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Gaining insight into corrosion rate and secondary mineral paragenesis from numerical simulations of integrated iron-claystone experiments

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DE LA RECHERCHE À L'INDUSTRIE



GAINING INSIGHT INTO CORROSION PROCESSES AND SECONDARY MINERAL PARAGENESIS FROM NUMERICAL SIMULATIONS OF INTEGRATED IRON- CLAYSTONE EXPERIMENTS

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Andra (French Radioactive Waste Management Agency)



www.cea.fr

Clays In Natural And Engineered Barriers For Radioactive Waste Confinement -
march 23-25, 2015

- description of the « ArCorr » integrated experiment
- observations to be matched by the modeling
- numerical model implementation and parameters
- first results :
 - base case
 - sensitivity to kinetics parameters
 - sensitivity to transport parameters
- conclusions and perspectives

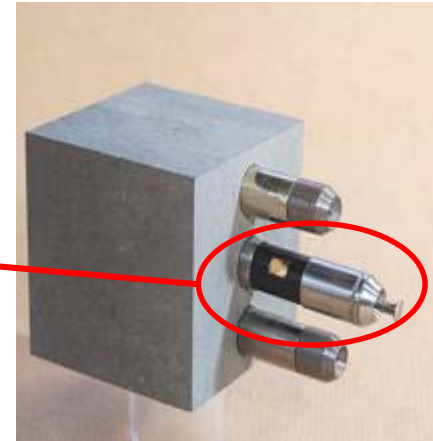
THE « ARCORR » EXPERIENCE

Experimental conditions

Isothermal 90°C
Pressure 40 bars

2 interfaces :

- iron/argilites
- glass/argilites

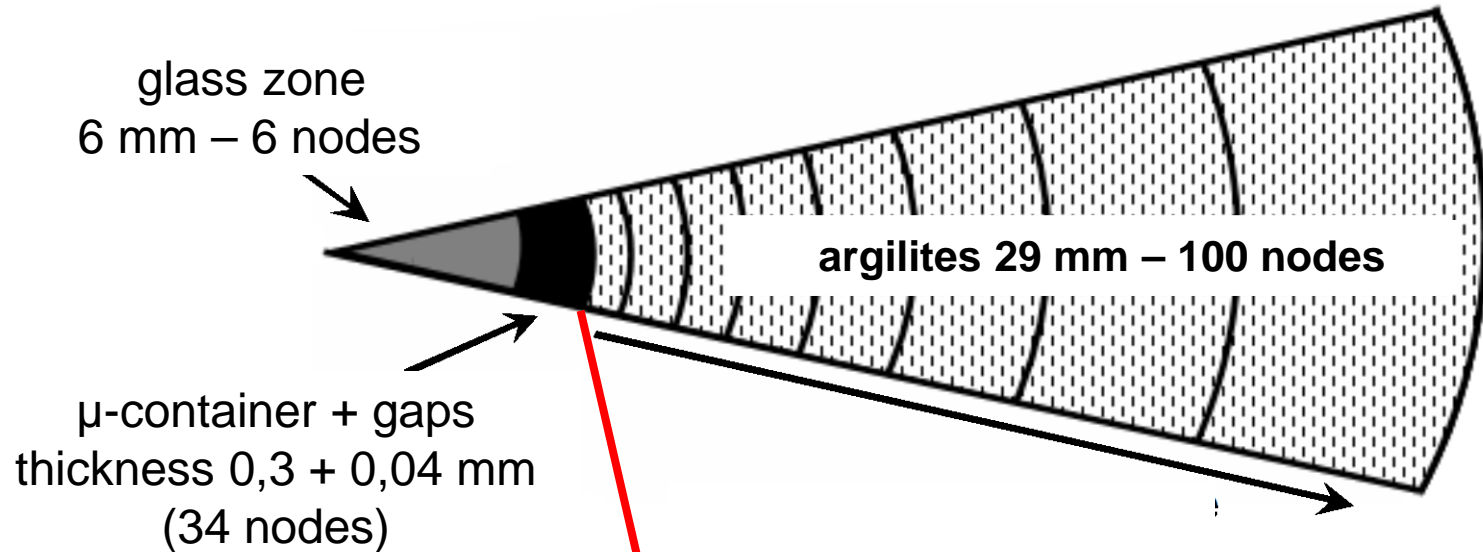


Modeling options

- only the iron/argilites interface is treated in this presentation
- « ThermoChimie V8 » thermodynamic database
- kinetic parameters and diffusion coefficients at 90°C
- dissolution kinetics parameters from Palandri & Kharaka (1984)
- precipitation kinetics = $k_{\text{diss}}/100$
- use BET specific surface areas

SIMULATION GEOMETRY AND PARAMETERS

- Geometry



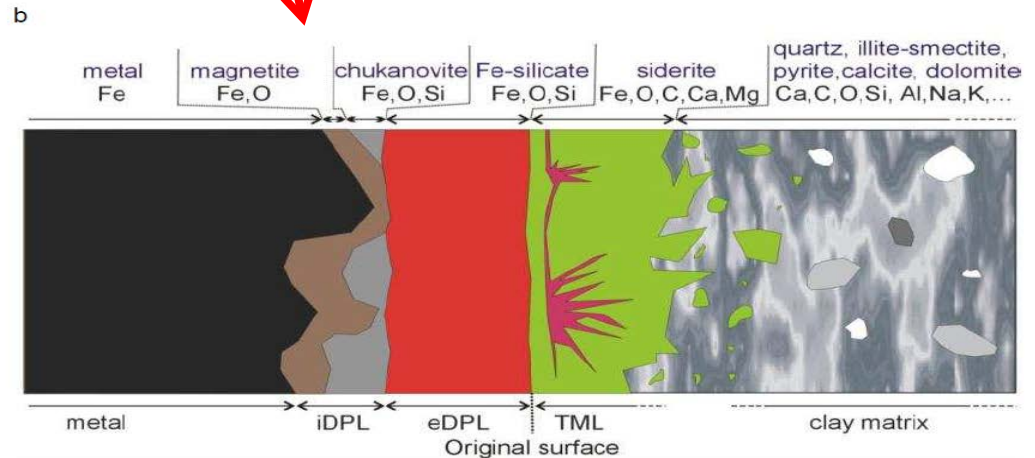
- base case parameters

- Iron zone

- porosity = 0.15
- $D_{\text{eff}} = 2,61 \cdot 10^{-11} \text{ m}^2/\text{s}$

- Argilites (38 mm)

