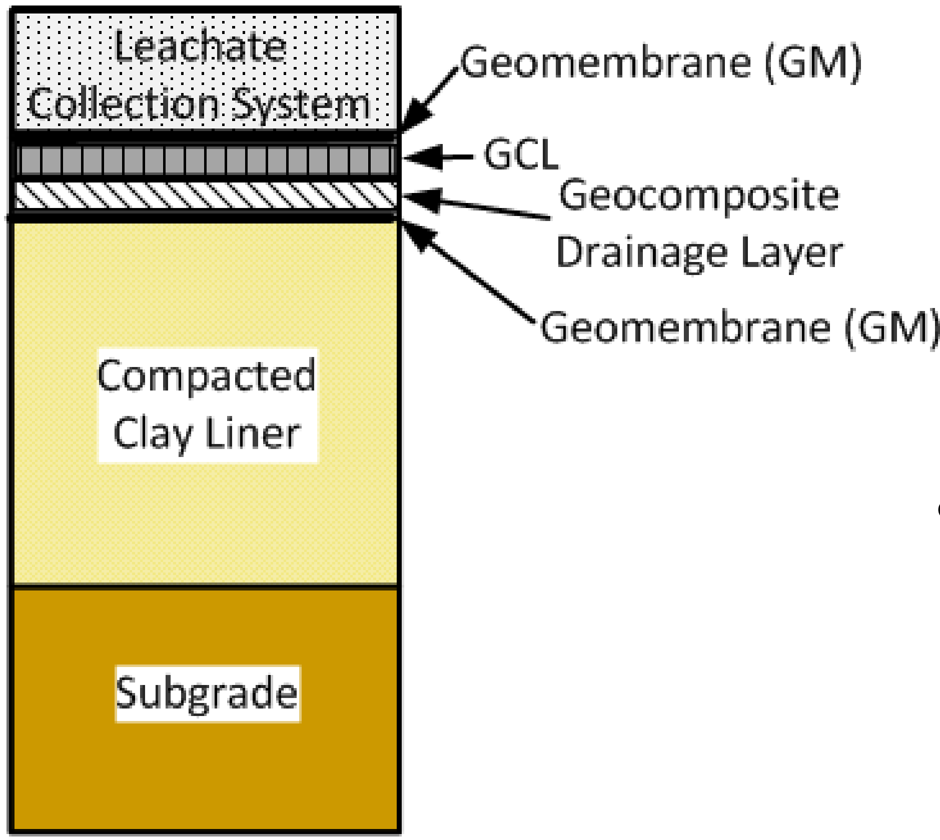
Multi-Component Liner Systems Used in LLW and MW Near Surface Disposal Facilities



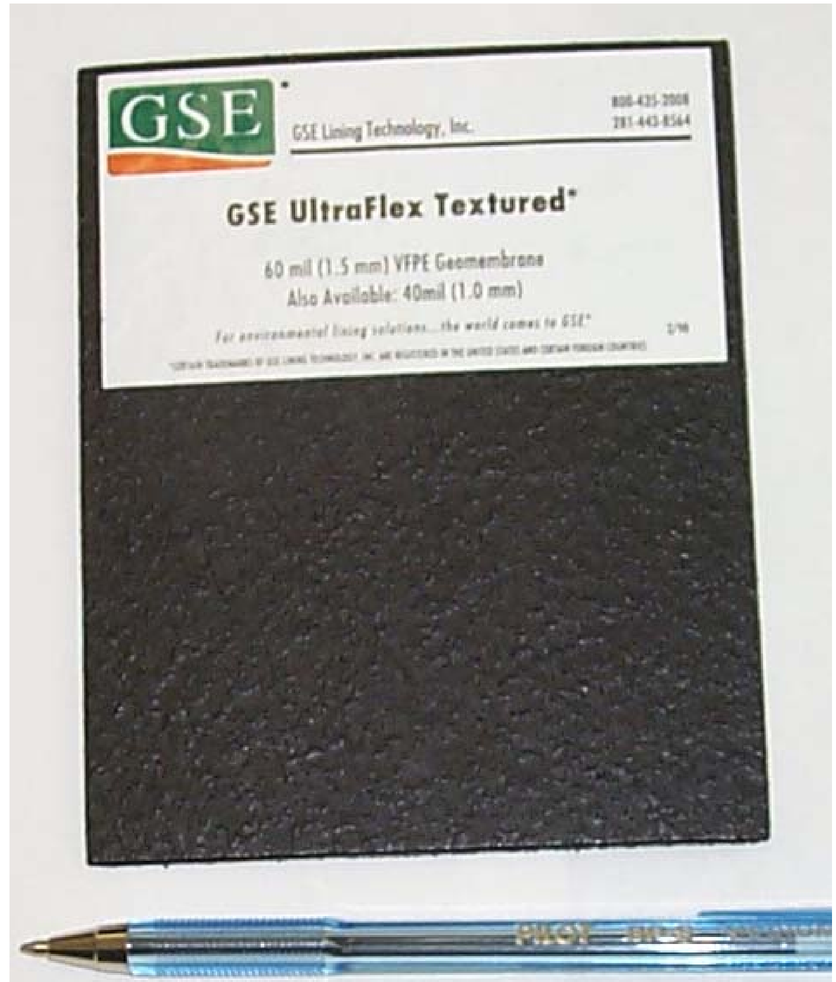
- Double lining system with two composite liners
  - Geomembrane over geosynthetic clay liner (upper)
  - Geomembrane over clay liner (lower)
- Double collection system
  - Upper leachate collection system
  - Lower “leak detection zone” with geocomposite drainage layer

Composite Barriers: Geomembranes & Soil Liners

Geomembrane:

- Heavy polymer sheet to block flow. 1.5-2.5 mm thick & often comprised of polyethylene. Generally textured to provide physical stability.

- Nearly impervious, but holes & seam defects inevitable.



Composite Barriers: Geomembranes & Soil Liners

Soil liner or Geosynthetic Clay Liner (GCL):

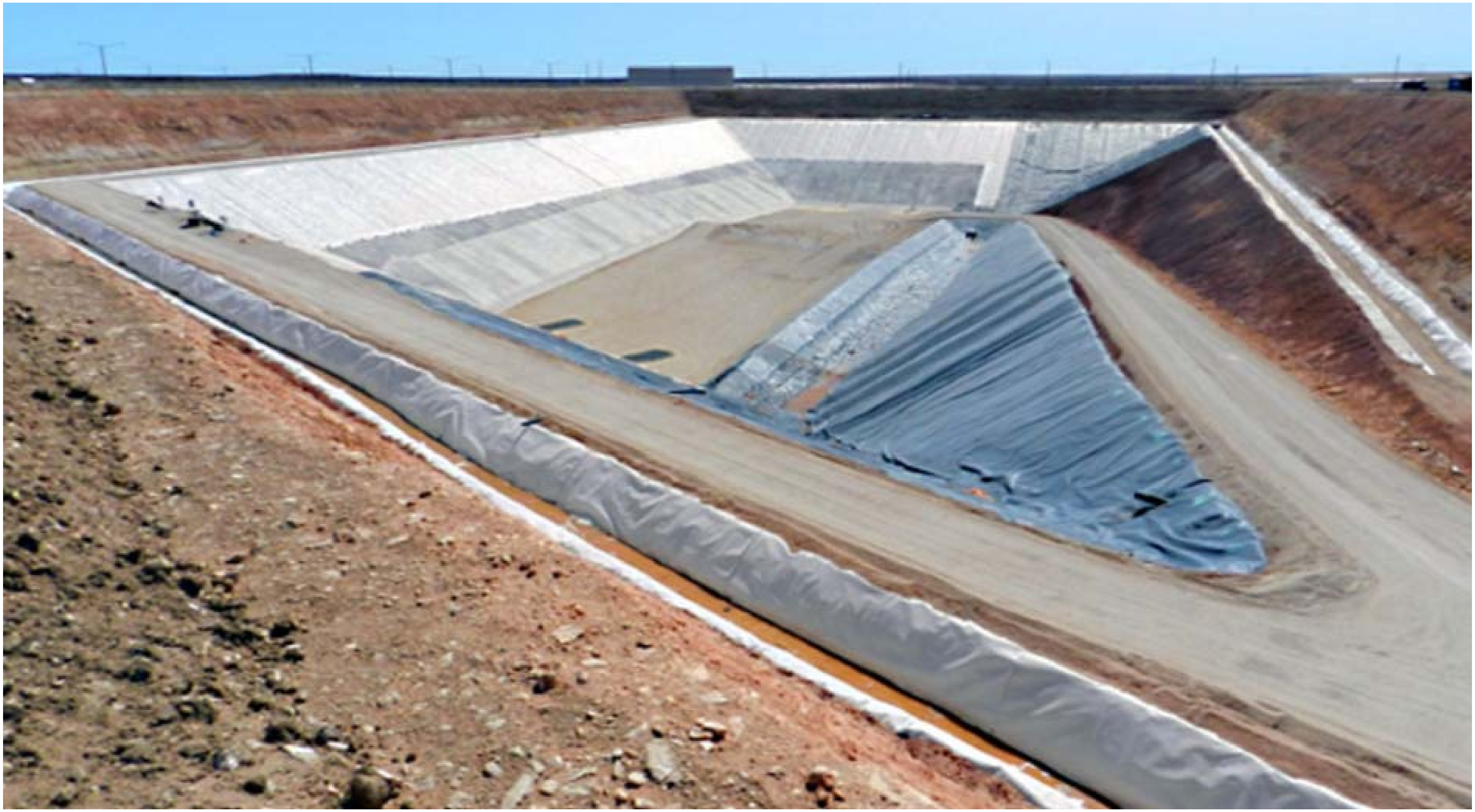
- Mineral barrier with low hydraulic conductivity. Blocks flow passing through defects in geomembrane.

- GCL is prefabricated clay liner constructed in factory with bentonite clay

Compacted Clay Liner (CCL)

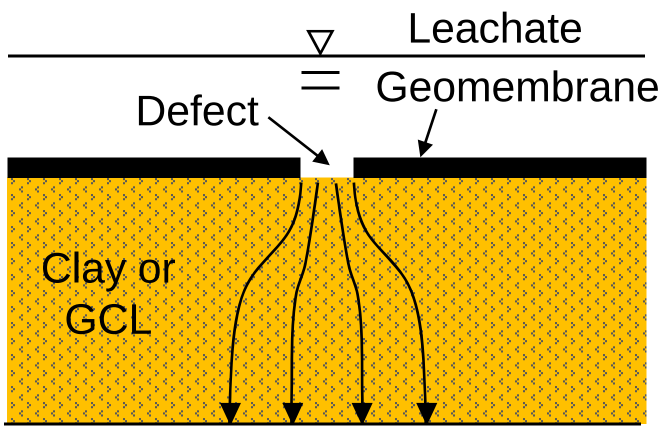
Geosynthetic Clay Liner (GCL)

Example of Composite Lined Cell WCS in Andrews, TX

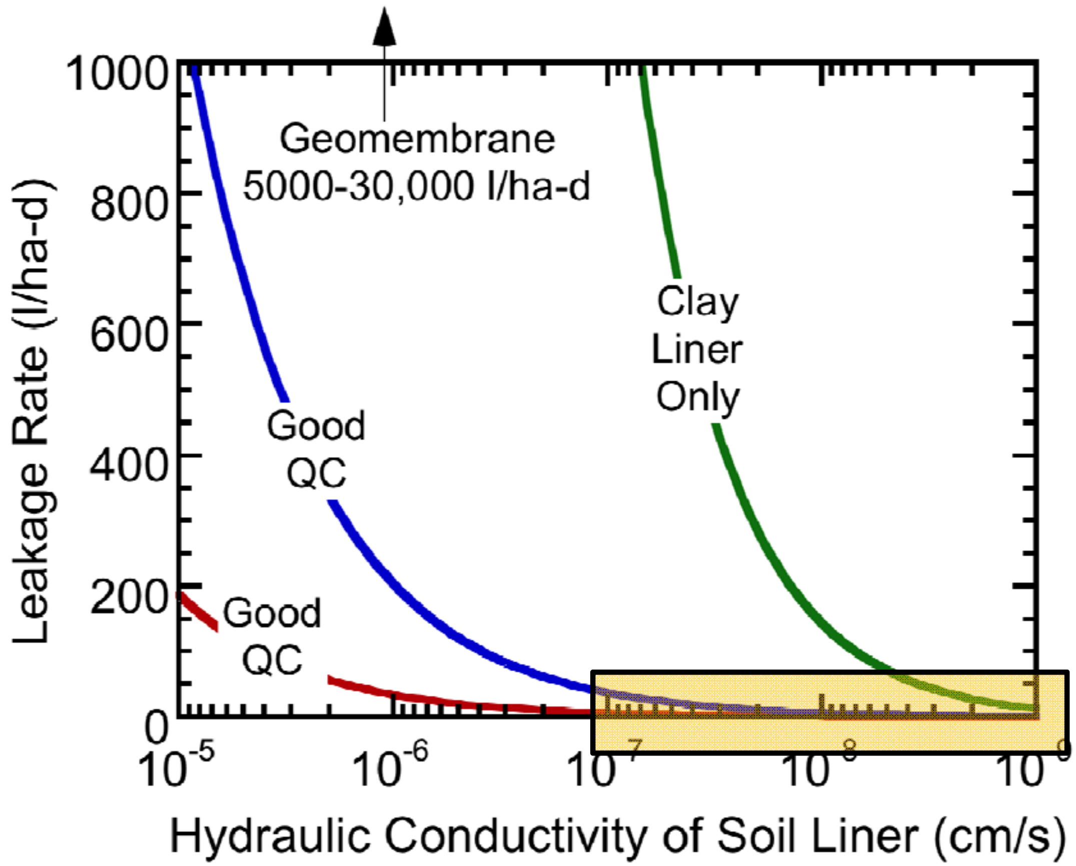


http://www.wcstexas.com/

Single Composite Liner Leakage Rates Very Low



- 1 L/ha-d = 0.04 mm/y
- Typical *primary liner* leakage rates < 10 L/ha-d, or 0.4 mm/yr



The Challenge – Extreme Service Life

- Regulations require service life > 1000 yr
- Analyze for 10,000 yr or peak.
- How long will geomembranes last?
- 10 yr, 50 yr, 100 yr, 5000 yr???

