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AREVA

Solid State Transport of Reactive Charged Particles

Application to Metal Oxidation

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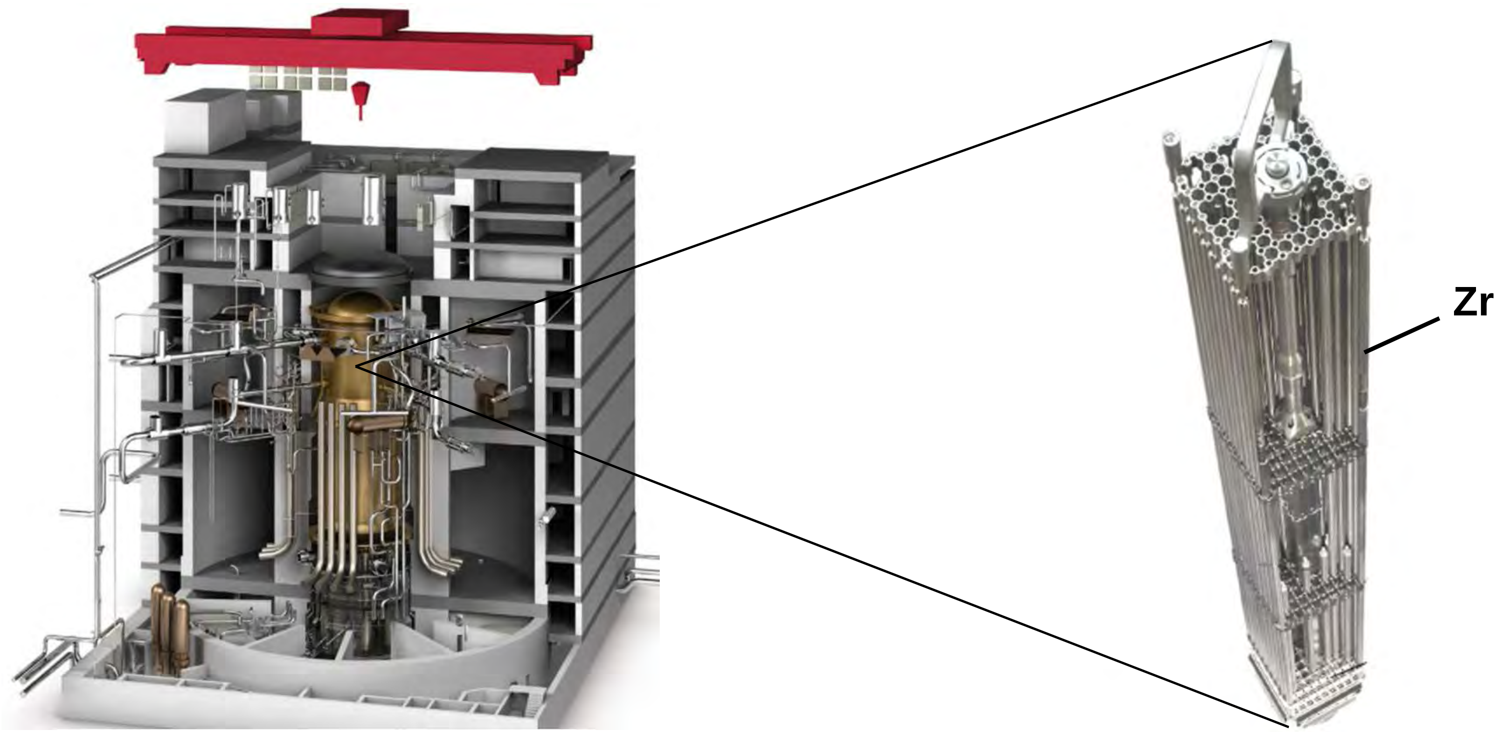
FUEL

