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Modeling of Spatially Dependent Oxidative Polymer Degradation

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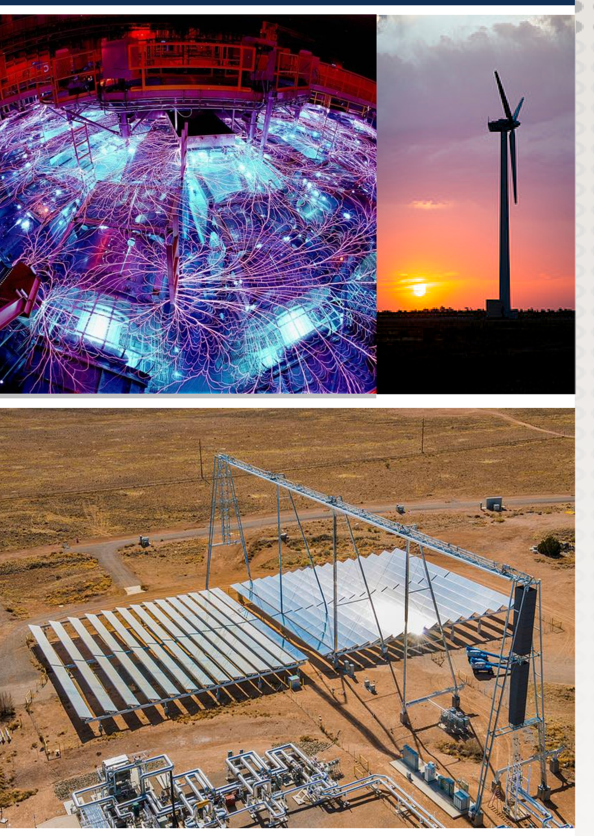

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GOALS AND MOTIVATION OF THIS WORK

- What happens during thermo-oxidative aging and thermal cycling of polymeric materials and components?
- Understand heterogeneous polymer degradation processes Diffusion Limited Oxidation (DLO)
- Predict spatially resolved degradation of materials
- Quantify integrated oxidative reactivity of materials
- Develop visualization tools to demonstrate expected material behavior
- Use predictive models for oxidative damage
- Foundation for changes in mechanical properties

MODEL CONCEPT - OXIDATION & DIFFUSION

Oxidation rate derived from the Basic Auto-Oxidation Scheme (BAS):

$$-r_{O_2} = \phi = \frac{k_a[O_2]}{k_b[O_2]+1}$$

Incorporation into Fick's second law:

$$\frac{\partial\theta}{\partial\tau} = \nabla^2\theta - \frac{\alpha\theta}{\beta\theta+1}$$

Pressure dependence of oxidation rate:

$$\frac{\phi}{\phi_0} = \frac{\beta+1}{\beta+1/\theta}$$

DLO model parameters:

$$\frac{\alpha}{\beta+1} = \frac{\phi_0 L^2}{P_{ox}p_0}$$

Initiation	$\text{Polymer} \xrightarrow{R_i} R^\bullet$
Propagation	$R^\bullet + O_2 \xrightarrow{k_2} RO_2^\bullet$
	$RO_2^\bullet + RH \xrightarrow{k_3} ROOH + R^\bullet$
Bimolecular termination	$R^\bullet + R^\bullet \xrightarrow{k_4} \text{Products}$
	$RO_2^\bullet + R^\bullet \xrightarrow{k_5} \text{Products}$
	$RO_2^\bullet + RO_2^\bullet \xrightarrow{k_6} \text{Products} + O_2$
Unimolecular termination	$RO_2^\bullet \xrightarrow{k_7} \text{Products}$
	$R^\bullet \xrightarrow{k_8} \text{Products}$

MODEL PARAMETERS

$$\alpha = \frac{k_1L^2}{D}$$
$$\beta = k_2Sp_0$$
$$\theta = {}^{P}/_{p_0}$$
$$\tau = \frac{tD}{L^2}$$
$$\chi = {}^{x}/_{L}$$
$$P_{ox} = DS$$
$$[O_2] = Sp_0 \text{ (Henry's Law)}$$

