

FROM RESEARCH TO INDUSTRY



CORROSION MODELLING OF IRON FOR LONG TERM PREDICTION IN NUCLEAR WASTE REPOSITORY

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Introduction: Andra underground radioactive waste repository, the DPCM and the CALIPSO code

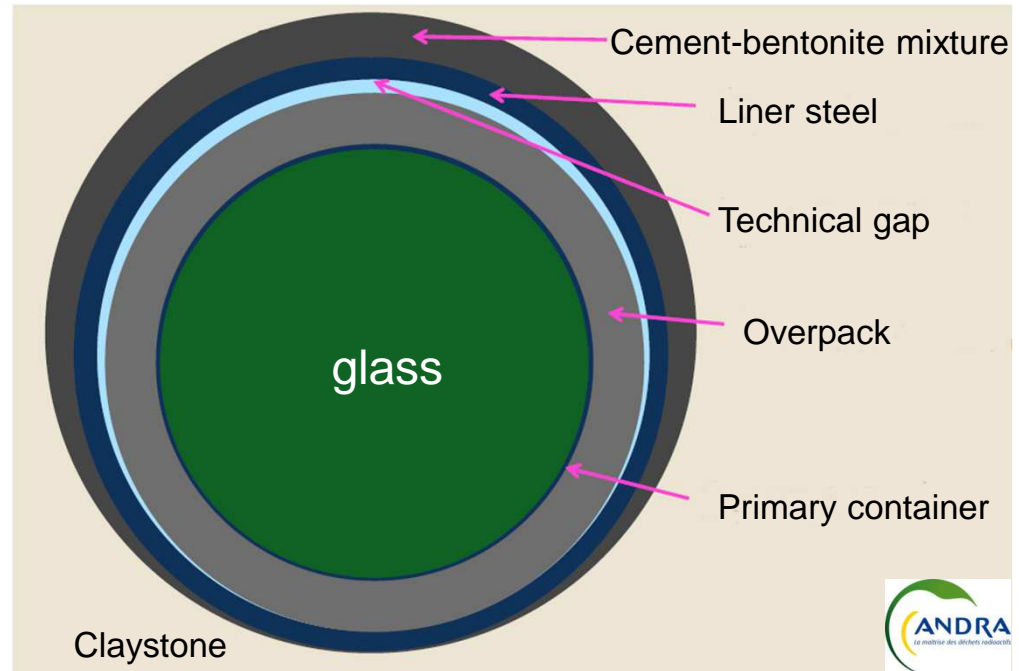
Objectives and methods: Setup parameters of the CALIPSO code associated to the DPCM

Results and discussions:

- Thermodynamic approach
- XANES study of the cathodic reduction of artificial iron oxide passive films
- Oxide Host Lattice Growth reaction

Conclusions

500-meter deep disposal concept



Long-term behavior of nuclear waste canisters in geological repository depends on:

- Metallic materials
- Geochemical features of the surrounding (pH and redox potential)

1000-years behavior from link geochemical and corrosion models

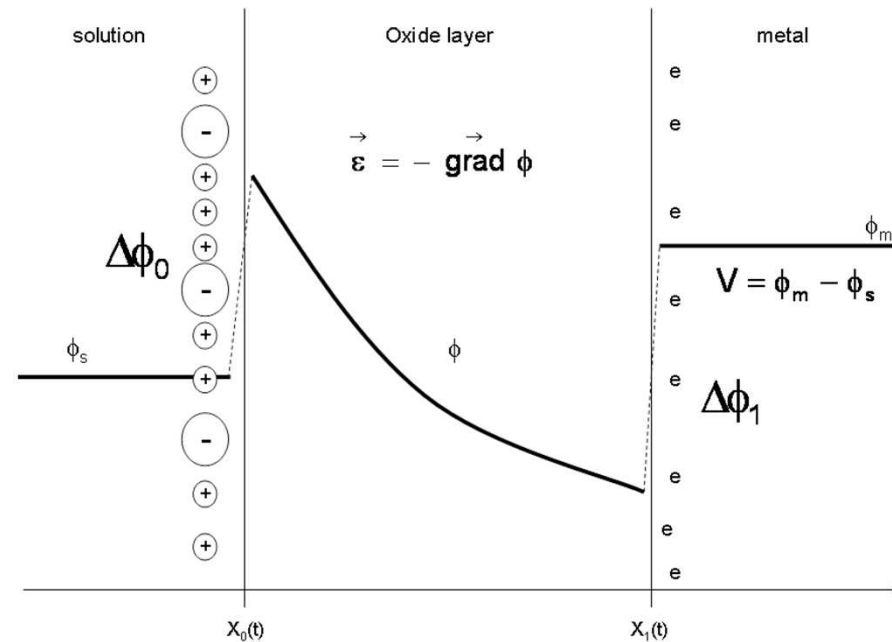
- Numerical methods

- Based on a fully implicit resolution of coupling between:

- Fick
- Poisson
- Moving interfaces equations

- Steady or dynamic situation

- Finite volume scheme with a discretization of Sharfetter & Gummel for convective-diffusive flux



Objectives:

- Setup parameters of the CALIPSO code associated to the DPCM

Methods:

- Presentation of the strategy from:
 - Literature data [3]
 - Thermodynamic equilibrium [4]
 - Specific experiments dedicated to elementary fluxes [5,6]

[2] Bataillon, C et al. *J. Comput. Phys.* **2012**, 231, 6213-6231.