Introduction

Zirconium corrosion in power plant coolant ➡ **Fuel assembly life**



Nuclear Power Plant

Picture AREVA NP

Fuel assembly

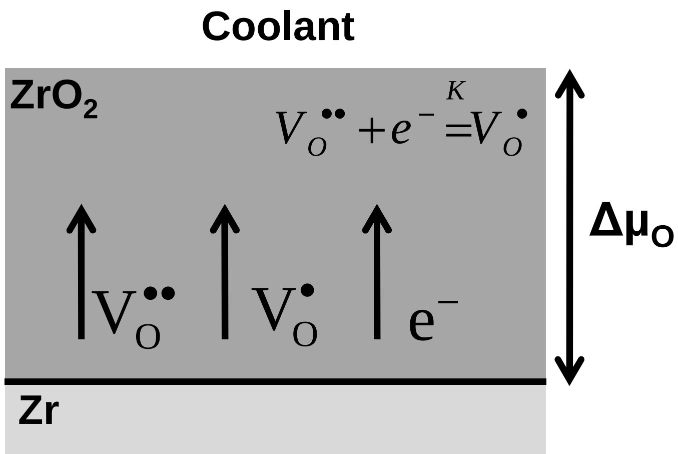
Picture AREVA NP

Understanding corrosion key factor impact on oxide growth

Objectives

- **Develop a numerical model for zirconium oxidation**
- **Simulation using <u>COMSOL Multiphysics</u>**

➡ **Multicomponent transport coupled with internal chemical reaction**



Anionic conductivity transport

$$V_O^{\bullet\bullet}, V_O^{\bullet}, e^-$$

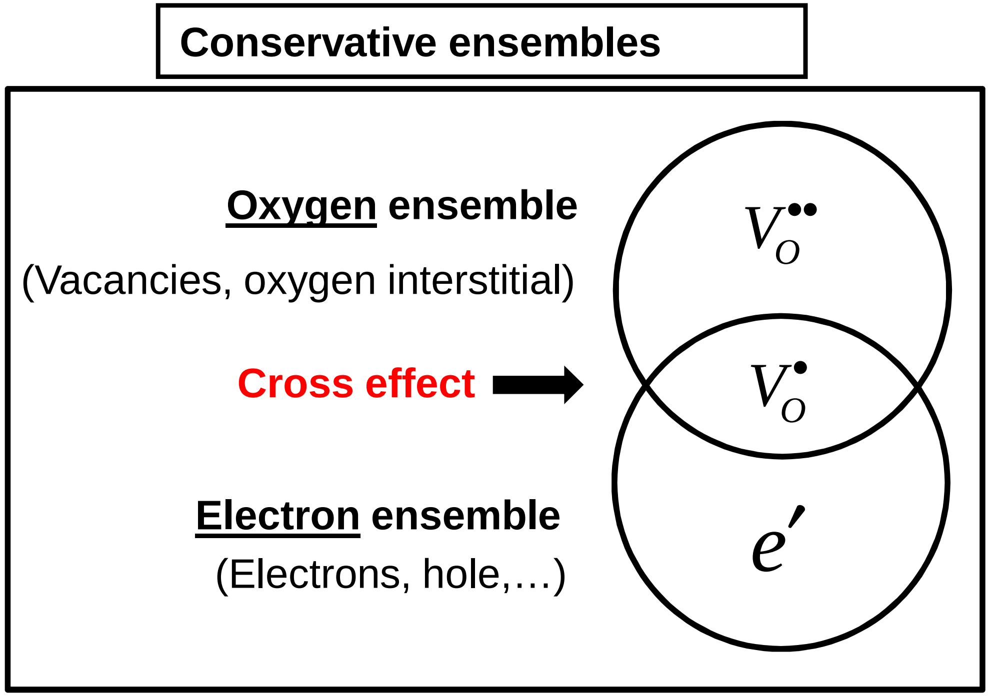
Electrons trapping

$$V_O^{\bullet\bullet} + e^- = V_O^{\bullet}$$

<u>Constraints on system :</u> **Electroneutrality + Stoichiometry + Chemical reaction**

