A kinetic model of the oxide growth and restructuring on structural materials in nuclear power plants

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Outline

- Introduction
- The Mixed Conduction Model for oxide films in high-temperature water
- Procedure for the calculation of kinetic parameters
- Comparison with experimental results
- Relevance of kinetic and transport parameters
- Conclusions and future trends

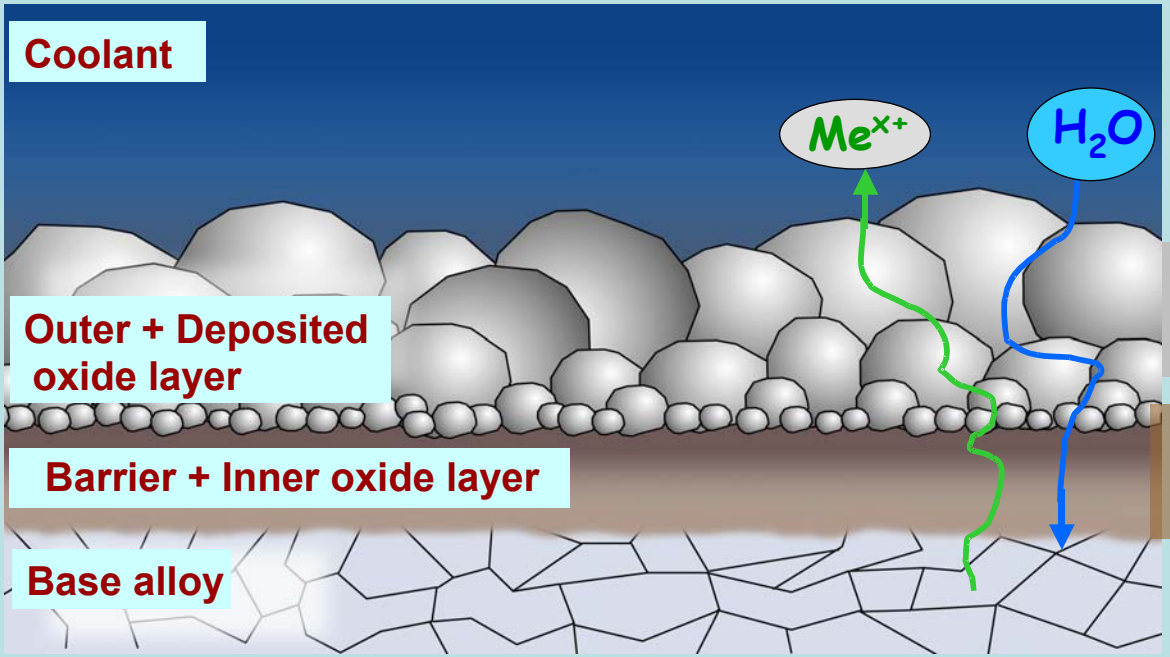
Introduction

The well-controlled growth of the passivating oxide on construction materials in light water reactors (LWRs):

- limits the impact of the coolant on such materials
- minimises the concentration of impurities that reach nuclear fuel surfaces and become radioactive

Introduction (2)

The oxide film has a duplex structure



grows via dissolution/precipitation

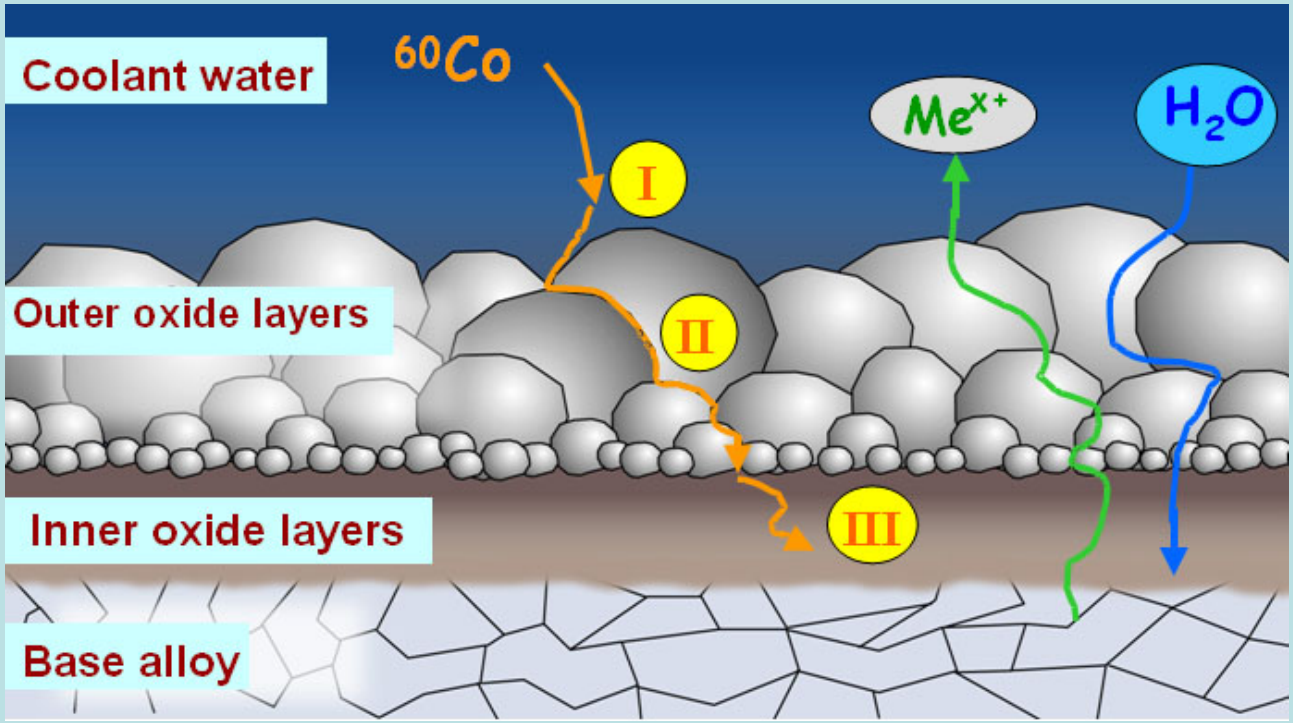
grows via a solid-state mechanism

The inner layer contains a significant number of ionic defects:

- ionic species transported through the film
- dissolution of the metal through the film an important process in addition to film growth – corrosion release

Introduction (3)

