

**A Mixed-Potential Model for the Prediction of the
Effects of Alpha-Radiolysis, Precipitation and
Redox Processes on the Dissolution of Used Nuclear Fuel**

by

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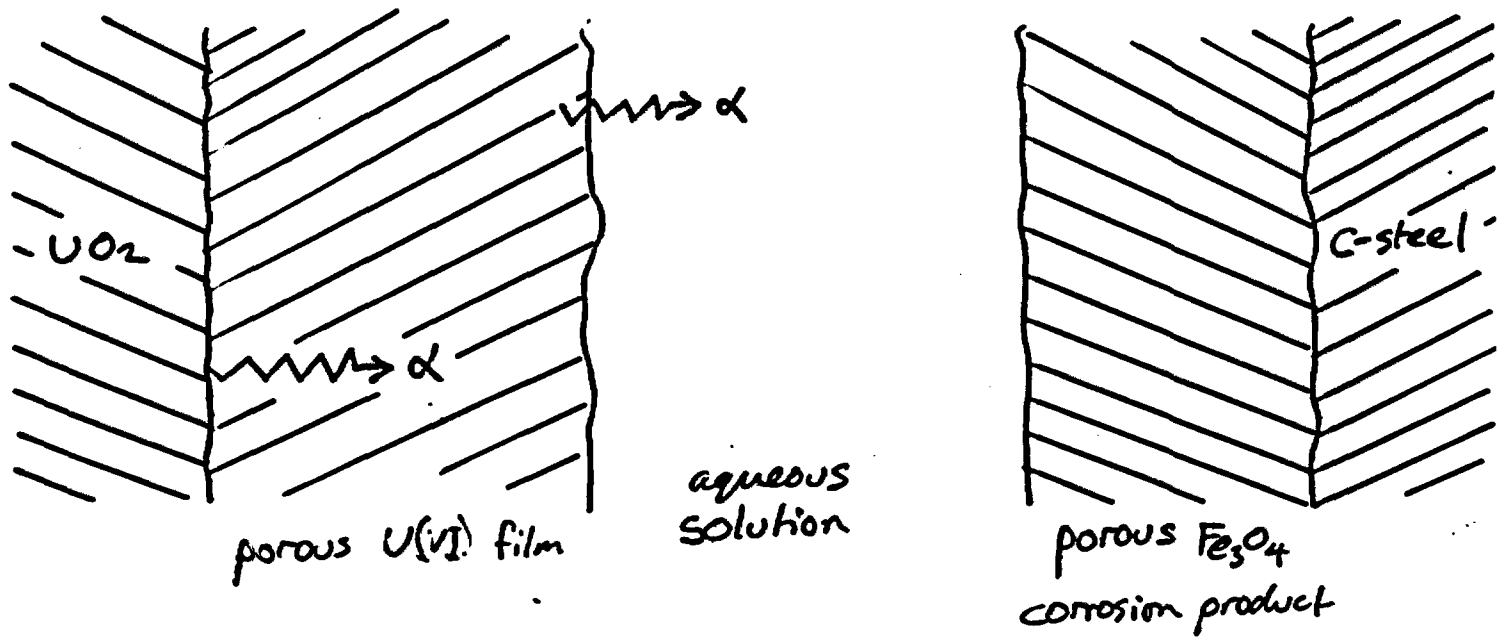
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1998 Spent Fuel Workshop, Las Vegas, 18-20 May 1998.

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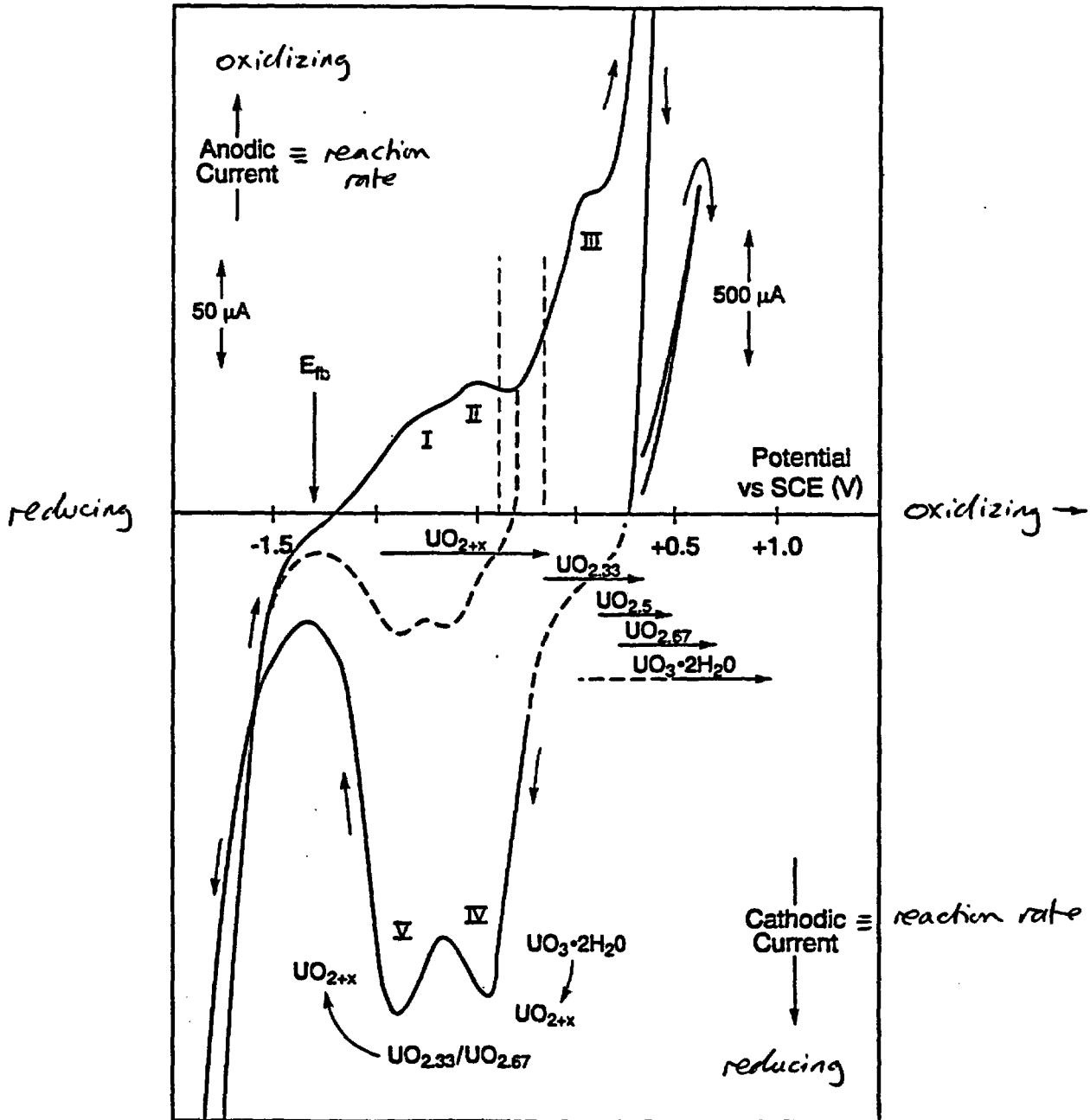
What are we trying to model?



- Summary of existing data on UO_2 electrochemistry
- Outline of mixed-potential model (MPM)
 - reaction scheme
 - reaction-diffusion equations
 - model geometry
 - boundary conditions
 - assumptions
- "Model predictions"
 - validation/verification of MPM
 - effects of α -radiolysis, precipitation and redox processes