- porosity = 0.18 ;
- $D_{\text{eff}} = 8 \cdot 10^{-11} \text{ m}^2/\text{s}$



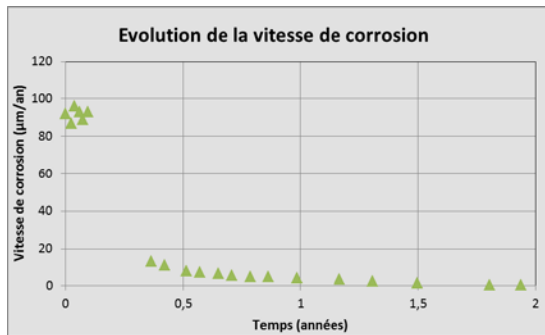
REACTIVITY OF THE DIFFERENT MATERIALS

Argilites

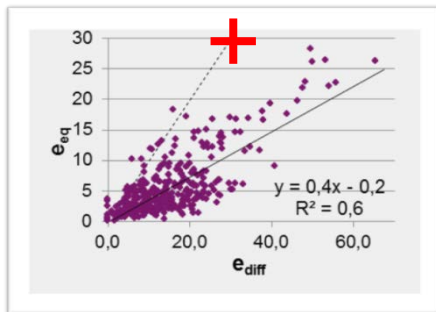
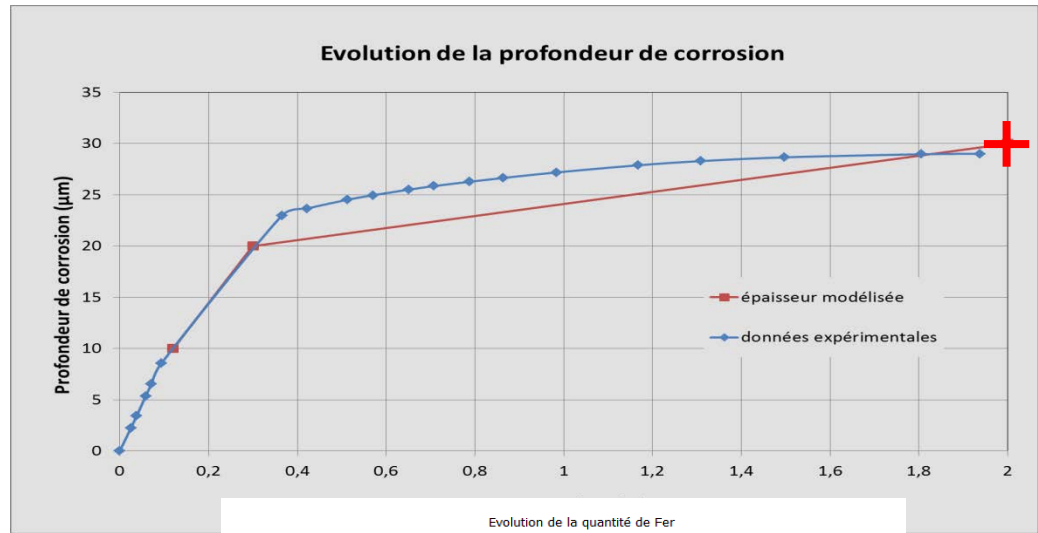
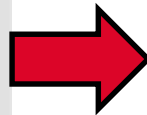
- no ion-exchange or surface complexation reactions

Iron

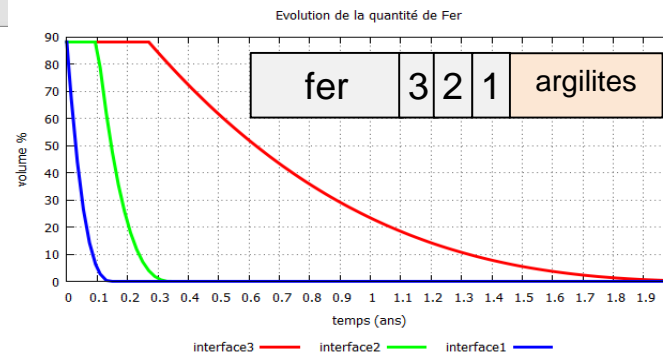
- time-dependent corrosion rate (matching experimentally measured rate)



(data from Schlegel et al. 2014)

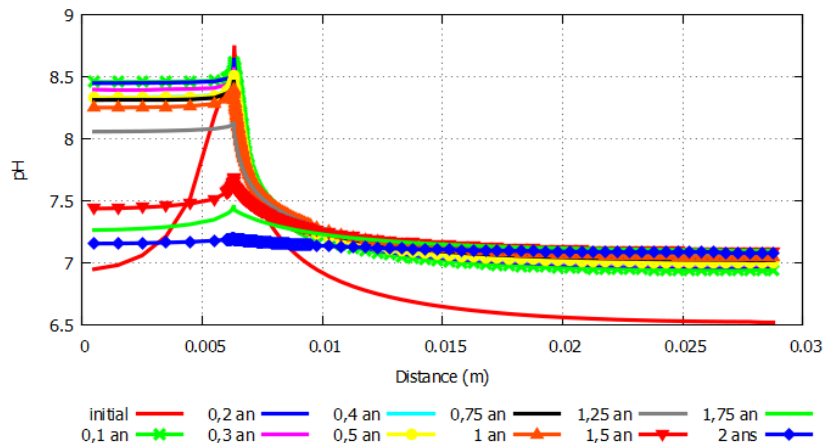


(data from Brucker and Schlegel, 2012)

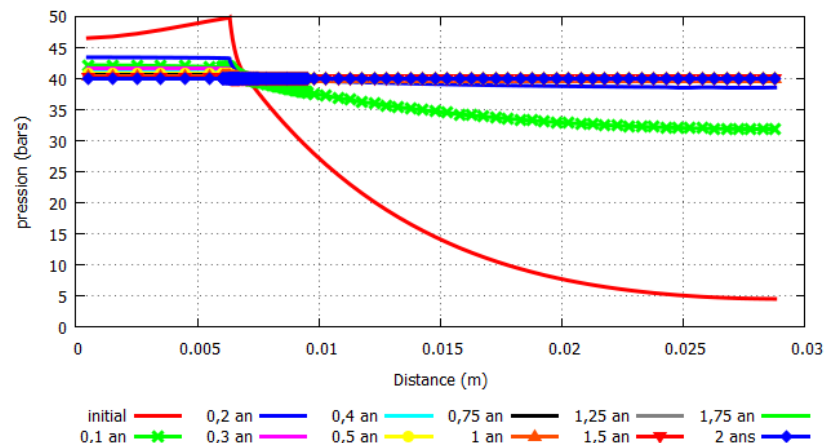


RESULTS FOR THE BASE CASE (1)