[3] M. Backhaus-Ricoult, R. Dieckmann, *Ber. Bunsenges. Phys. Chem.*, **1986**, 90, 690-698.

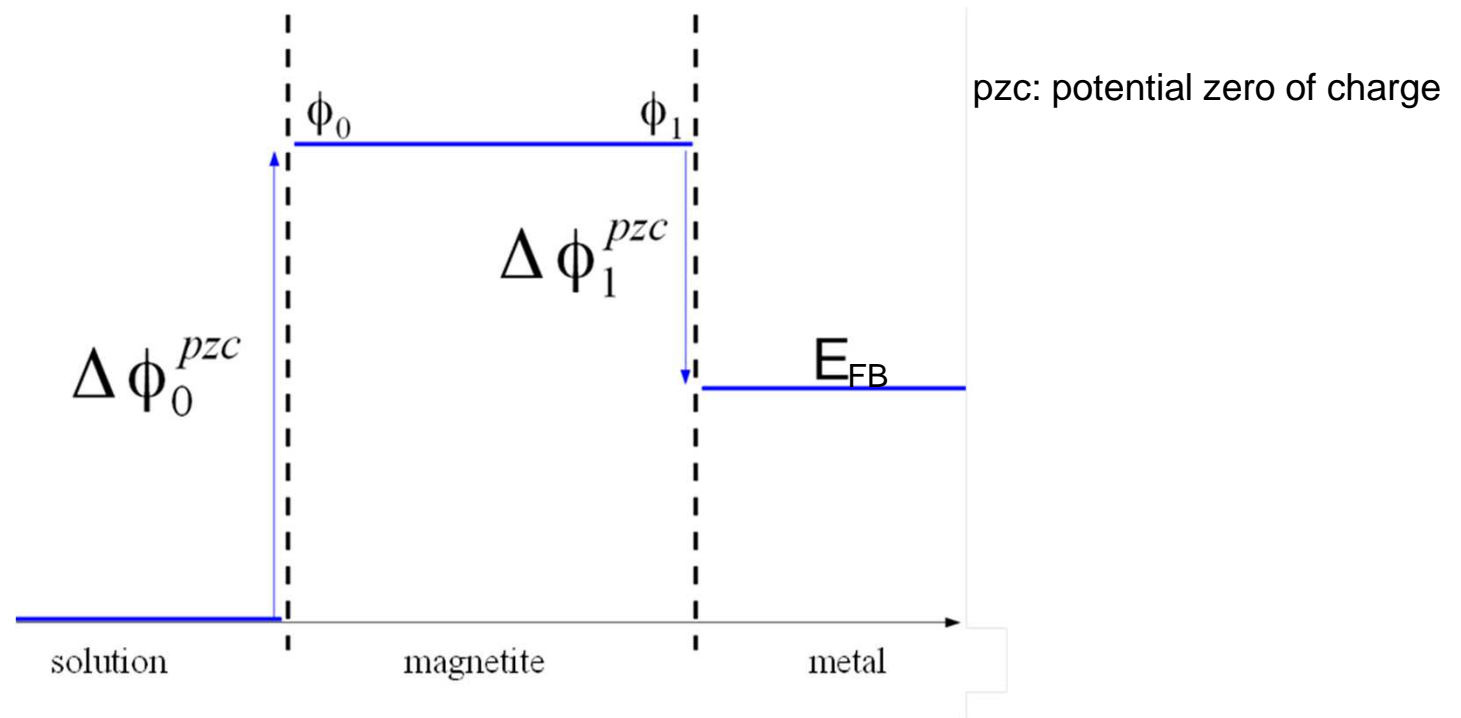
[4] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, National Association of Corrosion Engineers 1974.

[5] Schmuki, P et al. *J. Electrochem. Soc.* **1996**, 143 (2), 574-582.

[6] Lu, Z. and Macdonald, D. D., *Electrochim. Acta* **2008**, 53 (26), 7696-7702

THERMODYNAMIC EQUILIBRIUM: POTENTIAL PROFILE IN SOLUTION/MAGNETITE/METAL SYSTEM

- Potential homogeneity in all phases for electrochemical equilibrium
- Interfaces always assumed uncharged



THERMODYNAMIC EQUILIBRIUM: ELECTRONIC EQUILIBRIUM OF SOLUTION/MAGNETITE/METAL SYSTEM → INNER INTERFACE

In DPCM, kinetic of the electronic exchange between iron and the oxide is:

$$J_e = m_e^1 c_e^1 - k_e^1 c_e^{metal}$$

c_e^1 and c_e^{metal} : electron concentrations in the oxide at the inner interface and in metal, respectively.
 m_e^1 and k_e^1 : kinetic constants of Richardson