Monument on Final Cover over U tailings in disposal facility in Falls City, TX

Tian, K., Benson, C., and Tinjum, J. (2016), ANTIOXIDANT DEPLETION AND SERVICE LIFE PREDICTION FOR HDPE GEOMEMBRANES EXPOSED TO LOW-LEVEL RADIOACTIVE WASTE LEACHATE, *J. Geotechnical & Geoenvironmental Eng.*

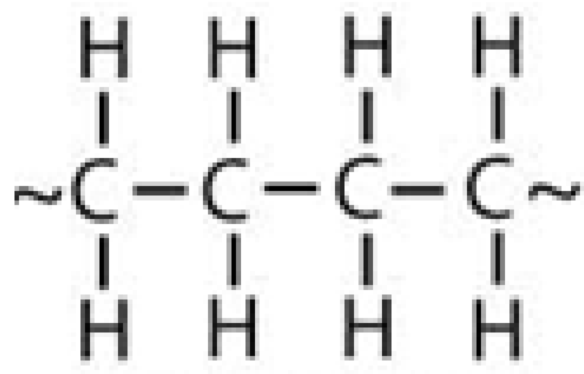
CRESP Research on HDPE Geomembranes in LLW & MW Facilities

- **Objective 1:** predict service life of HDPE geomembranes in LLW and MW disposal facilities based on current leachate composition (current conditions). – ***today's webinar***

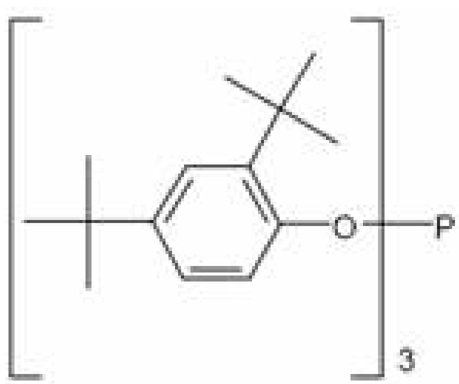
- **Objective 2:** evaluate if service life affected by higher activity environment associated with higher activity waste acceptance criteria.

Composition of HDPE Geomembranes

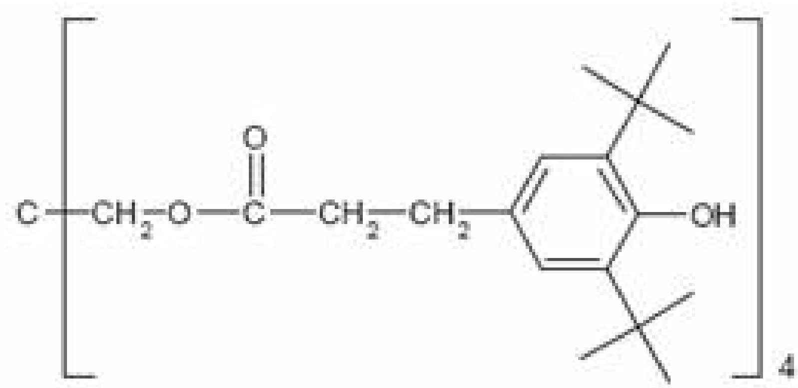
- Polyethylene (96-98%)
- Carbon black (2-3%) for ultraviolet light stabilization
- Antioxidants (<1%) to inhibit oxidation: hindered phenols, hindered amines, phosphites



Antioxidant 168



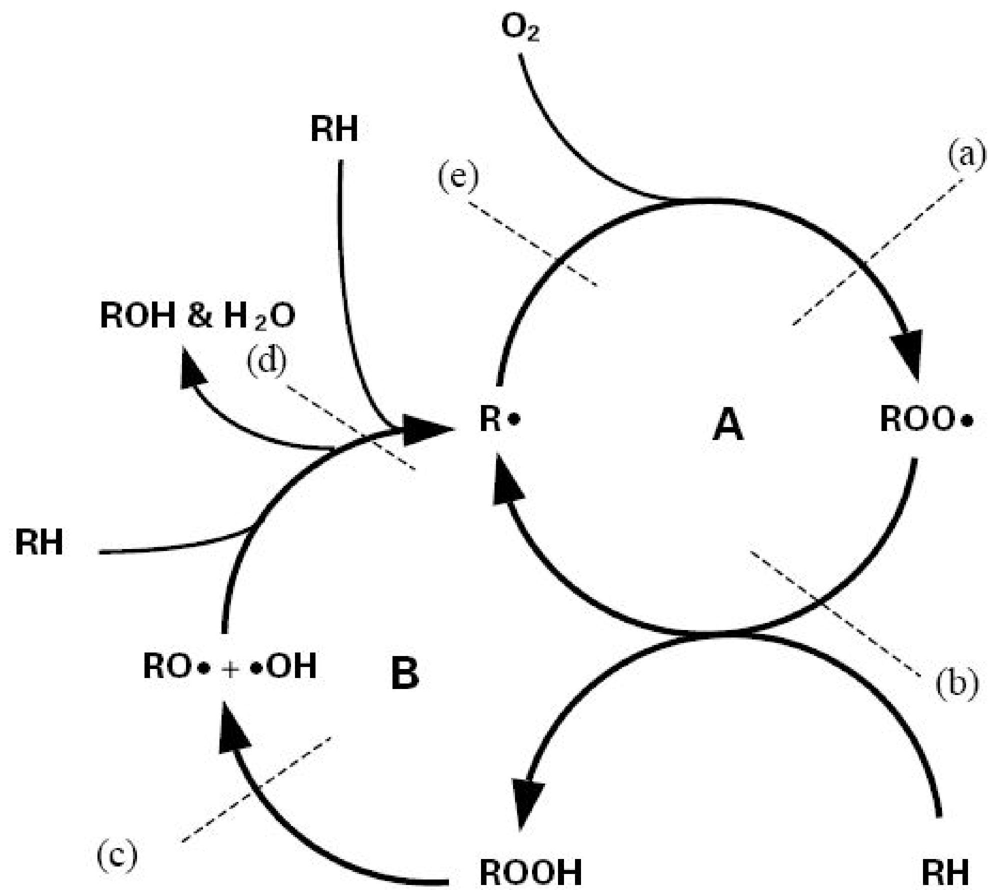
Antioxidant 1010



Oxidation:
Primary Chemical Degradation Mechanism

RH = polyethylene chain
R ● = reactive free radical
ROOH ● = hydroperoxide
ROO ● =hydroperoxy radical

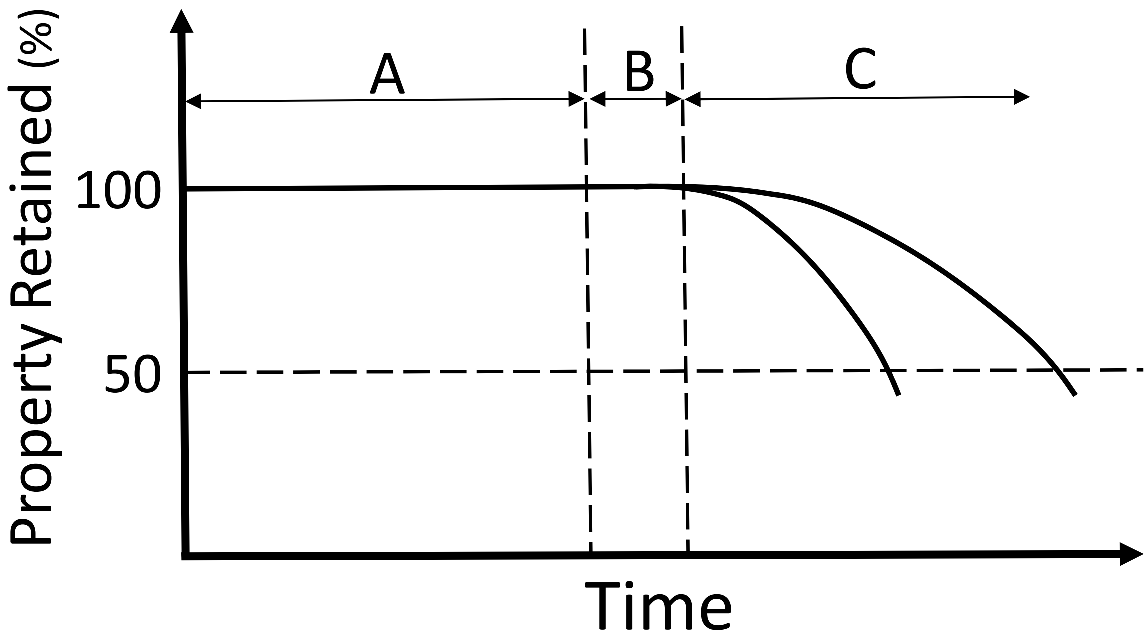
Dashed line represents antioxidant interrupting oxidation reactions by donating or capturing an electron OR reacting with free radicals to form a stable product



Modified from Grassie & Scott (1985) and Rowe & Sangam (2002)

Three Stages of Polyethylene Degradation

Service Life $T = T_A + T_B + T_C$

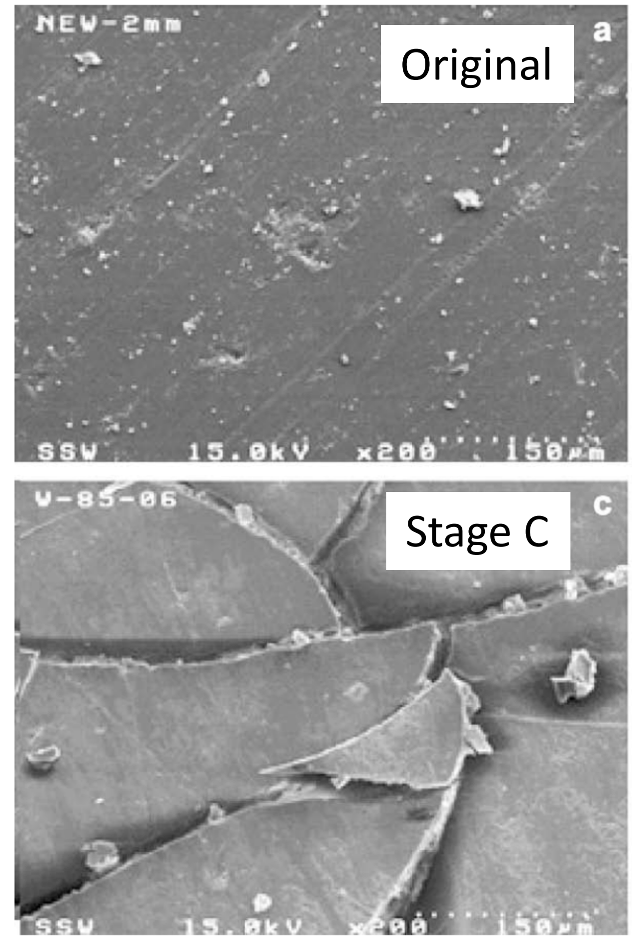


A = Antioxidant Depletion

B = Induction Time

C = 50% property degradation time

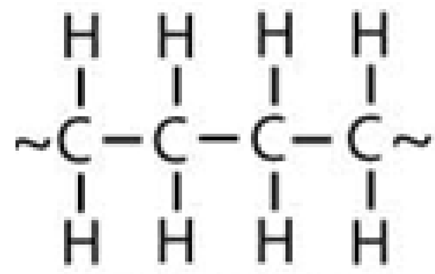
from Hsuan & Koerner (1998) and Koerner et al. (2011)



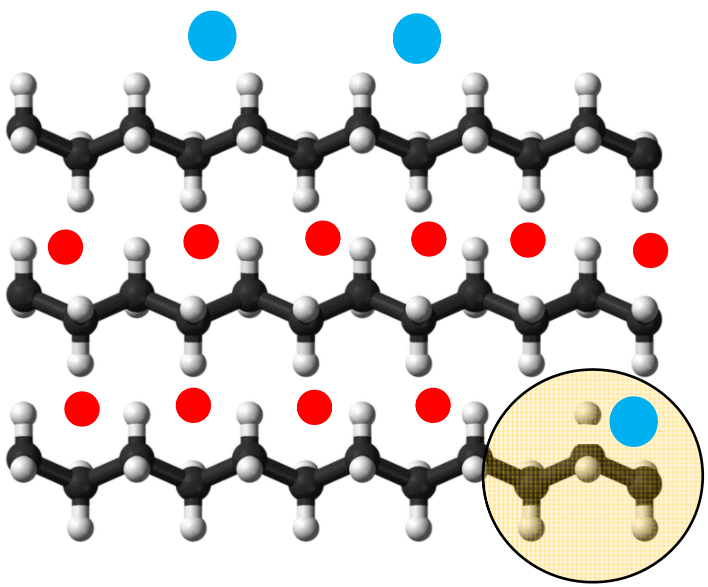
Photos from Rowe et al. 2009

Antioxidants: Function & Depletion

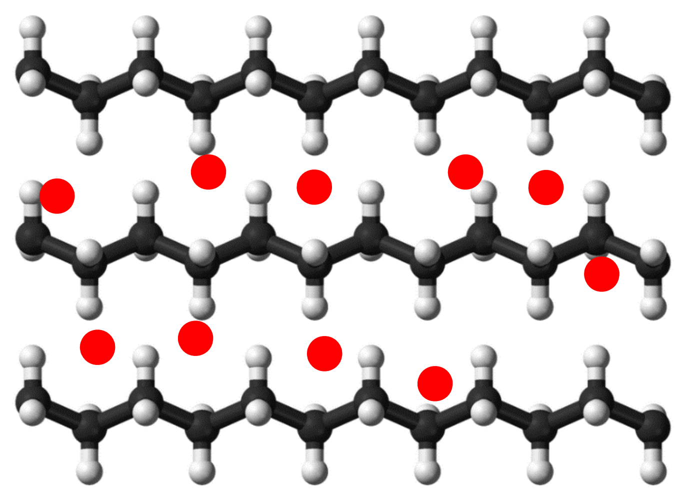
- Antioxidants
  - stabilize free radicals
  - react with oxygen
  - diffuse in water



Consumption Preventing Oxidation



Loss Via Diffusion



● **Antioxidants** ● **Oxygen**

Accelerated Testing Using Time-Temperature Superposition.