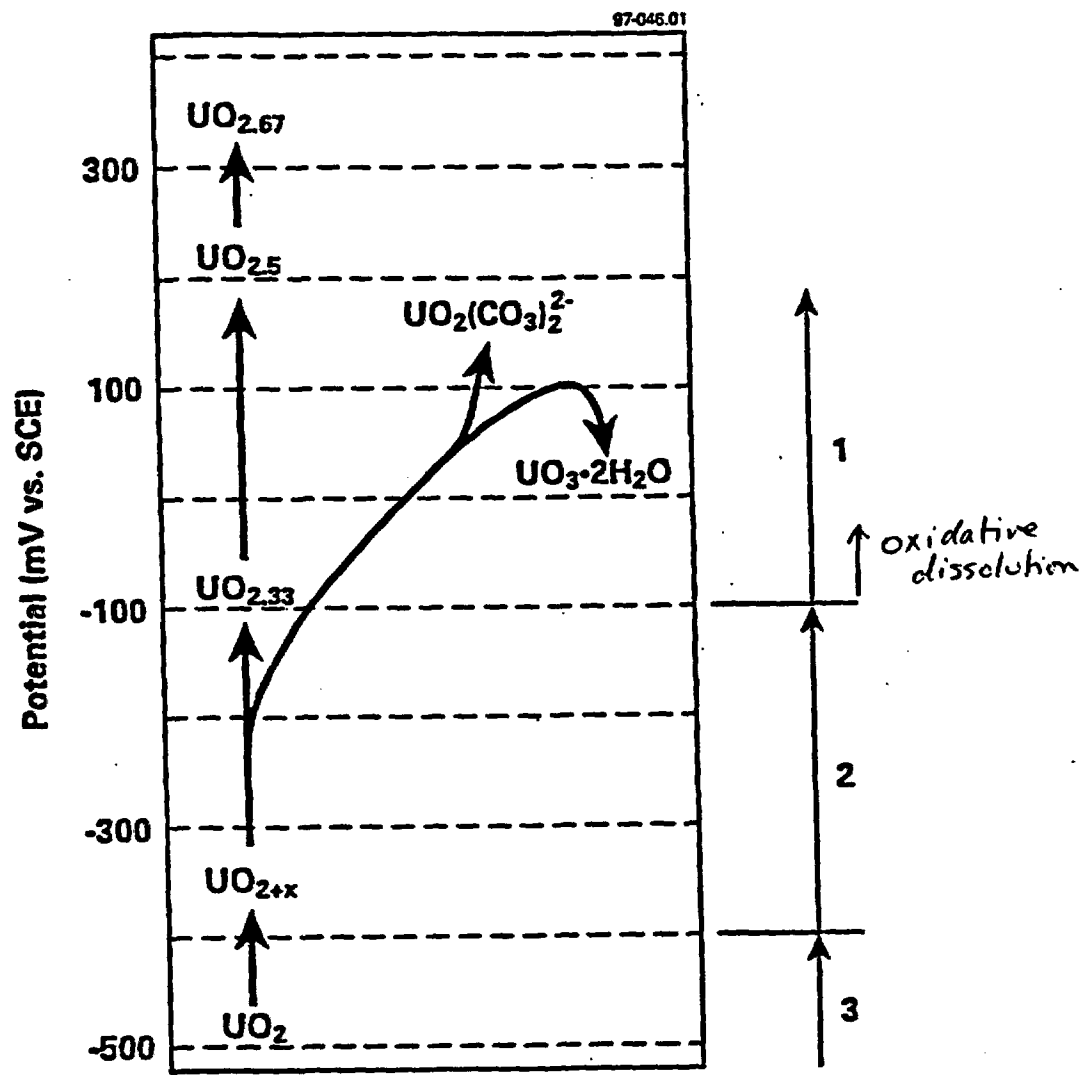
Summary of UO_{2+x} Electrochemistry (1)

- Behaves like a p-type semiconductor
- Rates of reaction dependent on potential (E)



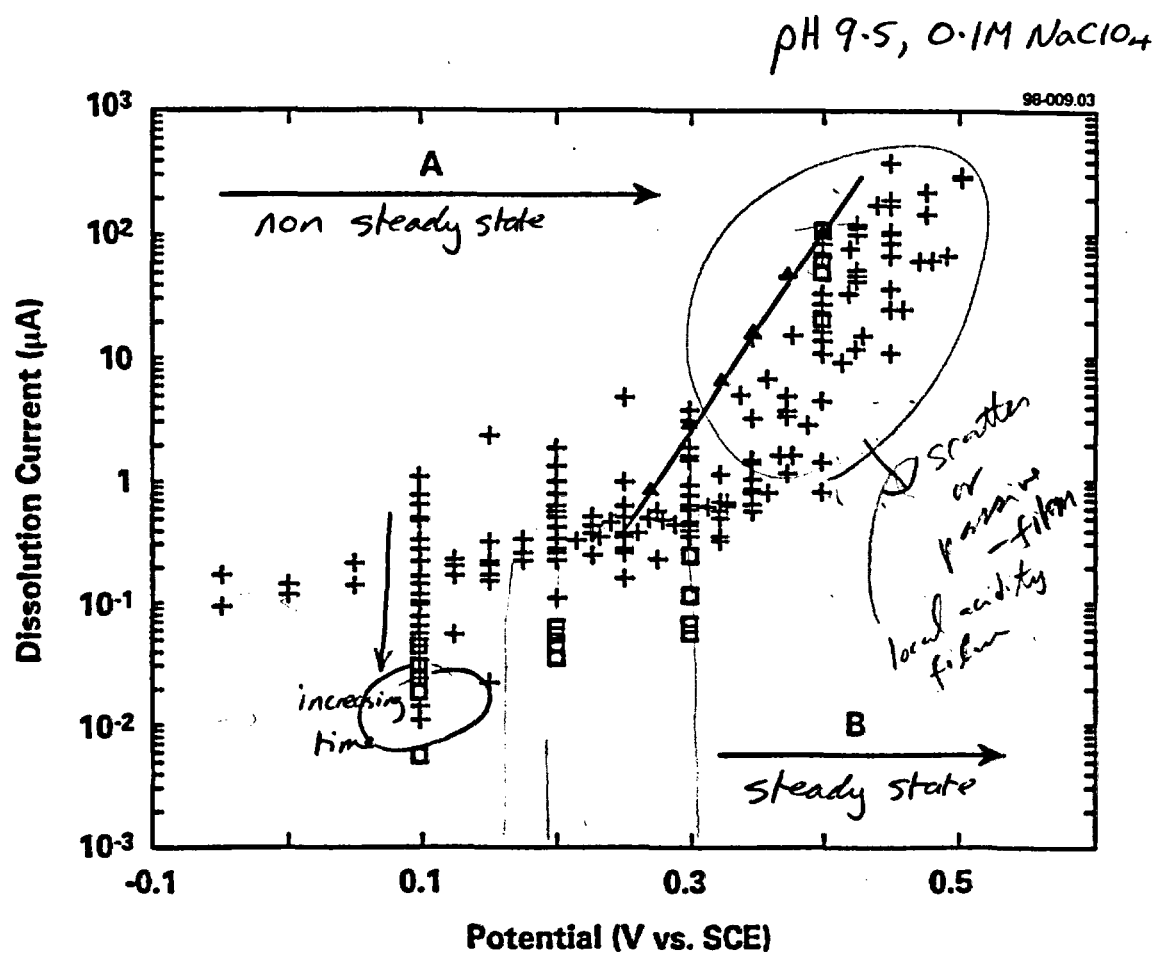
Summary of UO_{2+x} Electrochemistry (2)

- The degree of oxidation of the surface is E dependent
- Above a certain E, dissolution becomes oxidative in nature (i.e., the anodic dissolution to U(VI) is electrochemically coupled to the cathodic reduction of a suitable oxidant).



Summary of UO_{2+x} Electrochemistry (3)

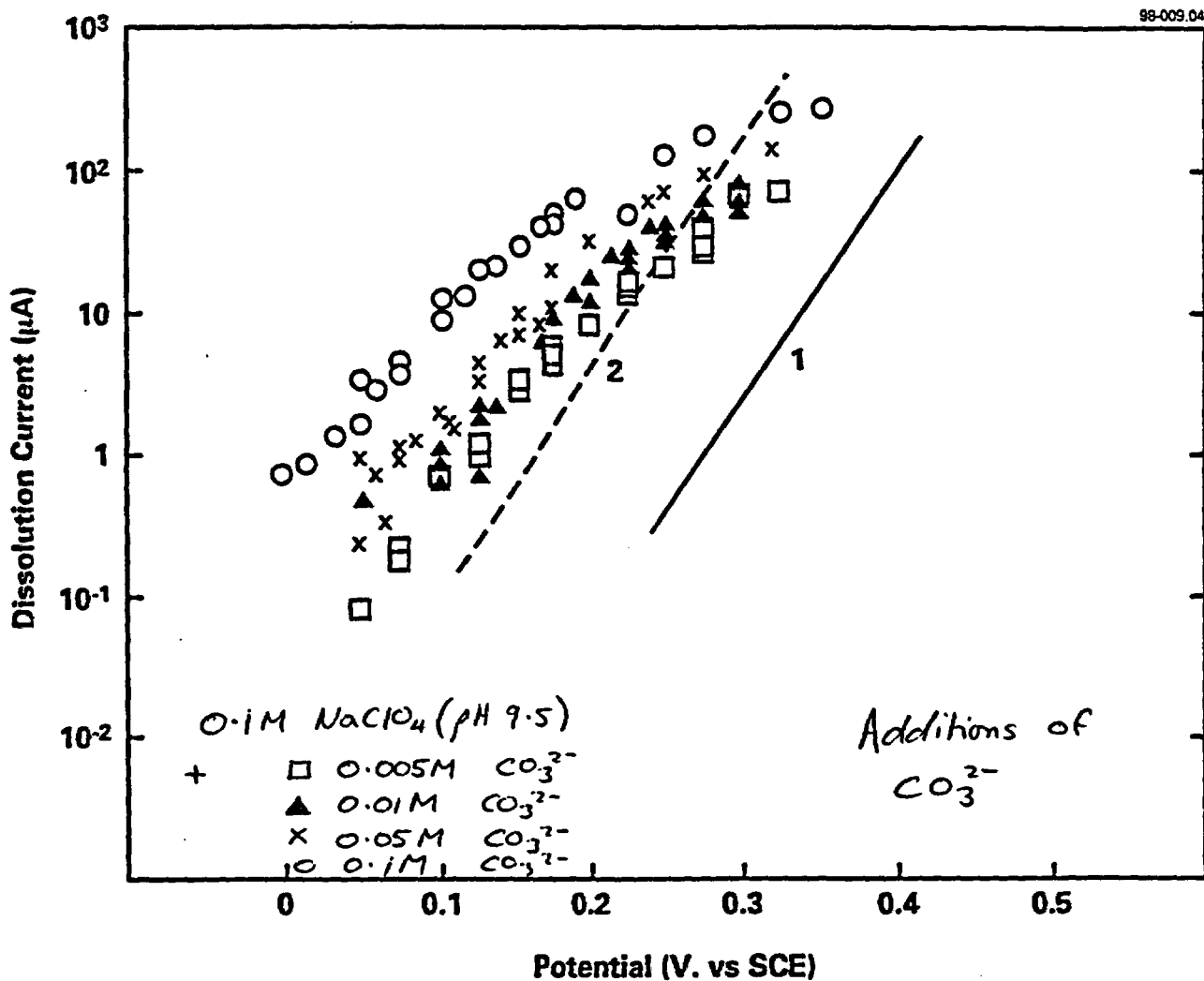
- In non-complexing environments, corrosion product films build up on the UO_2 surface, leading to a decrease in the dissolution rate.