Conservative Ensembles

Considering ensemble transport (J. Maier, 1994)



Thermodynamic of irreversible processes

$$J_O^* = -s_{OO}^* \nabla \eta_O^* - s_{Oe}^* \nabla \eta_e^*$$
$$J_e^* = -s_{eO}^* \nabla \eta_O^* - s_{ee}^* \nabla \eta_e^*$$

(Lankhorst, 1996)

Ensembles are conservatives for the chemical reaction

Chemical reaction : <u>Cross effect between ensembles fluxes</u>

Oxygen Flux

Oxygen flux given by:
(Wagner, 1977)

$$J_O = \frac{-\sigma_{amb}}{4F^2}\nabla\mu_O = -D^\delta \nabla c_O$$

Chemical diffusion coefficient

$$D^\delta = \frac{\sigma_{amb}}{4F^2}\left(\frac{d\mu_O}{dc_O}\right)$$

σ_{amb} **: Ambipolar conductivity**

$\frac{d\mu_O}{dc_O}$ **: Chemical capacity**

Constraints on system

$c_{V_O^{\bullet}} + 2c_{V_O^{\bullet\bullet}} - c_{e'} = 0$	Electroneutrality
$\partial c_O + \partial c_{V_O^{\bullet\bullet}} + \partial c_{V_O^{\bullet}} = 0$	Stoichiometry
$K = \frac{c_{V_O^{\bullet\bullet}} c_{e'}}{c_{V_O^{\bullet}}}$	Chemical Reaction

Transport equation:

$$\frac{\partial c_O}{\partial t} = \nabla D^\delta \nabla c_O$$

All system's information are given by D^δ

Oxide Growth

<u>**Oxide growth given by:**</u>

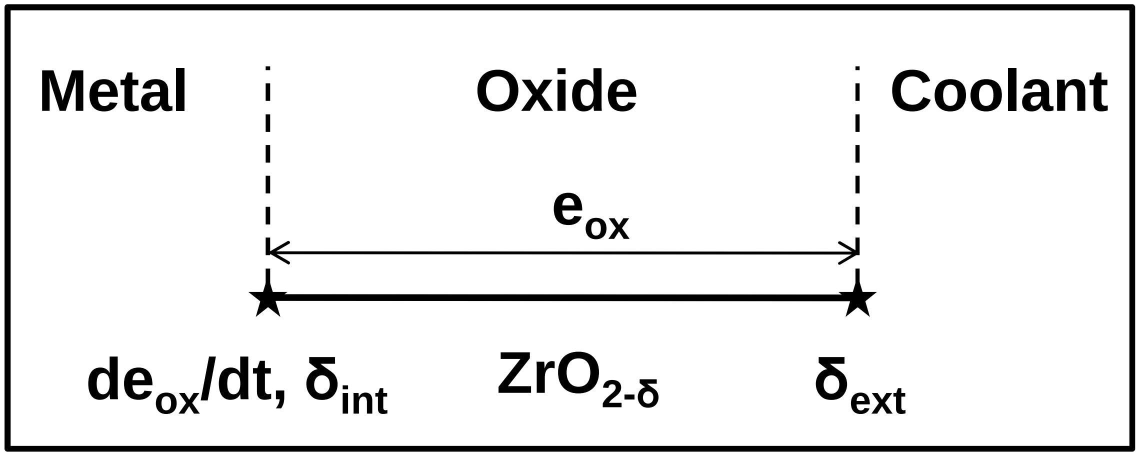
$$\boxed{\frac{de_{ox}}{dt} = \frac{1}{c_{o,\text{int}}} J_O}$$

Boundary condition on internal interface

Keeping subdomain constant: $x_{reduced} = \frac{x_{real}}{e_{ox}}$; $\nabla\big|_{real} = \frac{1}{e_{ox}} \nabla\big|_{reduced}$