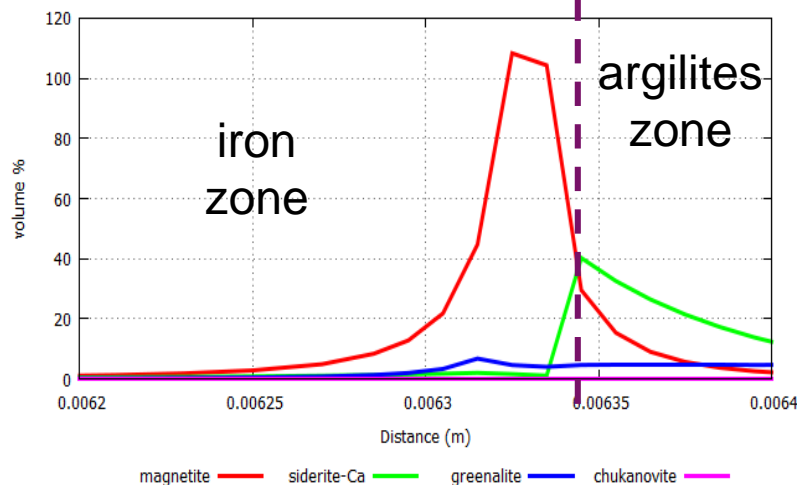
Evolution du profil de pH



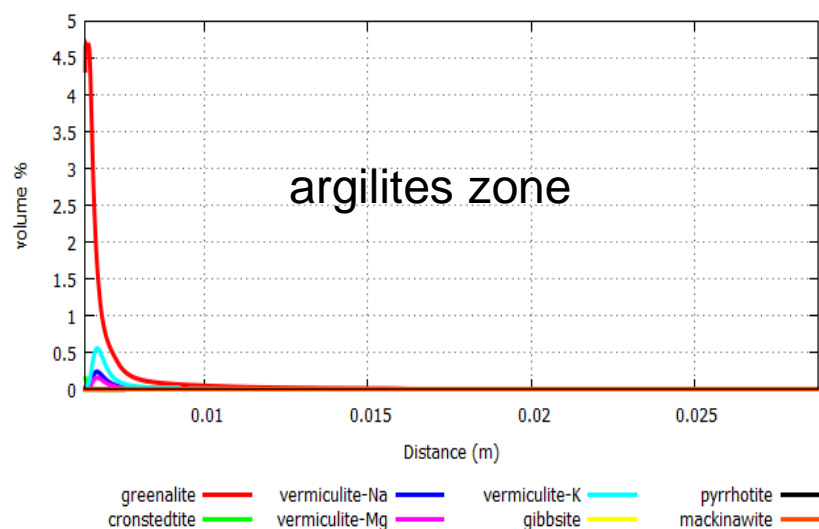
H2 gaz



Principaux produits de corrosion à t = 2 ans



Minéraux secondaires des argilites à t = 2 ans

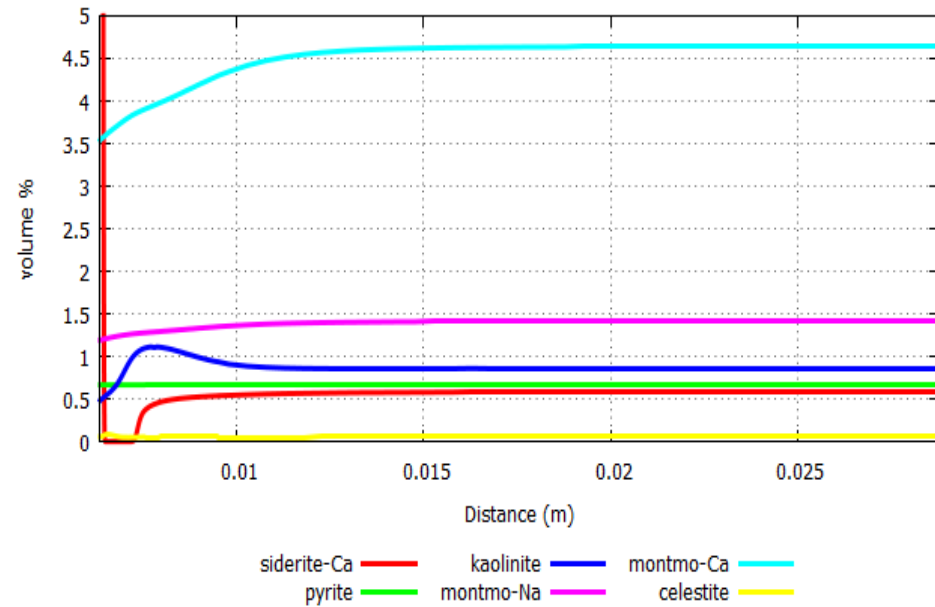


- maximal pH value of 8.7
- secondary mineral paragenesis dominated by magnétite

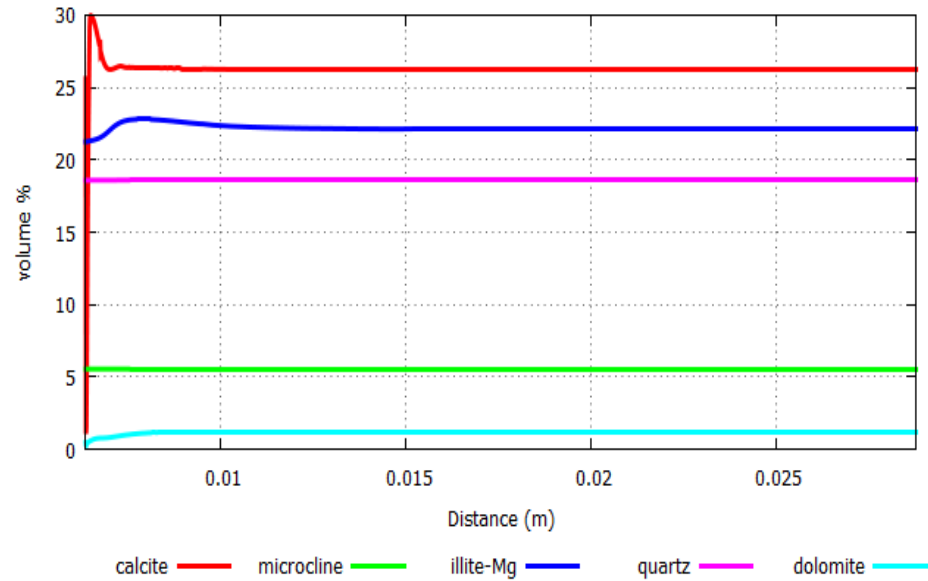
RESULTS FOR THE BASE CASE (2)

- reactivity of primary minerals

Minéraux primaires des argilites à t = 2 ans



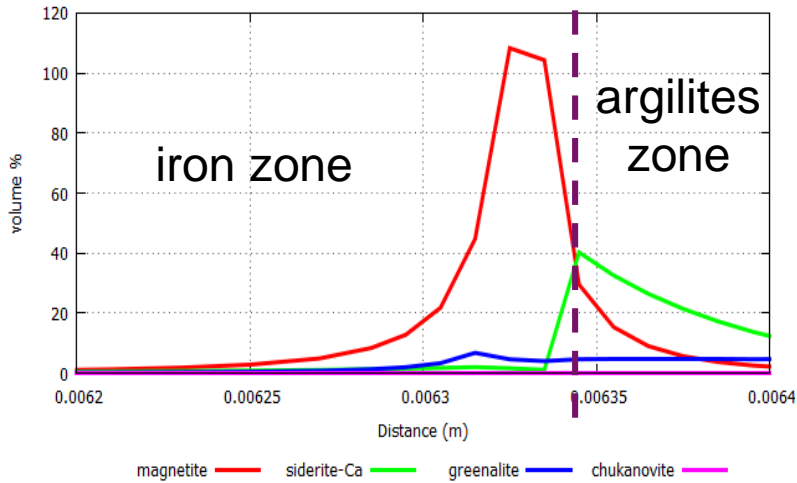
Minéraux primaires des argilites à t = 2 ans



RESULTS FROM SENSITIVITY TO KINETICS (1)