Incorporation of radioactive species in the film

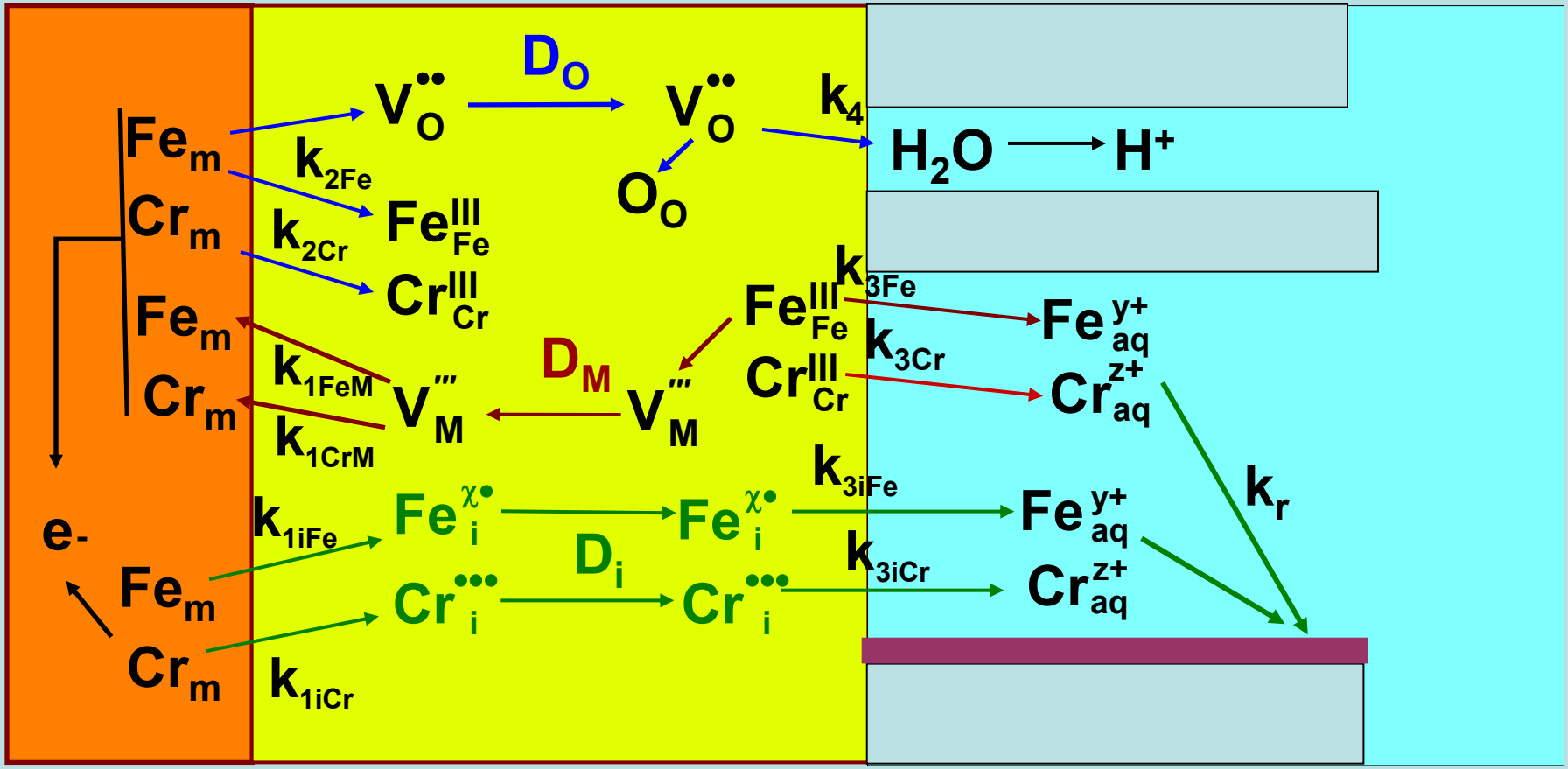


Involves adsorption/surface complexation (I), incorporation in the outer layer crystallites (II) and incorporation in the compact inner layer (III)

Aims of the work

- To elaborate a procedure for the estimation of the kinetic and transport parameters of film growth and restructuring on the basis of ex-situ analytical data
- To assess the rates of incorporation of minor species in the oxide films

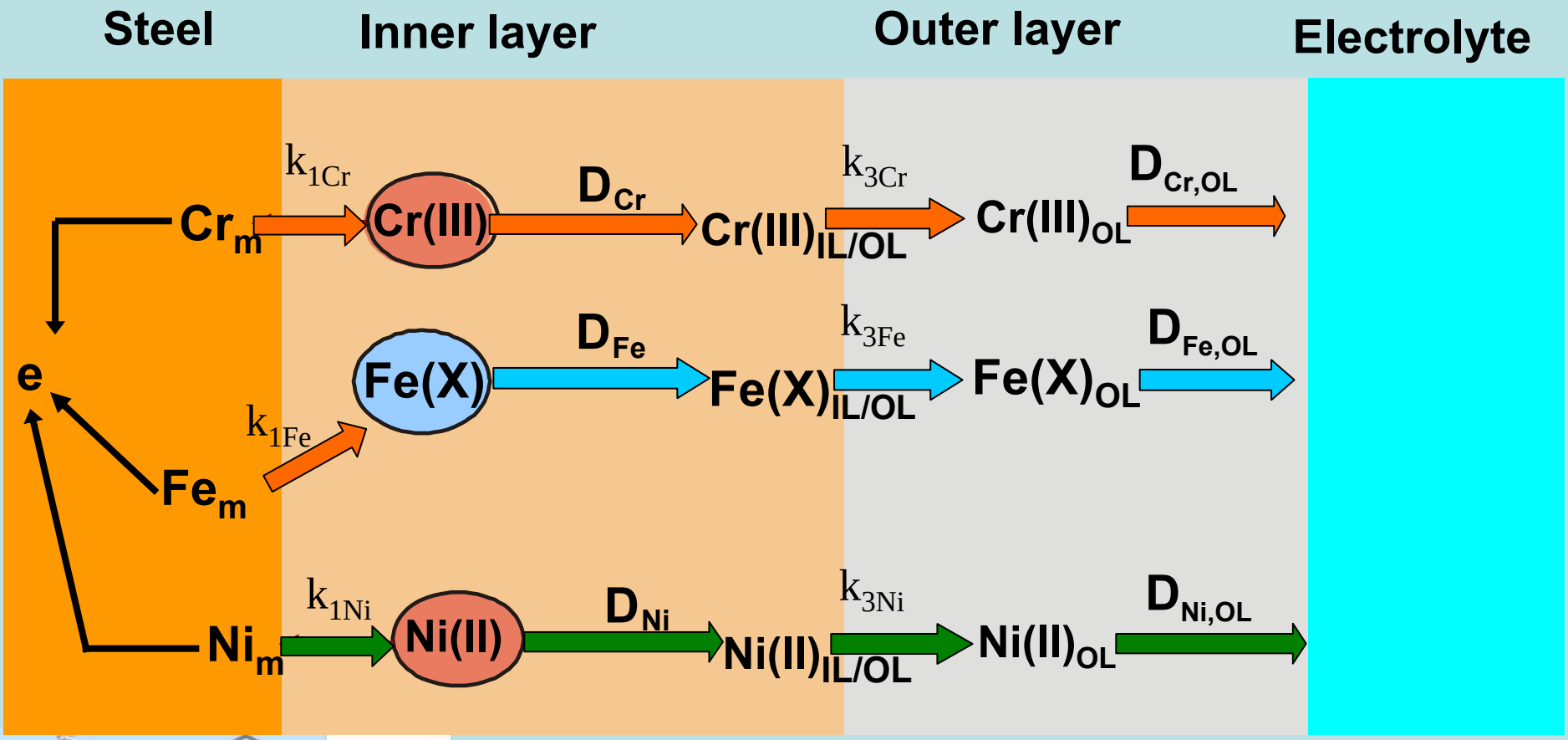
Mixed-Conduction Model for oxide films in high-temperature electrolytes