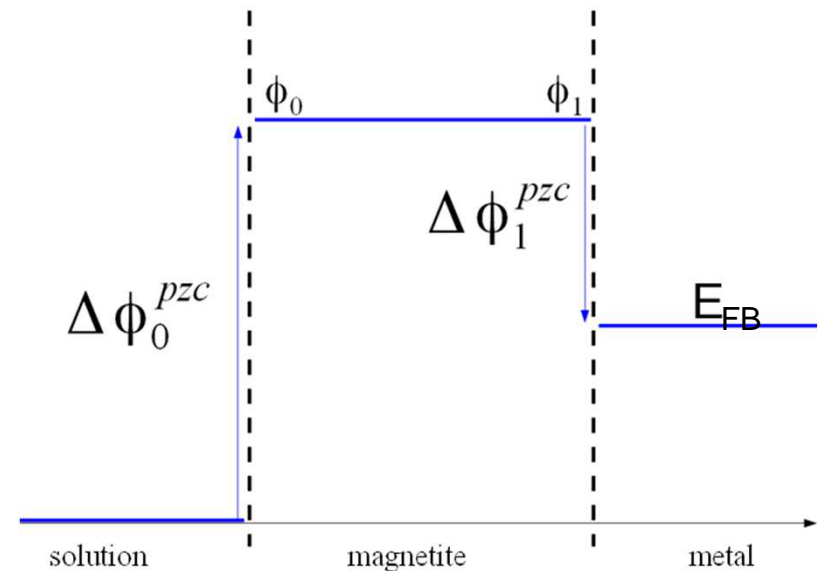
At the equilibrium $J_e = 0$

$$\Rightarrow N_e^1 = c_e^{1(eq)} \Omega_{ox} \quad \Omega_{ox}: \text{molar volume of the oxide}$$

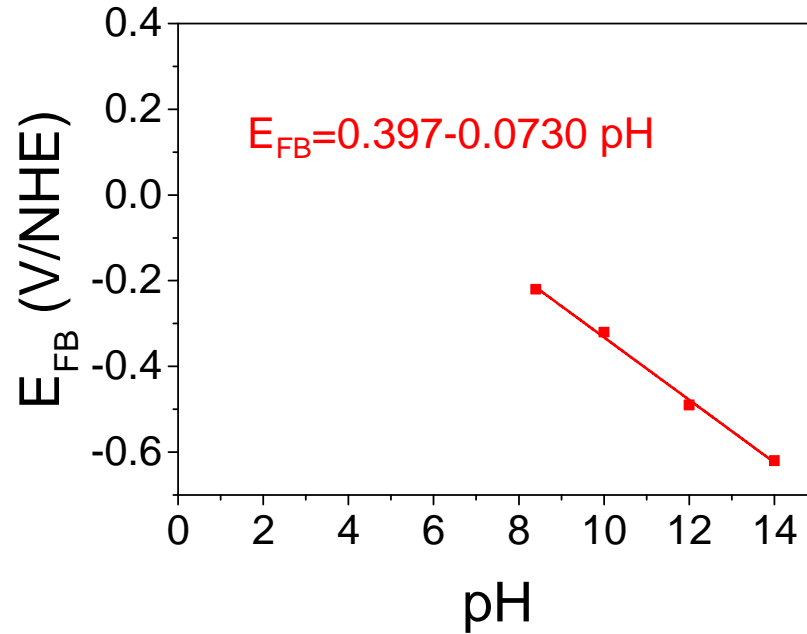
$$\Rightarrow N_e^1 = N_{metal} \ln[1 + \exp(-\gamma \Delta\Phi_1^{pzc})] \quad \gamma = \frac{F}{RT}, N_{metal}: \text{constant given by Friedel's model for iron}$$

$$\Rightarrow N_e^1 = 1 \text{ for magnetite} \quad \Rightarrow \boxed{\Delta\Phi_1^{pzc}}$$

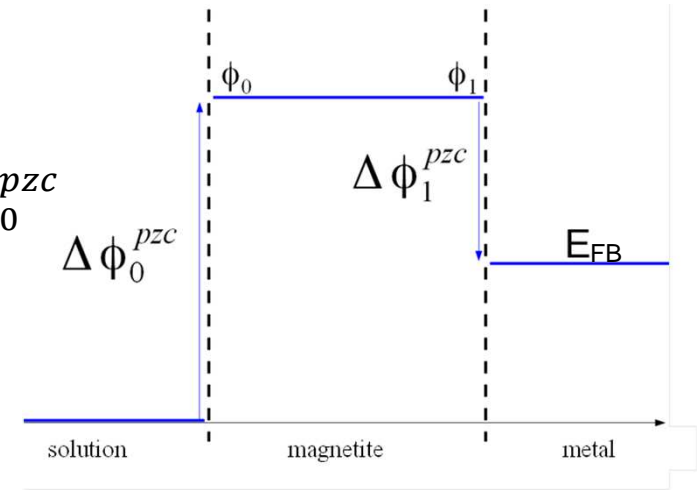
$$\Rightarrow \Delta\Phi_1^{pzc} - E_{FB} = \boxed{\Delta\Phi_0^{pzc}}$$



THERMODYNAMIC EQUILIBRIUM: ELECTRONIC EQUILIBRIUM OF SOLUTION/MAGNETITE/METAL SYSTEM → INNER INTERFACE



$$E_{FB} = \Delta\Phi_1^{pzc} + \Delta\Phi_0^{pzc}$$



$$\frac{\partial \Delta\Phi_1^{pzc}}{\partial pH} = 0 \Rightarrow \frac{\partial E_{FB}}{\partial pH} = \frac{\partial \Delta\Phi_0^{pzc}}{\partial pH}$$

$$\Delta\Phi_0^{pzc} \propto \frac{\ln 10}{\gamma} pH$$

$$\Delta\Phi_0^{pzc} \text{ (V/NHE)}$$

THERMODYNAMIC EQUILIBRIUM: ELECTRONIC EQUILIBRIUM OF SOLUTION/MAGNETITE/METAL SYSTEM → OUTER INTERFACE

- Butler-Volmer type law
- Kinetic of the electronic exchange between the oxide and the solution is kinetic redox of H⁺/H₂ couple:

$$J_e = m_e^0 a_{H_2}^{n_e^{H_2}} \exp(b_e^0 \gamma \Phi_0) - k_e^0 10^{-n_e^{pH} pH} c_e^0 \exp(-a_e^0 \gamma \Phi_0)$$