➡ **Oxide growth model formulated as <u>boundary weak form</u>**

<u>**Simulation in one dimension:**</u>



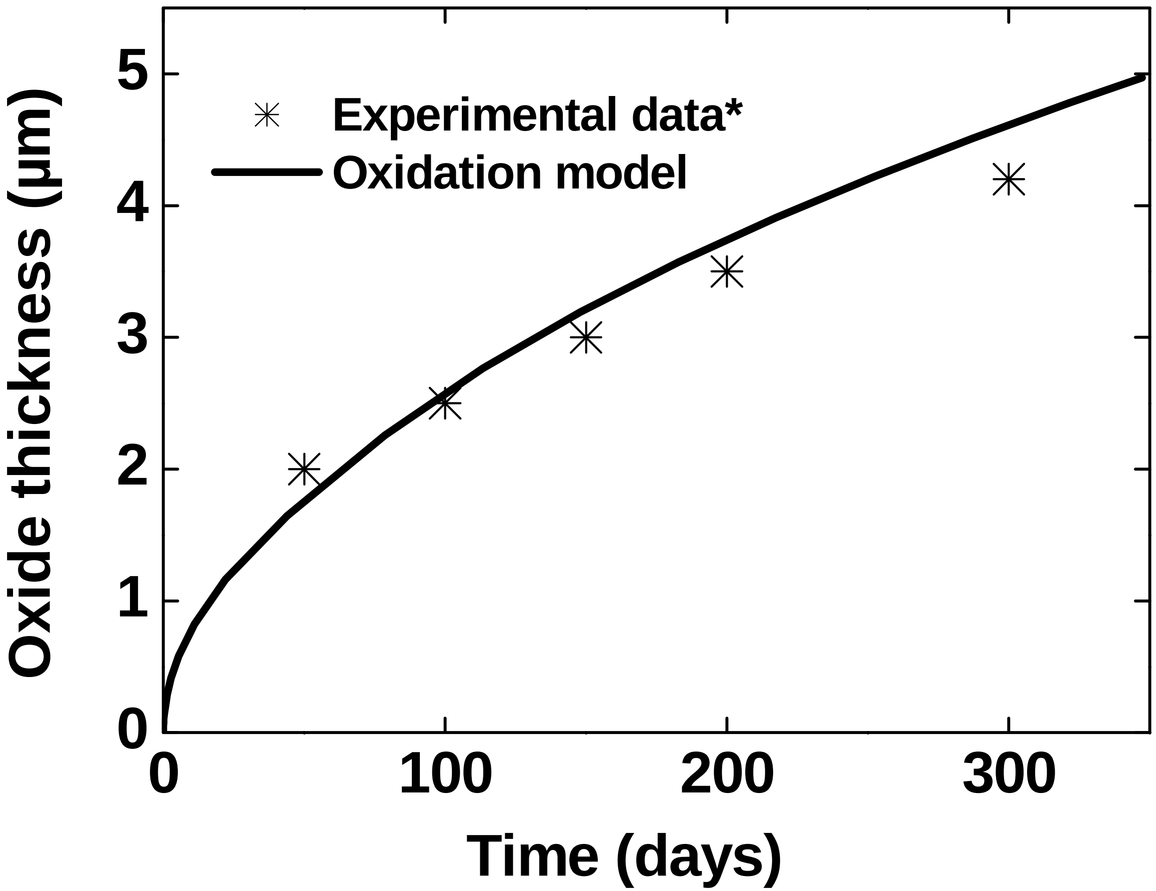
Oxide Growth

Model parameters

Symbol	Description
K	Chemical equilibrium between vacancies
$D_{V^{\bullet\bullet}}$	Diffusion coefficient of vacancies $V^{\bullet\bullet}$
$D_{V^{\bullet}}$	Diffusion coefficient of vacancies $V^{\bullet}$
D_e	Diffusion coefficient of electrons
δ_{int}	Zirconia non stoichiometry at the M/O interface
δ_{ext}	Zirconia non stoichiometry at the surface
T	Temperature