Main assumptions

- Applied potential distributed as potential drops at the interfaces and in the inner layer
- Steady-state thickness of the inner layer depends linearly on the applied potential (field strength in the layer constant)
- Rates of the interfacial reactions exponentially dependent on the potential drop at the respective interface
- Transport of ionic point defects governed by usual diffusion-migration equations, diffusion coefficients of interstitials and vacancies assumed equal
- Ionic defect transport assumed to proceed mainly via grain boundaries that occupy a significant part of the volume due to the nanocrystalline barrier layer structure

Approximation used in the calculation procedure



Transport equations (inner layer)

$$\frac{\partial y_{Fe}}{\partial t} = D_{Fe}\frac{\partial^2 y_{Fe}}{\partial x^2} + 2.7F\vec{E}D_{Fe}\frac{\partial y_{Fe}}{\partial x}$$

$$\frac{\partial y_{Cr}}{\partial t} = D_{Cr}\frac{\partial^2 y_{Cr}}{\partial x^2} + 3F\vec{E}D_{Cr}\frac{\partial y_{Cr}}{\partial x}$$

$$\frac{\partial y_{Ni}}{\partial t} = D_{Ni}\frac{\partial^2 y_{Ni}}{\partial x^2} + 2F\vec{E}D_{Ni}\frac{\partial y_{Ni}}{\partial x}$$

$$\frac{\partial y_{Co}}{\partial t} = D_{Co}\frac{\partial^2 y_{Co}}{\partial x^2} + 2F\vec{E}D_{Co}\frac{\partial y_{Co}}{\partial x}$$

Oxide constituents

$$\frac{\partial y_{Zn}}{\partial t} = D_{Zn}\frac{\partial^2 y_{Zn}}{\partial x^2} - \frac{2F\vec{E}D_{Zn}}{RT}\frac{\partial y_{Zn}}{\partial x}$$

Zinc from the electrolyte

Boundary conditions

$$y_{Fe}(x,0) = y_{Fe,a}, y_{Cr}(x,0) = y_{Cr,a}, y_{Ni}(x,0) = y_{Ni,a}, y_{Co}(x,0) = y_{Co,a}, y_{Zn}(x,0) = 0$$

$$y_{Fe}(0,t) = y_{Fe,a}, y_{Cr}(0,t) = y_{Cr,a}, y_{Ni}(0,t) = y_{Ni,a}, y_{Co}(x,0) = y_{Co,a}, y_{Zn}(0,t) = 0$$

$$y_{Fe}(L,t) = \frac{k_{1Fe} y_{Fe,a}}{V_{mo}} \left[\frac{1}{k_{3Fe}} + \frac{RT}{2F\vec{E}D_{Fe}} \right],$$

$$y_{Ni}(L,t) = \frac{k_{1Ni} y_{Ni,a}}{V_{mo}} \left[\frac{1}{k_{3Ni}} + \frac{RT}{2F\vec{E}D_{Ni}} \right]$$

$$y_{Cr}(L,t) = \frac{k_{1Cr} y_{Cr,a}}{V_{mo}} \left[\frac{1}{k_{3Cr}} + \frac{RT}{2F\vec{E}D_{Cr}} \right],$$

$$y_{Co}(L,t) = K_{enr,Co} c_{Co}(sol) + \frac{k_{1Co} y_{Co,a}}{V_{mo}} \left[\frac{1}{k_{3Co}} + \frac{RT}{2F\vec{E}D_{Co}} \right]$$

$$y_{Zn}(L,t) = K_{enr,Zn} c_{Zn}(sol)$$

Transport equations (outer layer) – formal description

- Pure diffusional transport – no field in the outer layer (discrete crystallites + electrolyte in between)

- Boundary conditions at the inner layer / outer layer interface – similar to those at the inner layer / electrolyte (continuity of composition)

- Boundary conditions at the outer layer / electrolyte interface – stoichiometry of oxide as found by XPS (agreement with thermodynamics)

$$\frac{\partial y_{Fe,OL}}{\partial t} = D_{Fe,OL}\frac{\partial^2 y_{Fe,OL}}{\partial x^2}$$

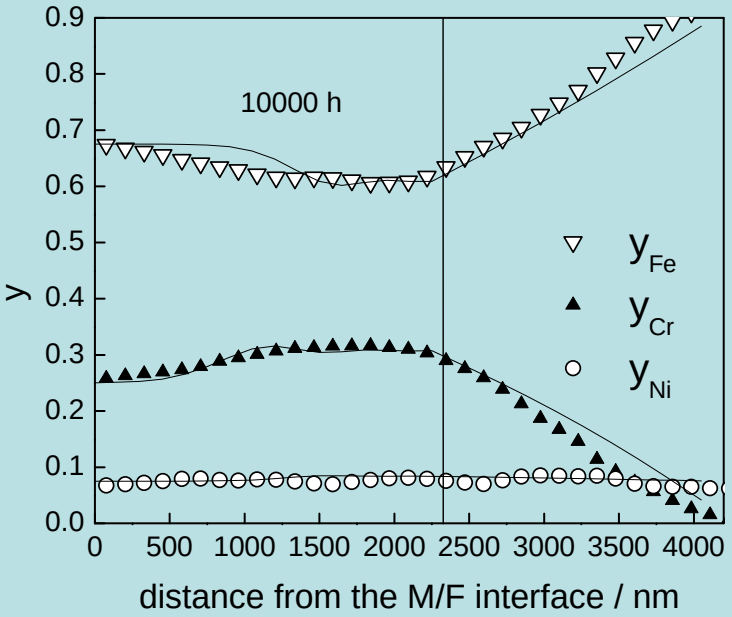
$$\frac{\partial y_{Cr,OL}}{\partial t} = D_{Cr,OL}\frac{\partial^2 y_{Cr,OL}}{\partial x^2}$$

$$\frac{\partial y_{Ni,OL}}{\partial t} = D_{Ni,OL}\frac{\partial^2 y_{Ni,OL}}{\partial x^2}$$