$a_{H_2}^{n_e^{H_2}}$ and b_e^0 : Butler-Volmer coefficients

- Same processing for Fe³⁺/Fe couple

$$J_e = m_r^0 a_{Fe^{2+}}^{sol} \exp(a_r^0 \gamma \Phi_0) - k_r^0 a_{Fe^{3+}}^{sol} c_e^0 \exp(-b_r^0 \gamma \Phi_0)$$

$a_{Fe^{2+}}^{sol}$, $a_{Fe^{3+}}^{sol}$ and b_r^0 : Butler-Volmer coefficients

- At the equilibrium $J_e = 0$

THERMODYNAMIC EQUILIBRIUM: KINETIC CONSTANTS RATIO FOR INTERFACIAL REACTION FOR SOLUTION/MAGNETITE/METAL SYSTEM

Mobile charge	Outer interface	Inner interface
Cations	$\frac{m_{Fe}^0}{k_{Fe}^0} = \frac{2}{P_m - 2} \exp(3\gamma (E_{Fe^{3+}/Fe}^0 - \Delta\Phi_1^{pzc}))$ $a_{Fe}^0 + b_{Fe}^0 = 1$	$\frac{m_{Fe}^1}{k_{Fe}^1} = \left(\frac{P_m}{2} - 1\right) \exp[3(a_{Fe}^1 + b_{Fe}^1)\gamma\Delta\Phi_1^{pzc}]$
Electrons	$\frac{k_e^0}{m_e^0} = \Omega_{ox} \exp(\gamma (E_{H^+/H_2}^0 - \Delta\Phi_1^{pzc}))$ $n_e^{pH} = a_e^0 + b_e^0 = 1$	$\frac{k_e^1}{m_e^1} = \sqrt{\frac{m^{**}}{m^*}}$

m^* and m^{**} : effective masses of electron in the oxide and in metal respectively

$$\gamma = \frac{F}{RT}$$

Ω_{ox} : molar volume of the oxide

P_m : oxide characteristic

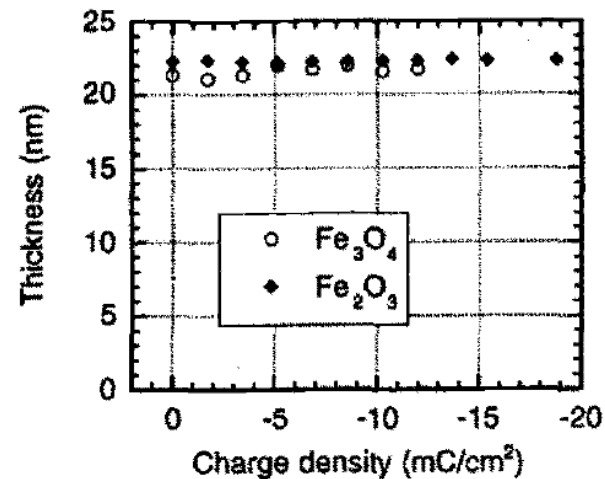
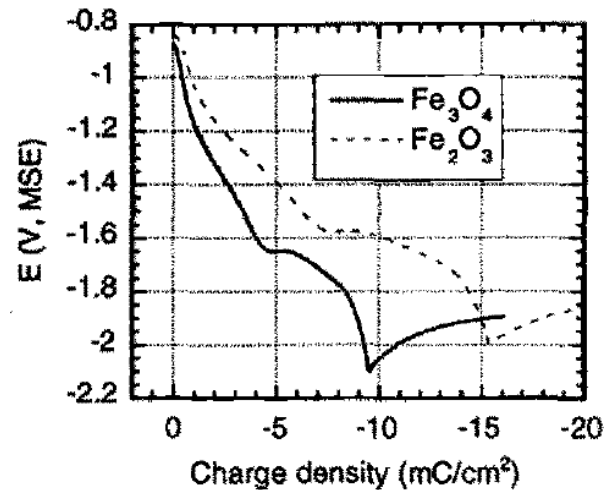
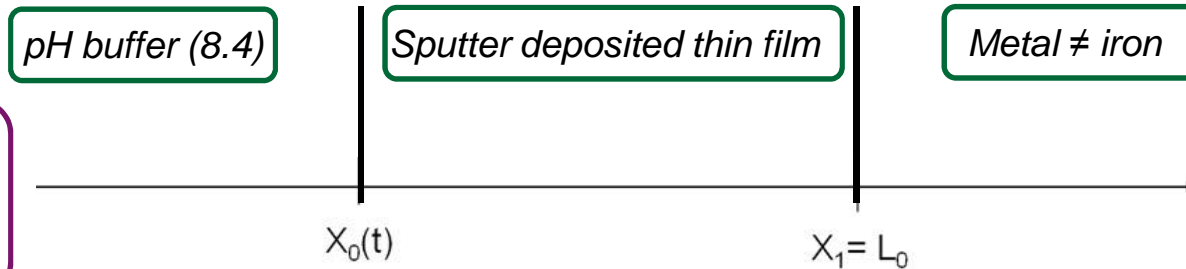
Reduction of number of independent parameters since kinetic ratio are constant