\downarrow
-300
reducing

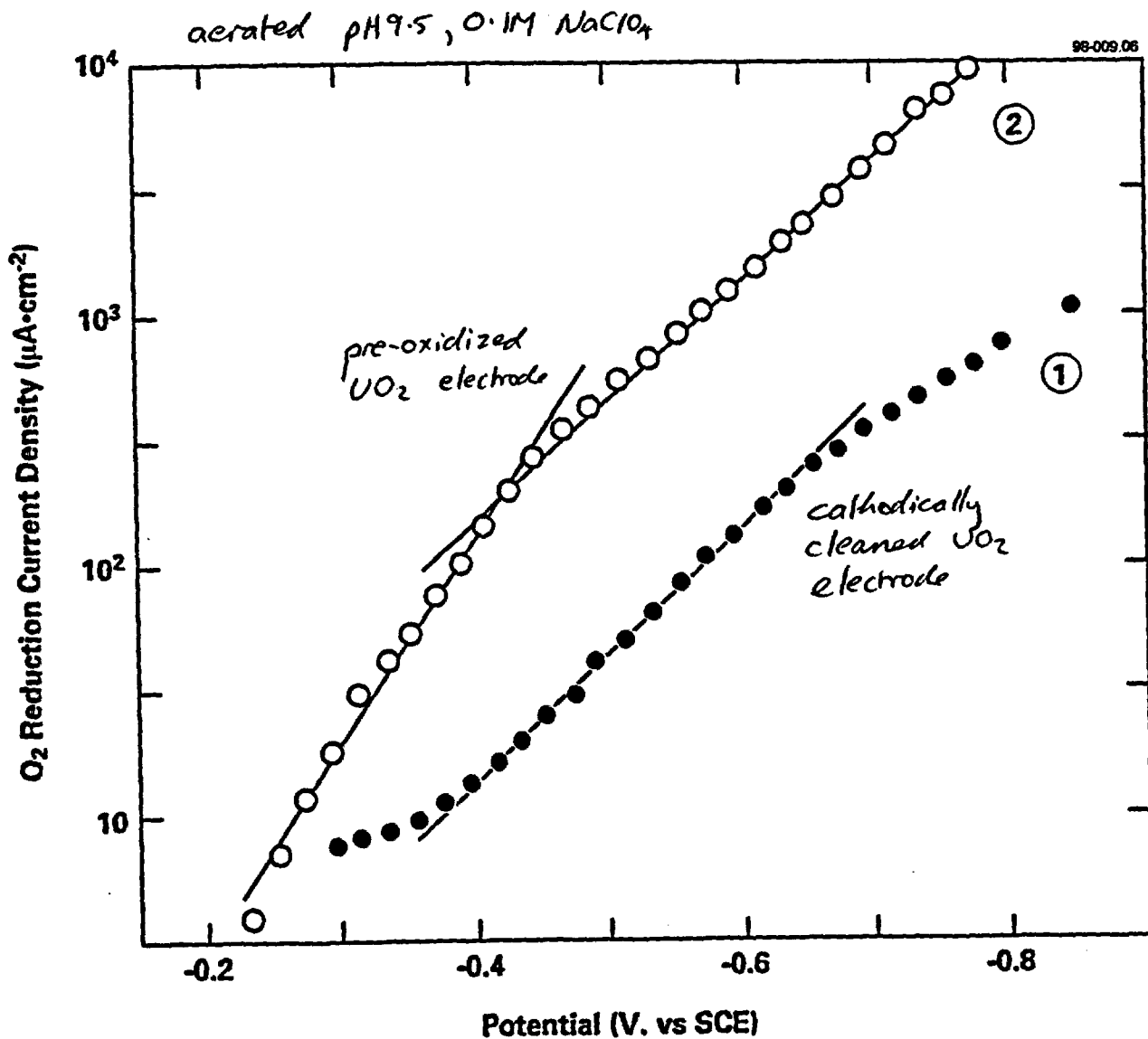
Summary of UO_{2+x} Electrochemistry (4)

- The addition of complexants for U(VI) increases the rate of dissolution.



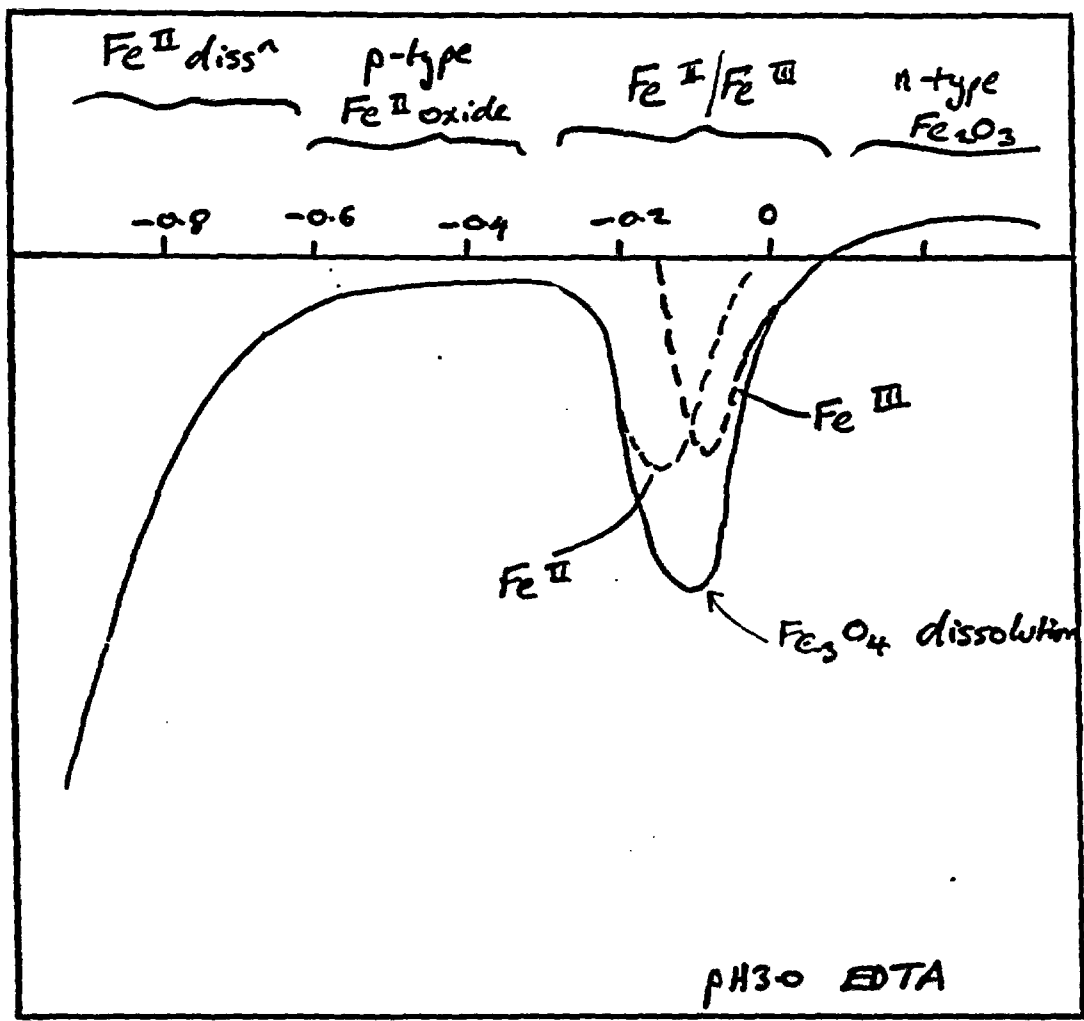
Summary of UO_{2+x} Electrochemistry (5)

- The cathodic reduction of O_2 on UO_2 has been extensively studied.
- Less is known about the cathodic reduction of H_2O_2 , or the surface-mediated decomposition of H_2O_2 .