- Oxidation reactions are temperature dependent, increasing rate at higher temperature.
- Conduct tests over range of temperatures, understand how rate varies with temperature.
- Use theory (Arrhenius model) to predict rate (s) for field conditions.

$$s = Ae^{-E_a/(RT)}$$

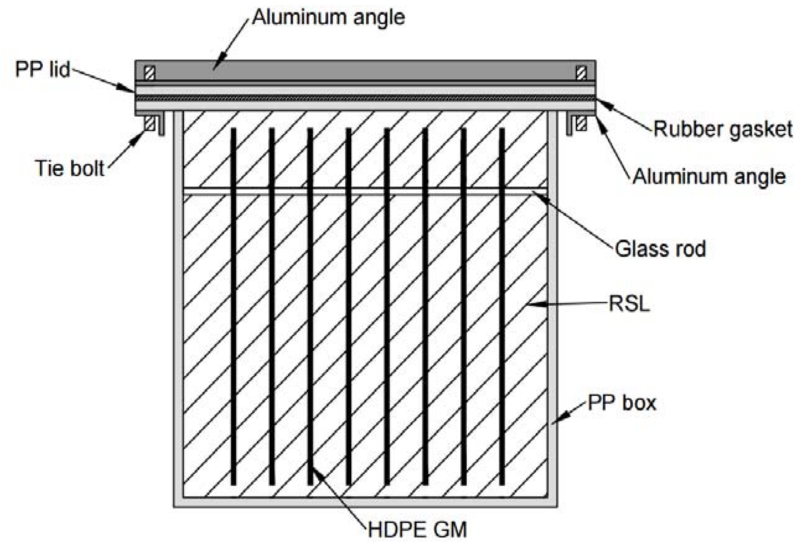
E_a is the activation energy, R is the universal gas constant, T is absolute temperature (°K), and where A is a constant.

Stage A:
Antioxidant Depletion Experiments

- Geomembranes contacted with synthetic LLW leachate at 25, 50, 70, and 90 °C.
- Immersion tests (two side exposure) & column tests (one side exposure) at elevated temperatures.
- Measure antioxidant depletion using oxidation induction time (OIT) using differential scanning calorimetry (DSC).
- Predict antioxidant depletion time using Arrhenius model.
- Evaluate physical properties: molecular weight, melt flow index, crystallinity. ***Consistent with Stage A?***

Immersion Tests in Synthetic LLW Leachate

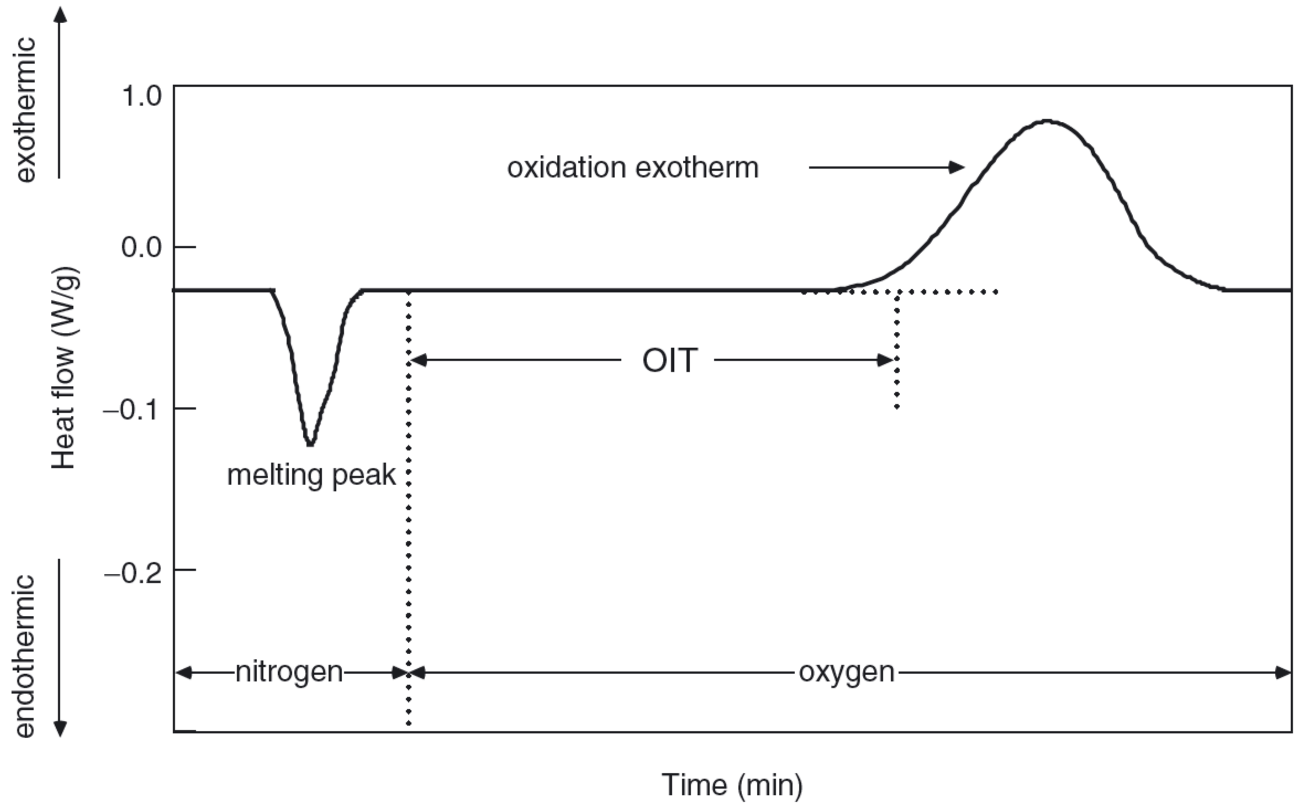
- RSL, NSL, & DI water at 25, 50, 70, and 90 °C
- Samples removed monthly
- OIT tests conducted to monitor antioxidant depletion.

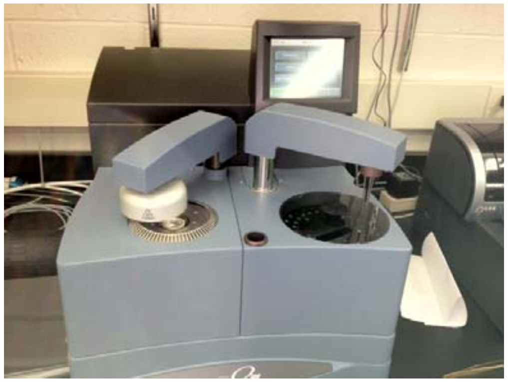


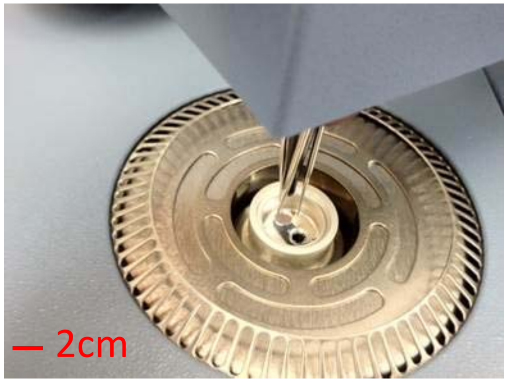
RSL = radioactive synthetic LLW leachate
NSL = non-radioactive synthetic LLW leachate

Measuring Antioxidant Depletion

- Standard oxidative induction time **(OIT)** Test (ASTM 3895) by Differential Scanning Calorimetry (DSC)