- k_a, k_b .. BAS overall rate constants
- α, β.... DLO model parameters
- ϕ ..... Oxidation rate [mol/g/s]
- θ ..... Relative oxygen partial pressure
- P_{ox}.... Oxygen Permeability [ccSTP/cm/s/cmHg]
- D ..... Diffusivity [cm²/s]
- S ..... Solubility [mol/cc/cmHg]
- p_0 ..... Oxygen partial pressure (reference) [cmHg]
- χ ...... Relative position
- L ...... Thickness (reference) [cm]
- τ ...... Normalized time
- t ...... Time [s]
- Ω ..... Spatial integrator depending on dimension
- φ ..... Simplex interpolation function

MATHEMATICAL APPROACH

Application of Galerkin Weighted Residual Finite Element Method (FEM)

Solution for the weak formulation of the partial differential equation

FEM uses triangle simplex subspaces

Approximate solution: $\theta_{i,j} \approx u_{i,n} = \sum_{j=1}^{n} u_{i,j}\varphi_j$

DLO weak formulation after divergence theorem:

$$\int_{\Omega_j}\boldsymbol{\varphi}^T\frac{\partial\boldsymbol{u}}{\partial\tau}d\,\Omega = \int_{n_j}(\boldsymbol{\varphi}^T\nabla\boldsymbol{\varphi}\cdot\boldsymbol{u})\cdot d\boldsymbol{n} - \int_{\Omega_j}\nabla\boldsymbol{\varphi}^T\nabla\boldsymbol{\varphi}\cdot\boldsymbol{u}\,d\,\Omega - \int_{\Omega_j}\boldsymbol{\varphi}^T\frac{\alpha\boldsymbol{\varphi}\cdot\boldsymbol{u}}{\beta(\boldsymbol{\varphi}\cdot\boldsymbol{u})+1}d\,\Omega$$

Summation over all simplex interpolation functions:

$$\mathbb{M}\frac{\partial\boldsymbol{u}}{\partial\tau} = (\mathbb{f}+\mathbb{K})\boldsymbol{u} - \boldsymbol{r}$$

$\mathbb{M}$ is the mass matrix ($\mathbb{M} = \underline{\mathbf{0}}$ for steady state)

$\mathbb{f}$ defines the surface flux ($f_n = \frac{P_{ox\,i}}{P_{ox\,l}}$ is necessary for the laminar boundary condition, which is 0 for non-boundary)

$$\mathbb{M} = \sum_{n=1}^{N}\int_{\Omega_n}\boldsymbol{\varphi}^T\boldsymbol{\varphi}\,d\,\Omega \qquad \mathbb{f} = \sum_{n=1}^{N} f_n\overline{\boldsymbol{\varphi}^T}\nabla\boldsymbol{\varphi}\big]_{\varphi_n}$$

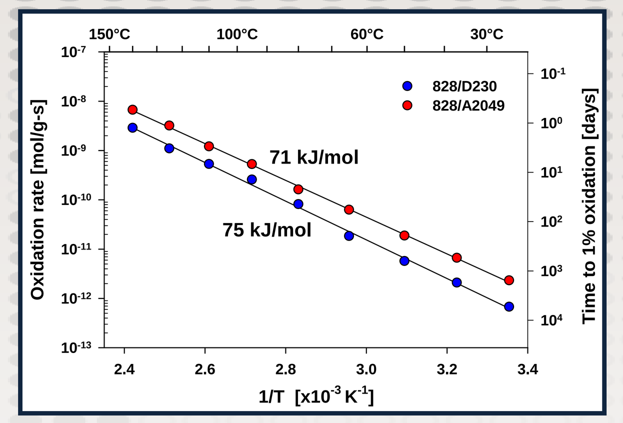
$\mathbb{K}$ is the stiffness matrix

$\boldsymbol{r}$ is summation of averaged element rate expressions using mean value theorem

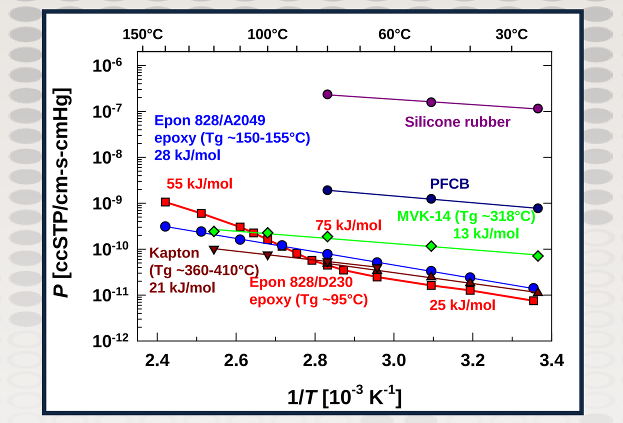
$$\mathbb{K} = -\sum_{n=1}^{N}\Omega_n\nabla\boldsymbol{\varphi}^T{}_n\nabla\boldsymbol{\varphi}_n \qquad \boldsymbol{r} = \sum_{n=1}^{N}\overline{\boldsymbol{\varphi}^T}_n\frac{\overline{\alpha u_n}}{\beta\boldsymbol{u}_n+1}$$