XANES STUDY OF THE CATHODIC REDUCTION OF ARTIFICIAL IRON OXIDE PASSIVE FILMS AT $-5 \mu\text{A}/\text{cm}^2$ [5]

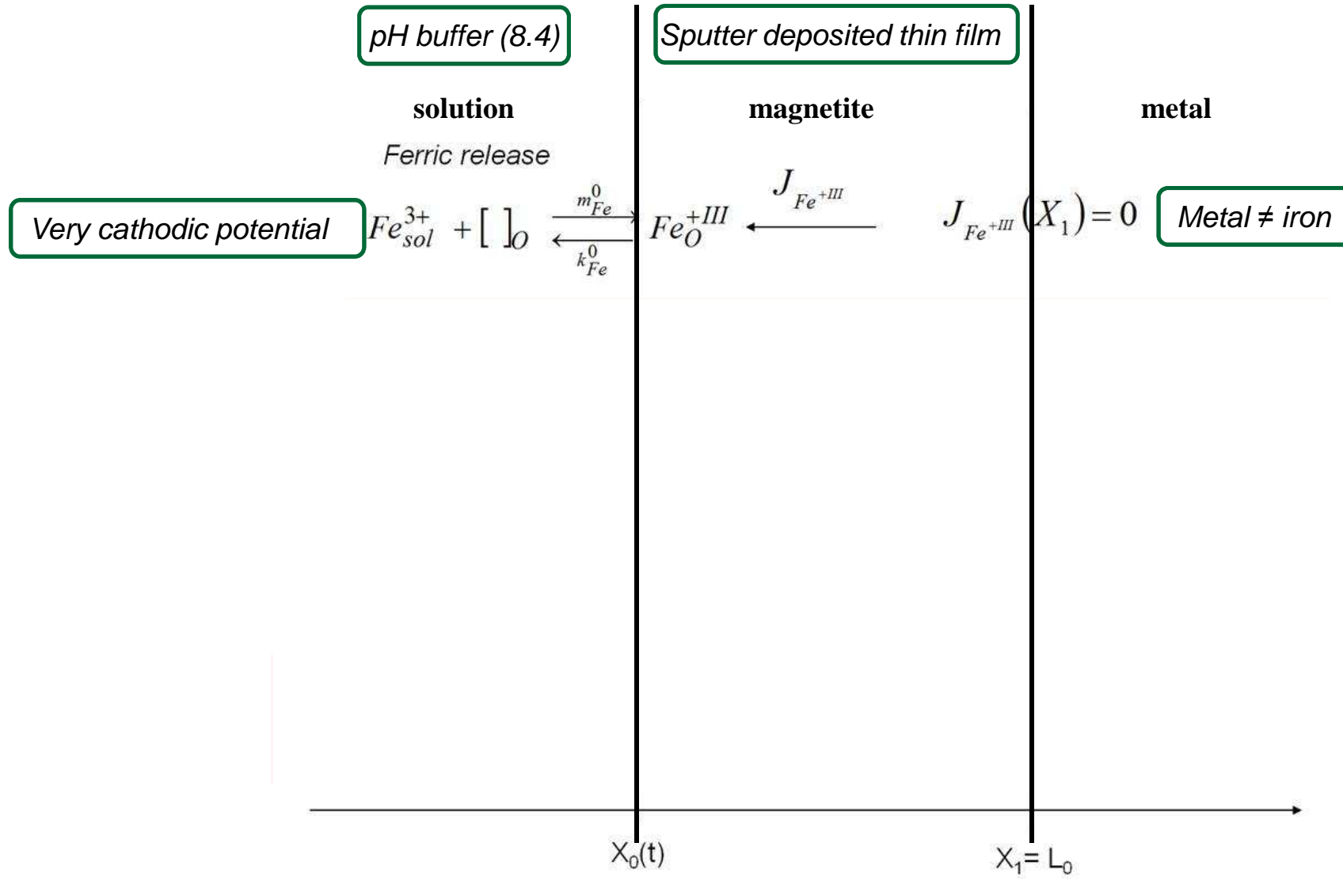
Available:
2 informations with
charge density