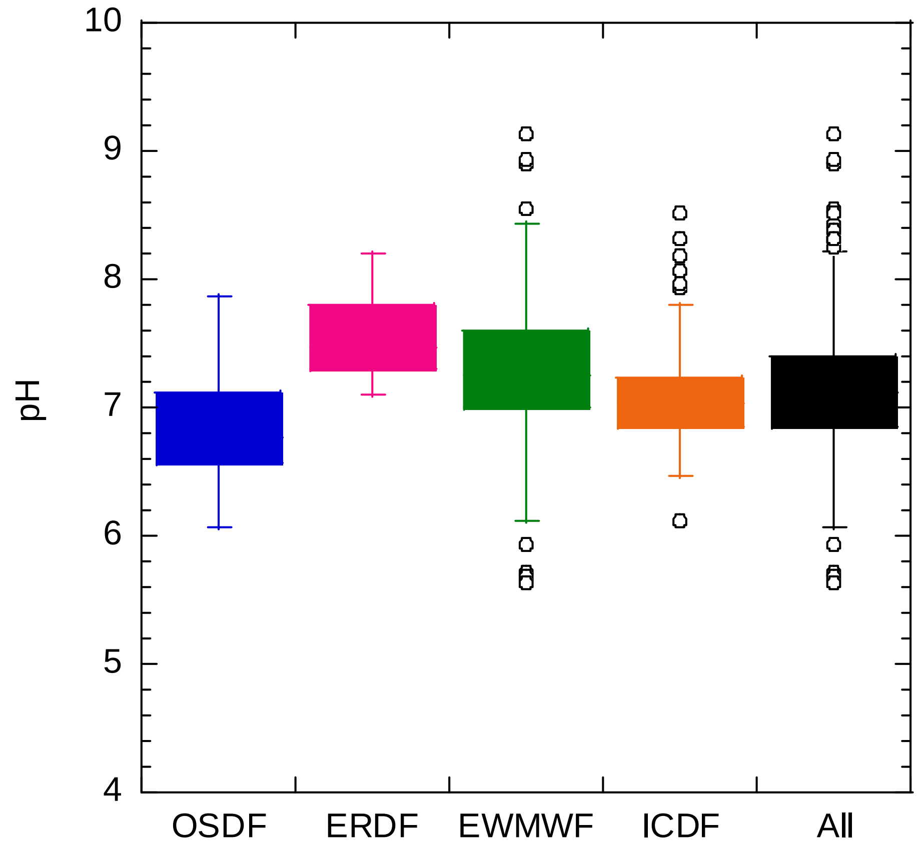


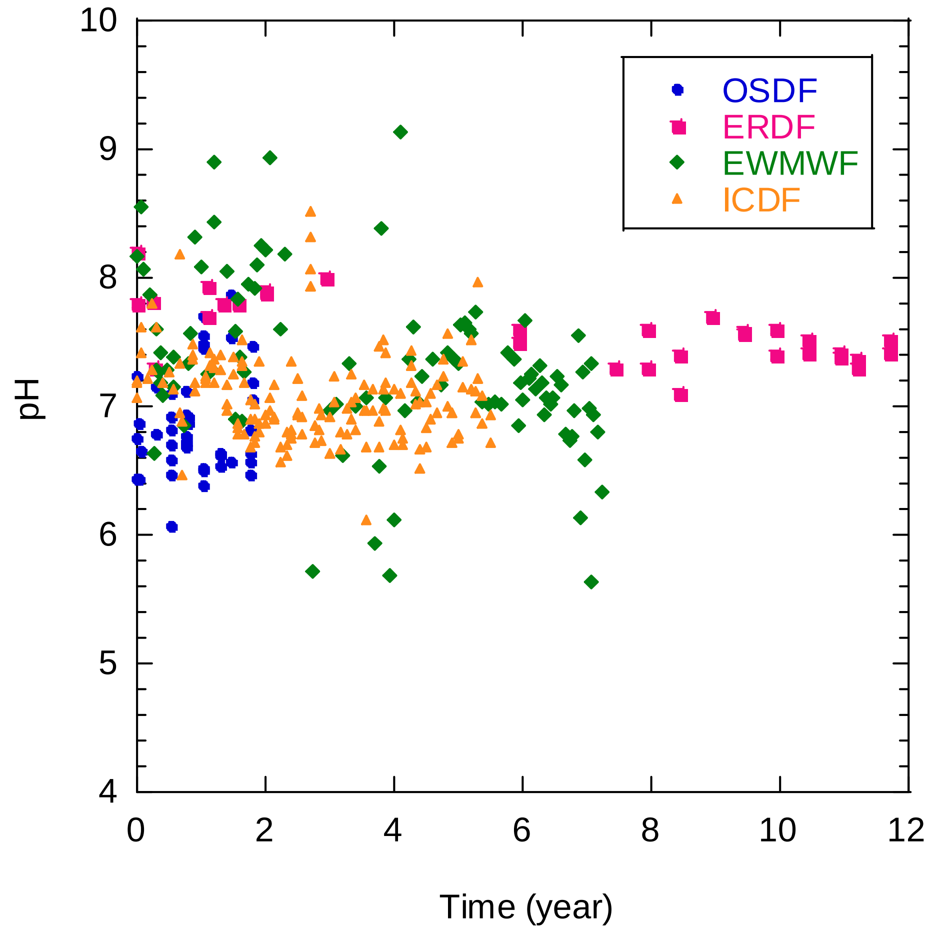


Data Sources for Leachate

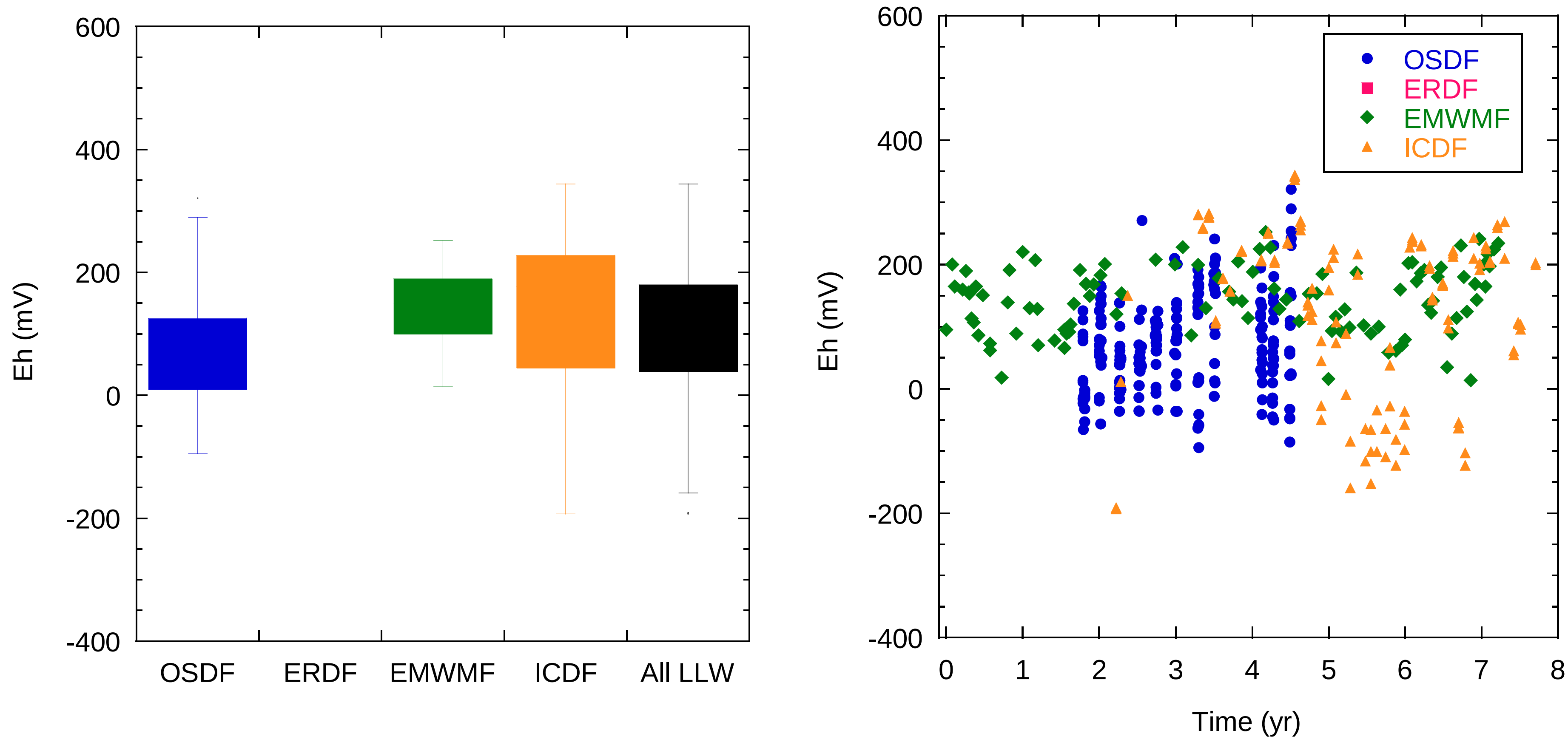
- ERDF, OSDF, ICDF, and EMWMF disposal facilities
- Segregated components into:
  - Inorganic macro-components - major cations (Ca, Mg, Na, and K) and major anions (Cl, SO_4^{2-}, HCO_3^-, and NO_3^-/NO_2^-)
  - Trace heavy metals, such as Al, As, Ba, Cu, Fe, Li, Mn, Ni, Sr, and Zn
  - Radionuclides: e.g., uranium, Tc-99, Sr-90, and H-3
  - Organic compounds (Mean ~ 8 mg/L)