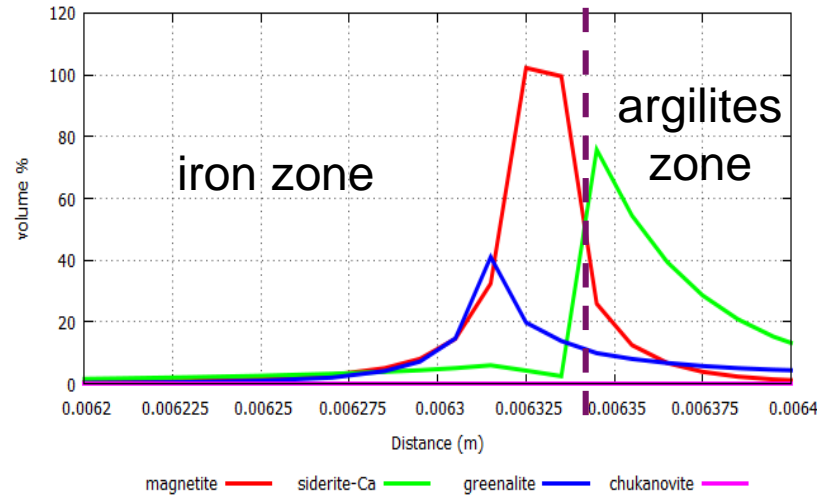
base case

Principaux produits de corrosion à t = 2 ans



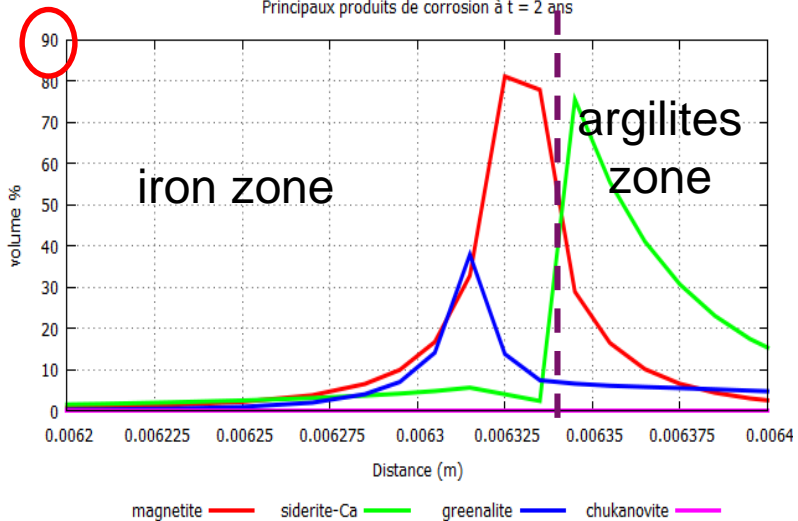
quartz dissolution x100

Principaux produits de corrosion à t = 2 ans



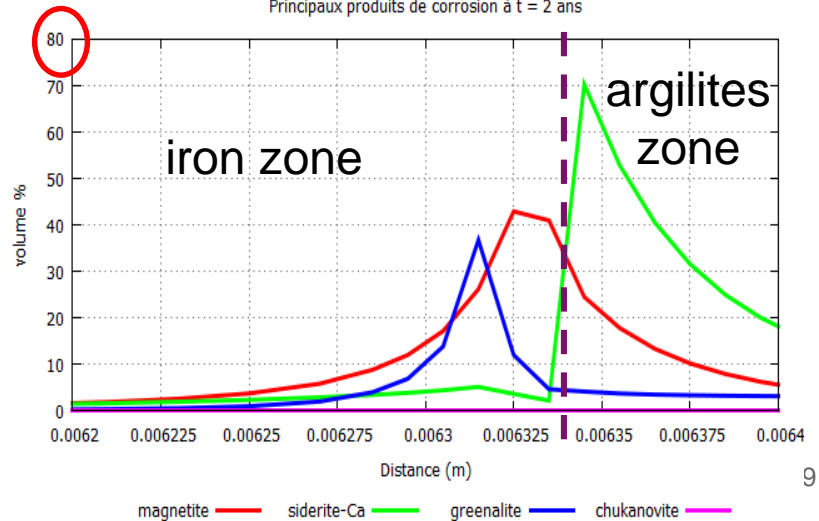
magnetite reactivity/100

Principaux produits de corrosion à t = 2 ans



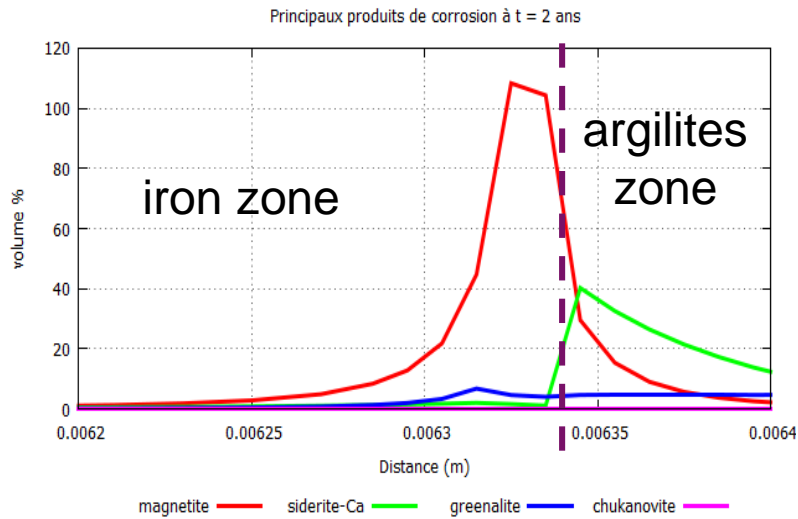
magnetite reactivity/1000

Principaux produits de corrosion à t = 2 ans

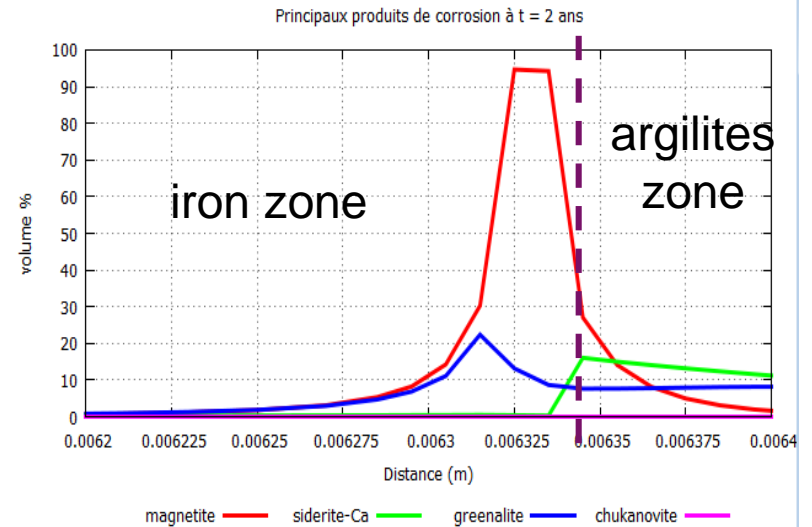


RESULTS FROM SENSITIVITY TO KINETICS (2)