Potential evolution
during the reduction

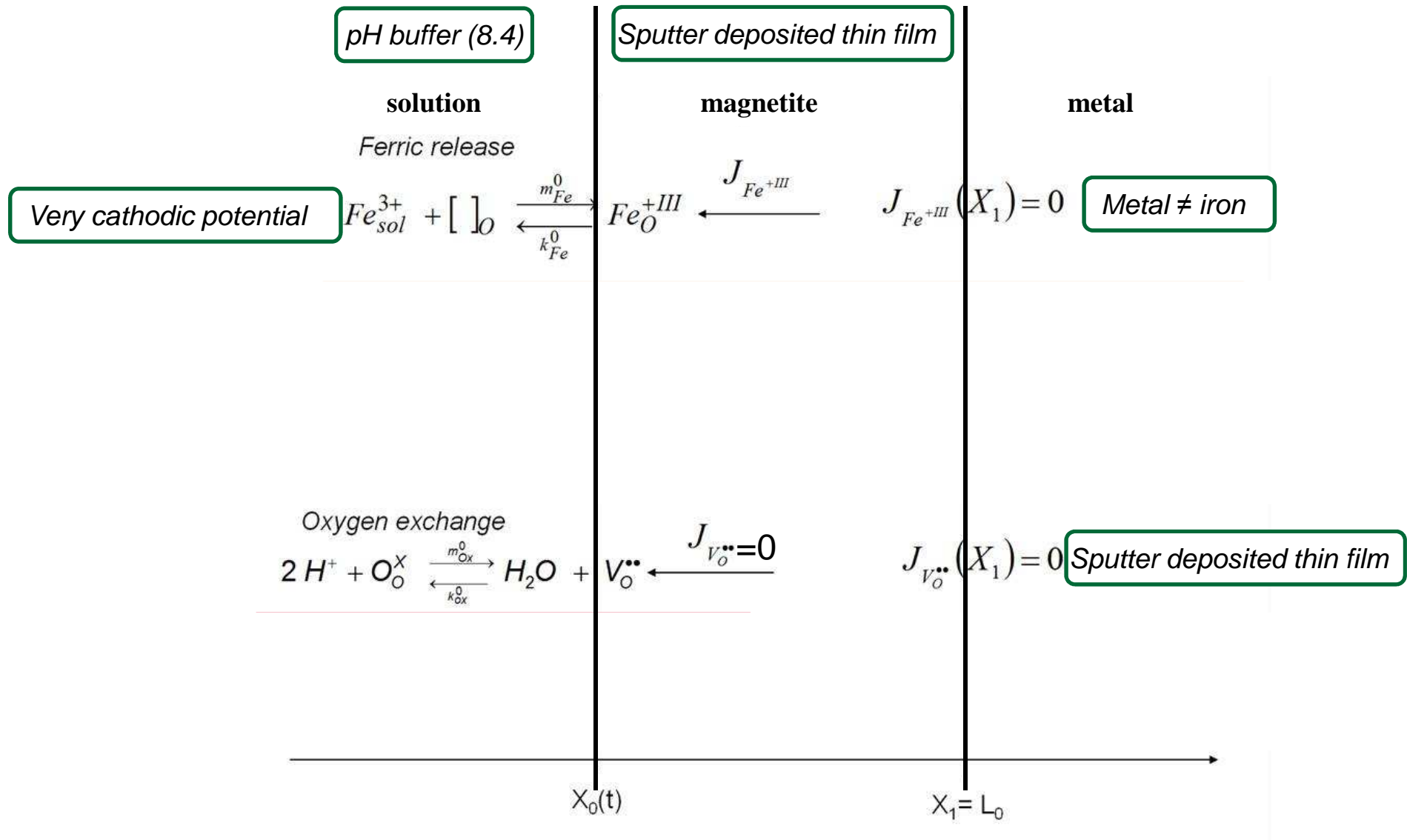
Thickness
decrease
measurements



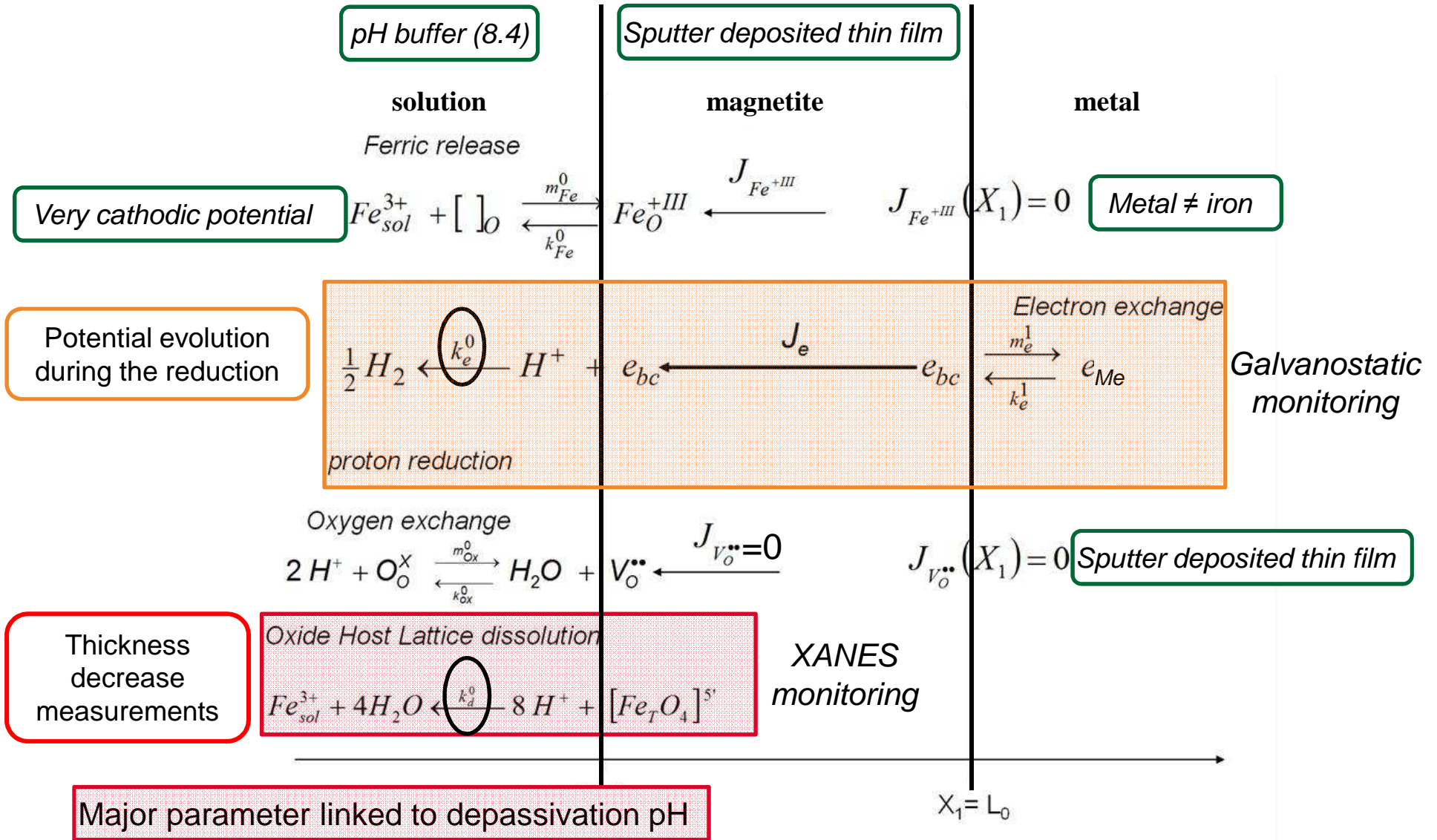
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