MODEL REQUIREMENTS

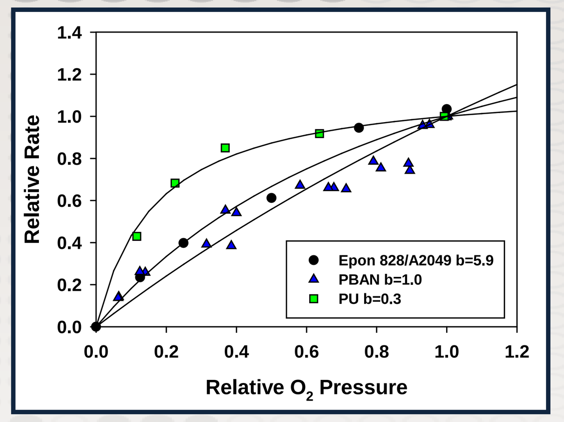
- Material oxidation rates with temperature
- Permeation with temperature
- Definition of oxidative degradation chemistry (basic autoxidation scheme)
- Theoretical DLO model; i.e. mathematical linkage between degradation mechanism and the physical process for O2 diffusion
- Mathematical approaches to provide solutions for material characterization of 1D (analytical) to 2D FEM complex geometries (numerical Galerkin methods)



Oxidation rates are experimentally determined and available for many polymers including thermosets. Data provide consumed oxygen under non-DLO conditions. SNL has led this research activity.

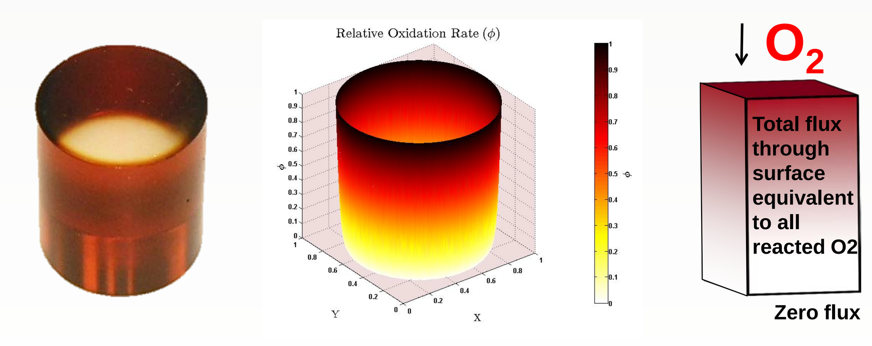


Oxygen permeability is obtained from flux measurements through thin films. O2 diffusion and solubility are available via Fickian diffusion fits.

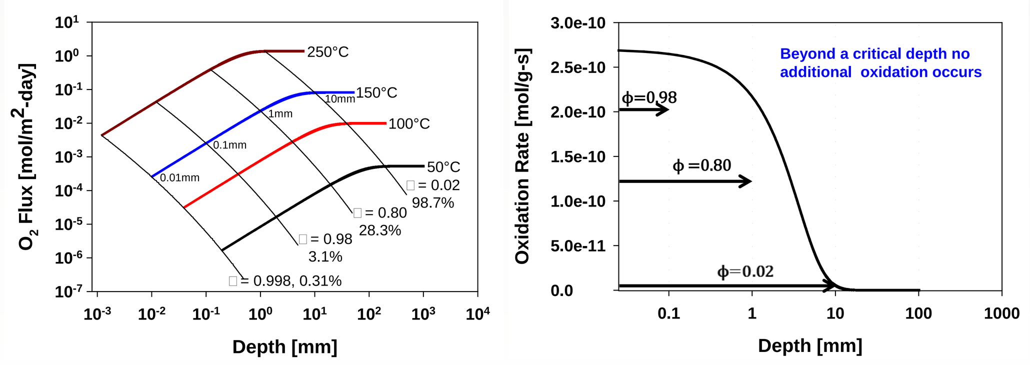


Oxygen rate dependence on local concentration, referenced to surface, is part of the mechanistic description and available from special rate experiments as well as DLO analysis.