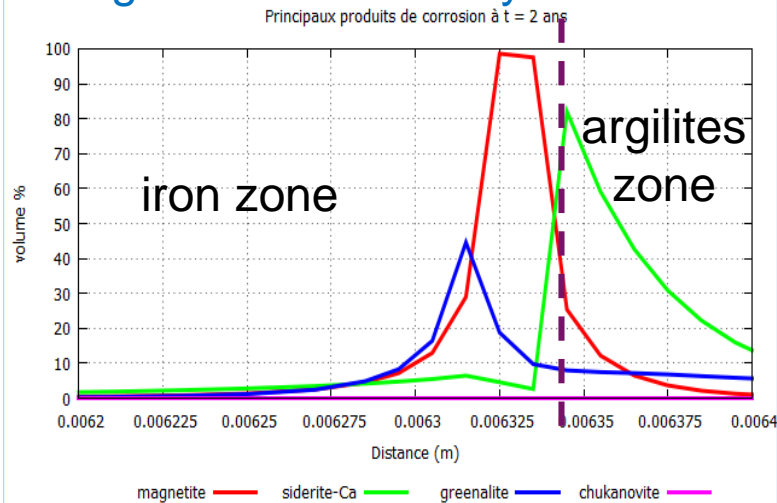
base case



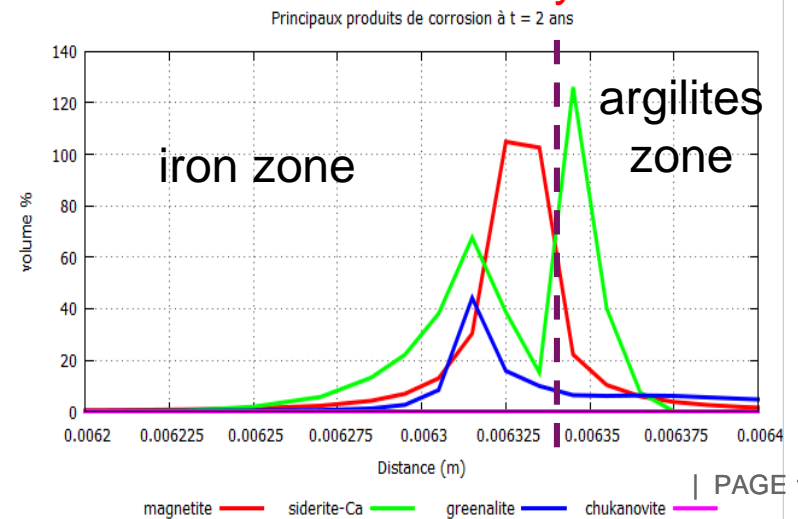
siderite-Ca reactivity /10



greenalite reactivity x100

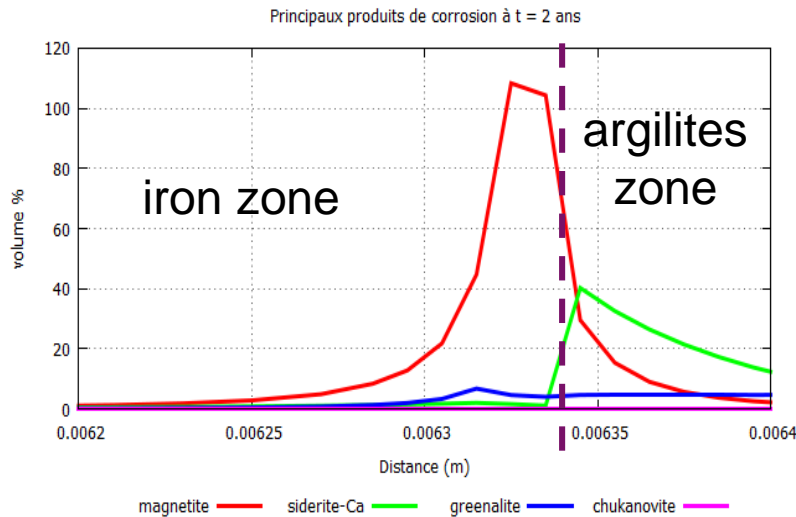


siderite-Ca reactivity x100

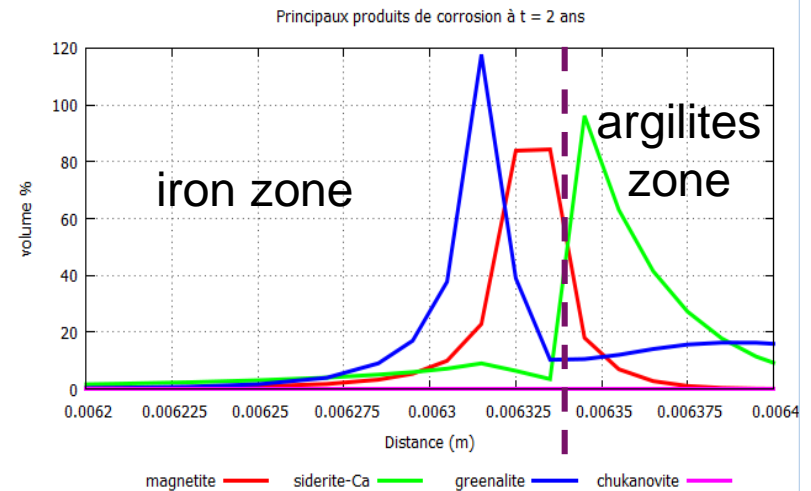


RESULTS FROM SENSITIVITY TO KINETICS (3) QUARTZ

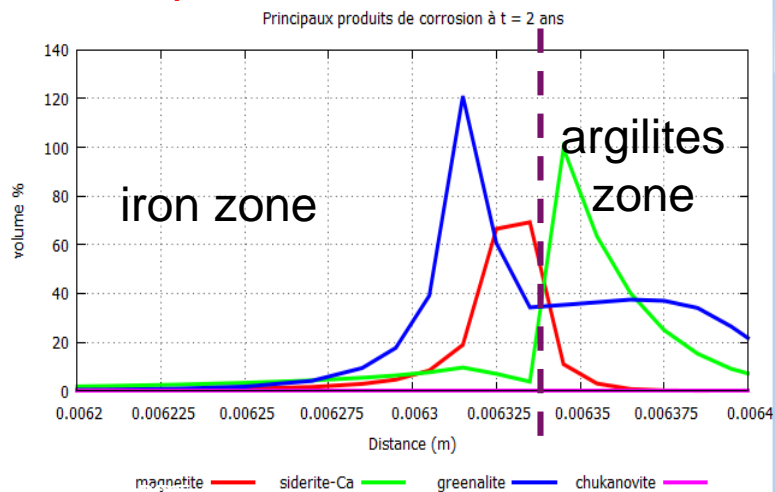
base case



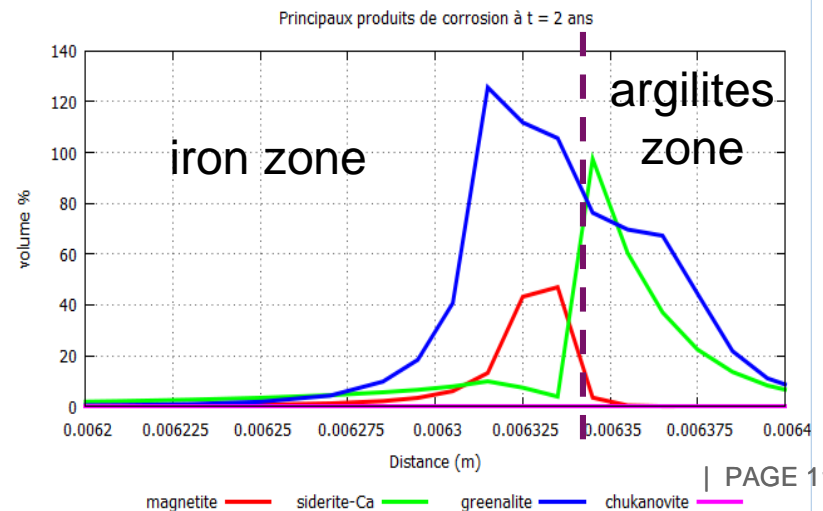
quartz dissolution x10



quartz dissolution x30

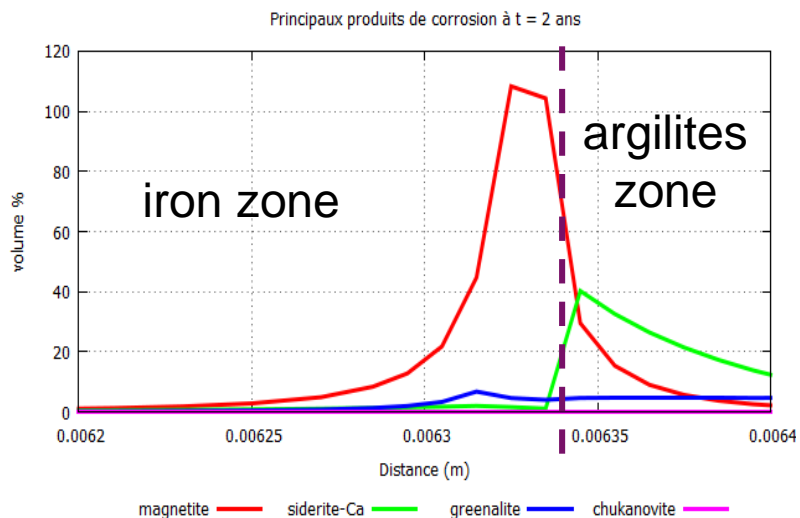


quartz dissolution x100

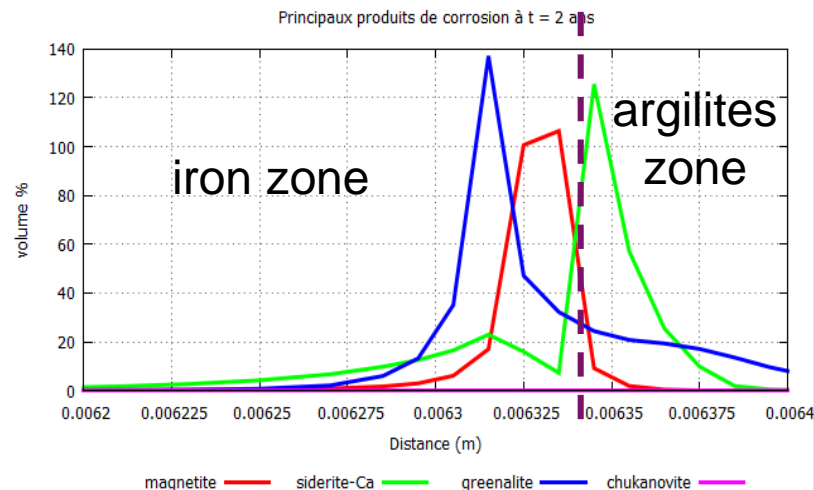


RESULTS FROM GLOBAL SENSITIVITY TO KINETICS

