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COUPLED THCM MODELS OF HEATING AND HYDRATION TESTS TO STUDY THE INTERACTIONS OF FE CORROSION PRODUCTS AND BENTONITE

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1. INTRODUCTION

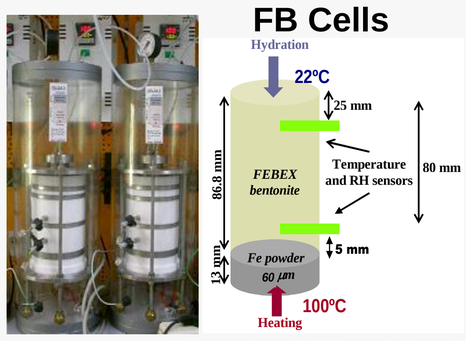
- Compacted bentonite is foreseen as a backfill and sealing material in radioactive waste repositories
- The strong interplays among thermal (T), hydrodynamic (H), mechanical (M) and chemical (C) processes during the hydration and thermal stages of a repository call for coupled THMC models.
- Many laboratory experiments have been performed on canister corrosion, corrosion-bentonite interactions and concrete-bentonite interactions.
- There is a clear need to test the models used in performance assessment analyses with laboratory data.

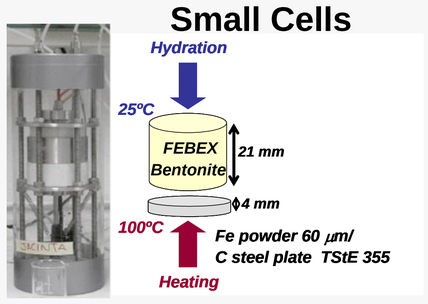
2. OBJECTIVES

- We present coupled THMC models of heating and hydration corrosion experiments performed at the Ciemat facilities to study the corrosion products generated at the canister/bentonite interface under repository conditions and analyze how the corrosion products could affect bentonite properties

3. HEATING & HYDRATION CORROSION TESTS

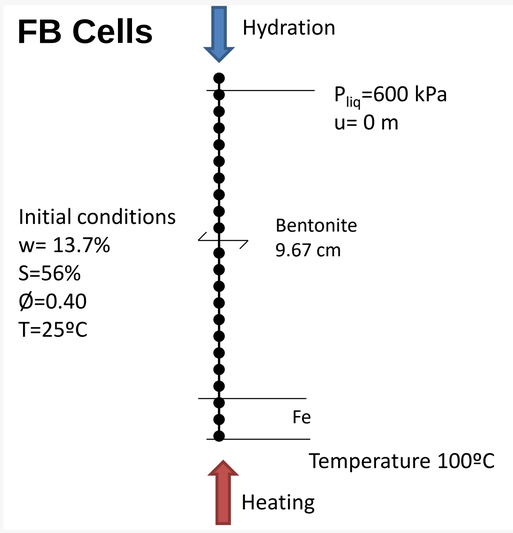
- Some of these experiments were performed within the NF-PRO and PEBS Projects (ENRESA, 2008, Turrero et al., 2011) while others are being dismantling within EURAD Project.

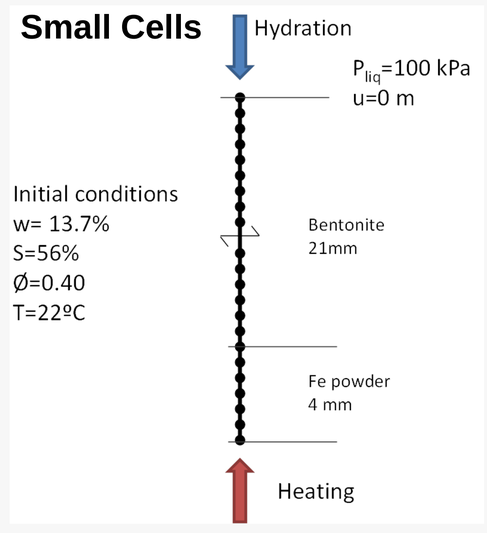




4. THCM MODEL OF CORROSION EXPERIMENTS

- 1D finite element grid
- A temperature of 100ºC is imposed at the heating boundary
- THMC parameters were taken from Zheng et al. (2010)
- The numerical model was performed with INVERSE-FADES-CORE (Zheng et al., 2011; Mon, 2017) a code which solves multiphase flow and multicomponent reactive transport problems in deformable porous media