EXAMPLES OF DLO MODEL APPLICABILITIES AND PREDICTIONS

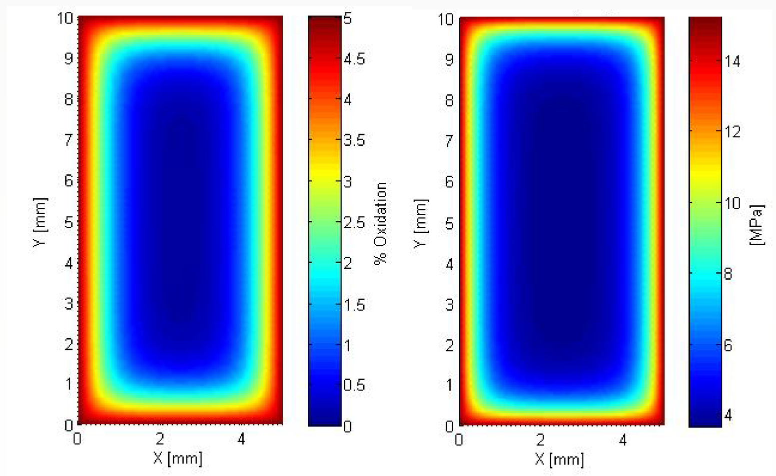


Actual degradation and model of an epoxy material where severe oxidation is limited to surface layer.

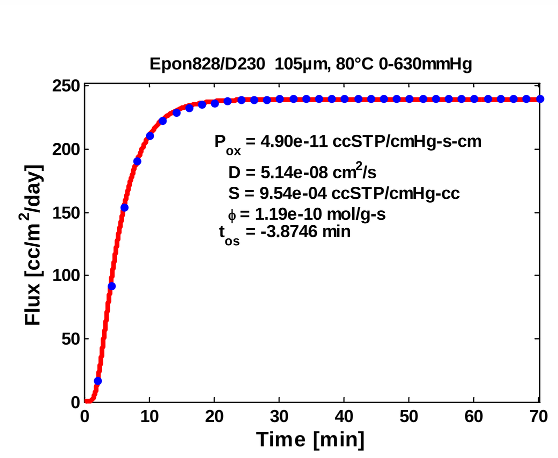


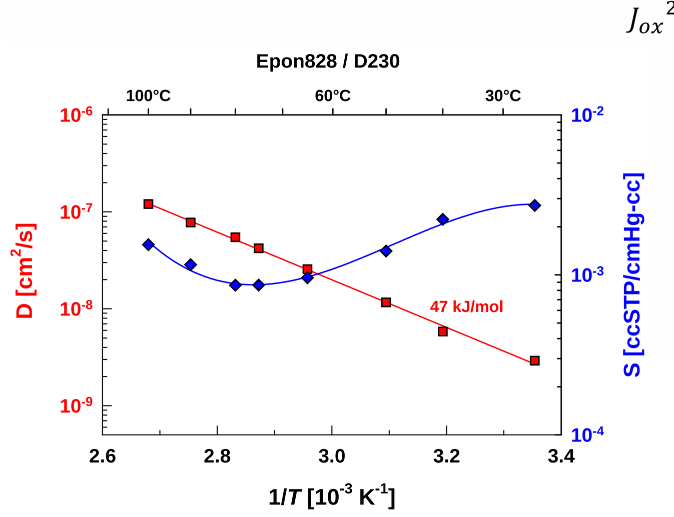
Prediction of oxygen flux and oxidation rate with respect to depth into an EPDM material for total material oxidation reactivity. The total flux can be analytically expressed:

$$J_{ox}{}^2 = \phi P_{ox}p_0\gamma, \qquad \gamma \equiv 2\frac{(\beta+1)(\beta-\ln(\beta+1))}{\beta^2}$$