pH of LLW leachate

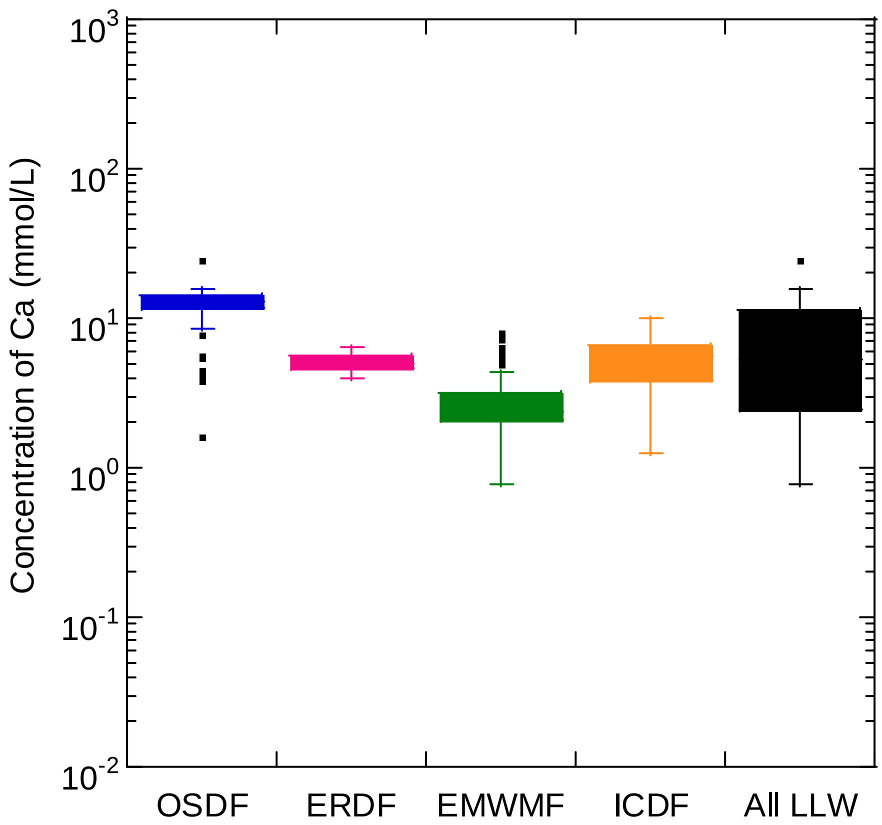


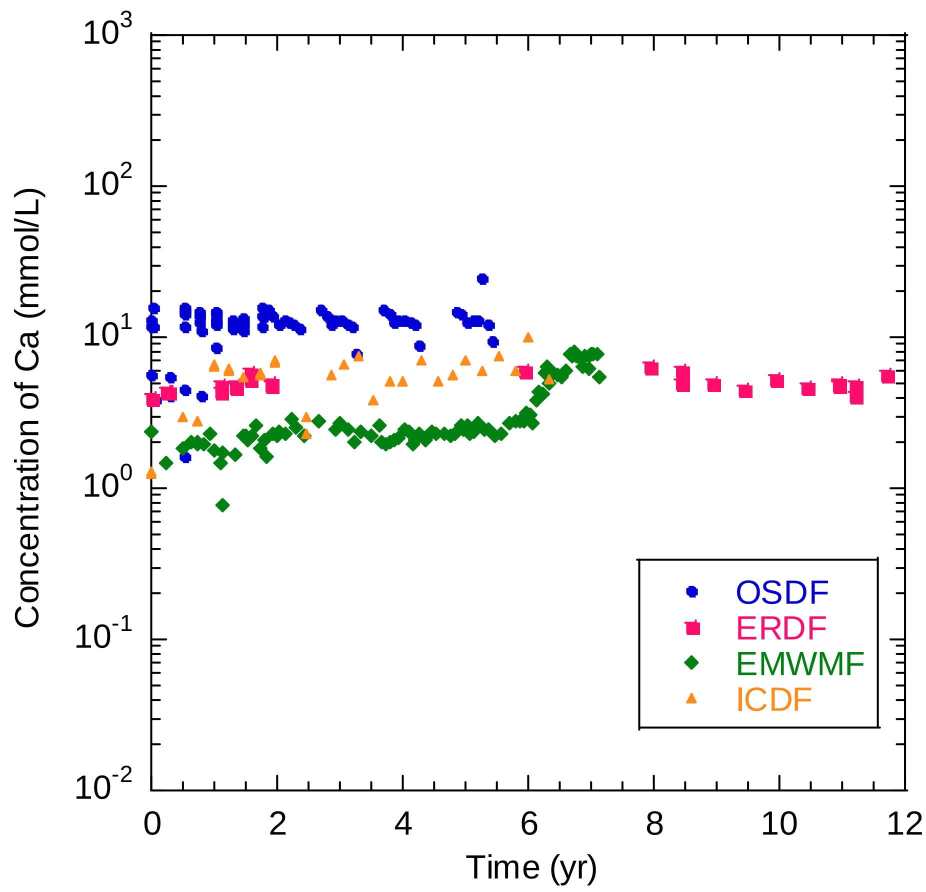


Eh of LLW leachate

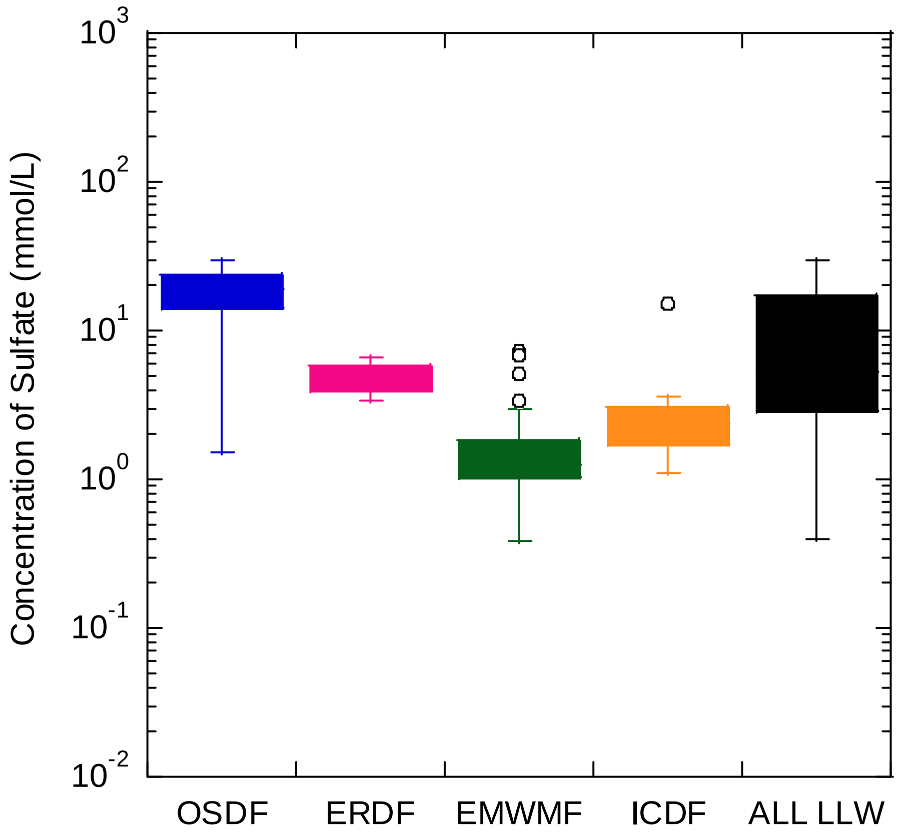


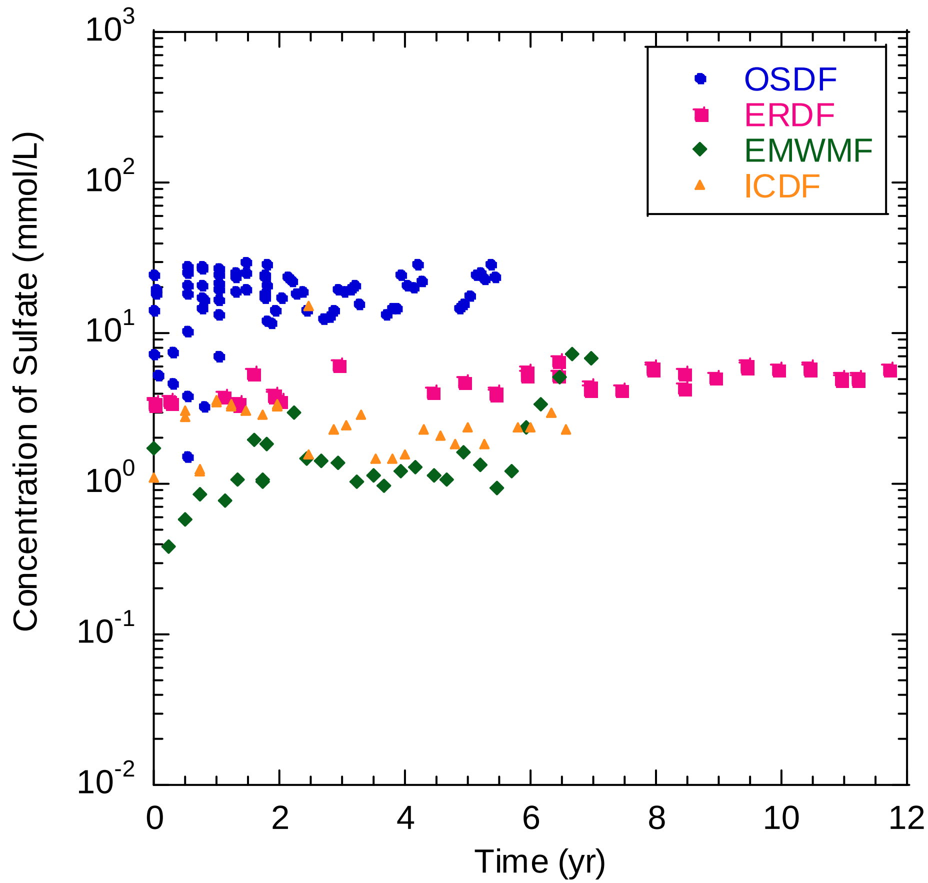
Major Cations: Calcium



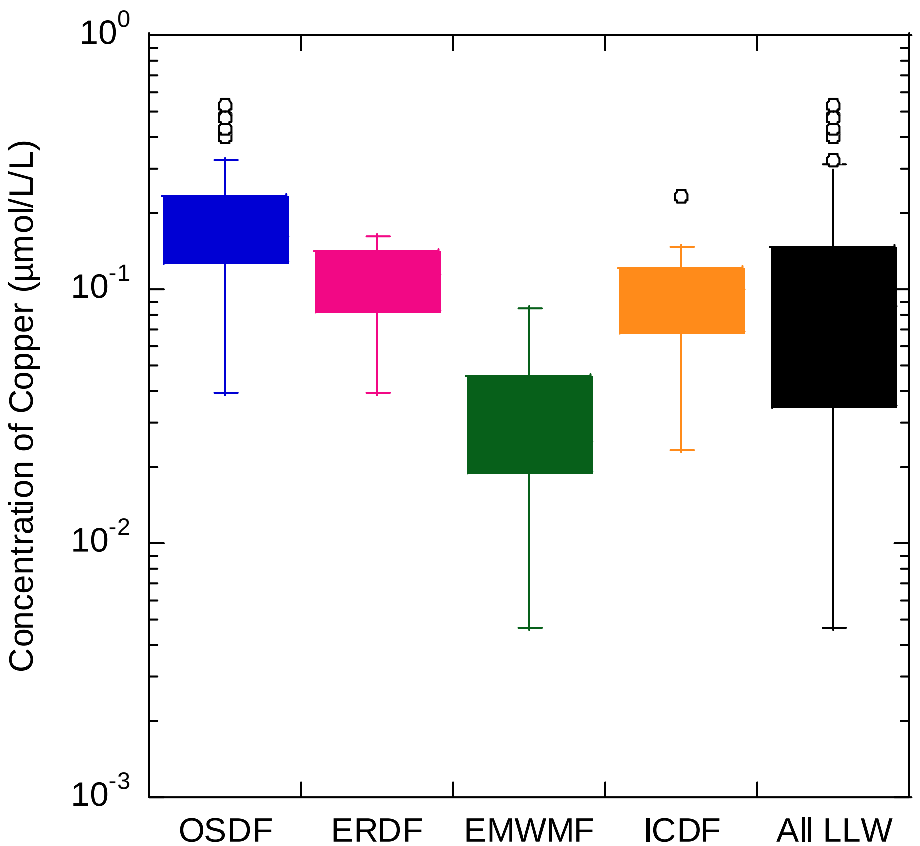


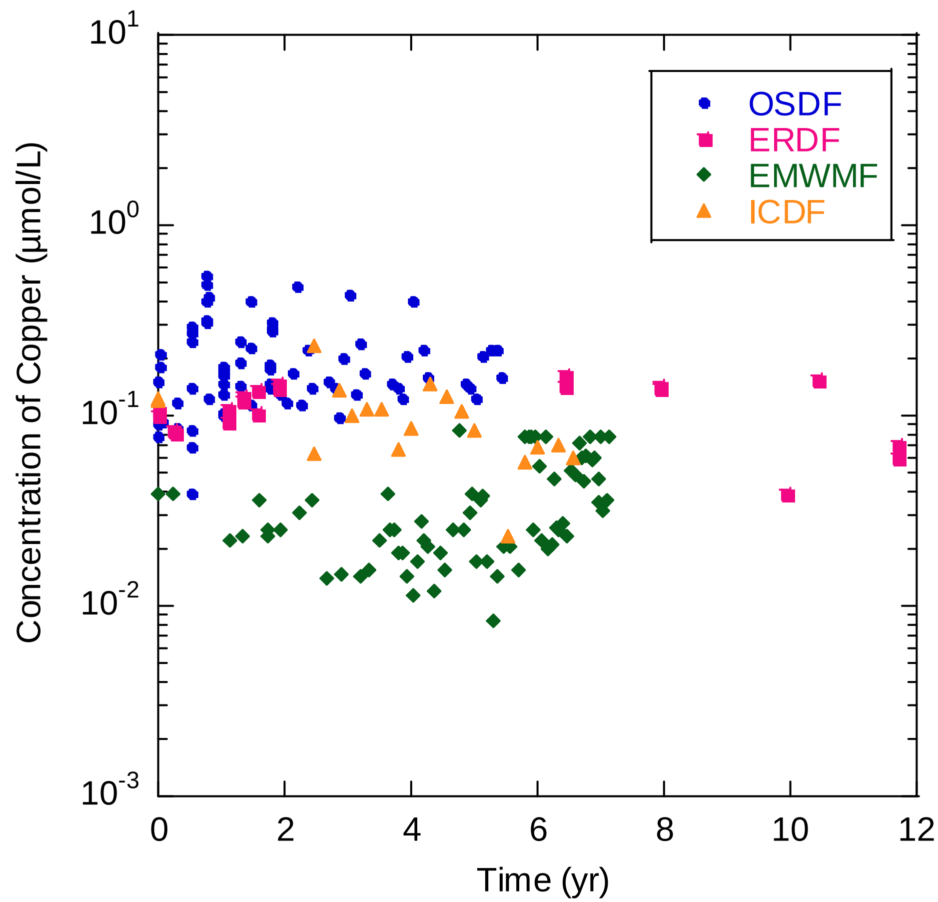
Major Anions: Sulfate



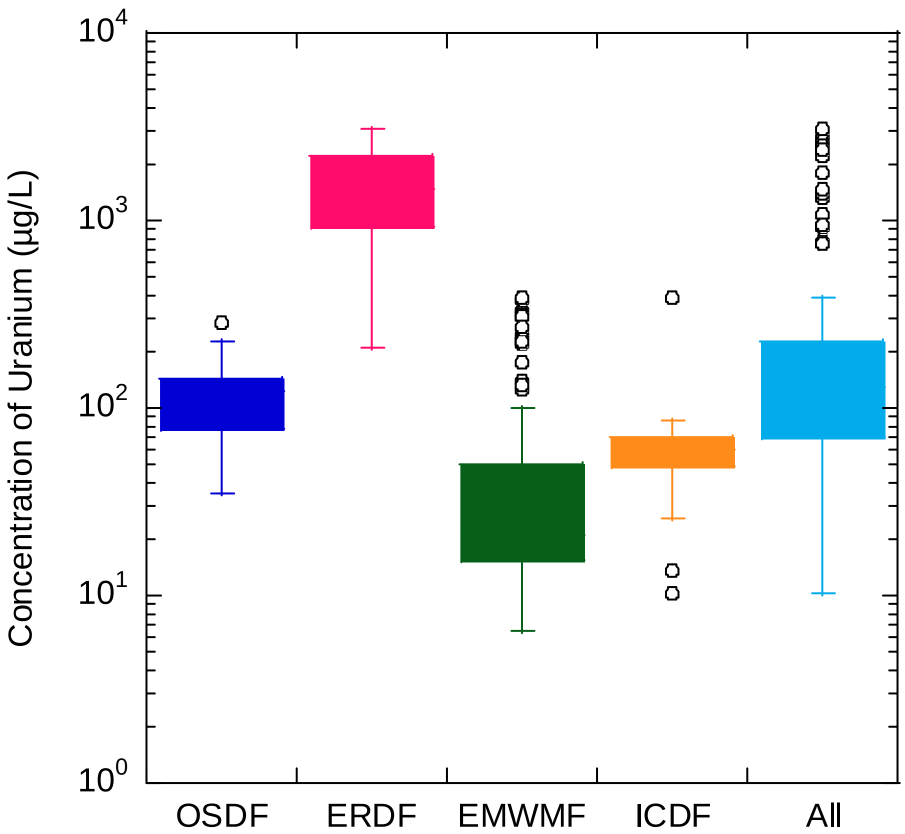


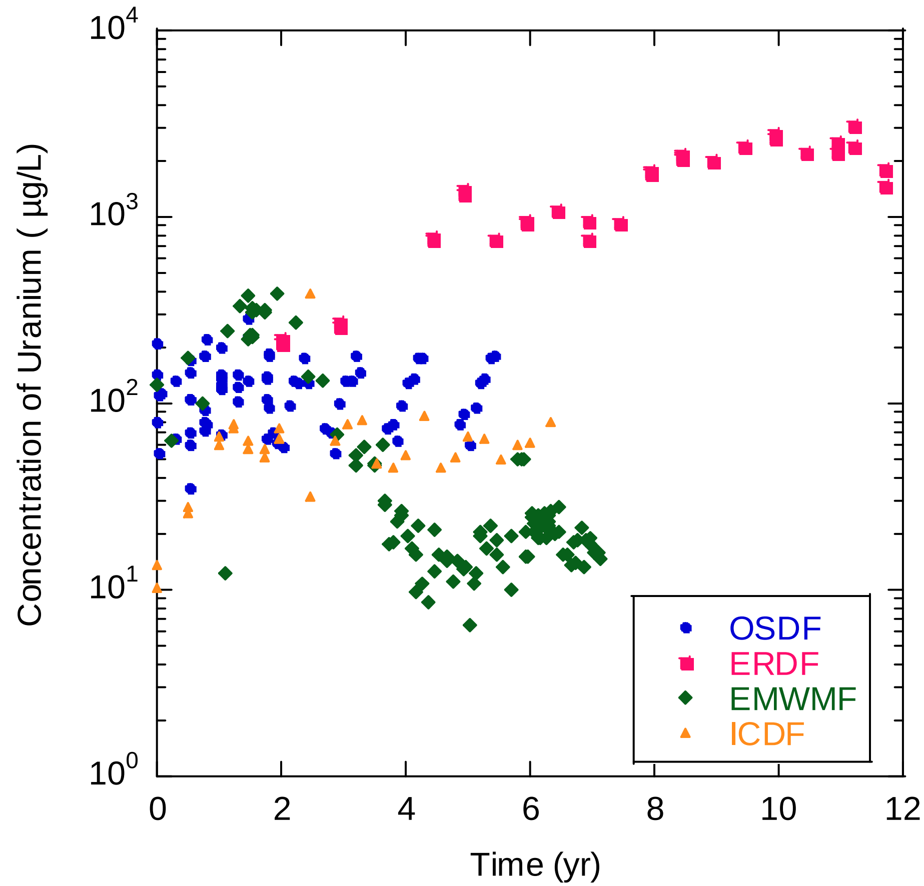
Trace Metal: Copper



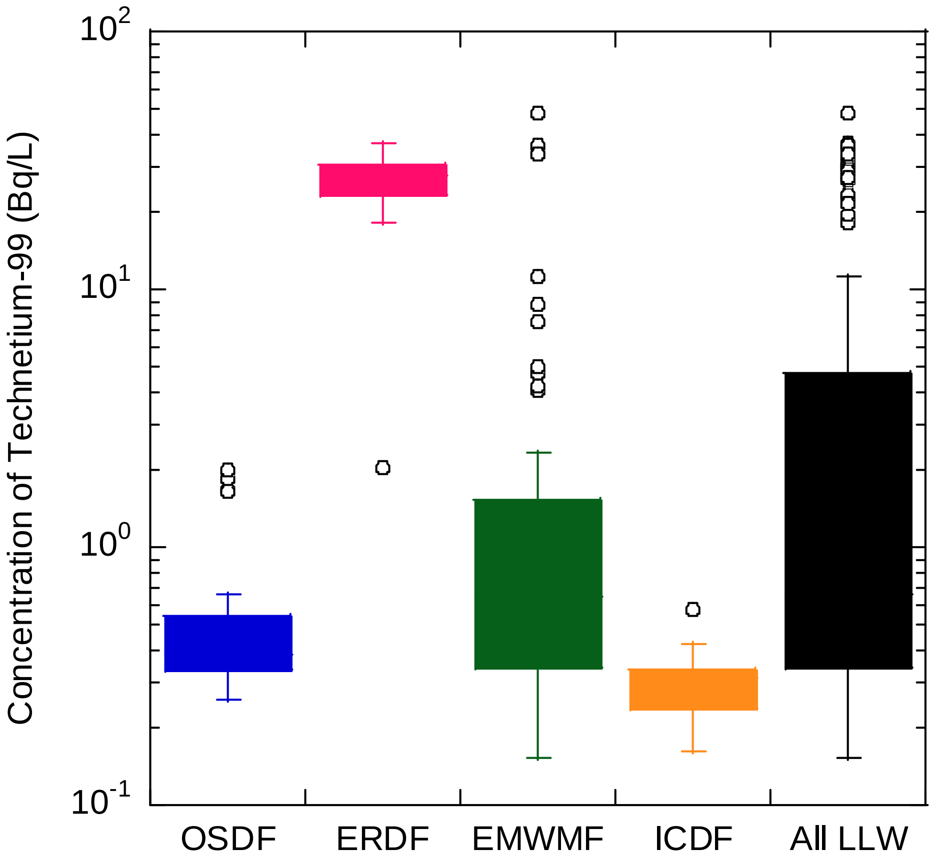


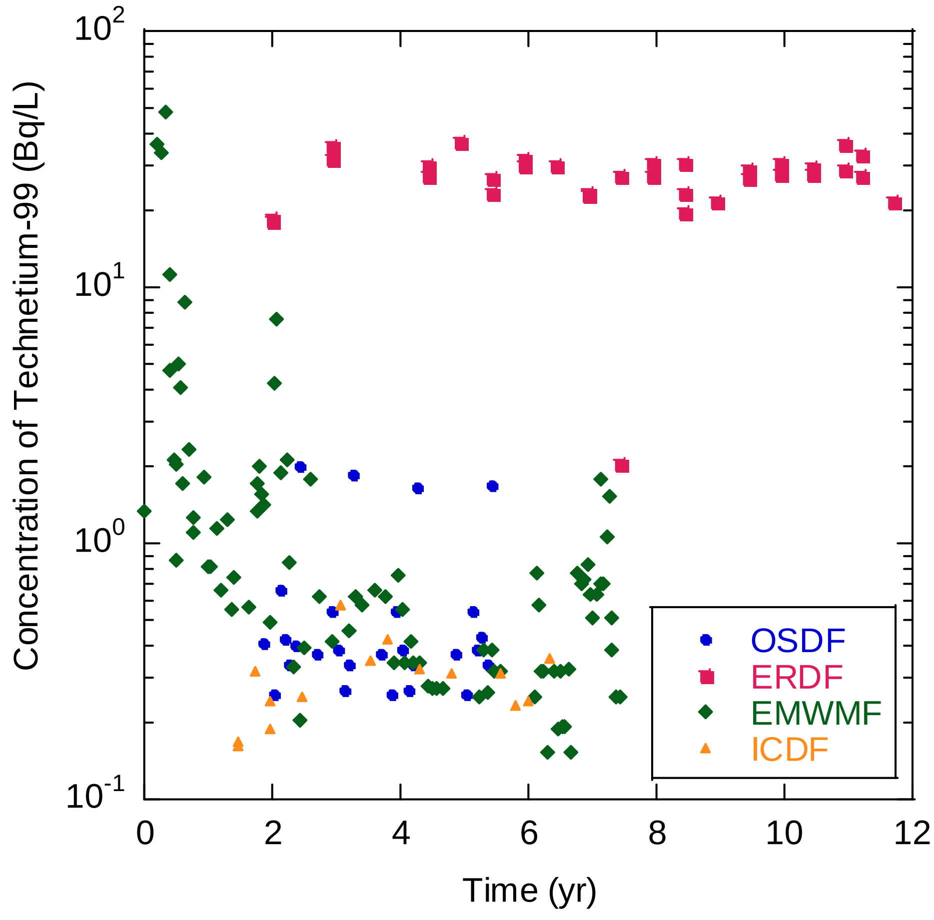
Radionuclides: Uranium





Radionuclides: Tc-99



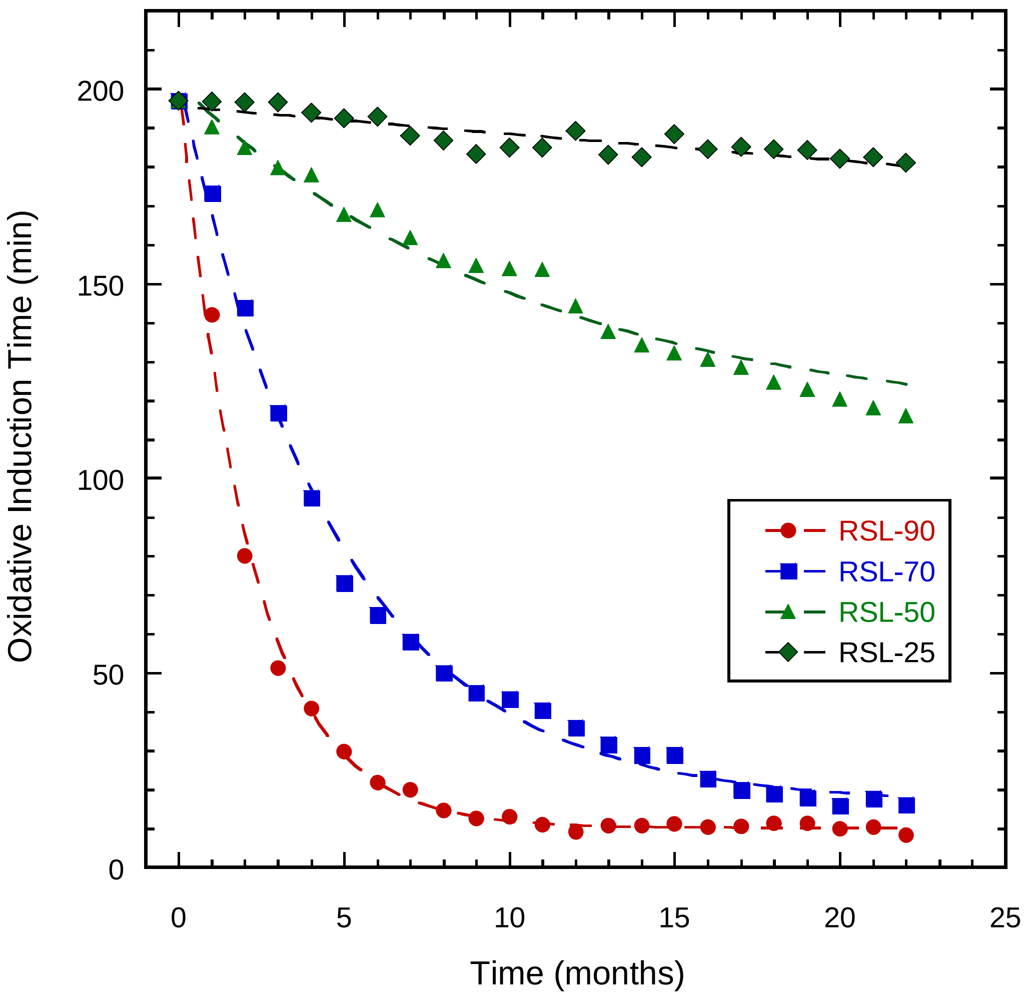


Synthetic Leachate for Immersion Test

1) Radioactive Synthetic Leachate **(RSL)**
2) Non-radioactive Synthetic Leachate **(NSL)**
3) Deionized Water (control)

Major Cations/Anions (mM)		**Trace Metals (mM)**			
Ca^{2+}	4	As	0.001	Al	0.03
Mg^{2+}	6	Ba	0.002	Mn	0.01
Na^{+}	7	Cu	0.0002	Ni	0.0003
K^{+}	0.7	Fe	0.04	Sr	0.02
Sulfate	7.5	Li	0.02	Zn	0.0005
Chloride	8	**Chemical Characteristics**			
Nitrate	1.5	TOC (mg/L)			8
Alkalinity	3.5	Eh (mv)			120
Radionuclides		pH			7.2
U-238 (μg/L)	1500	*Ionic Strength (mM)*			***43.6***
H-3 (Bq/L)	4400	*Ratio of monovalent to divalent cations ($M^{1/2}$) (Kolstad et al. 2004)*			***0.077***
Tc-99 (Bq/L)	29				