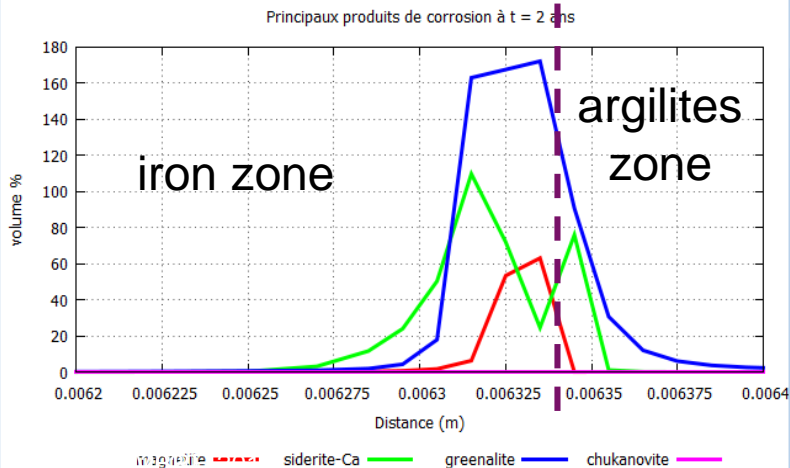
base case



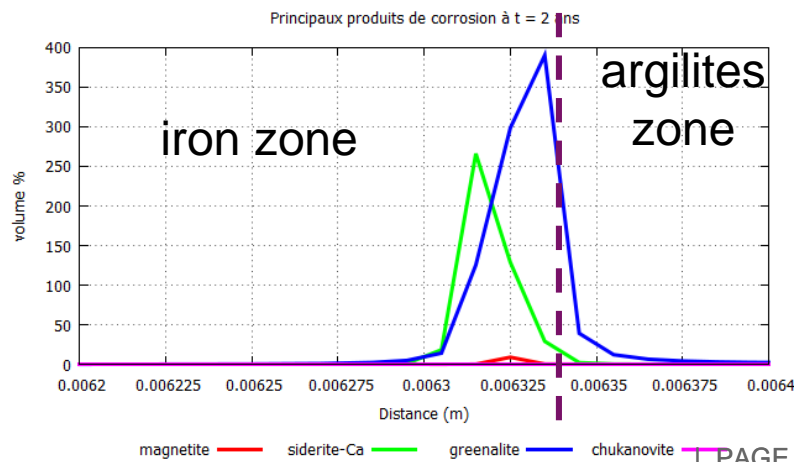
quartz siderite magnétique greenalite x 10



all reactivity x 100

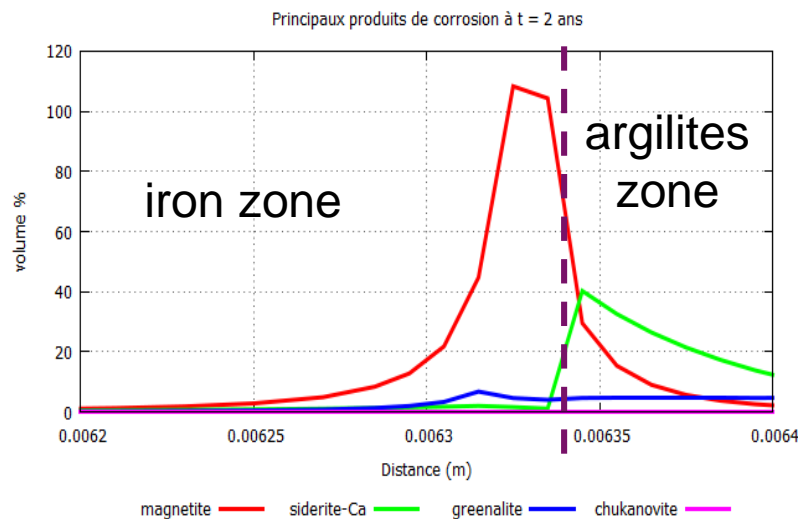


all reactivity x 1000



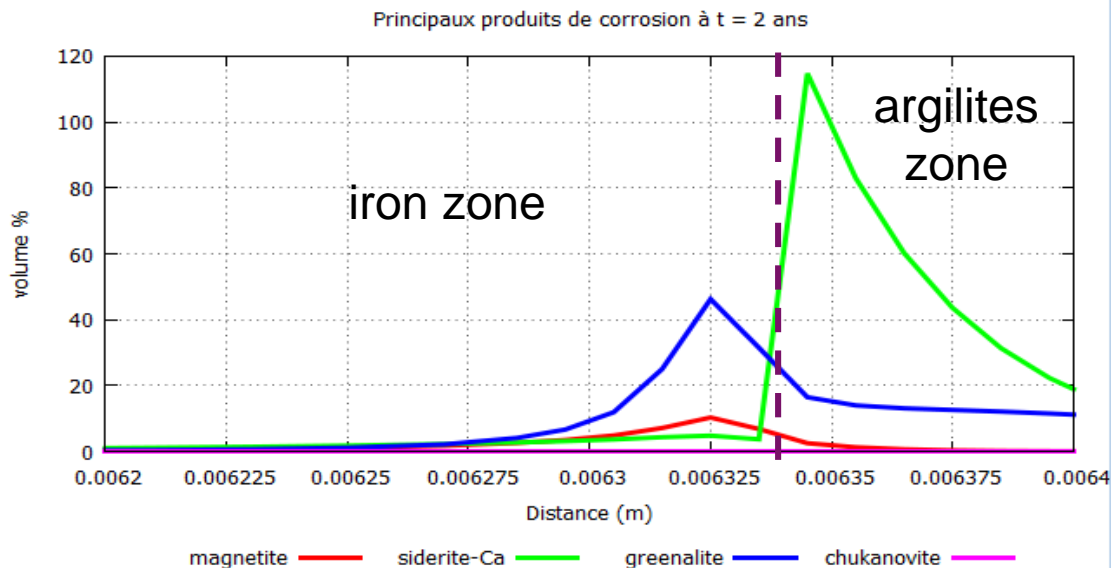
RESULTS FROM SENSITIVITY TO CORROSION RATE

base case



corrosion rate /10

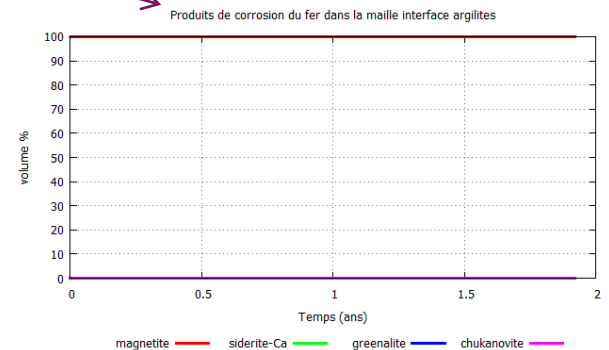
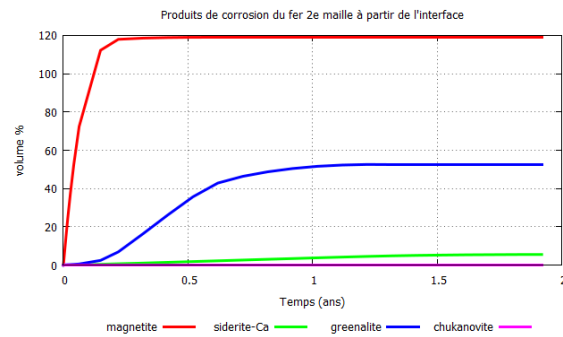
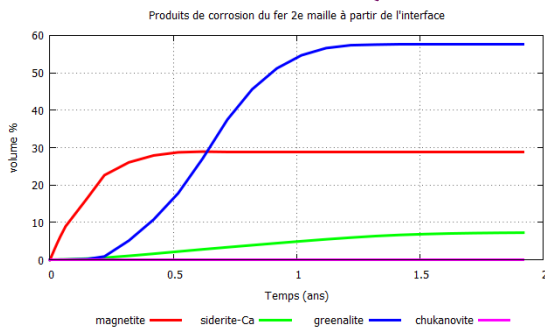
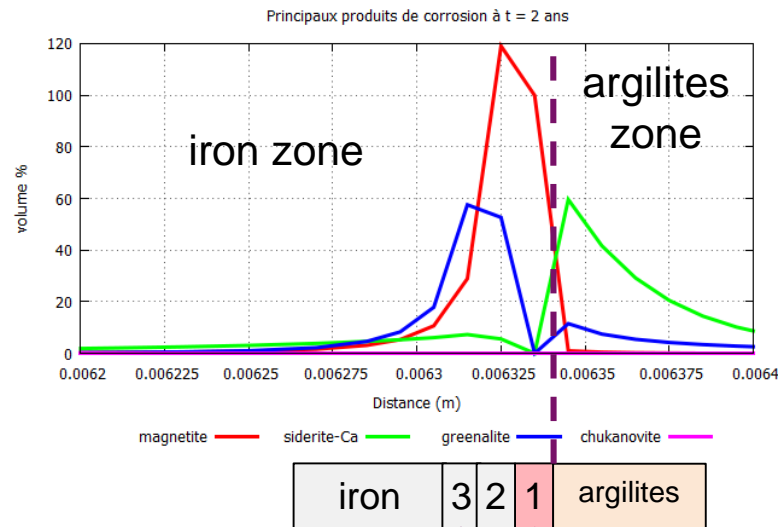
- **attention : interface fer-argilite**
- **greenalite becomes dominant**
- **more iron migration towards the argilites**