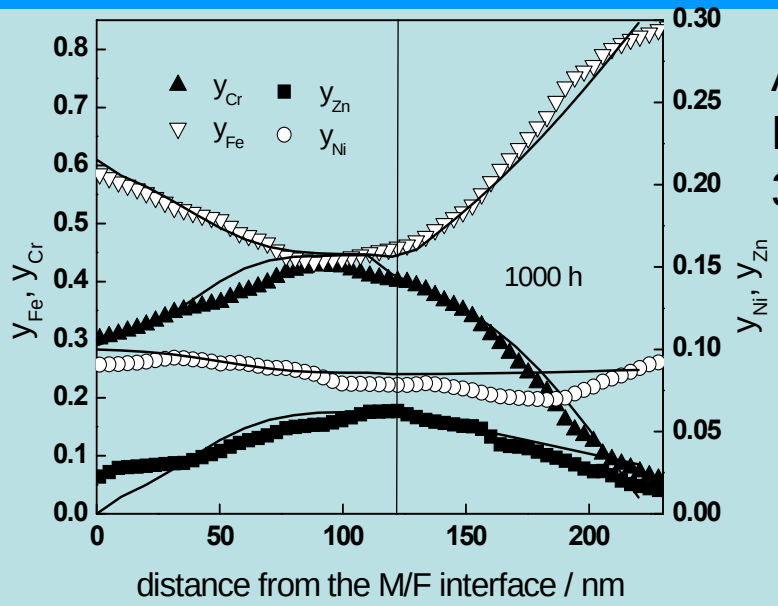
$$\frac{\partial y_{Zn,OL}}{\partial t} = D_{Zn,OL}\frac{\partial^2 y_{Zn,OL}}{\partial x^2}$$

$$\frac{\partial y_{Co,OL}}{\partial t} = D_{Zn,OL}\frac{\partial^2 y_{Co,OL}}{\partial x^2}$$

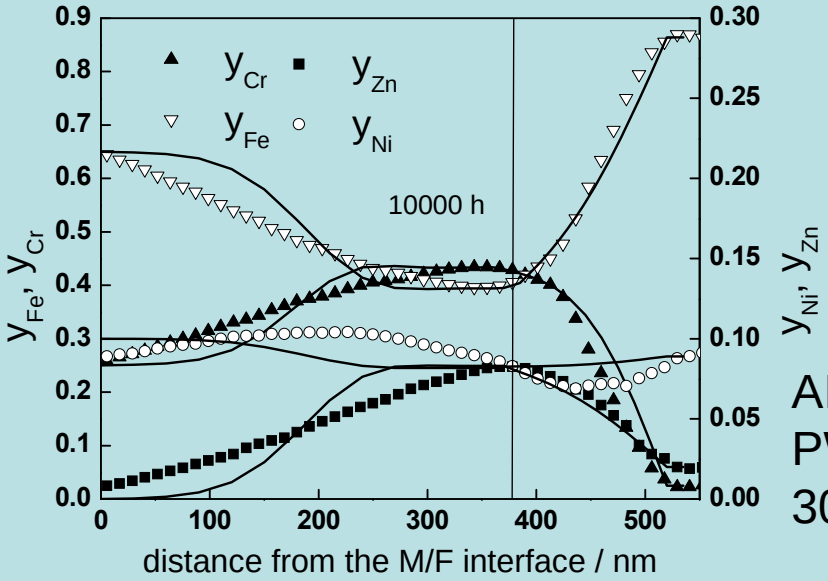
Calculational results – influence of Zn on film growth / restructuring



