Complex multi-physics multi-layers modelling approaches for iron-environment interactions

upscaling to a cell scale of geological repository radioactive waste

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Steel in the geological disposal is present at different levels and in different forms:

- Iron concrete, bolts, liner to assure mechanical stability of the galleries/cells and ILW-LL overpack
- HLW overpack to delay the coming of water

Multi interfaces between steel components and environment

- Voids
- Cement
- Argillite
Corrosion processes are function of thermodynamic and fluid composition environment:

- **Dry corrosion**
- **Water corrosion:**
  - atmospheric corrosion
  - aqueous corrosion

Corrosion modes are function of interface conditions:

- General corrosion
- Localized corrosion
- ...

**Three macro-processes:**

- Cathodic process: input and reduction of oxidizing species
- Anodic process: metal oxidation and metallic cation release
- Formation process and corrosion products growth
Context

- **Space scale heterogeneity**
- **Coupled effects of physical processes**
  - Electrochemistry
  - Geochemistry
  - THM (Thermal, Hydraulic and Mechanical processes)

Needs multilevel modelling
Oxide-hydroxide layer modelling
Conceptualisation

- Modelling oxide-hydroxide layer (rust) result of the oxidation by dissolved oxygen in a water film (electrolyte)
- Electrolyte formation depends on air condition
- Consume iron Velocity depends on wetting-drying cycle

Electrolyte formation depends on air condition

Consume iron Velocity depends on wetting-drying cycle
Assumption

- A first rust layer exists
- Thickness rust layer is of constant size

Modelling approach:

- Modular approach (CEA / CAST3M)
  - Thermo-hydrodynamic module
    - Predict the characteristics of wetting-drying cycle
    - Assessment of the characteristics electrolyte film
  - Electrochemical module
    - Mechanistic description of physical-chemical phenomena
    - Prediction of iron damage

Rust layer actively participates in corrosion mechanisms

- Its properties determine its electrochemical reactivity
- Its properties control the diffusive phenomena
**Conceptualisation**

- Modelling the oxidation of a metal covered by an oxide layer
- Dedicated software: Calipso (Andra/CEA)

**Assumption**

- The metal (iron) is assumed to be covered by a spinel iron oxide layer \( \text{Fe}_{(3-\delta)} \text{O}_4 \)
- The metal is a pure electronic conductor
- The solution is a pure ionic conductor
Modelling approach

- **DPC (Diffusion Poisson Coupled) Model (C. Bataillon – CEA)**
  - convection-diffusion equations for the charge carrier concentrations coupled with a Poisson equation for the electric potential
  - discretization of the fluxes by the Scharfetter-Gummel scheme
  - Robin boundary conditions and variable boundaries

**Chemical Reactions and Fluxes**

- **Ferric release**
  - $\text{Fe}^{3+}_{\text{sol}} + \frac{m_0}{k_{Fe}} \rightarrow \text{Fe}^{3+}_{\text{sol}}$

- **Ferrous release**
  - $\text{Fe}^{2+}_{\text{sol}} + \frac{m_0}{k_{Fe}} \rightarrow \text{Fe}^{3+}_{\text{sol}}$

- **Oxygen exchange**
  - $2H^+ + O_2 \rightarrow \text{H}_2O + \frac{m_0}{k_{ox}}$

- **Oxide Host Lattice dissolution**
  - $\text{Fe}^{3+}_{\text{sol}} + 4H_2O \rightarrow \frac{m_0}{k_{ox}} 8H^+$

**Electrical Fluxes**

- **Hopping conduction mechanism**
  - $J_{\text{Fe}^{3+}}$

- **Electron exchange**
  - $J_e$

**Vacancy mechanism**

- $J_{V_{Fe}}$

- **Oxide growth and expansion**
  - $X_0(t)$ to $X_0(t + \Delta t)$
  - $X_1(t)$ to $X_1(t + \Delta t)$

**Interface motion**

**Chemical Equations**

- **Iron oxidation**
  - $3e_{Fe} \rightarrow \frac{m_0}{k_{Fe}} \rightarrow \text{Fe} + \frac{m_0}{k_{ox}}$

- **Oxide lattice growth**
  - $3e_{Fe} \rightarrow \frac{m_0}{k_{Fe}} \rightarrow \text{Fe} + 4O_{\text{x}}$
Some results

pH influence on oxide layer thickness  
Temporal evolution of oxide layer
corrosion products layer modelling
Corrosion products layer modelling

Conceptualisation
- Transport reactive approach
- Electrochemical laws of Butler-Volmer type (iron flux imposed)

Assumption
- Electroneutrality
- Chemical system reduced
- Porosity changes are not taken into account

Modelling approach
- COMSOL
- Nernst-Planck equations
Some results: effects on the porosity
Conceptualisation

- Evaluation of the velocity of corrosion products layer growth are given by empirical formulation
- Relation between velocity and layer thickness
- Modelling mechanical constraints evolution
- Not numerical corrosion/reactive transport model

Corrosion products layer modelling: mechanical coupling

Species transport

Steel corrosion

Cracking section reduction

Occurrence of spalling

Species transport

Cl CO₂ O₂

Cl CO₂ O₂

Corrosion products layer modelling: mechanical coupling
Example: ILW-LL overpack damage at 10,000 years
Electro-geochemistry coupling

2 levels
Electro-geochemistry coupling: 2 levels

Conceptualisation
- Electrochemical / reactive transport coupling

Assumption
- Corrosion product layer are not simulated

Modelling approach
- Coupling Kirmat (1D reactive transport model – LHyGeS) / Calipso (corrosion model – Andra/CEA)
Electro-geochemistry coupling: 2 levels

Some result: Test argillite/concrete/iron at 25°C

1 **argillite zone:**
- Length: 1m (20 cells 0.05 m)
- Section: 4E-4m²
- Porosity: 0.18
- Permeability: 1.62E-20 m²
- Diffusion: 3.15E-3 m²/an
- pH: 7.2
- Eh: -171 mV

1 **concrete zone:**
- Length: 0.04 m (4 cells 0.01 m)
- Section: 4E-4m²
- Porosity: 0.13
- Permeability: 5.0E-21 m²
- Diffusion: 3.15E-3 m²/an
- pH: 12.4
- Eh: -50.5 mV

1 **iron zone:**
- Length: 0.01 m (1 cell)
- Section: 4E-4m²
- Porosity: 0.075
- Permeability: 1.5E-30 m²
- Diffusion: 3.15E-3 m²/an
- pH: 12.4
- Eh: -50.5 mV
Electro-geochemistry coupling: 2 levels

Result after one year of reaction

Without coupling

With coupling

Dense oxide layer
Electro-geochemistry coupling

3 levels
Electro-geochemistry coupling: 3 levels

Conceptualisation

- Electrochemical / reactive transport coupling
- Passivante layer modelling
- Protective layer of corrosion products modelling
- Geochemistry interaction modelling

Work in progress

- University of Bourgogne (ICB) thesis
- Support collaboration Andra/CEA/LHyGeS
That’s all folks!