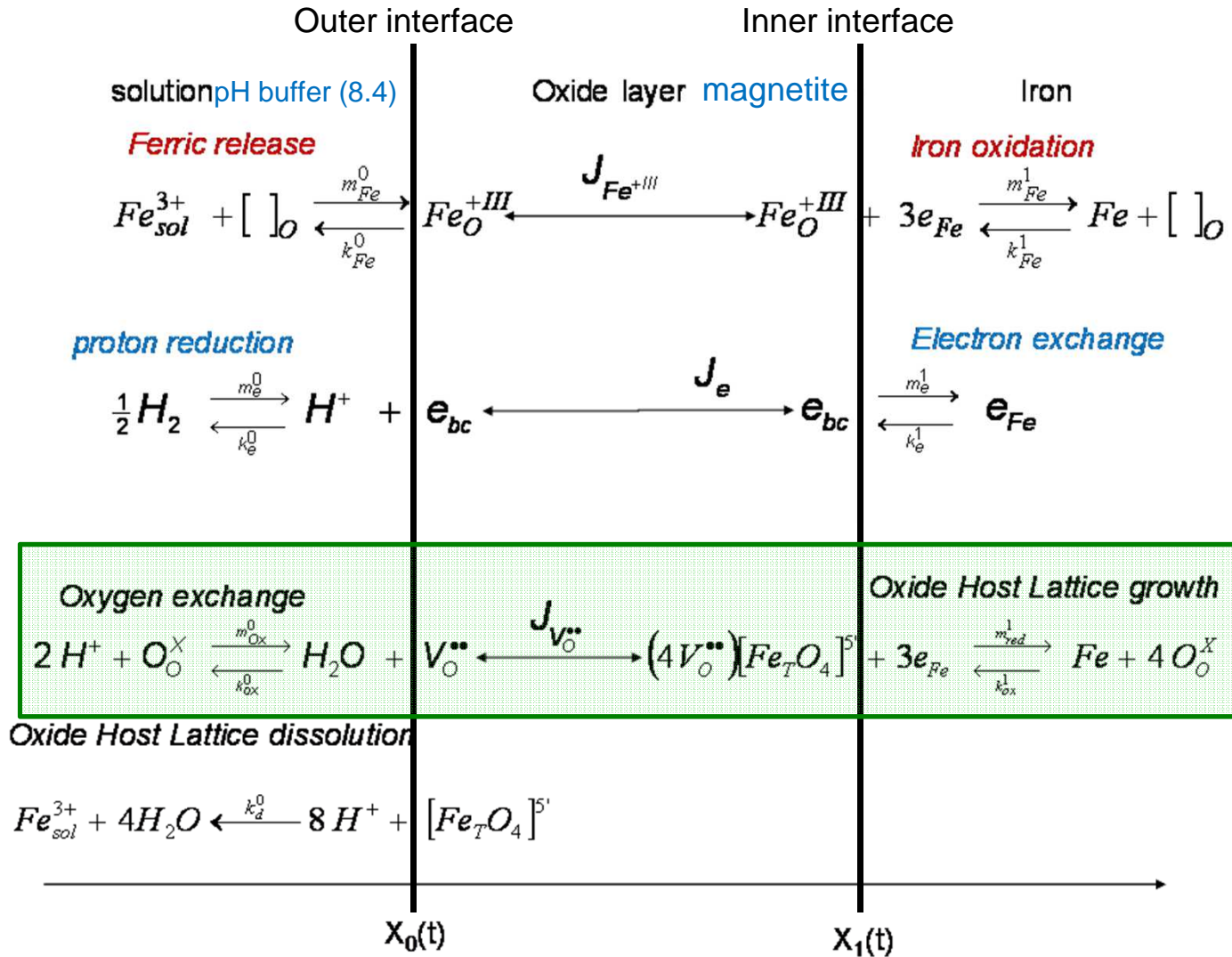
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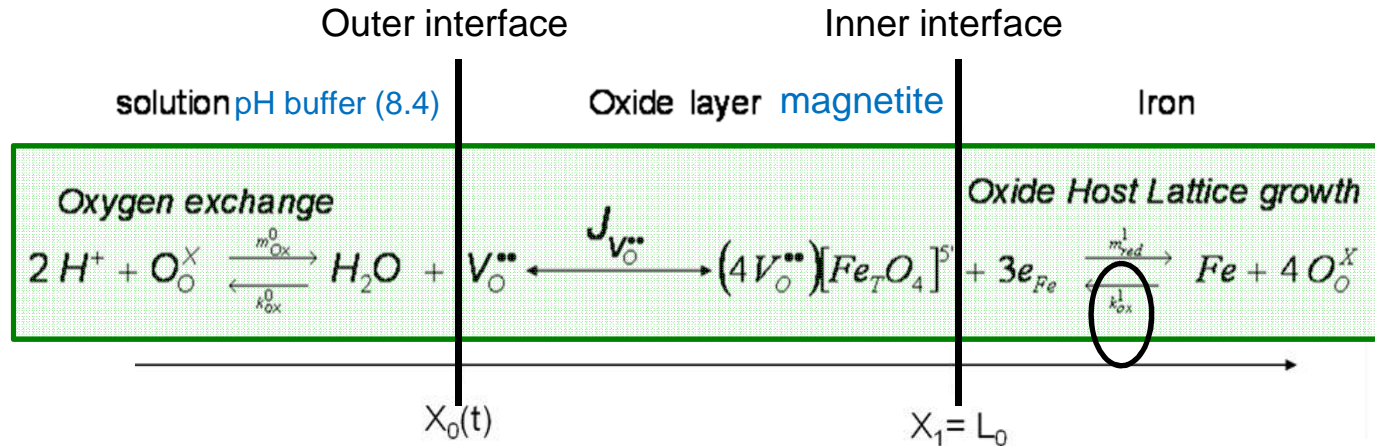
OXIDE HOST LATTICE GROWTH REACTION [6]: MOTION RATE OF INNER INTERFACE