AISI 304, 260 °C, PWR, 10 000 h, no Zn

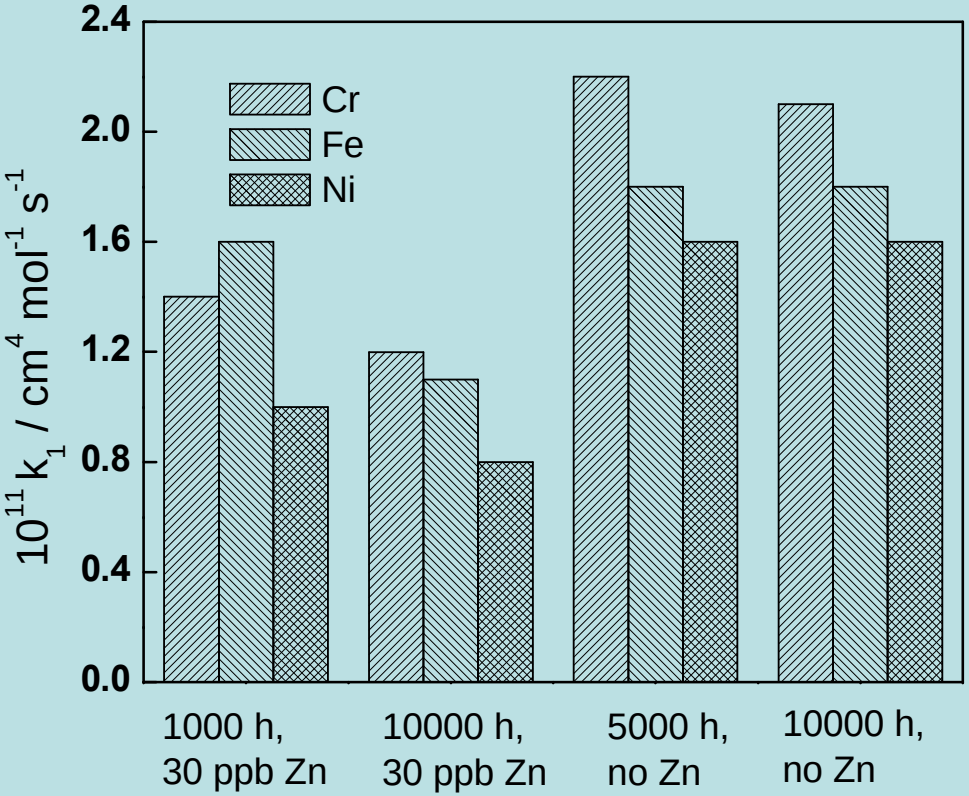


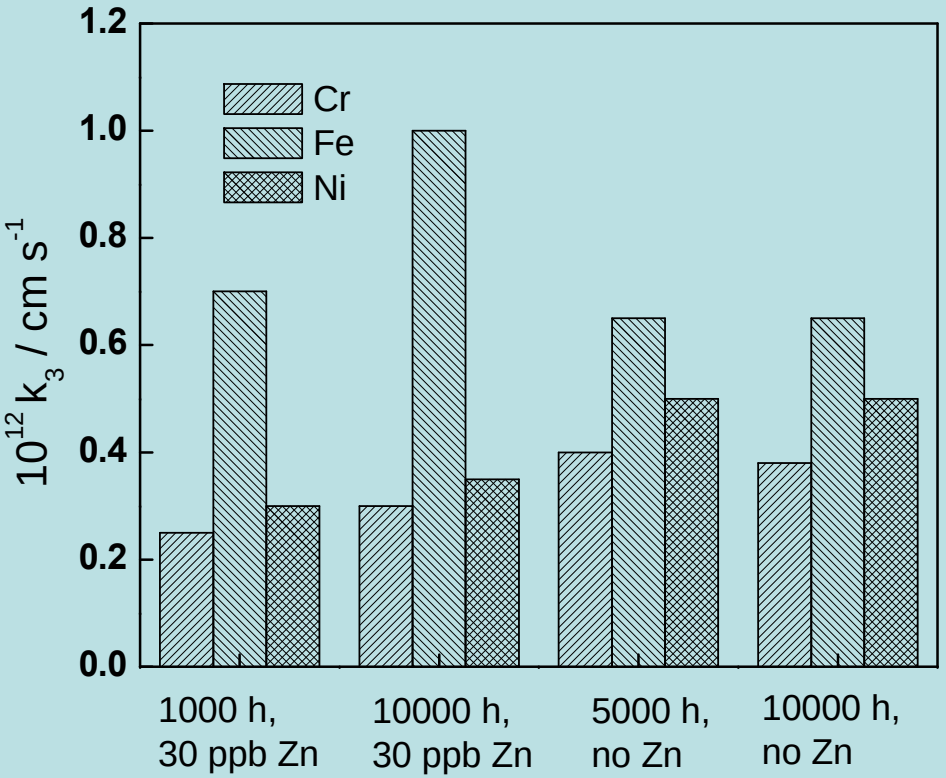
AISI 304, 260 °C, PWR, 1000 h, 30 ppb Zn



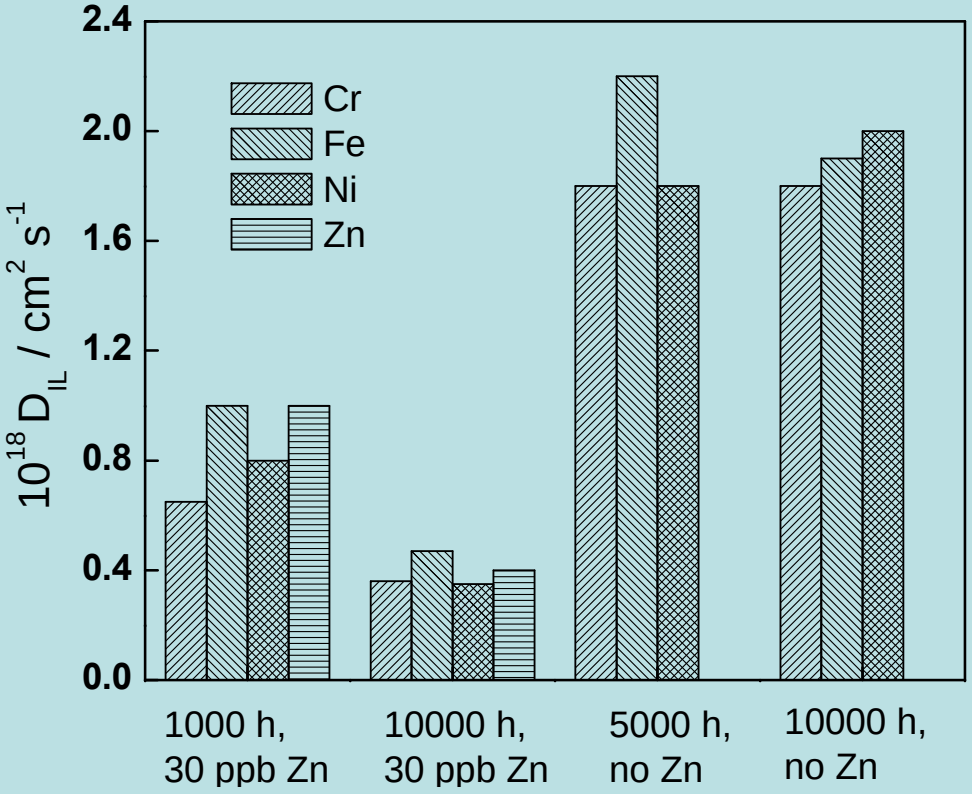
AISI 304, 260 °C, PWR, 10 000 h, 30 ppb Zn

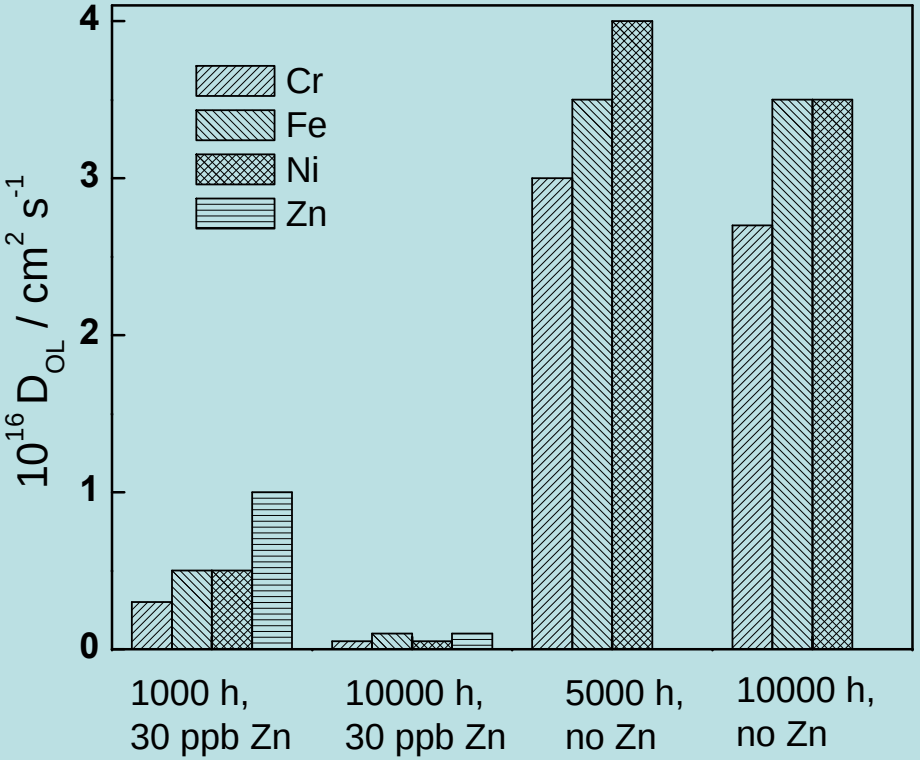
Calculational results – effect of Zn (continued) – kinetic parameters