Antioxidant Depletion in RSL



$$OIT_t = OIT_r + (OIT_0 - OIT_r)\exp(-st)$$

OIT_t = OIT after aging

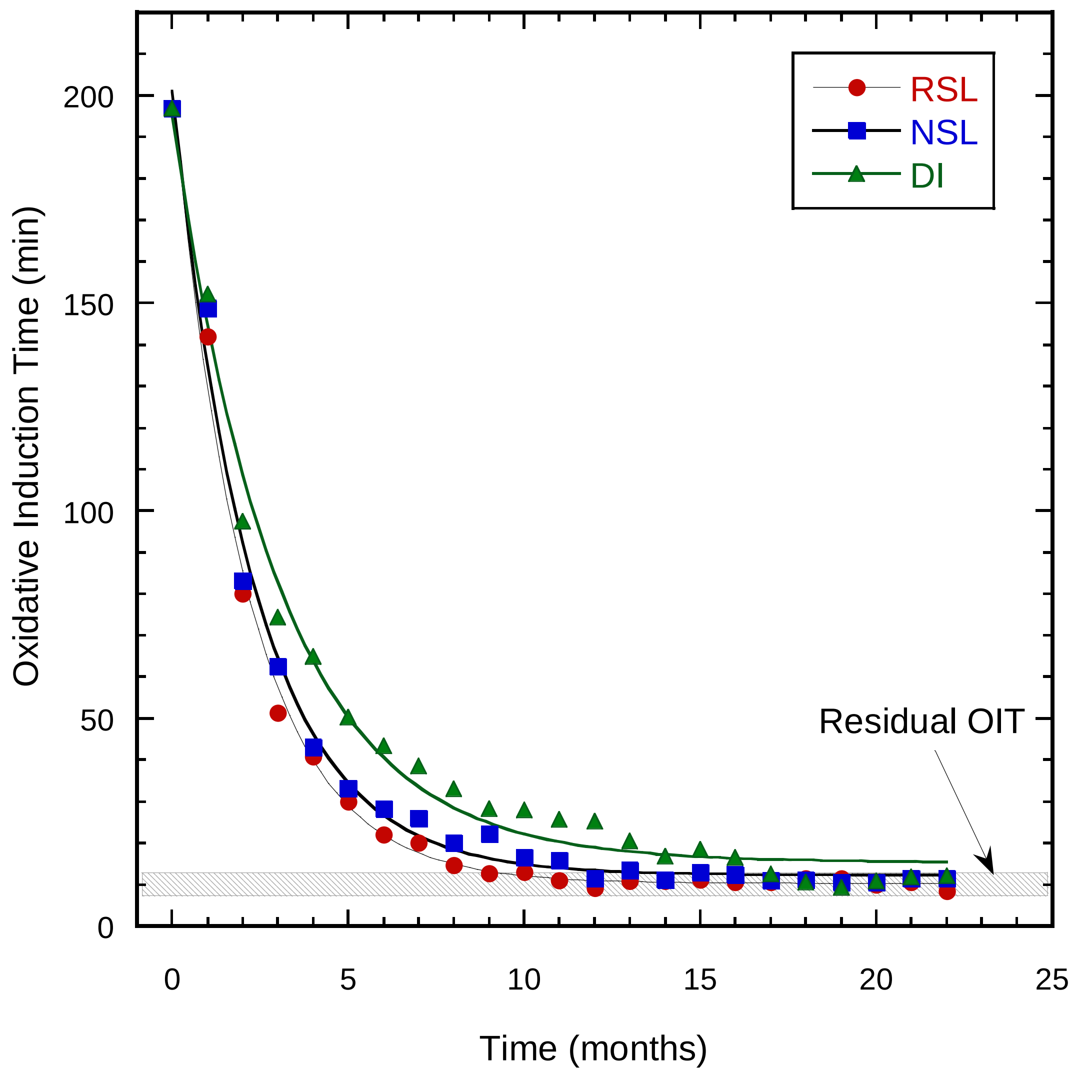
OIT_r = residual OIT time

OIT_0= initial OIT

s = antioxidant depletion rate

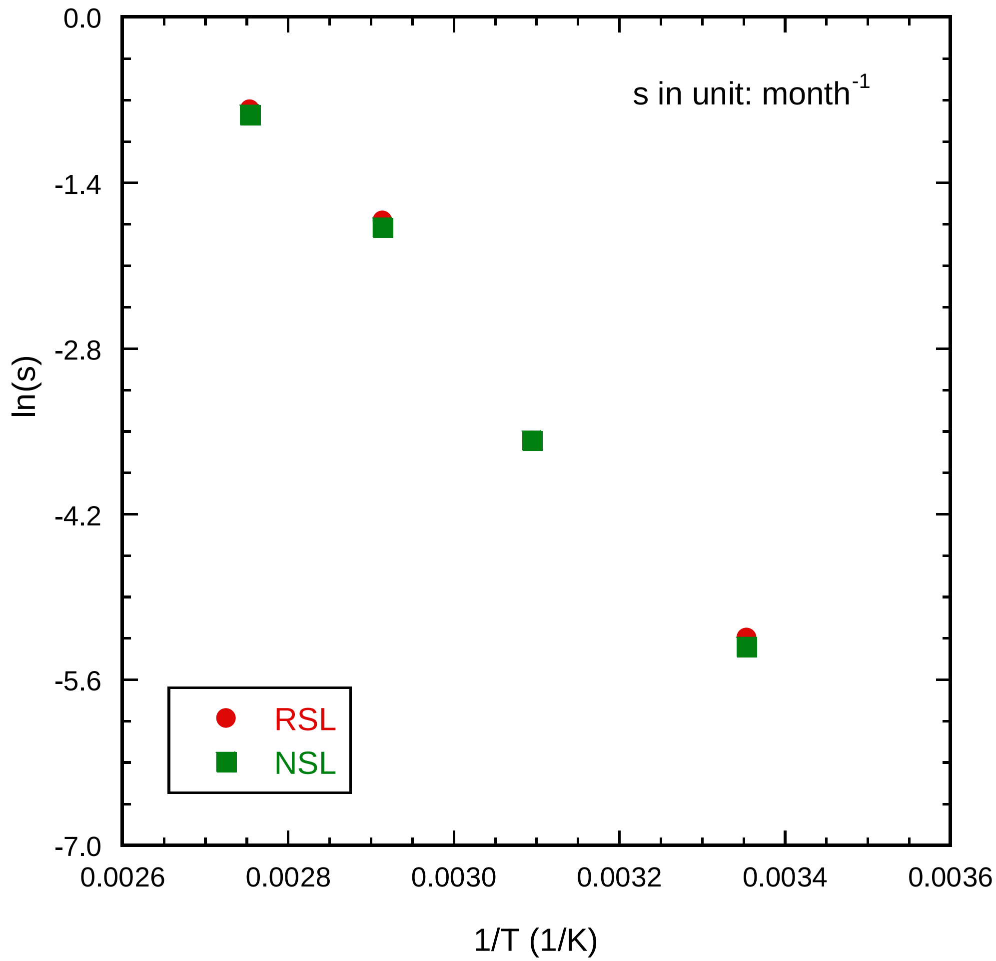
t =aging time

Residual OIT



- Relatively constant OIT at end of test for all test liquids.
- Not an artifact of methodology.
- Assume antioxidants remaining at residual no longer effective in preventing oxidation

Effect of Radionuclides in Leachate

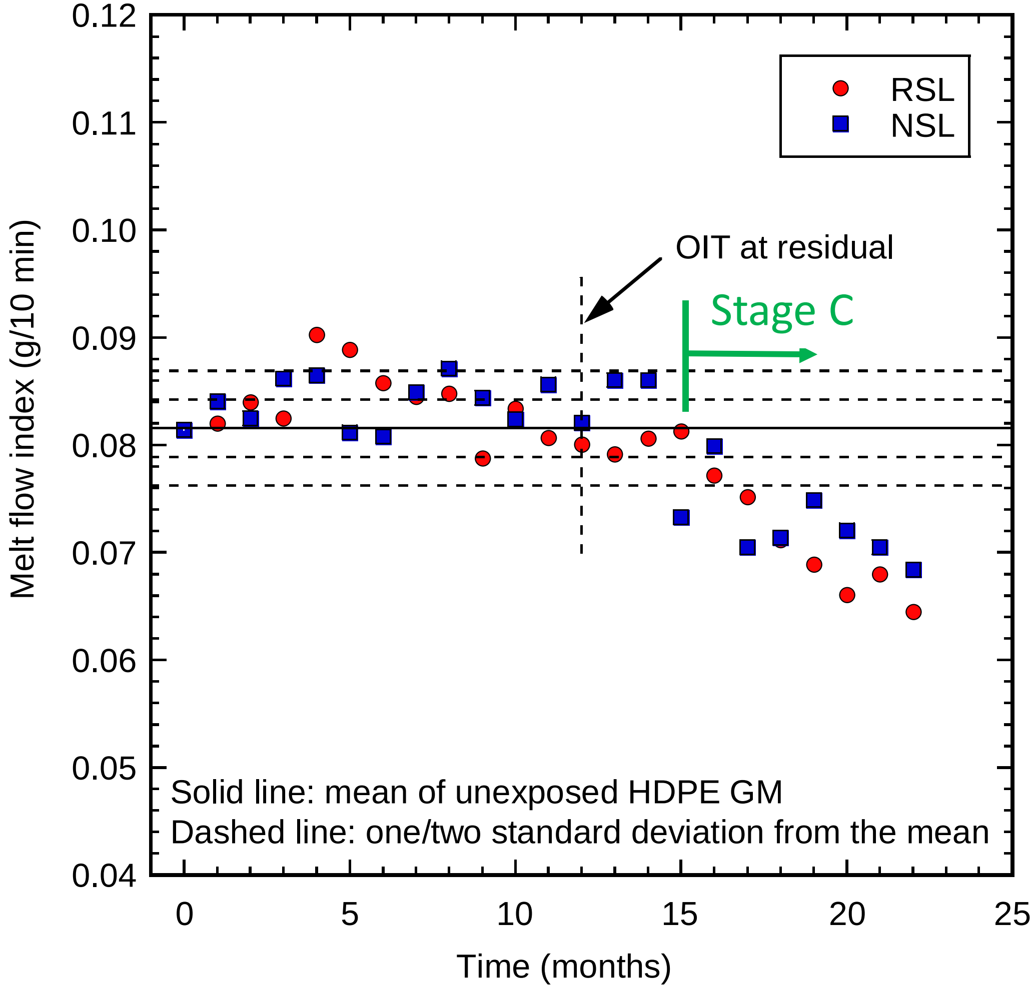


Temp (°C)	Antioxidant Depletion Rate, s ln(min)/month		Ratio
	NSL	RSL	RSL/NSL
25	0.0043	0.0047	**1.09**
50	0.0278	0.0277	**1.00**
70	0.1789	0.1862	**1.04**
90	0.4319	0.4569	**1.06**

Effect of radiation from RSL on antioxidant depletion subtle, ***not statistically significant***.

Rate ***slower than for municipal solid waste (MSW) leachate*** because little surfactants in LLW and MW leachates.

Physical Properties: Melt Flow Index



Similar findings for crystallinity and tensile strength. Stages B and C occurring after residual OIT reached.

- Oxidation breaks down polymer chains, making polymer less viscous under a standard heat and pressure.
- No change in MFI until after residual OIT reached. Consistent with no oxidation.
- Drop after 14 months indicates Stage C, oxidative degradation

Recap – Lessons Learned

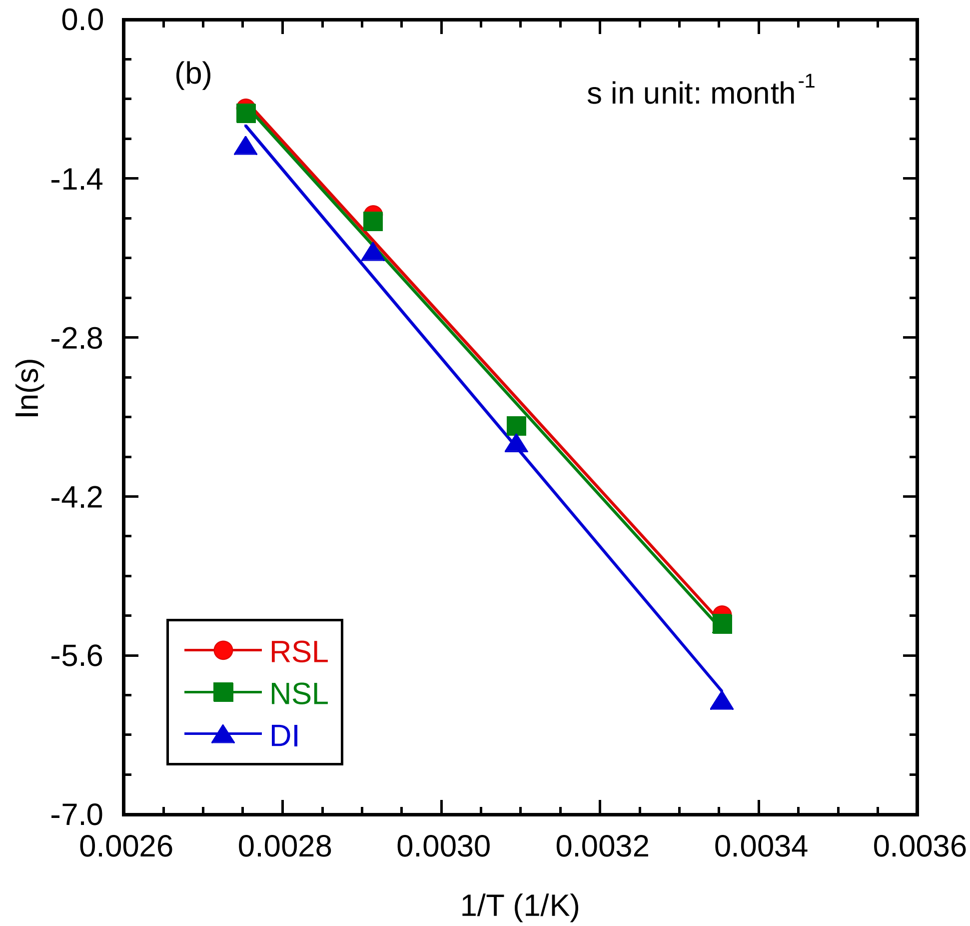
- Antioxidant depletion first order and sensitive to temperature (as expected).
- Reaching residual OIT indicates end of Stage A
- Physical properties (melt flow index, crystallinity, tensile strength) consistent with Stages B and C occurring after residual OIT reached.
- Similar rates in RSL and NSL liquids – slightly more with radionuclides but not statistically significant.

Predicting Field Conditions: Arrhenius Model

$$s = Ae^{-E_a/(RT)}$$

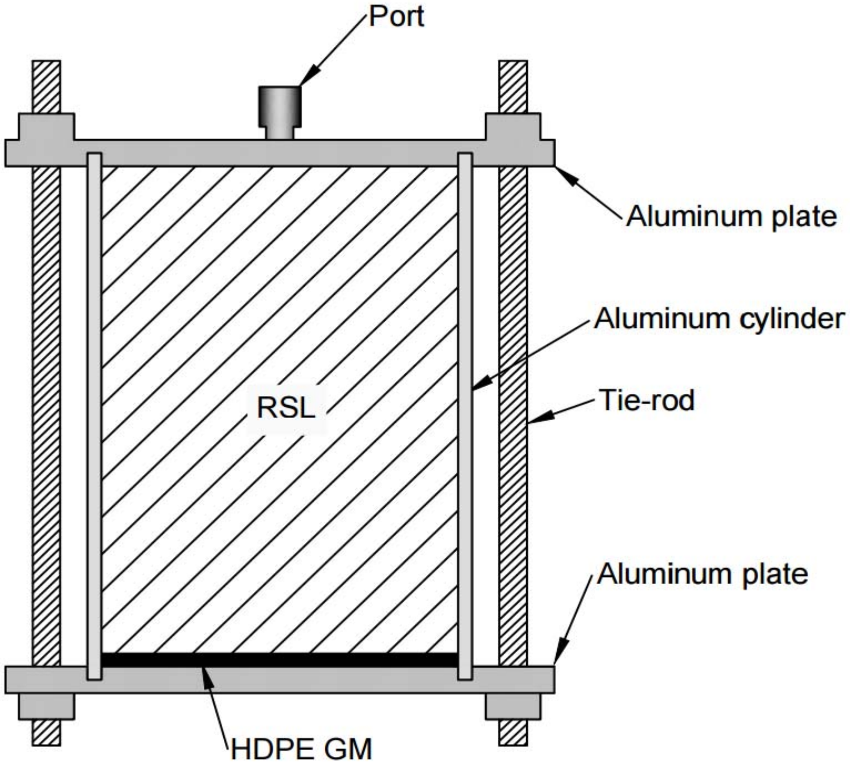
E_a = activation energy
R = universal gas constant
T = absolute temperature (°K)
A = constant

Use equation with parameters below to predict rate (s) at any temperature.