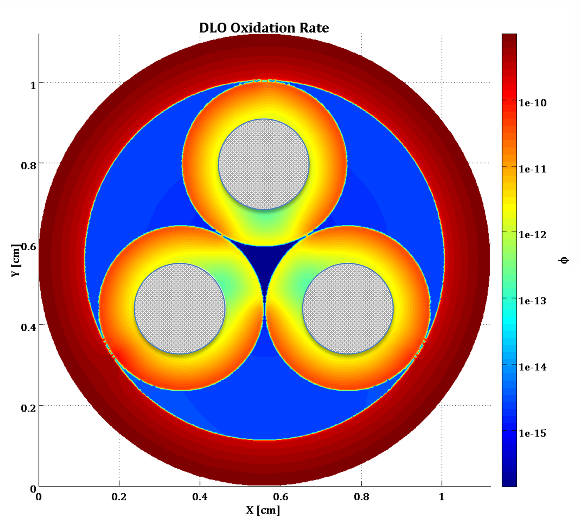


Prediction of DLO for cross-section of aged Neoprene at 125°C with changes in mechanical properties (oxidation level – modulus correlation from Modulus profiling).

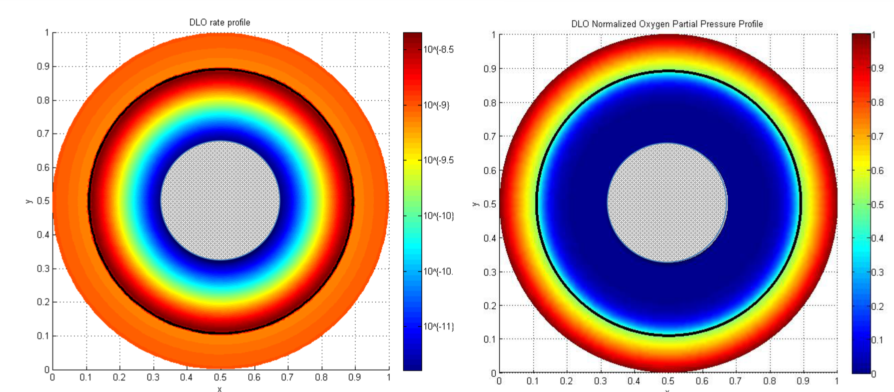




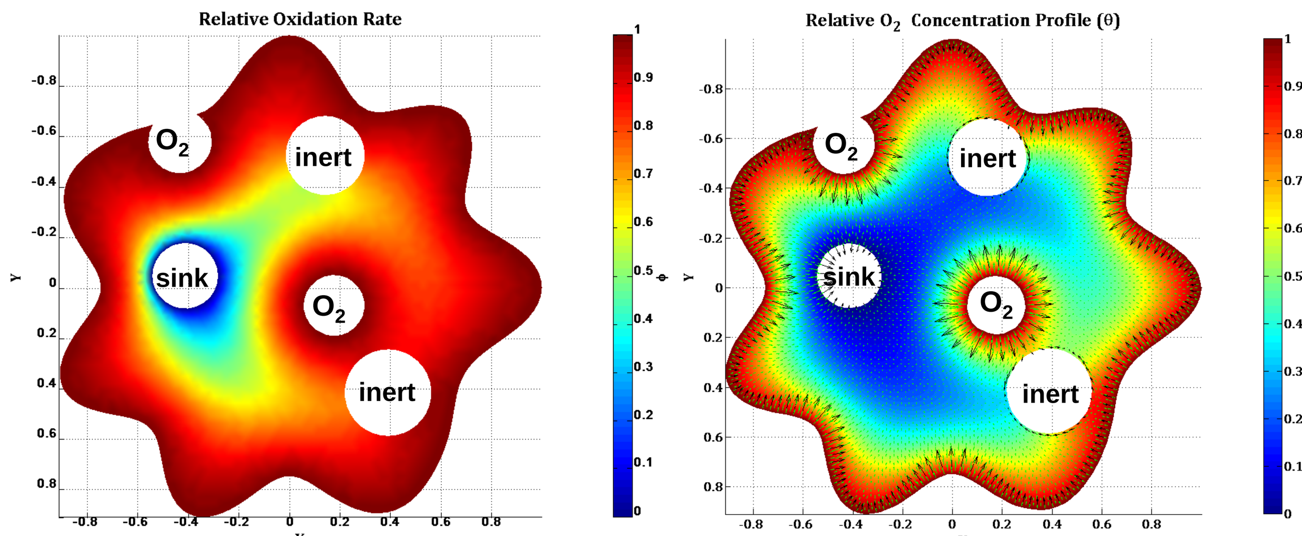
O_2 time – permeation flux measurements can be fitted with 1D film transport solution to extract permeability, diffusivity and solubility.