Calculational results – effect of Zn (continued) – transport parameters





Mechanism of Zn incorporation

Incorporation of Zn at the inner layer/electrolyte interface → filling of empty cation interstices and/or cation vacancies

$$V_i + Zn_{aq}^{2+} \rightarrow Zn_i^{\bullet\bullet}$$

$$V_M^{'''} + Zn_{aq}^{2+} \rightarrow Zn_M^{'}$$

Steady-state concentration of defects maintained ➔ additional amount of Fe dissolved according to the reactions

$$Fe_i^{\bullet\bullet} \rightarrow Fe_{aq}^{x+} + V_i + (x-2)e'$$

$$Fe_{Fe}^{X} \rightarrow Fe_{aq}^{x+} + V_M^{'''} + (x-X)e'$$

Sum of the rate constants of the above reactions = rate constant k_{3Fe} → observed to increase with the addition of Zn

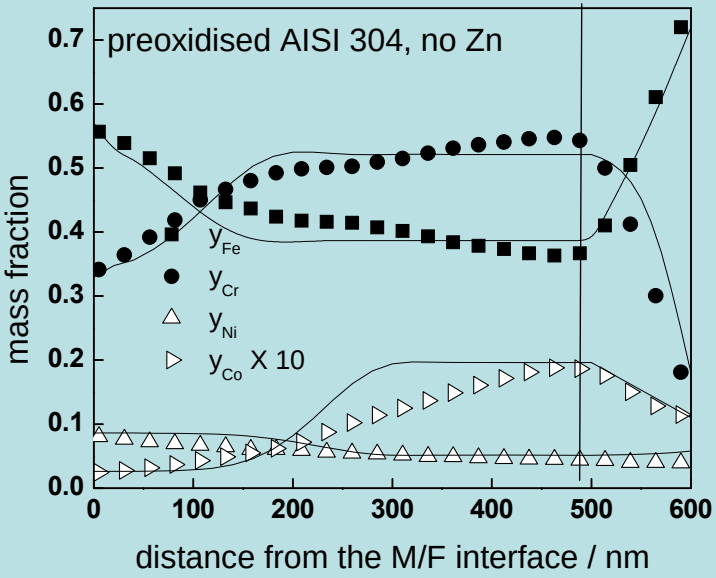
Mechanism of Zn incorporation (cont.)

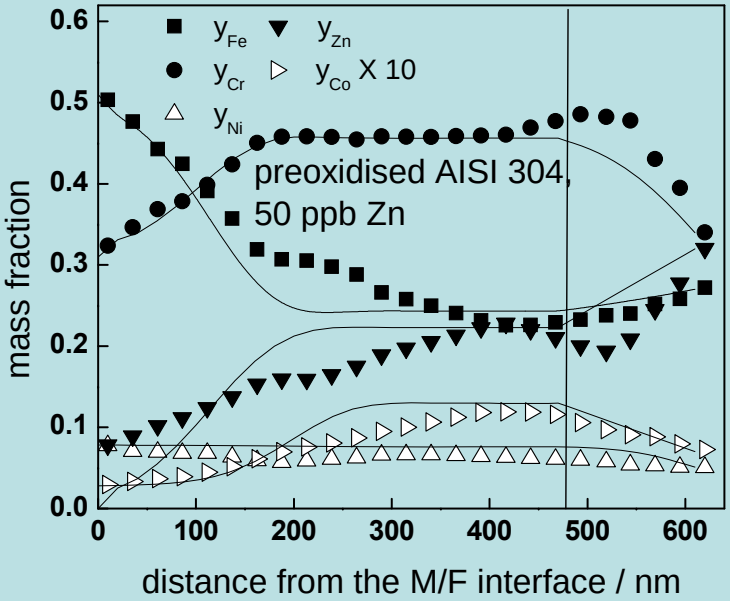
First step of Zn incorporation in the oxide - written as a surface complexation reaction

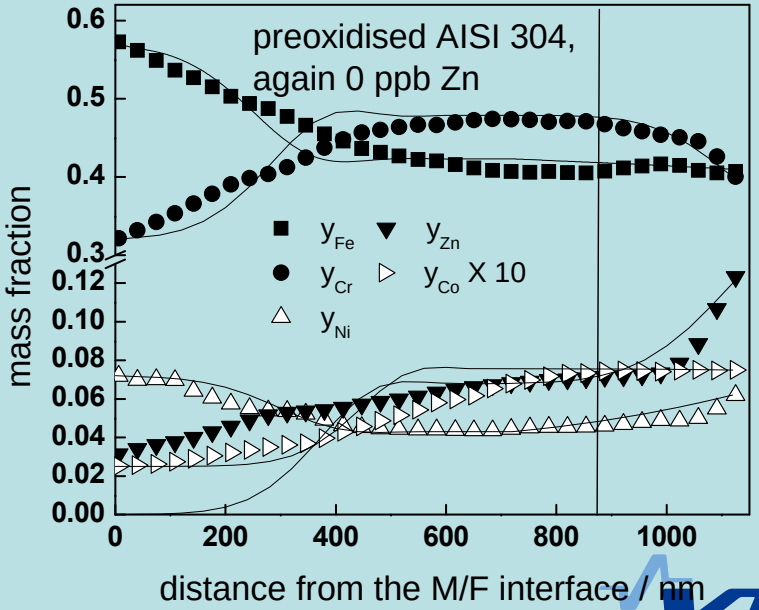
$$\equiv Fe-OH^{0}_{1/2} + Zn^{2+}_{aq} \rightleftarrows \equiv Fe-OZn^{1/2+} + H^{+}$$

Equilibrium constant of this reaction estimated at 280 ºC using the constant capacitance model to interpret high-temperature titration data in simulated PWR water –
good agreement with the present surface analytical measurements

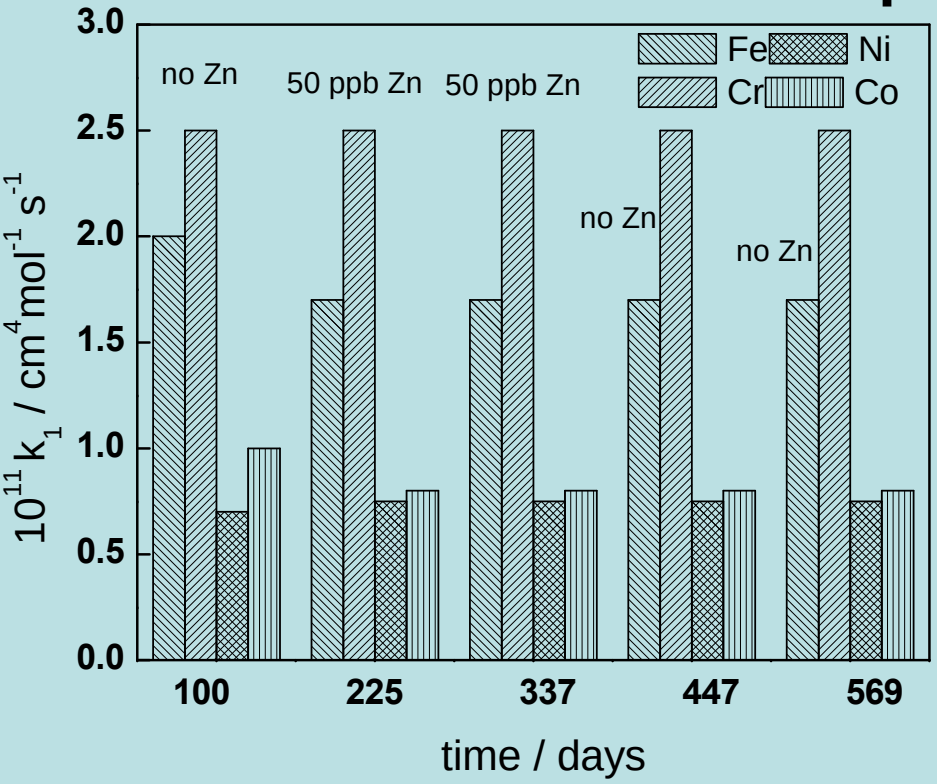
Effect of Zn on in-reactor Co incorporation