Immersion Liquid	Arrhenius Equation		Activation Energy (E_a) (kJ/mol)
	$\ln(s) = \ln(A) - (E_a/R) / T$	R^2	
RSL	$\ln(s) = 20.043 - 7879 / T$	0.99	**65.4**
NSL	$\ln(s) = 20.193 - 7922 / T$	0.99	**65.8**
DI	$\ln(s) = 22.203 - 8383 / T$	0.99	**69.7**

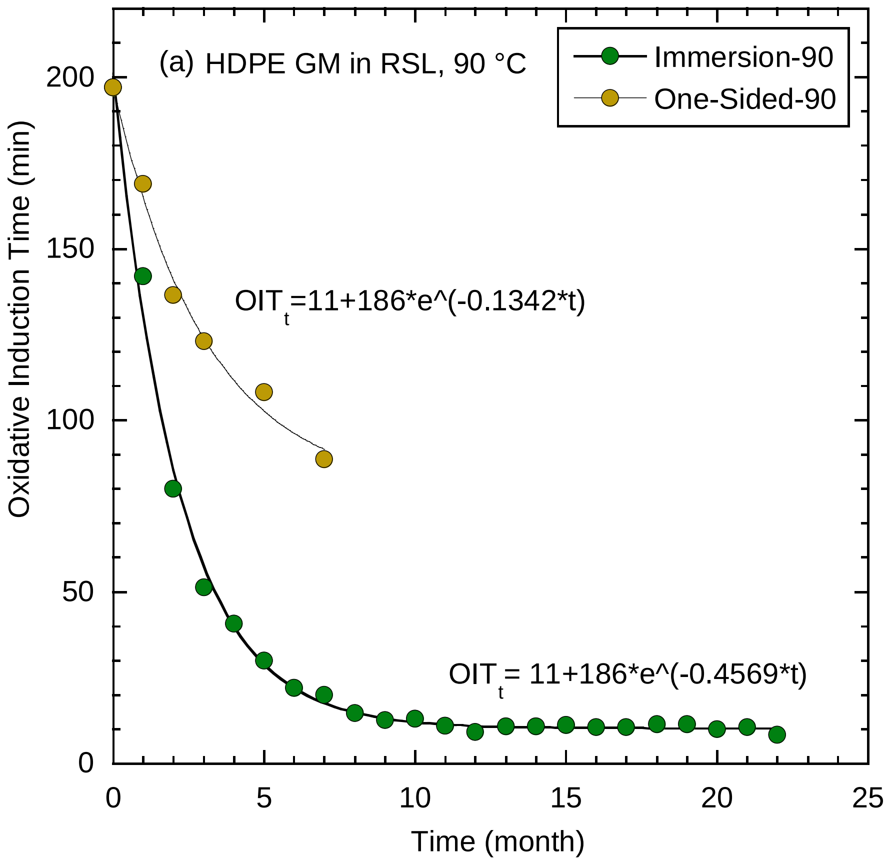
Scaling Two-Side Immersion Test to One-Sided Field Scenario

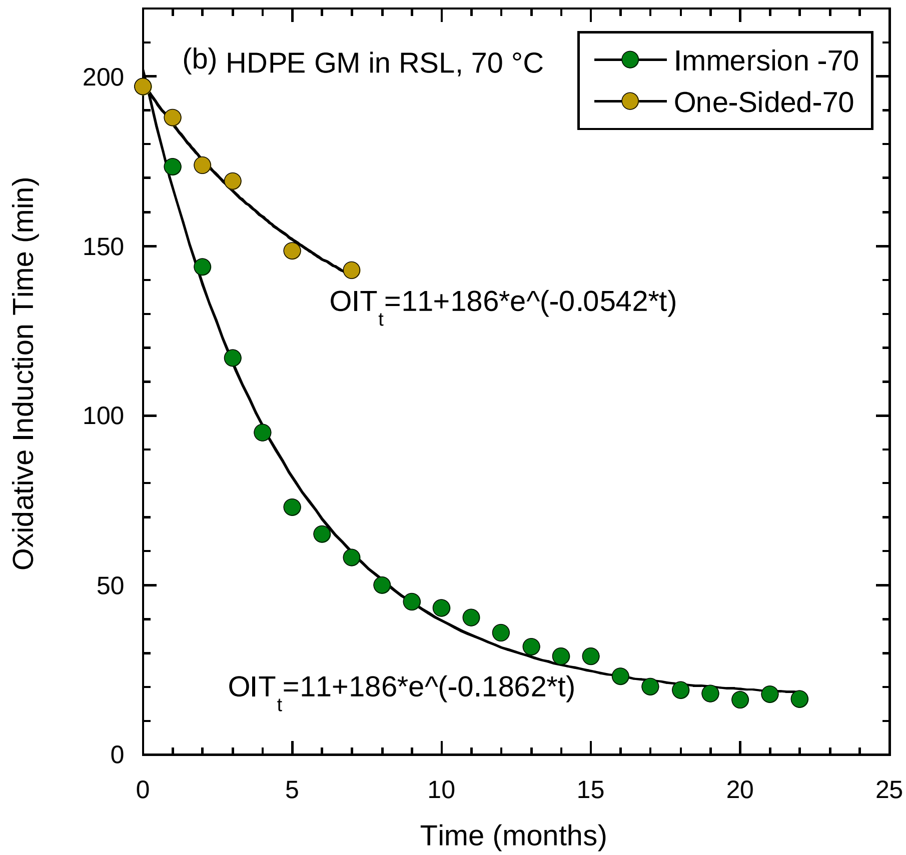


- One side exposed to represent field condition
- RSL or NSL over geomembrane at base.
- Lower surface of geomembrane not in contact with leachate.

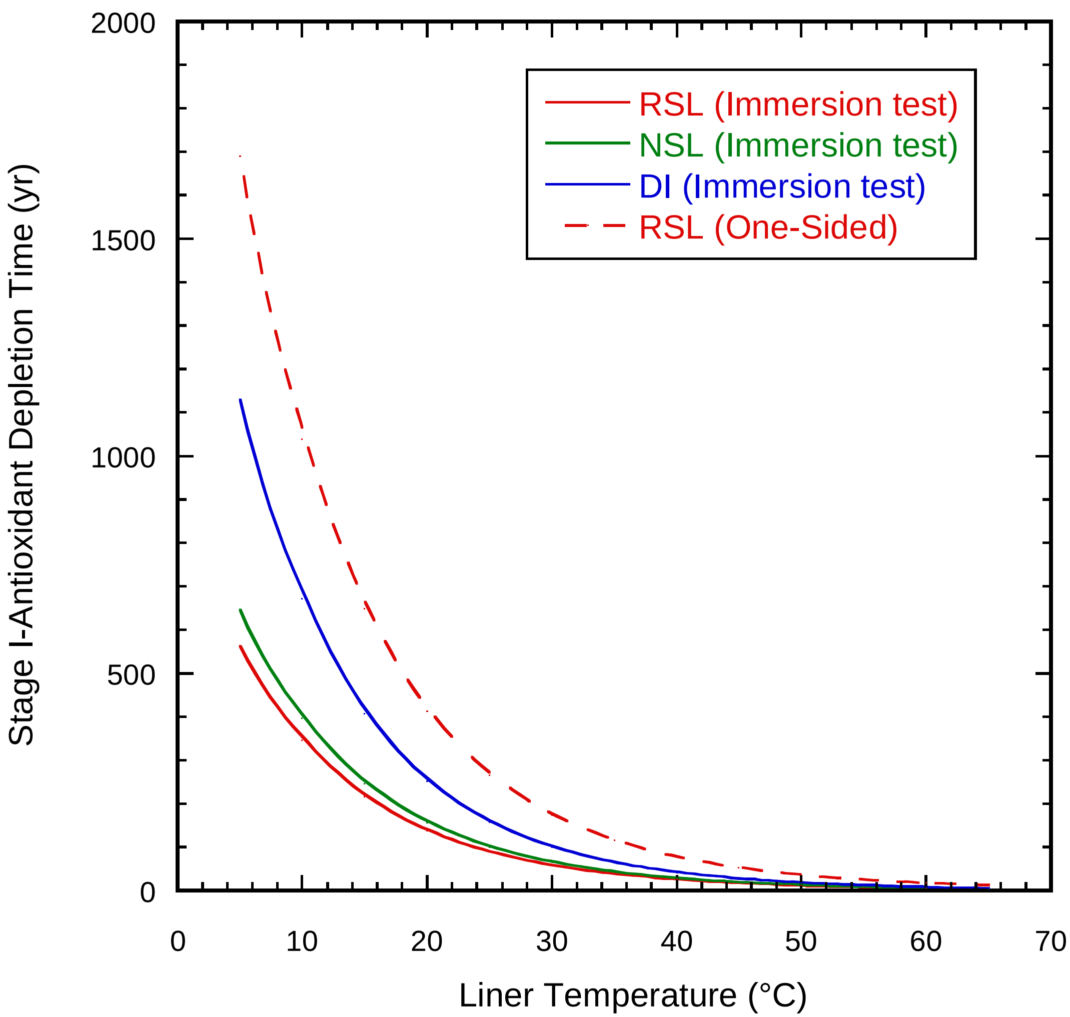
Impact of Single-Sided Exposure

Antioxidant depletion rate obtained from two-sided immersion tests 3.5 times higher than from one-sided test





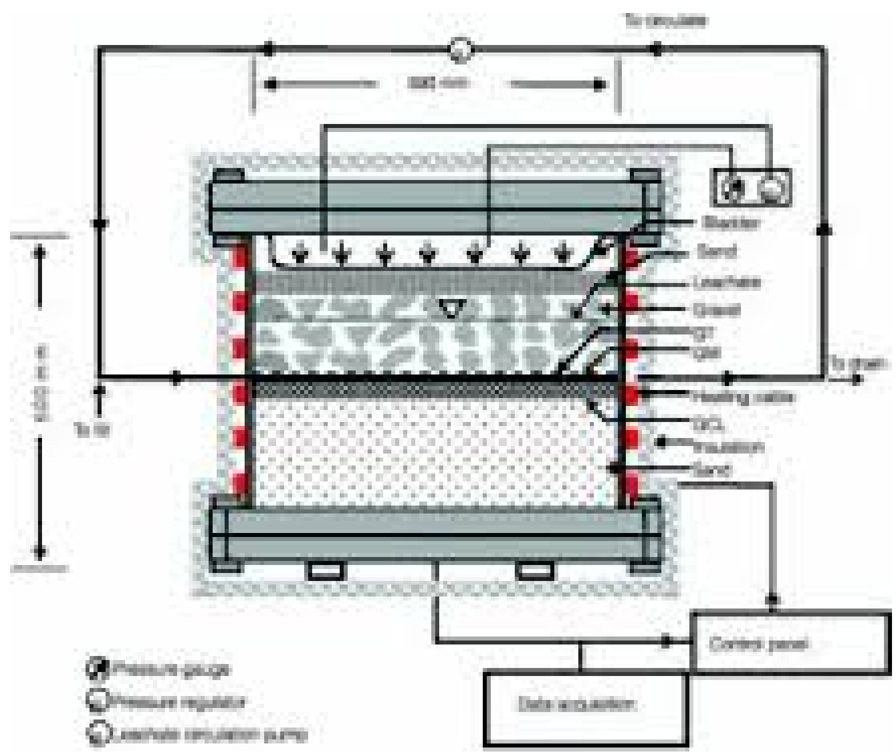
Predicting Duration of Stage A – Antioxidant Depletion



- Use Arrhenius parameters.
- Account for single-side exposure using 3.5x.
- Scale to liner temperature of 15 °C.
- Stage A completed in **730 yr**. *No deterioration in engineering properties at this time.*

Predicting Service Life: Stages B and C

- Use Stage C data from large-scale "landfill simulator" experiments by Rowe et al. (2009) using municipal solid waste leachates.
- Conservative, as MSW leachates more aggressive in degrading geomembranes.



Stage B - Induction Time – Rowe et al. (2009)

Properties	Analysis Method	Parameters for Arrhenius Eq.		Prediction Stage B	
		$\ln(s_T) = \ln(A) - (E_a/R)/T$	E_a (kJ/mol)	s_T at 15 °C ($month^{-1}$)	**Duration (yr)**
Break Strength	Best-Fit	$\ln(s_T) = 28.43 - 10682/T$	88.8	0.00017	**480**
	Interpreted	$\ln(s_T) = 22.04 - 8588/T$	71.4	0.00049	**200**
Break Stain	Best-Fit	$\ln(s_T) = 10.97 - 4957/T$	41.2	0.0019	**45**
	Interpreted	$\ln(s_T) = 6.38 - 4957/T$	28.7	0.0037	**25**
SCR (25%)	Interpreted	$\ln(s_T) = 31.33 - 11634/T$	96.7	0.00011	**720**
SCR (50%)	Interpreted	$\ln(s_T) = 23.24 - 8982/T$	74.7	0.00035	**235**
SCR (75%)	Interpreted	$\ln(s_T) = 18.46 - 7415/T$	61.7	0.00068	**120**

Stage C- 50% Property Degradation Time

Properties	Temp. (°C)	Analysis Method	Prediction for Stage C	
			$s_{T=85}/s_{T=15}$	**Duration (yr) at 15 °C**
Break Strength	85	Best-Fit	689.5	**2880**
		Interpreted	689.5	**2585**
Break Stain	85	Best-Fit	689.5	**1995**
		Interpreted	689.5	**1495**
SCR (25%)	85	Interpreted	689.5	**1400**
SCR (50%)	85	Interpreted	689.5	**1220**
SCR (75%)	85	Interpreted	689.5	**1045**

Total Service Life (A + B + C)

Determination Criteria	Service Life (yr)
Based on break strength	**3000–3575**
Based on break strain	**1735–2255**
Stress Crack Resistance	**1380–2335**

Summary of Findings

- Geomembranes undergo similar first-order degradation in LLW-MW leachate as observed in MSW leachate, but ***slower*** due to lack of surfactants. Radiation impact minimal for current waste streams.

- No degradation of engineering properties during Stage A, consistent with absence of oxidation.

- ***Stage A at least 730 yr for LLW and MW environments.***

- Use rate data for Stages B and C from large-scale experiments with MSW leachate (conservative). **Predict 1400 yr as shortest service life.**