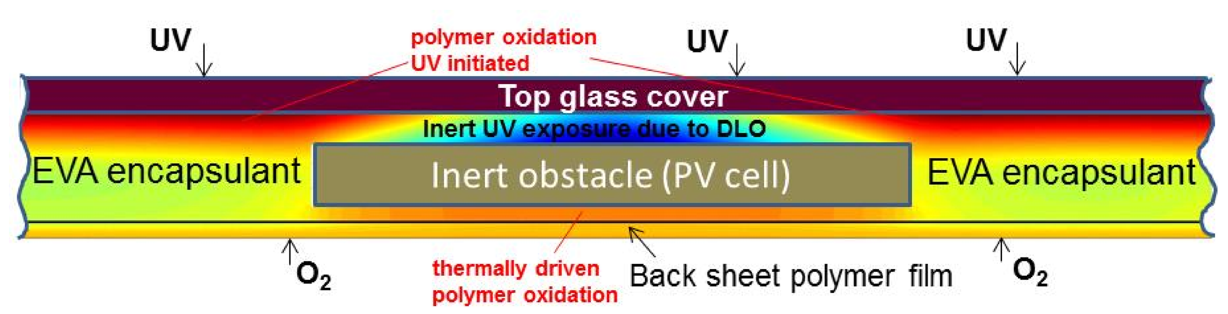
Potential aging in cable assembly. Weak gradient in jacket, DLO through insulation and restricted O2 access in cable center



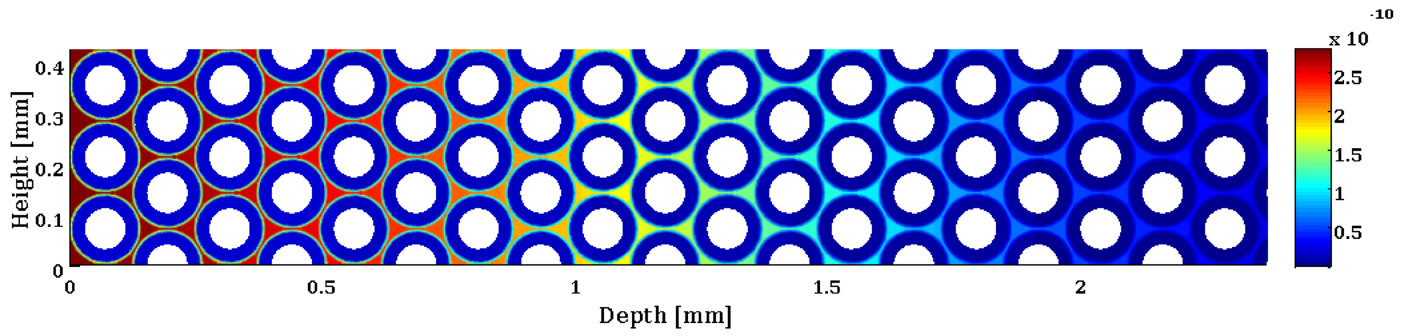
Possible aging of cable jacket/insulation, in this case the inner insulation has higher oxidation sensitivity and is DLO affected under accelerated aging conditions.



Model evaluation with multiple boundary conditions. Example of irregular domain, surface O_2 exposure, with internal inert voids, additional O_2 source, and an O_2 sink.



Perceived heterogeneous degradation in PV applications due to DLO. Competition between surface UV induced and thermal degradation is strongly dependent on local oxygen availability.



Spatially resolved oxidation rates for epoxy resin matrix and coated inert material assembly; two polymers with boundaries and complex permeation process; coating has a lower oxidation rate than matrix.

CAPABILITIES AND IMPACT

- **We have developed a comprehensive tool set to predict spatially resolved oxidative degradation processes for multiple materials**
- **Model enables extraction of P, D, S from permeation flux experiments**
- **Simple 1D models for thin film and multi-layered materials**
- **2D analytical models for simple geometries with numerical solutions**
- **2D FEM codes for complex geometries involving multiple materials**

- **This work supports predictive aging programs in energy, security and defense applications as well as material performance assessments and requalification needs in multiple areas.**

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