Simulations

Comparison with experimental data

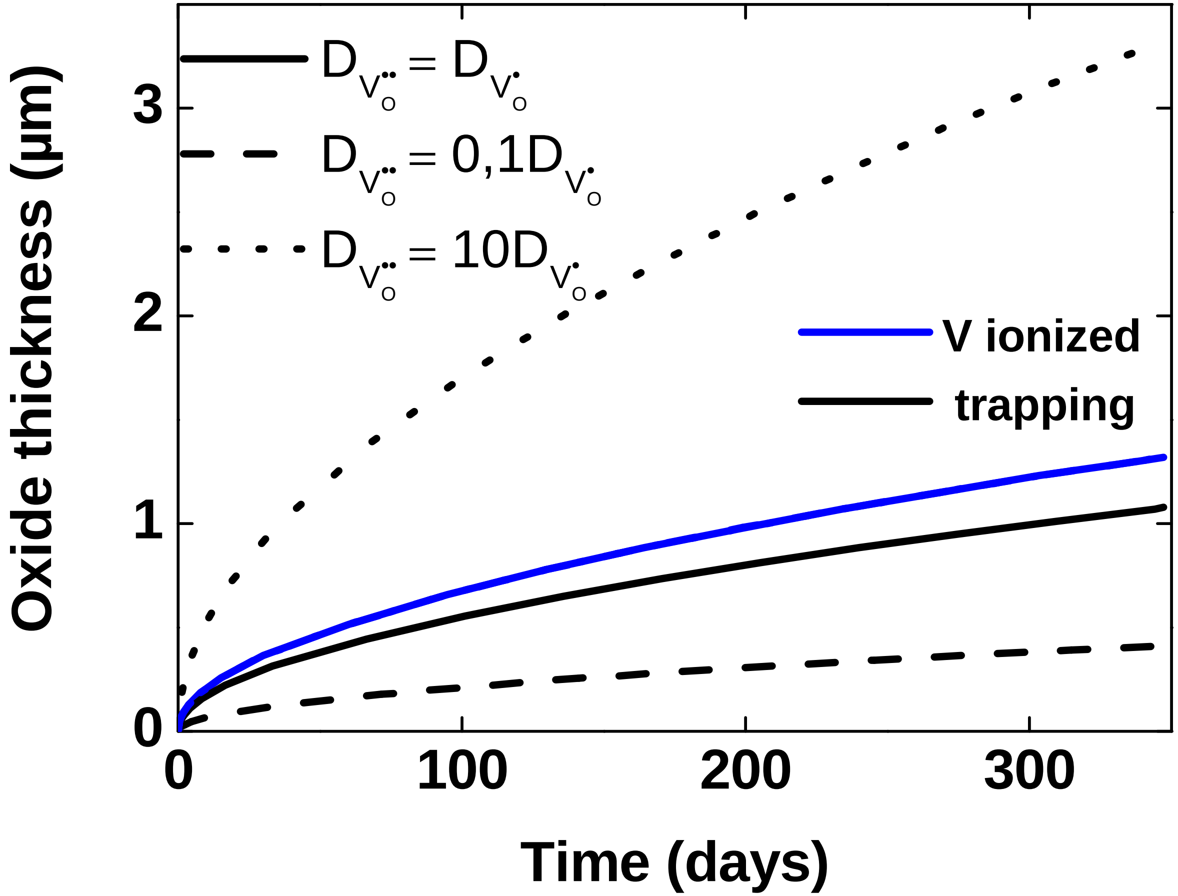


* J. Vermoyal, A. Hammou, L. Dessemond, A. Frichet, Elec. Acta, 2002

➡ **Simulation gives good results according to experimental data**

Simulations

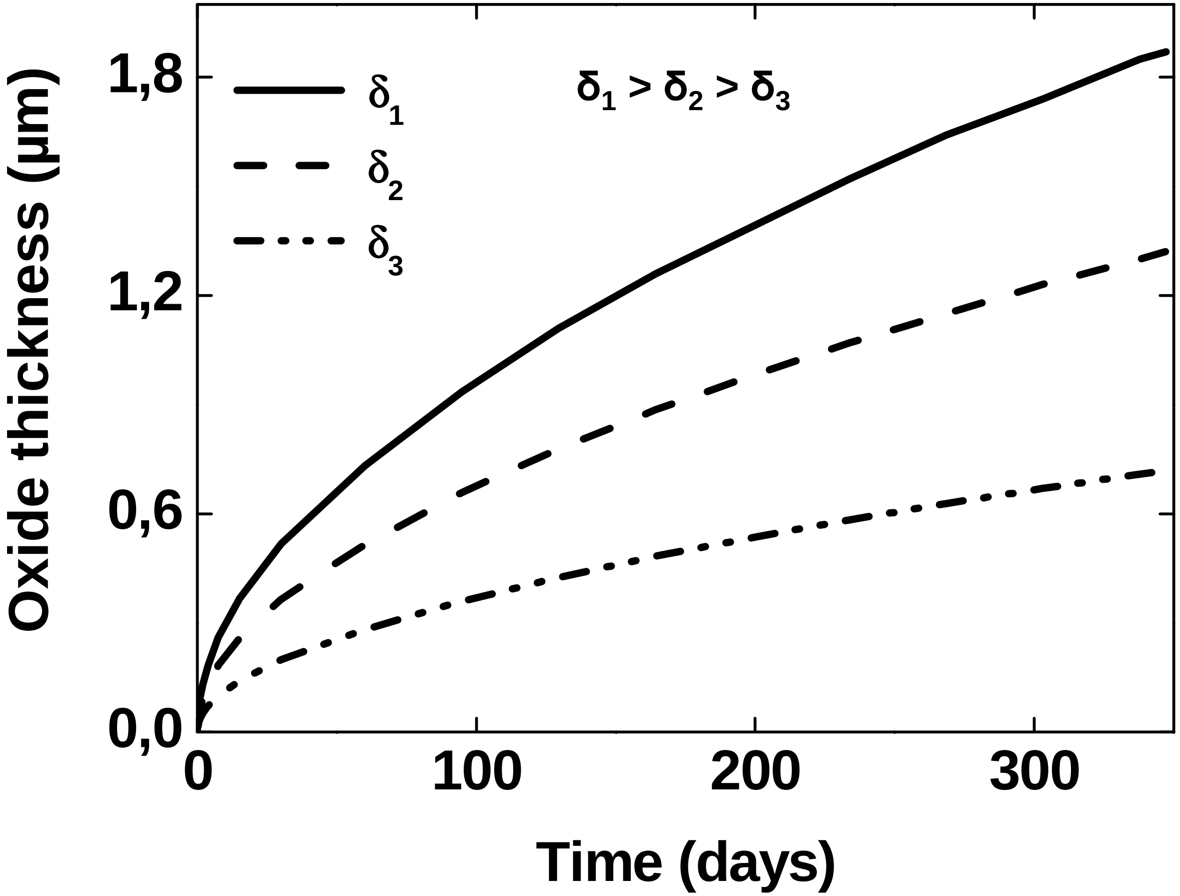
Effect on reaction and transport coefficient



➡ **Effect of electron trapping on oxide growth kinetic**

Simulations

Effect on zirconia non stoichiometry on inner interface $ZrO_{2-\delta}$



➡ **Effect oxygen chemical potential gradient through the oxide**

Conclusions

- **Development of an oxide growth model for anionic transport**

  Model is not specific for zirconium oxidation

- **Assessment of the control parameters on growth kinetics**

  Transport coefficient, stoichiometry, …

Environmental effect could be add on the model

2D model version when symmetry is broken

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