- no modification in the sequence of secondary minerals
- magnetite is destabilized only when global reactivity is increased
- magnetite DOES NOT FORM at « low » corrosion rate

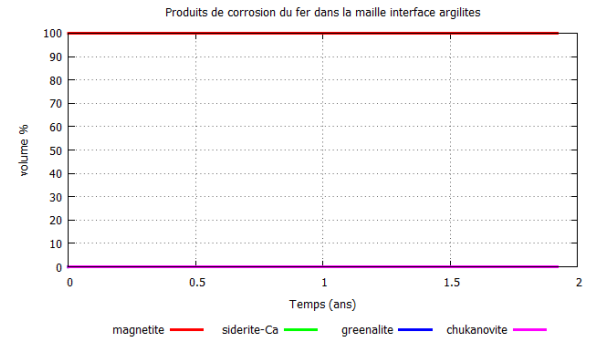
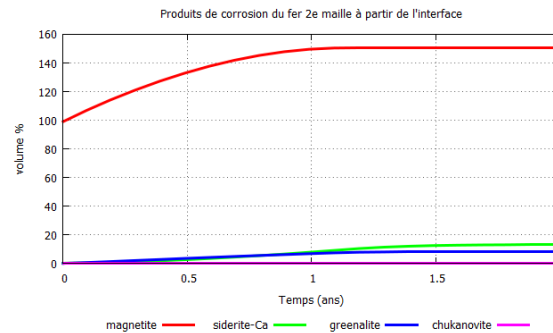
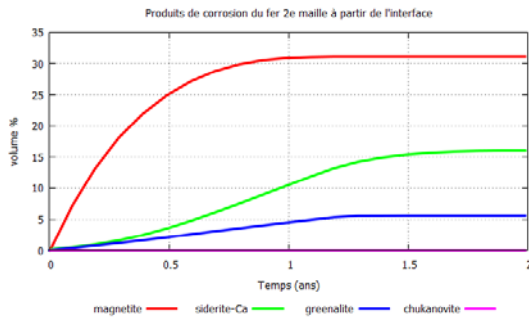
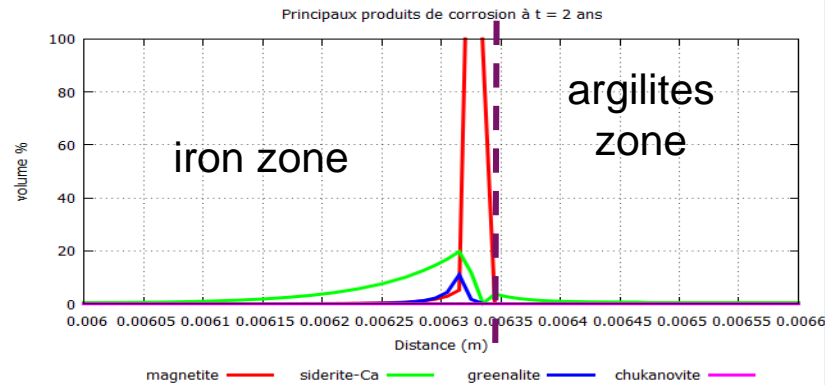
RESULTATS WITH 1 PRE-EXISTING MAGNETITE NODE

- 1 « magnetite » node (porosity = 0.1% → diffusion/10000), kinetics x10



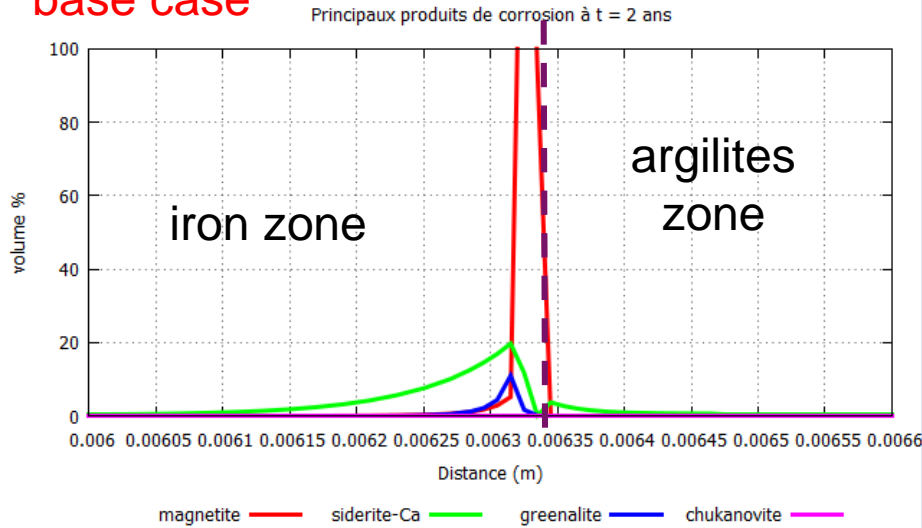
RESULTATS WITH 2 PRE-EXISTING MAGNETITE NODES

- magnetite node 1 (porosity = 1% → diffusion/100)
- magnetite node 2 (porosity = 0.1% → diffusion/10000)