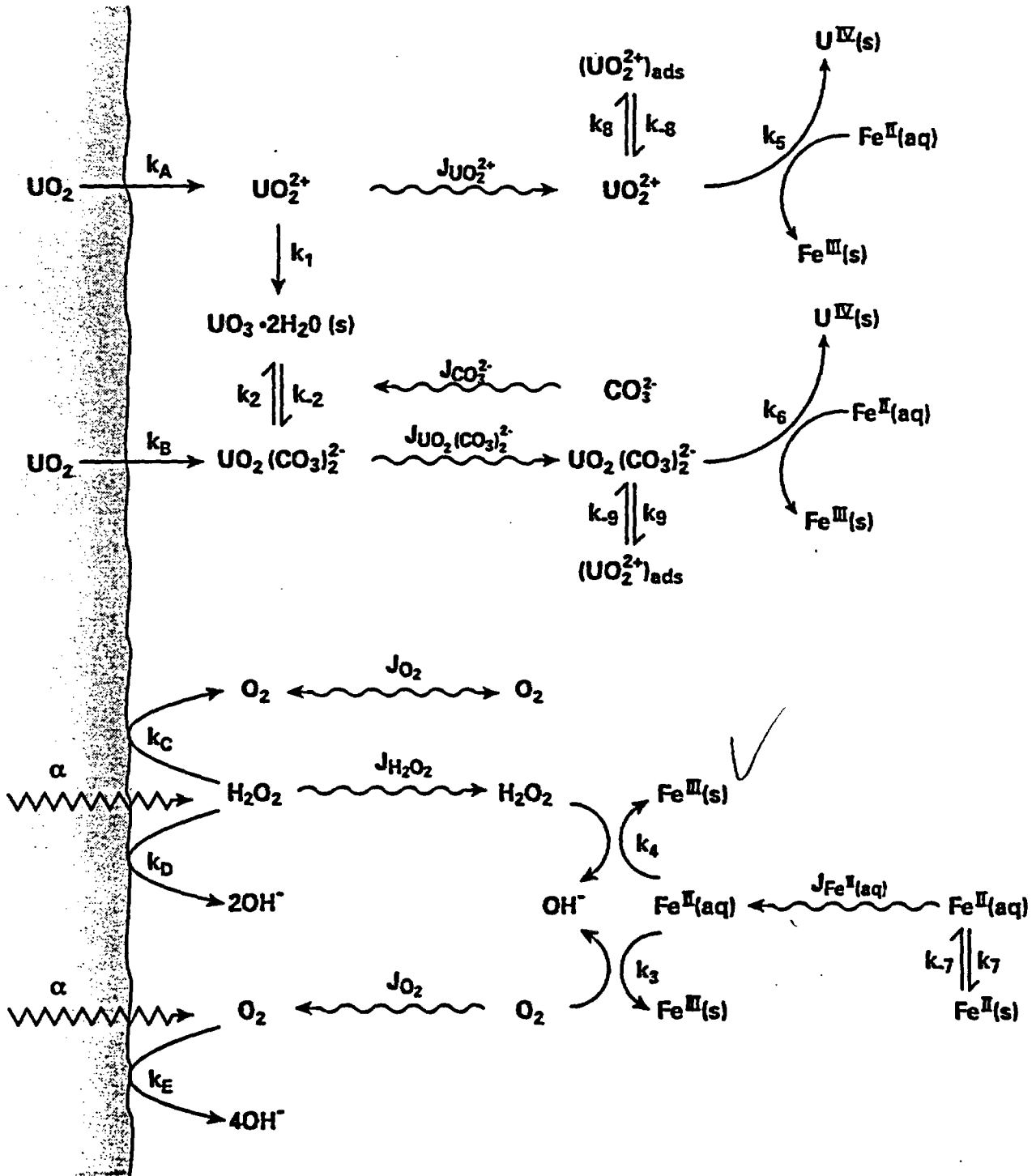
Summary of Electrochemical Data (6)

Potential-Dependent Dissolution Rate of Fe_3O_4



Outline of UO_2 Mixed-Potential Model (1)

The Reaction Scheme



Outline of UO₂ Mixed-Potential Model (2)

The Reaction-Diffusion Equations

The various mass-transport and chemical processes involving the ten species (UO₂²⁺, UO₂(CO₃)₂²⁻, UO₃ · 2H₂O(s), CO₃²⁻, O₂, H₂O₂, Fe(II)_{AQ}, Fe(II)_{PPT}, U(IV)_{PPT} and UO₂²⁺ (ads)) are described by reaction-diffusion equations of the general form

$$\varepsilon \frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(\tau \varepsilon D_i \frac{\partial c_i}{\partial x} \right) + \varepsilon \sum_{j=1}^9 R_j \quad \text{for } c = 1, \dots, 10$$

e.g., for O₂ (species #7)

$$\varepsilon \frac{\partial c_7}{\partial t} = \frac{\partial}{\partial x} \left(\tau \varepsilon D_7 \frac{\partial c_7}{\partial x} \right) + G_7 R(x, t) - \varepsilon k_3 c_7 c_9$$

and for UO₃ · 2H₂O(s) (species #3)

$$\varepsilon \frac{\partial c_3}{\partial t} = \varepsilon k_1 \max(0, (c_1 - c_1^{\text{sat}})) + \varepsilon k_2 \max(0, (c_2 - c_2^{\text{sat}})) - \varepsilon k_{-2} c_3 c_6^p$$

Since D_i and k_j are temperature dependent, we also solve a heat-conduction equation

$$\rho C \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(K \frac{\partial T}{\partial x} \right)$$

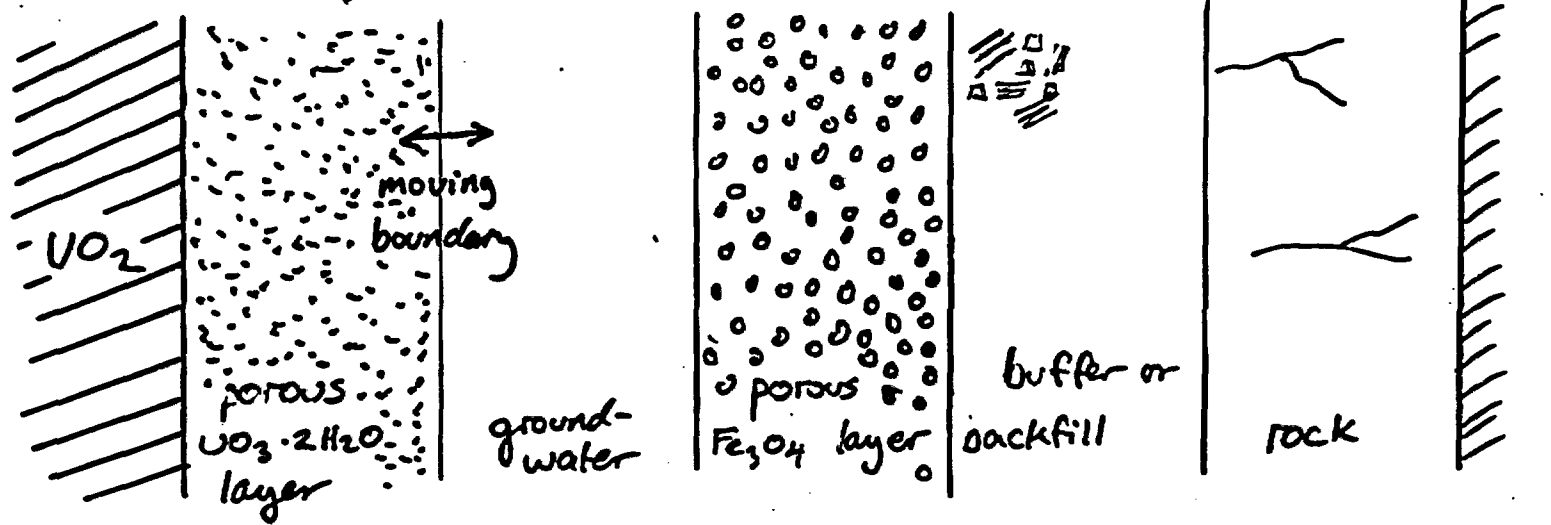
to predict $T(x, t)$ and, hence, $D_i(x, t)$ and $k_j(x, t)$ (depending upon model geometry, may assume $T(t)$ only).