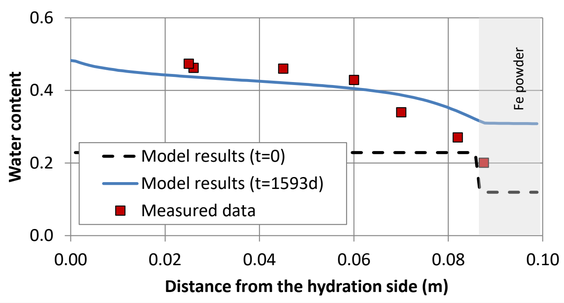


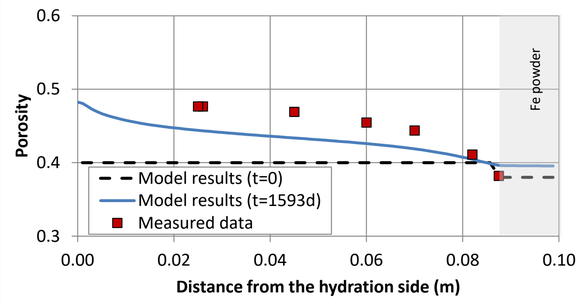
Geochemical system

Primary species	H_2O, H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, $SiO_2(aq)$, $O_2(aq)$, Fe^{2+}
Aqueous complexes	$CaCO_3(aq)$, $CaHCO_3^+$, $CaOH^+$, $CaSO_4(aq)$, $CO_2(aq)$, CO_3^{2-}, KSO_4^-, $MgCO_3(aq)$, $MgHCO_3^+$, $MgSO_4(aq)$, $MgOH^+$, $NaHCO_3(aq)$, $NaSO_4^-$, $NaCO_3^-$, $NaOH(aq)$, OH^-, $H_3SiO_4^-$, HSO_4^-, HS^-, Fe^{3+}, $FeHCO^{3+}$, $FeCO_3(aq)$, $FeCl^+$, $FeCl^{2+}$, $FeOH^+$, $FeOH^{2+}$, $Fe(OH)_3(aq)$, $Fe(OH)_2(aq)$, $Fe(OH)_4^-$, $Fe(OH)_2^+$, $Fe(SO_4)_2^-$, $FeSO_4(aq)$, $FeHSO_4^{2+}$, $Fe(OH)_2^{4+}$, $KOH(aq)$, $H_2(aq)$, $NaHSiO_3(aq)$, $HSiO_3^-$, $MgH_3SiO_4^+$
Minerals	calcite, quartz, gypsum/anhydrite, magnetite, siderite, goethite, Fe(s), $Fe(OH)_2(s)$
Exchangeable cations	Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}

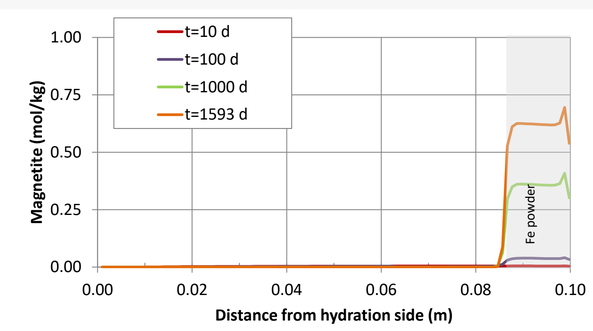
Cation exchange	$K_{Na\text{-}cation}$
$Na^+ + X\text{-}K \Leftrightarrow K^+ + X\text{-}Na$	0.138
$Na^+ + 0.5Ca\text{-}X_2 \Leftrightarrow 0.5Ca^{2+} + Na\text{-}X$	0.292
$Na^+ + 0.5Mg\text{-}X_2 \Leftrightarrow 0.5Mg^{2+} + Na\text{-}X$	0.280
$Na^+ + 0.5Fe\text{-}X_2 \Leftrightarrow 0.5Fe^{2+} + Na\text{-}X$	0.5
$Na^+ + X\text{-}H \Leftrightarrow H^+ + X\text{-}Na$	$3.16\cdot10^{-5}$
Surface complexation	**Log K_{int}**
$SOH_2^+ \Leftrightarrow SOH + H^+$	-4.5
$SO^- + H^+ \Leftrightarrow SOH$	7.9
$SOFe^+ + H^+ \Leftrightarrow SOH + Fe^{2+}$	0.6
$S^sOFeOH + 2H^+ \Leftrightarrow S^sOH + Fe^{2+} + H_2O$	10.0
$S^sOFe(OH)_2^- + 3H^+ \Leftrightarrow S^sOH + Fe^{2+} + 2H_2O$	20.0
$S^{W1}OH_2^+ \Leftrightarrow S^{W1}OH + H^+$	-4.5
$S^{W1}O^- + H^+ \Leftrightarrow S^{W1}OH$	7.9
$S^{W1}OFe^+ + H^+ \Leftrightarrow S^{W1}OH + Fe^{2+}$	3.3
$S^{W2}OH_2^+ \Leftrightarrow S^{W2}OH + H^+$	-6.0
$S^{W2}O^- + H^+ \Leftrightarrow S^{W2}OH$	10.5
Steel canister corrosion	
$Fe(s) + 2H_2O \Leftrightarrow Fe^{+2} + 2OH^- + H_2(g)$	