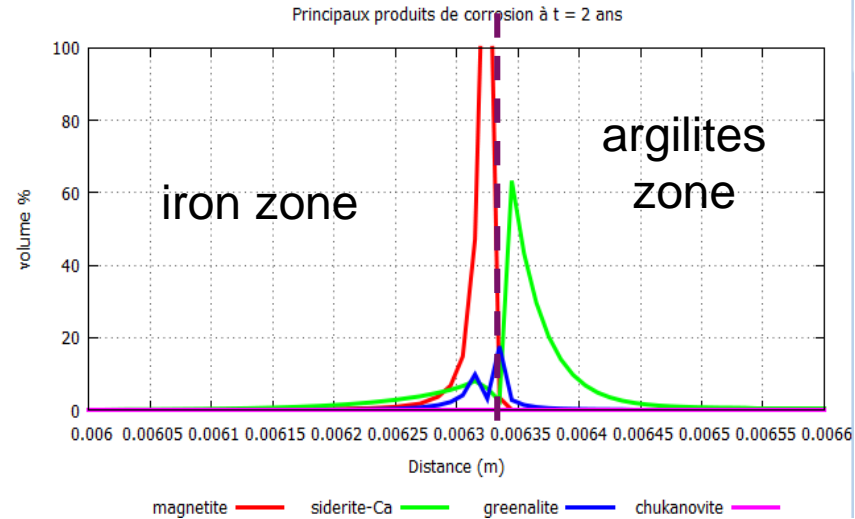


NEW SENSITIVITY TO MAGNETITE REACTIVITY

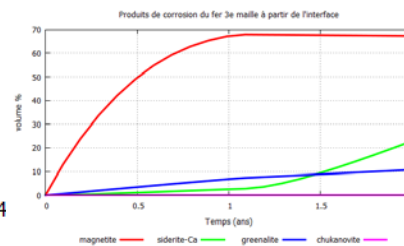
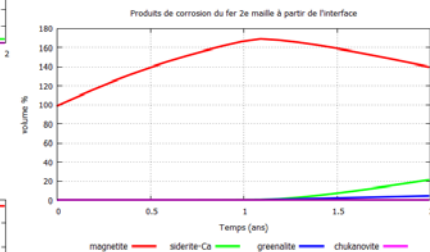
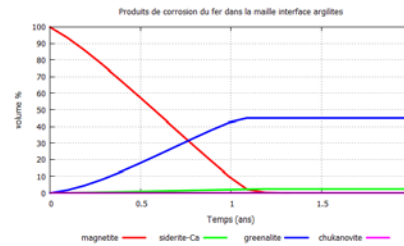
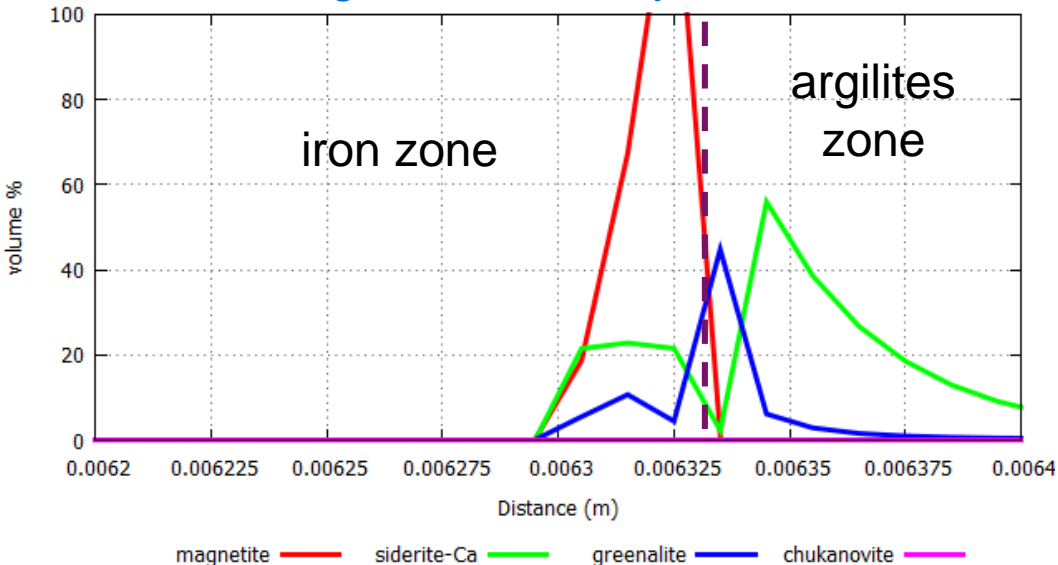
base case



magnetite reactivity x100

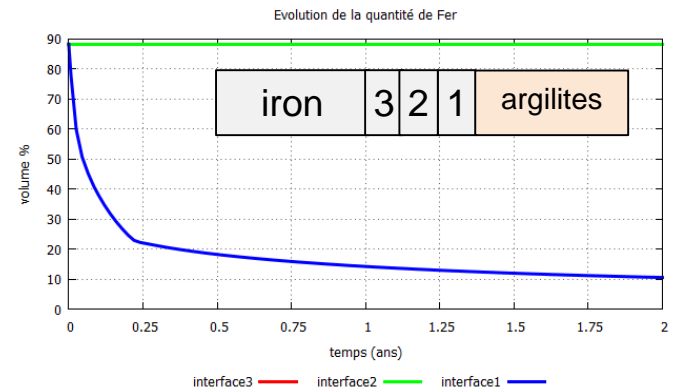
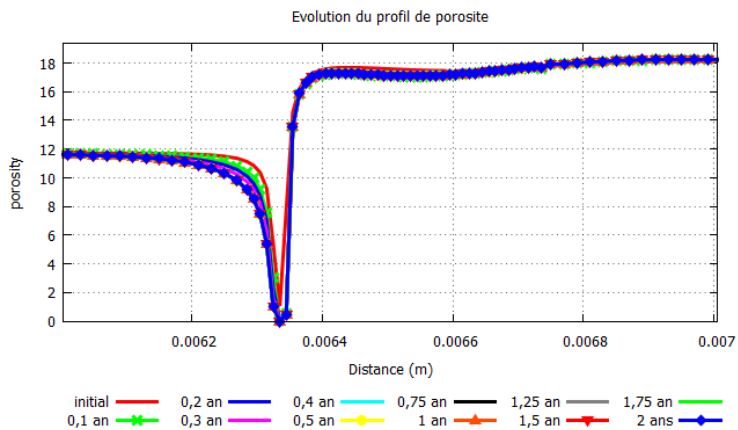
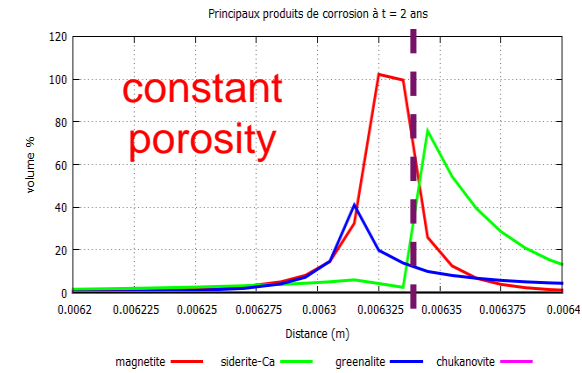
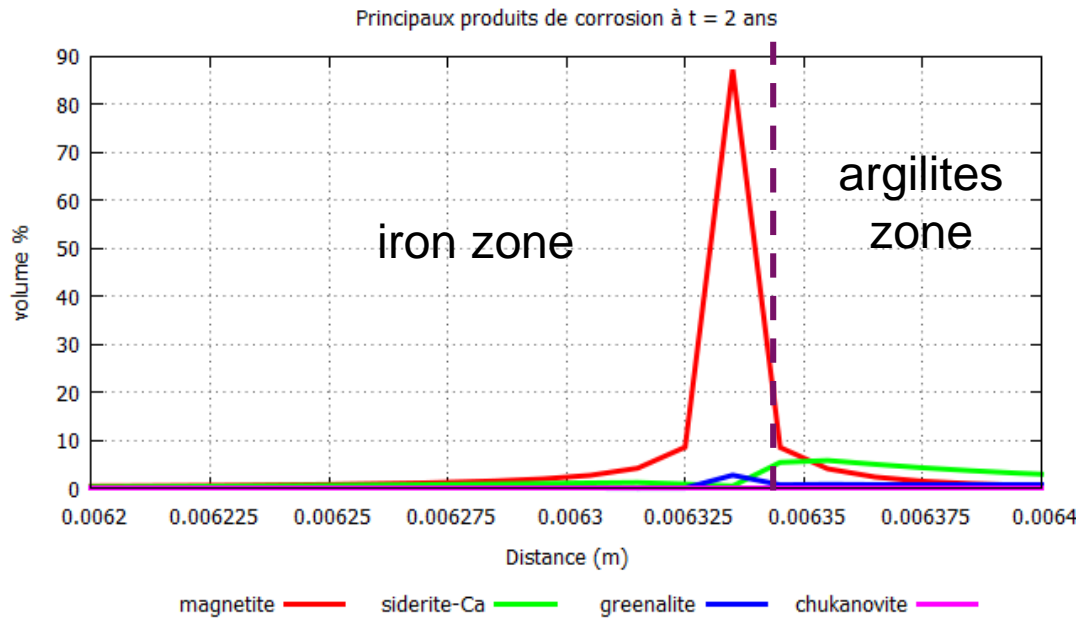


magnetite reactivity x1000



EFFECT OF VARIABLE POROSITY

- corrosion rate rapidly drops...



Modeling and sensitivity analysis:

- **modifying precipitation/dissolution kinetics affects only the amount of mineral precipitated, the mineral sequence remaining unchanged (unless a very high magnetite reactivity is used)**
- **a low corrosion rate changes the nature of corrosion products: greenalite and sidérite instead of magnetite**
- **a low diffusive barrier is necessary to avoid greenalite précipitation in the iron zone**
- **high magnetite dissolution rate is required to allow for its redissolution at the interface with argilites**

- **modify the tortuosity in the iron zone**
- **calculate the corrosion rate as controlled by the diffusion of reactants/products (H_2) in the internal corrosion layer (magnetite)**

THANK YOU FOR YOUR ATTENTION

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