Outline of UO_2 MPM (3)

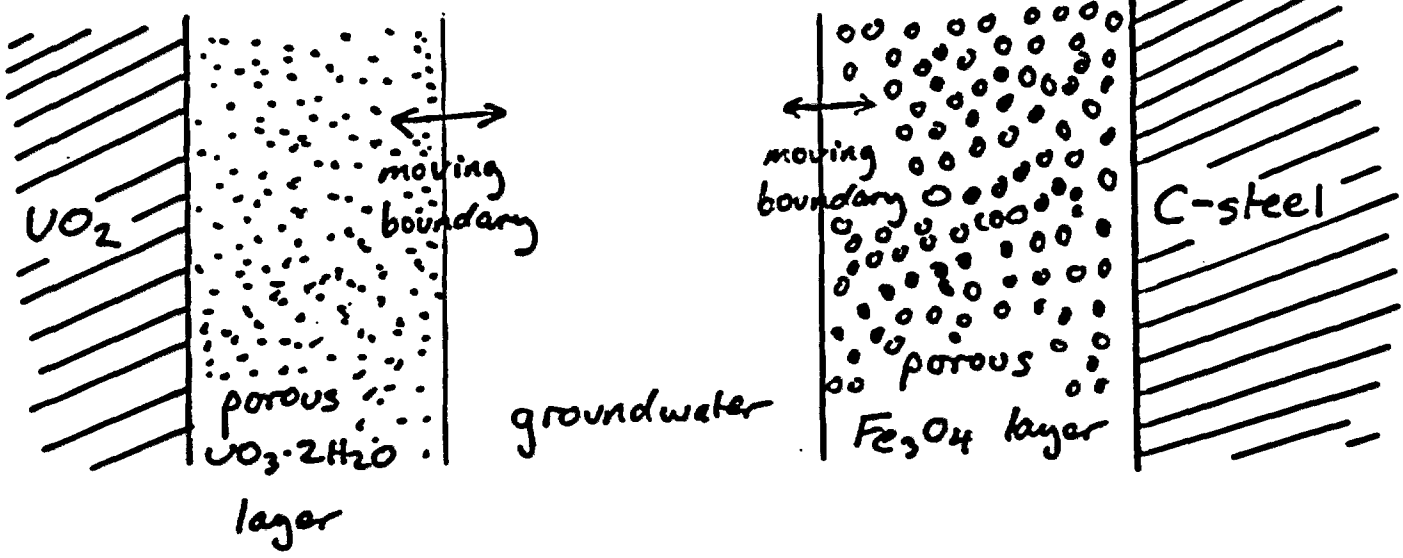
The Spatial Grid

- one-dimensional representation of the container and vault geometries
- two possible model geometries are:

(1) The "open" system:



(2) The "closed" system:

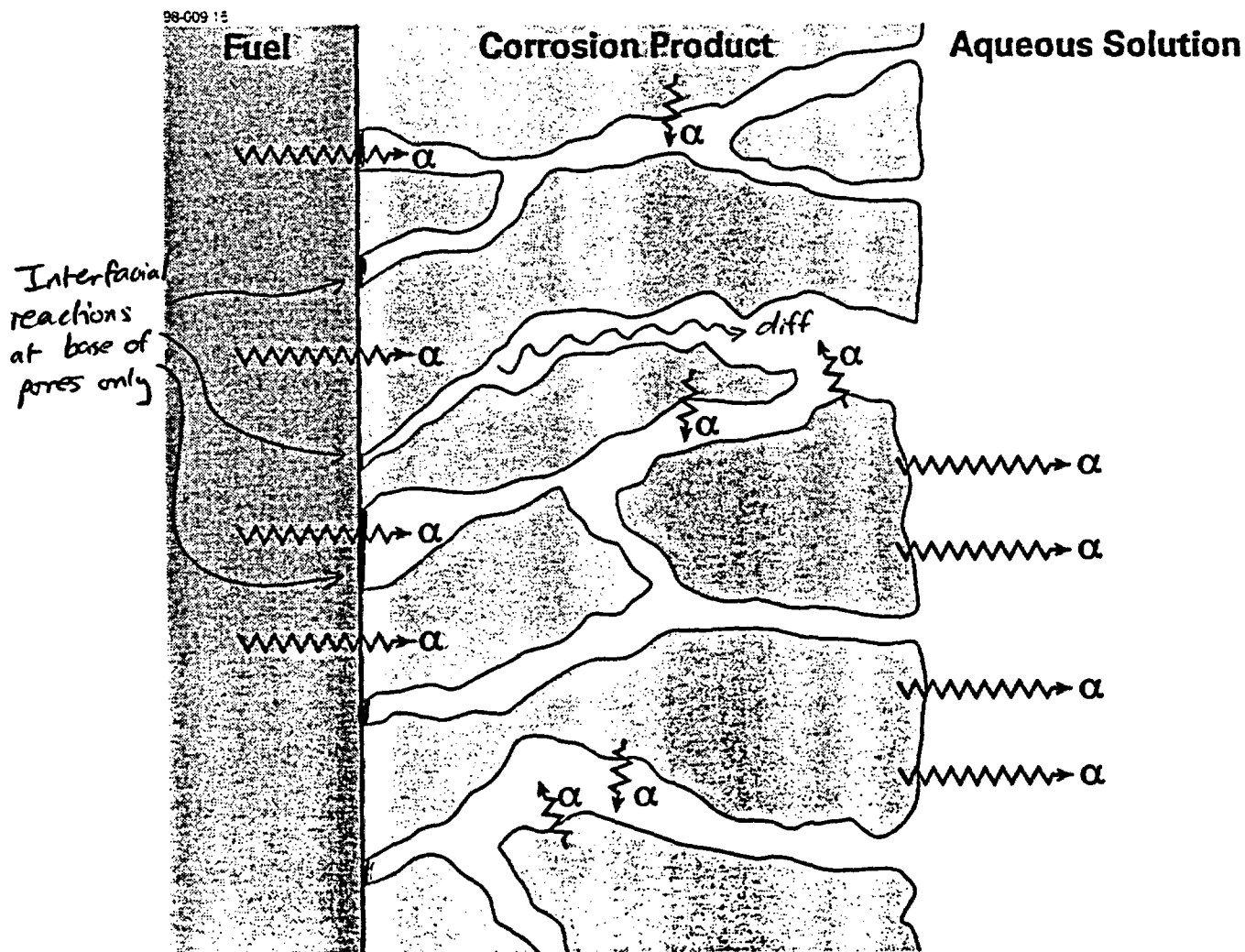


Outline of UO_2 MPM (4)

A Closer Look at the Porous U(VI) Layer

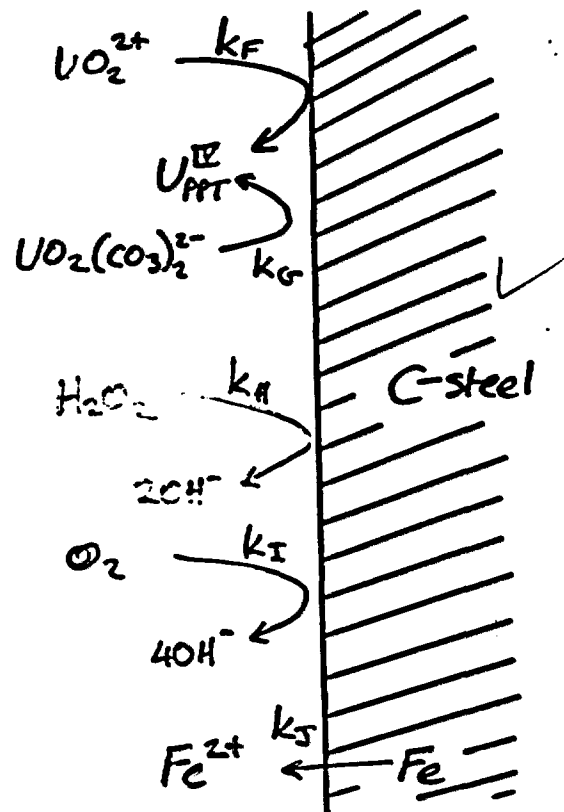
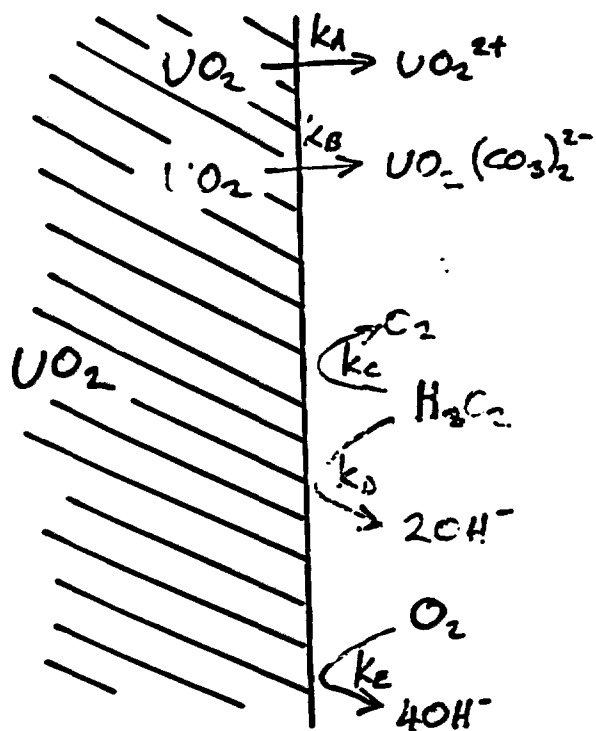
The U(VI) precipitate layer has several effects:

- blocks the surface electrochemical reactions
- inhibits mass transport to and from the UO_2 surface
- affects the yield and location of radiolysis products



Outline of UO₂ MPM (5)

Boundary Conditions



$$I_A + I_B + I_C = -(I_D + I_E)$$

$$I = \pm nF\tau\epsilon D \frac{\partial c(0,t)}{\partial x}$$

$$I = \pm nF\epsilon Ak c(0,t) \exp\left(\pm \frac{\alpha F}{RT} (E - E^0)\right)$$