Available:
Thickness = $f(E_{applied})$

Irreversible process
as in the Point
Defect Model

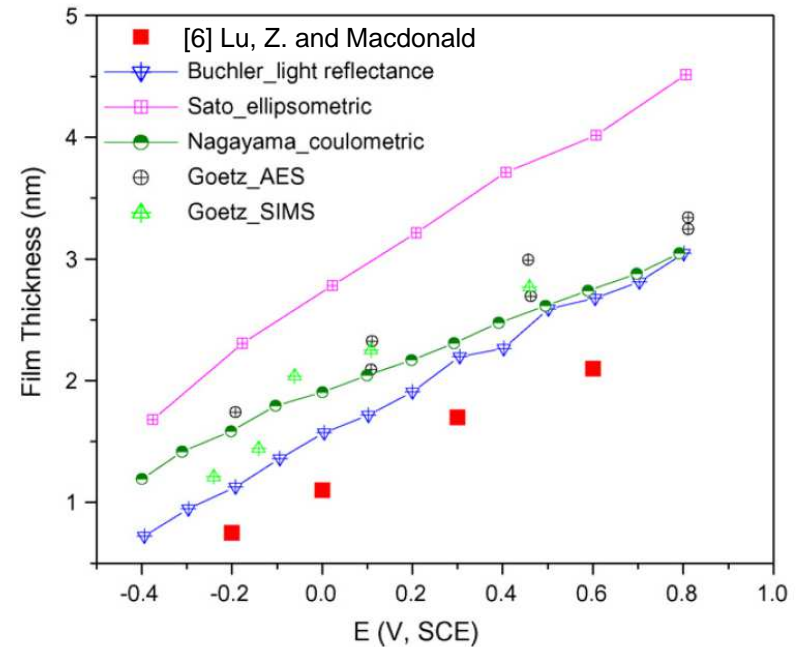
OXIDE HOST LATTICE GROWTH REACTION [6]: MOTION RATE OF INNER INTERFACE



Simulation of potential profile in the system with CALIPSO in searching

- k_{ox}^1
- a_{ox}^1 associated Butler-Volmer coefficient

in order to fit experimental curves



- Strategy organized step by step without using multifitting processing
- Step 1: Thermodynamic approach
 - based on equilibrium states
 - allows to reduce the number of independent parameters
- Step 2: Study of the Oxide Host Lattice dissolution reaction (outer interface)
 - based on experimental data in literature
 - allow to determine dissolution rate of magnetite
 - major parameter linked to pH of depassivation
- Step 3: Study of the Oxide Host Lattice growth reaction (inner interface)
 - based on experimental data in literature and CALIPSO simulation
 - allow to know potential and pH ranges of passive film existence
 - estimation of parameter value of the oxide growth
- Next step to setup k_{Fe}^0
- Setup based on no corrosion data or experiments
- Possibility to check parameters values in simulating corrosion experiments



Acknowledgements

- Andra (French Agency for Nuclear Waste Management)

THANK YOU FOR YOUR ATTENTION

Commissariat à l'énergie atomique et aux énergies alternatives
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