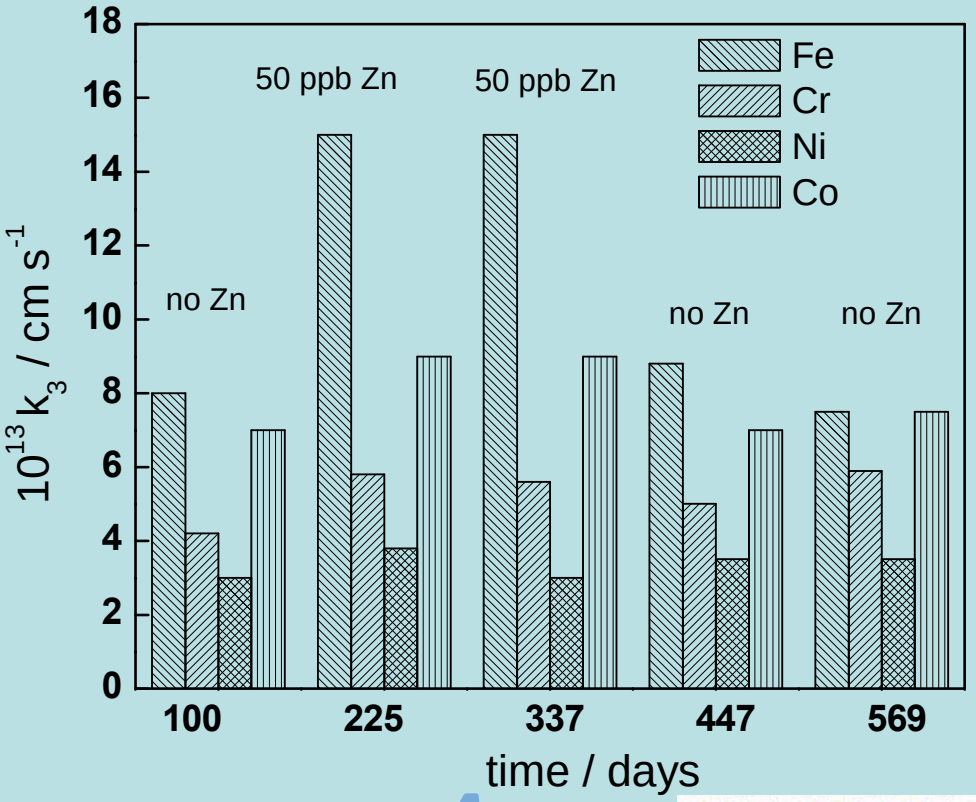




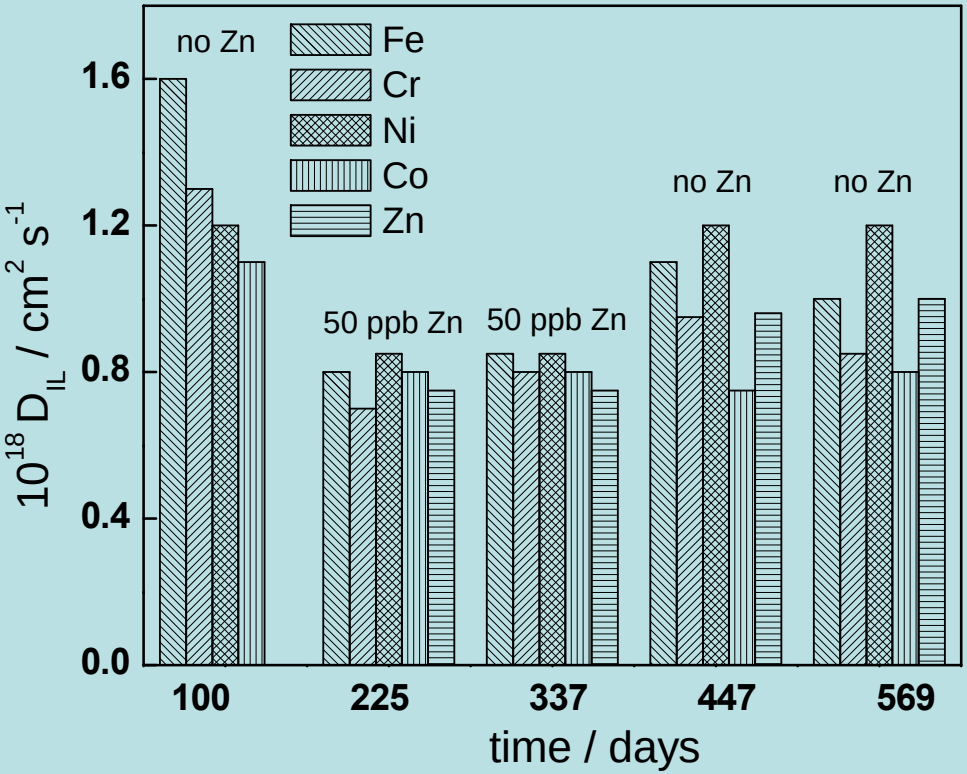


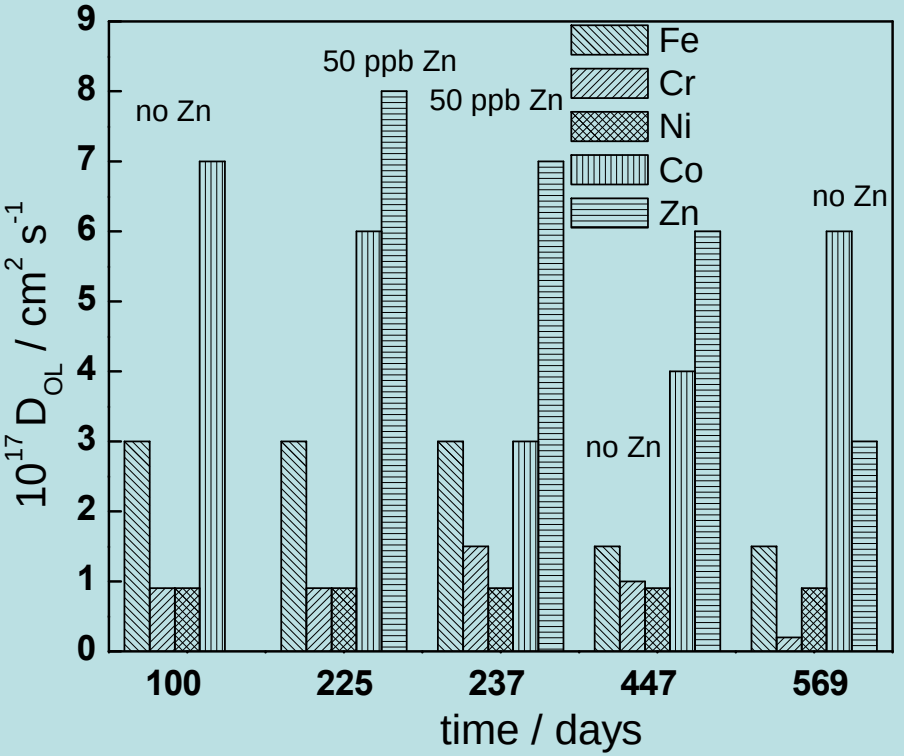
Effect of Zn on in-reactor Co incorporation – kinetic parameters





Effect of Zn on in-reactor Co incorporation – transport parameters

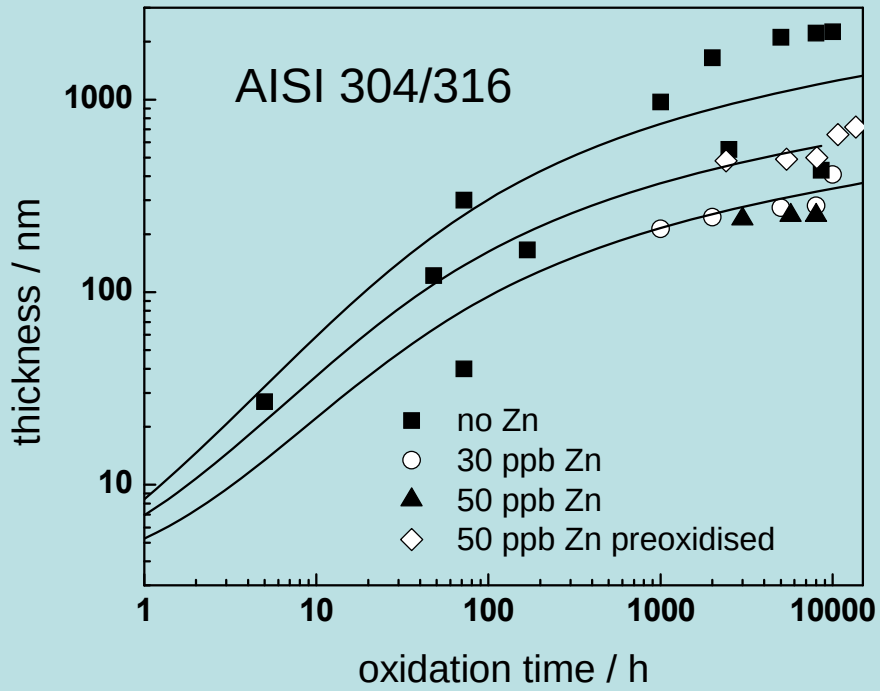


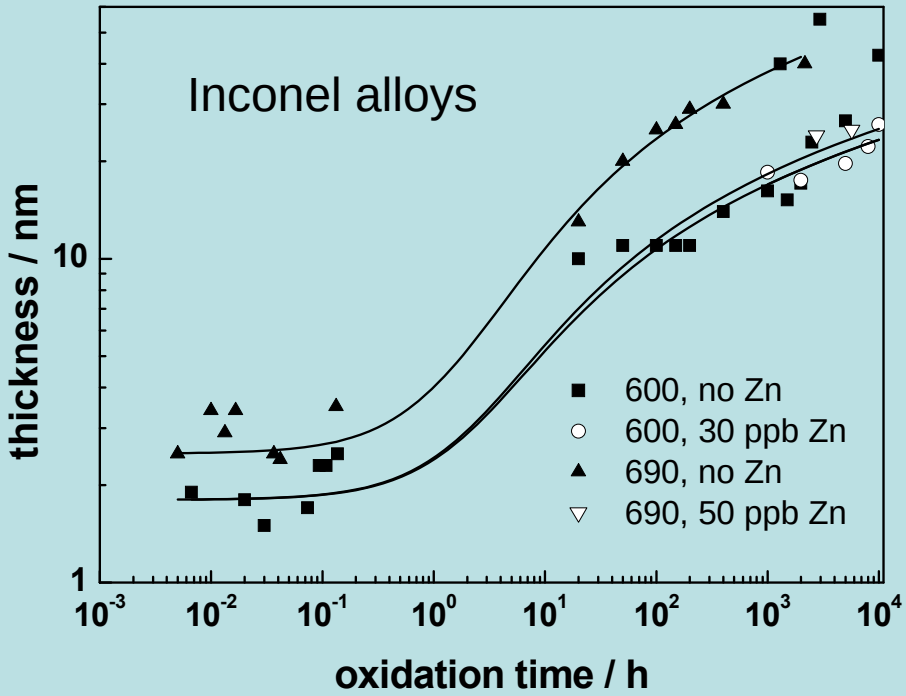


Layer growth kinetics

$$L(t) = L(t=0) + \frac{1}{b}\ln\left[1 + V_{m,MO}\left(k_{1,Cr}y_{Cr,a} + k_{1,Fe}y_{Fe,a} + k_{1,Ni}y_{Ni,a}\right)be^{-bL(t=0)}t\right]$$

$$b = \frac{3\alpha_1 F\vec{E}}{RT}$$





Conclusions (1)

- A quantitative procedure of determination of kinetic parameters for individual alloy constituents in the inner and outer layers has been developed
- It is based on available in-depth compositional data for oxides obtained from ex-situ analyses
- A fitting procedure for the calculation of the in-depth distribution of the individual alloy constituents in the compact layer is put forward
- On the basis of the obtained database of kinetic constants and transport parameters, the rate of transport of coolant-originating species (e.g. Co, Zn) is assessed

Conclusions (2)

- Oxide growth and incorporation of Co in the oxide retarded by Zn – the effect quantified by the model, kinetic and transport parameters estimated
- Main effects of Zn on the diffusion coefficients in both layers and to a certain extent on the rate constants at the outer interface – modification of both the oxide surface and the bulk oxide
- Incorporation of Zn in already existing oxides slower, restructuring less → on the overall less effective

Acknowledgement

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