Derived parameters:

$$I_{CORR} = I_A + I_B$$

$$E_{CORR} = E_A^0 + \frac{RT}{\alpha_A F} \ln \left\{ \frac{I_{CORR}}{2F\epsilon Ak_A} \right\}$$

$$I_J = -(I_F + I_G + I_H + I_J)$$

$$I = \pm nF\tau\epsilon' D \frac{\partial c(x_{right}, t)}{\partial x}$$

$$I = \pm nF\epsilon' Ak c(x_{right}, t) \exp\left(\pm \frac{\alpha F}{RT} (E - E^0)\right)$$

Derived parameters:

$$I_{CORR} = I_J$$

$$E_{CORR} = E_J^0 + \frac{RT}{\alpha_J F} \ln \left\{ \frac{I_{CORR}}{2F\epsilon' Ak_J} \right\}$$

Outline of UO₂ MPM (6)

① Pablo
② Granbrow
③ Serano
④ Making experiments (no effects) Fe? magnetite powder
⑤ remaining short-term
⑥ 14

Assumptions

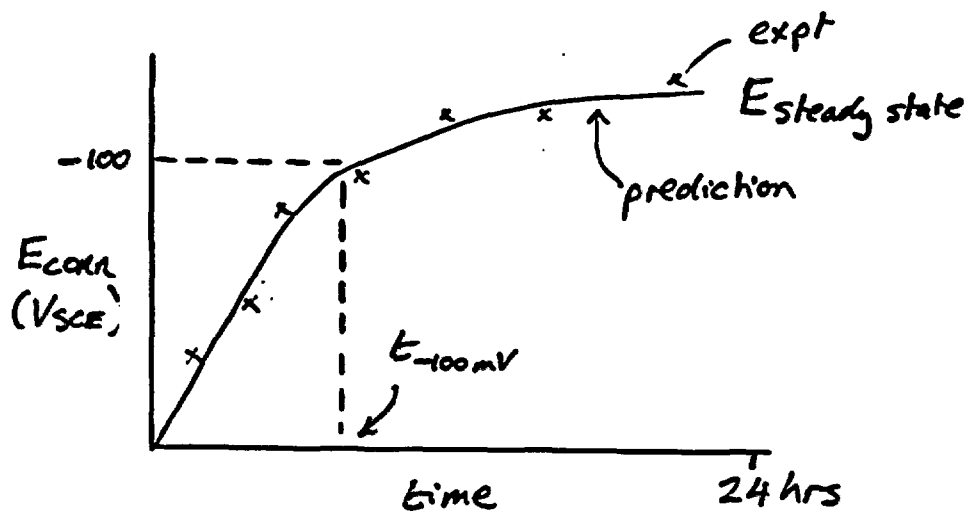
- the reaction scheme and 1-D model geometry adequately describe the oxidative dissolution of UO₂
- uniform dissolution of the fuel surface (no localized effects, such as gb etching)
- mass transport by diffusion only
- system is completely saturated and the supply of H₂O is not limiting
- no effect of Zircaloy fuel cladding
- effects of α -radiolysis can be simulated by O₂ and H₂O₂ only
- U(VI) and Fe₃O₄ films can be treated as equivalent porous media with spatially and temporally constant porosity and tortuosity
- U(VI) film is assumed to be electrically insulating with electrochemical reactions restricted to base of pores
- U(VI) film attenuates α -dose rate at the fuel surface and contains co-precipitated α -emitters
- film growth occurs at the film/solution interface with no precipitation within the pores
- Fe₃O₄ is the stable C-steel corrosion product
- constant pH throughout the system (pH 7)
- various assumptions involved in derivation of input data

UO₂ so
↓
observed difference
↓
rapid decrease
U⁶⁺ → U⁴⁺
decrease (Fe)
1.0 x 10⁻⁹ / d
granite
+ granite + bentonite
not effects in carbonate
model + Fe II
Yucca Mountain
(Fe(II) surface iron III no source

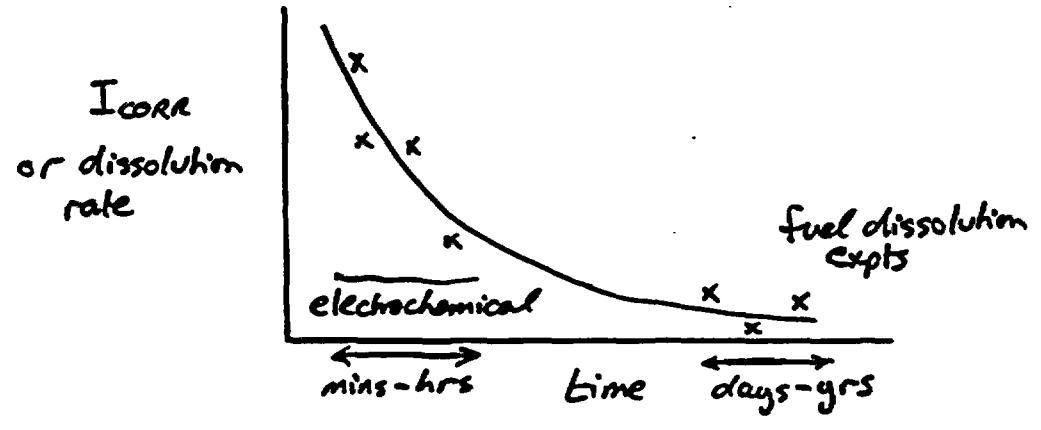
"Model Predictions" (1)

Validation/Verification of the Model

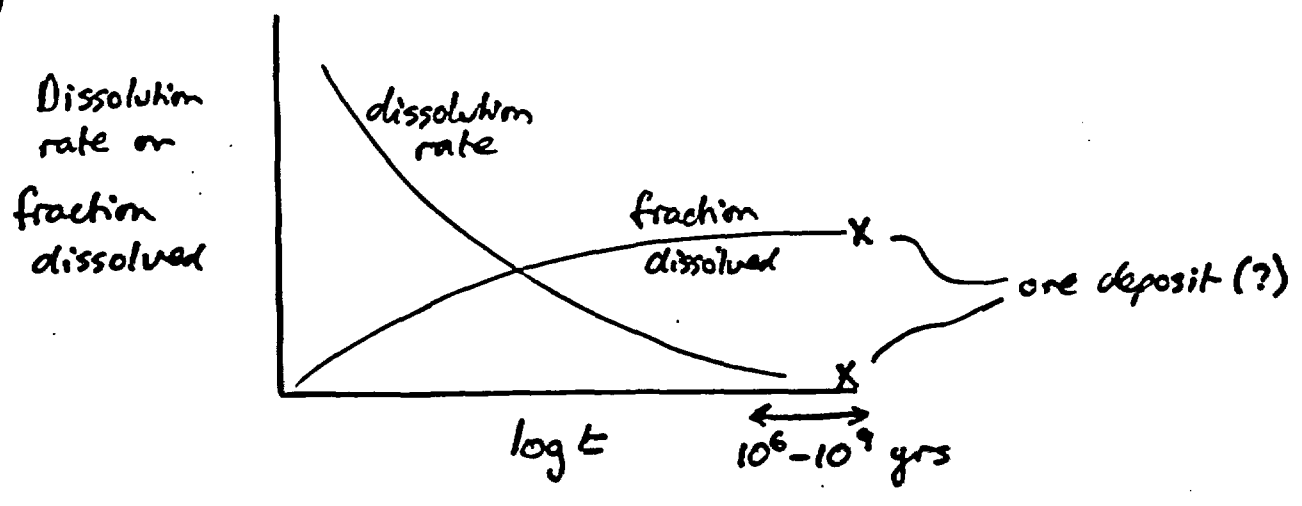
(a)



(b)



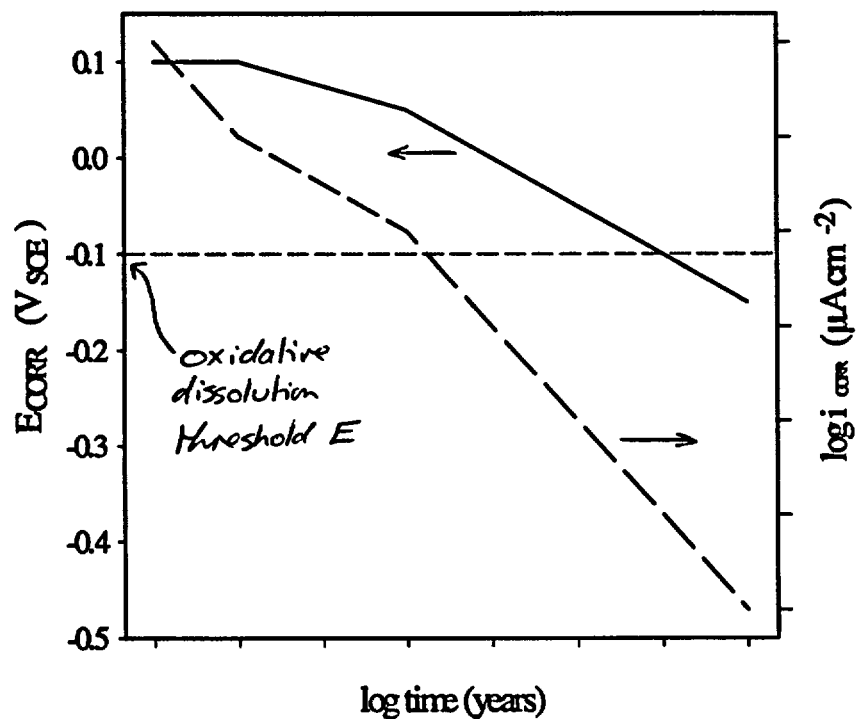
(c)