5. NUMERICAL MODEL RESULTS OF FB3 CELL





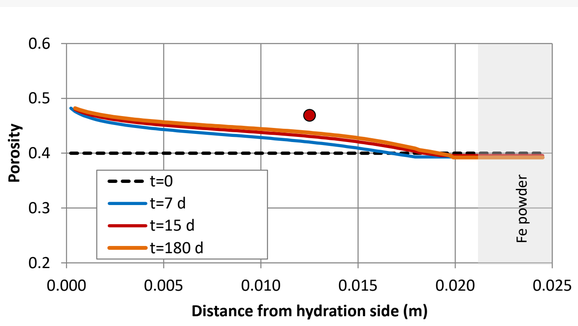
Data taken from Turrero et al. (2011)

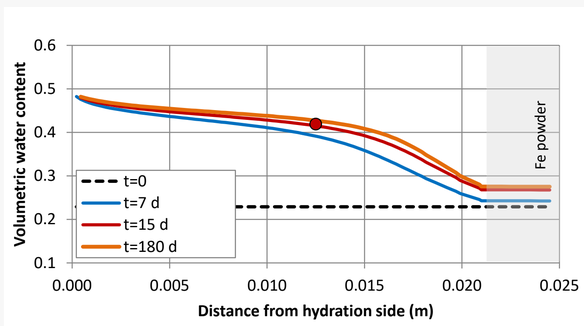


MAJOR FINDINGS

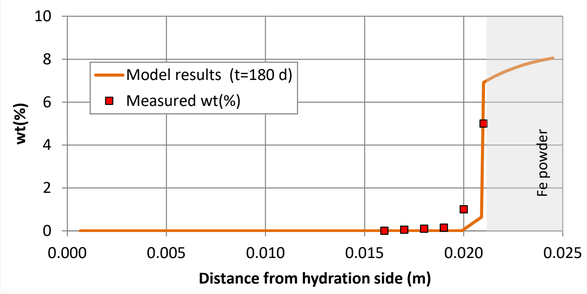
- Model results predict a small amount of magnetite precipitation computed at the bentonite/Fe powder interface which is consistent with magnetite precipitation observed at the interface.
- The precipitation of magnetite at chemical equilibrium is larger than that computed with a kinetically-controlled precipitation.
- Fe(OH)2(s) does not precipitate when magnetite precipitates at equilibrium and when the corrosion rate is decreased.

6. NUMERICAL MODEL RESULTS OF SMALL CELLS





Data taken from Torres et al. (2008) and De Windt et al. (2009)



MAJOR FINDINGS

- Magnetite and $Fe(OH)_2(s)$ are the main corrosion products which compete for Fe^{2+} precipitation.
- The corrosion products penetrate a few mm into the bentonite.
- The numerical results fit the measured iron weight data.
- Fe^{2+} sorbes by surface complexation.
- Fe^{2+} exchange is less relevant than Fe^{2+} sorption by surface complexation.

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Acknowledgements

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