"Model Predictions" (2)

The most basic prediction is of I_{CORR} and E_{CORR} of the UO_2 surface

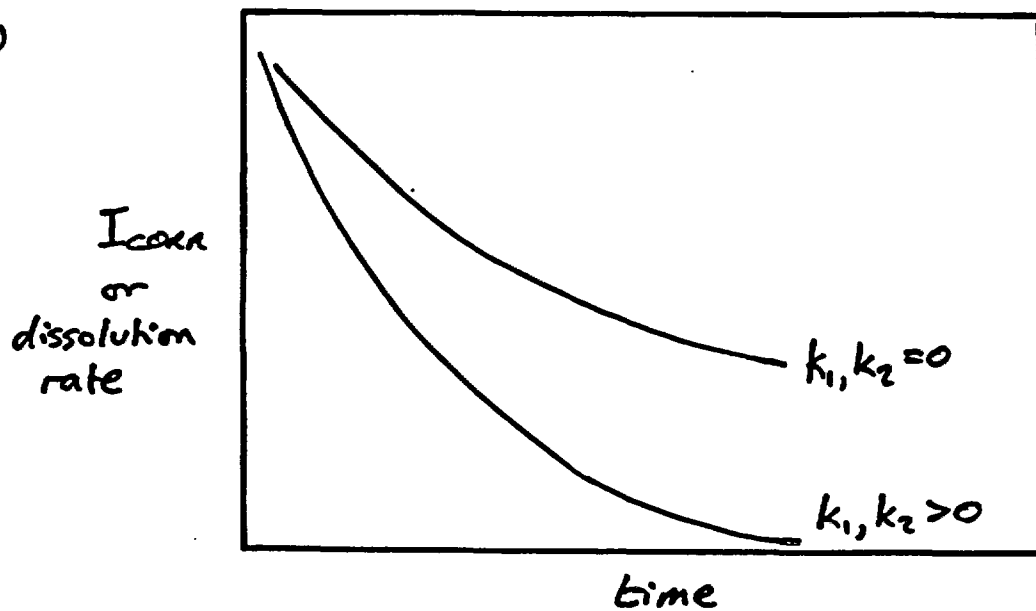
- I_{CORR} is equivalent to the dissolution rate
- E_{CORR} indicates the period of oxidative dissolution



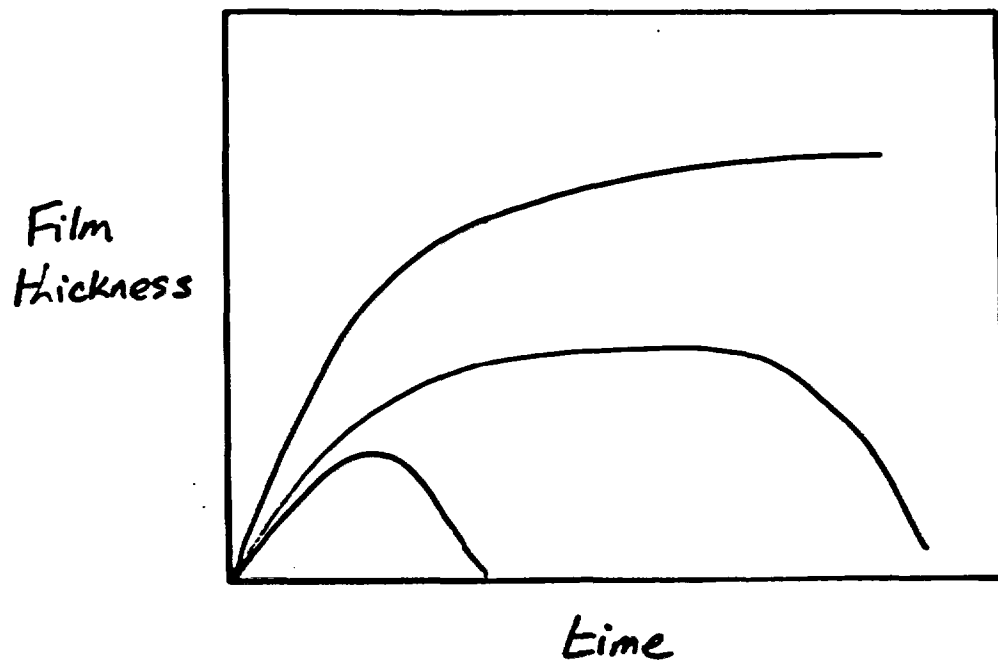
"Model Predictions" (3)

- To what extent does film growth inhibit UO_2 dissolution?

(a)



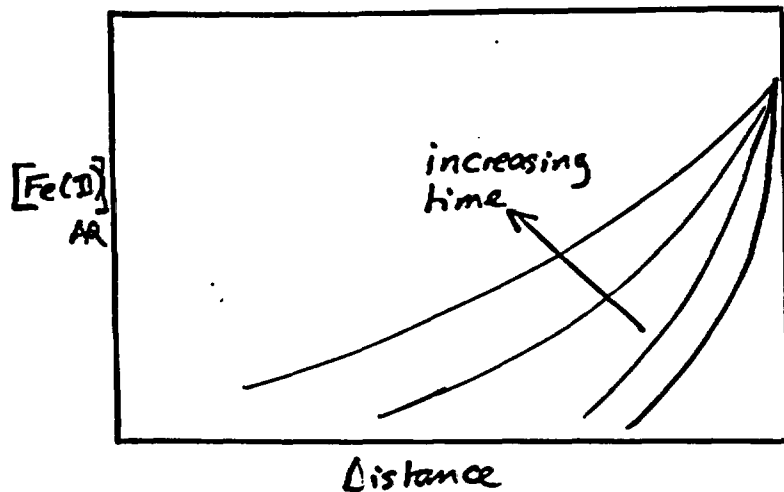
(b)



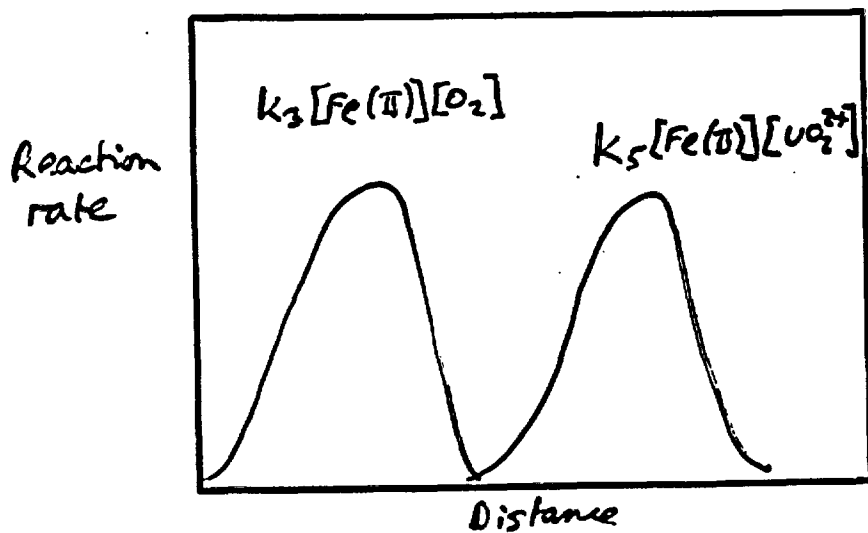
"Model Predictions" (4)

- The ability of the C-steel to act as a redox barrier

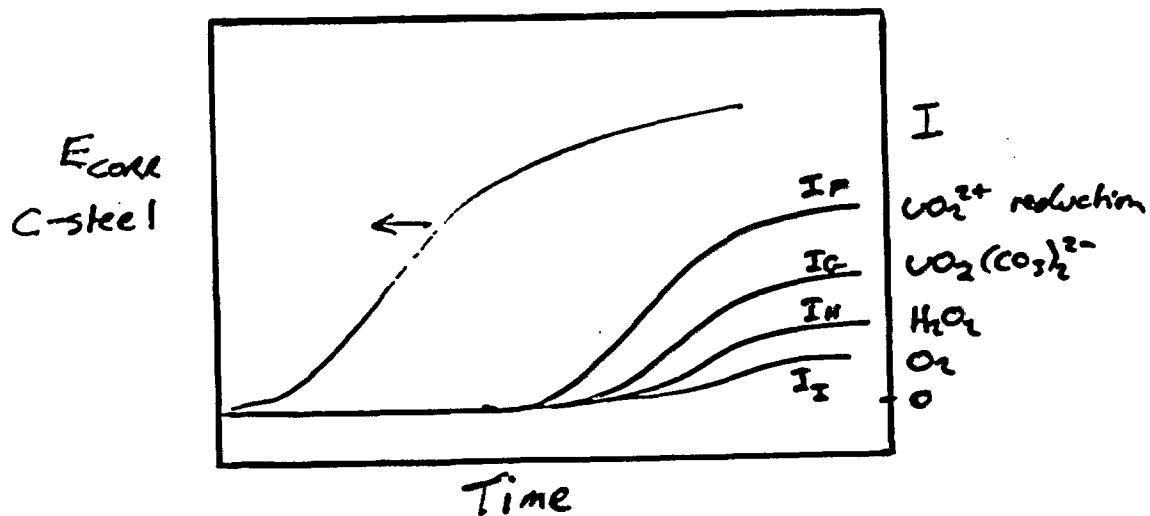
(a)



(b)

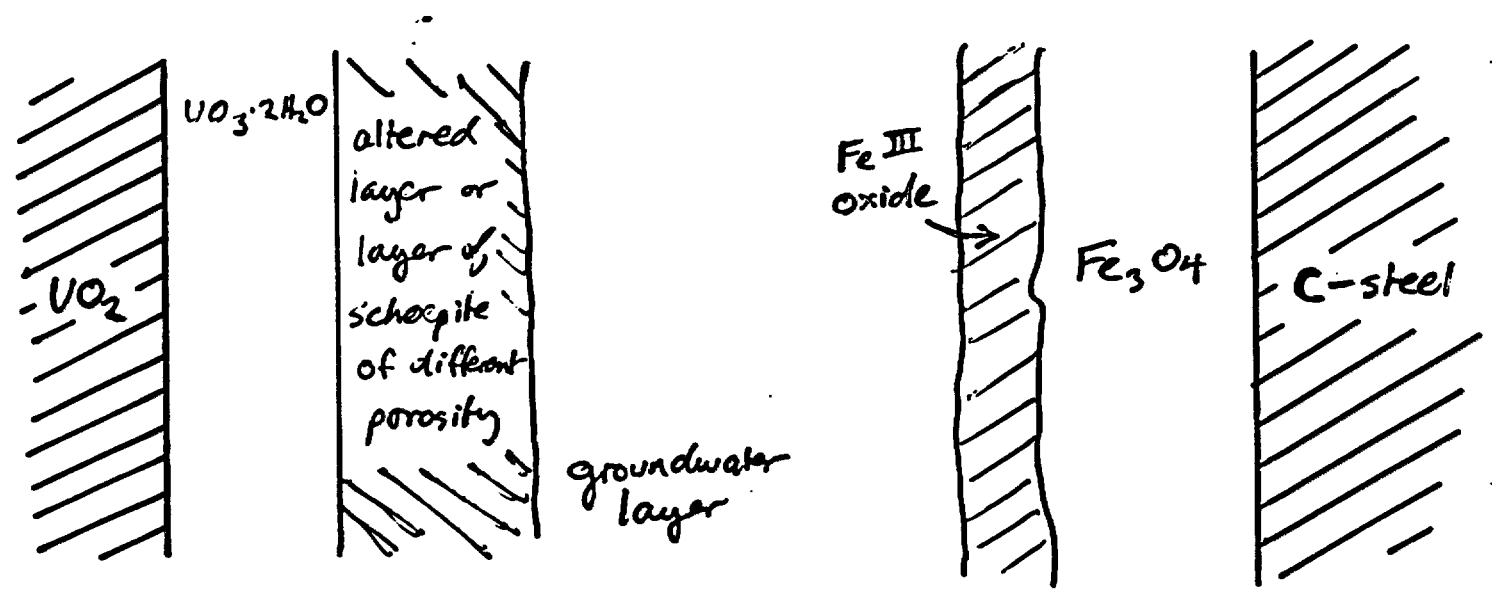


(c)

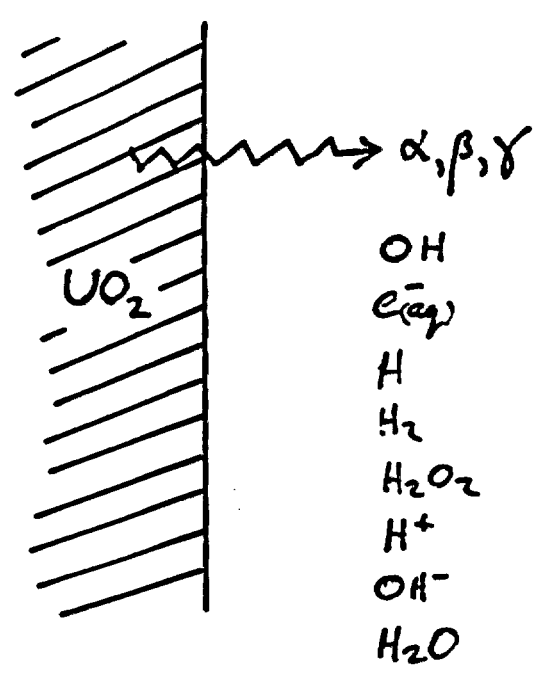


Future Developments (1)

(1) Inclusion of multiple growing layers

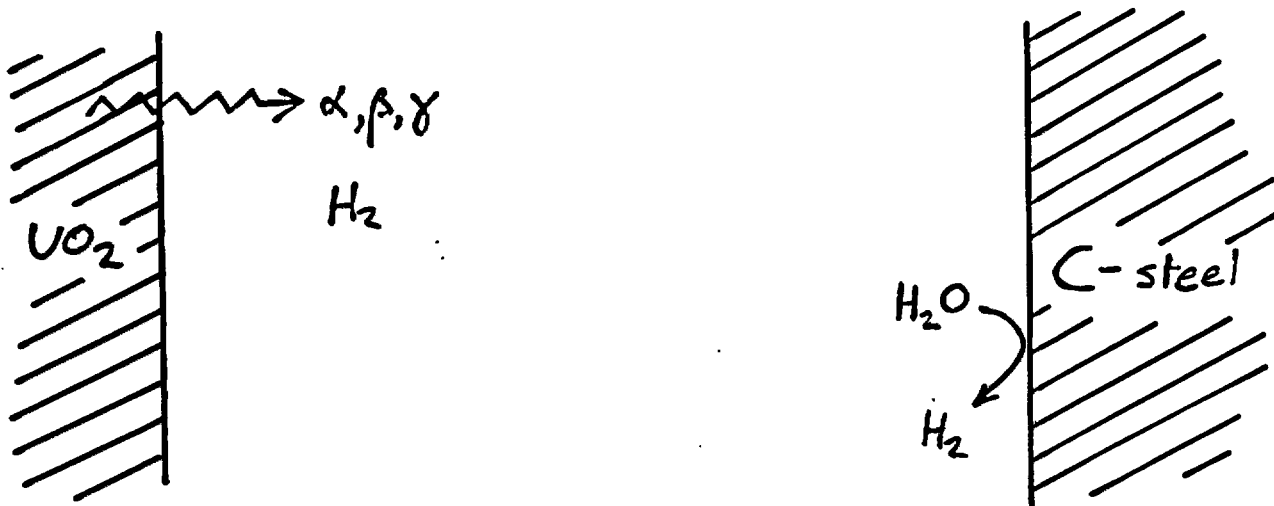


(2) More detailed radiolysis modelling

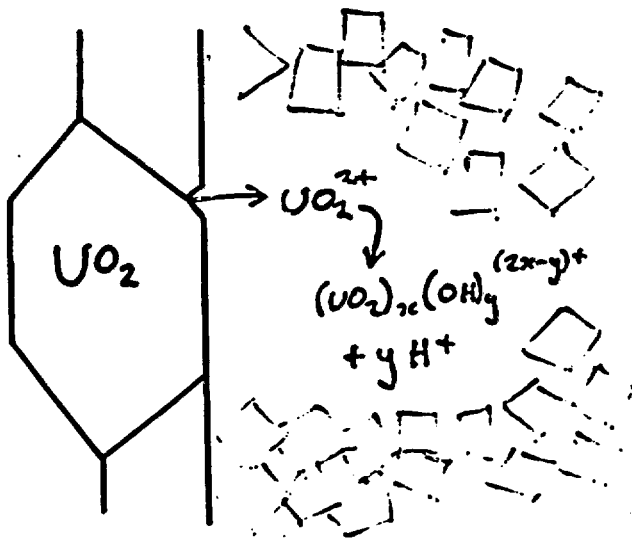


Future Developments (2)

(3) Inclusion of H_2 produced by radiolysis and corrosion



(4) Prediction of localized acidification and chemistry within deposits



requires a radically different model

(5) Improvements to treatment of Fe_3O_4/Fe interface

Conclusions

- An electrochemically based model has been developed for predicting the effects of α -radiolysis, precipitation and redox reactions on the dissolution behaviour of used fuel.
- The reaction-diffusion of ten chemical species is included in the model (UO_2^{2+} , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$, CO_3^{2-} , O_2 , H_2O_2 , $\text{Fe}(\text{II})_{\text{AQ}}$, $\text{Fe}(\text{II})_{\text{PPT}}$, $\text{U}(\text{IV})_{\text{PPT}}$ and $\text{UO}_2^{2+}(\text{ads})$).
- The container/vault system is described by a 1-D system of porous mass-transport barriers representing corrosion product films, the container and buffer and backfill materials.
- The use of electrochemical boundary conditions permits the prediction of the corrosion potential (E_{CORR}) and dissolution rate (I_{CORR}) of both the UO_2 and C-steel surfaces.
- As yet, no predictions have been made!