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2nd Mechanisms and modelling of waste/cement interactions
October 14, 2008, Le Croisic

Diffusion of an alkaline and hyperalkaline solution through compacted Mg-saturated bentonite

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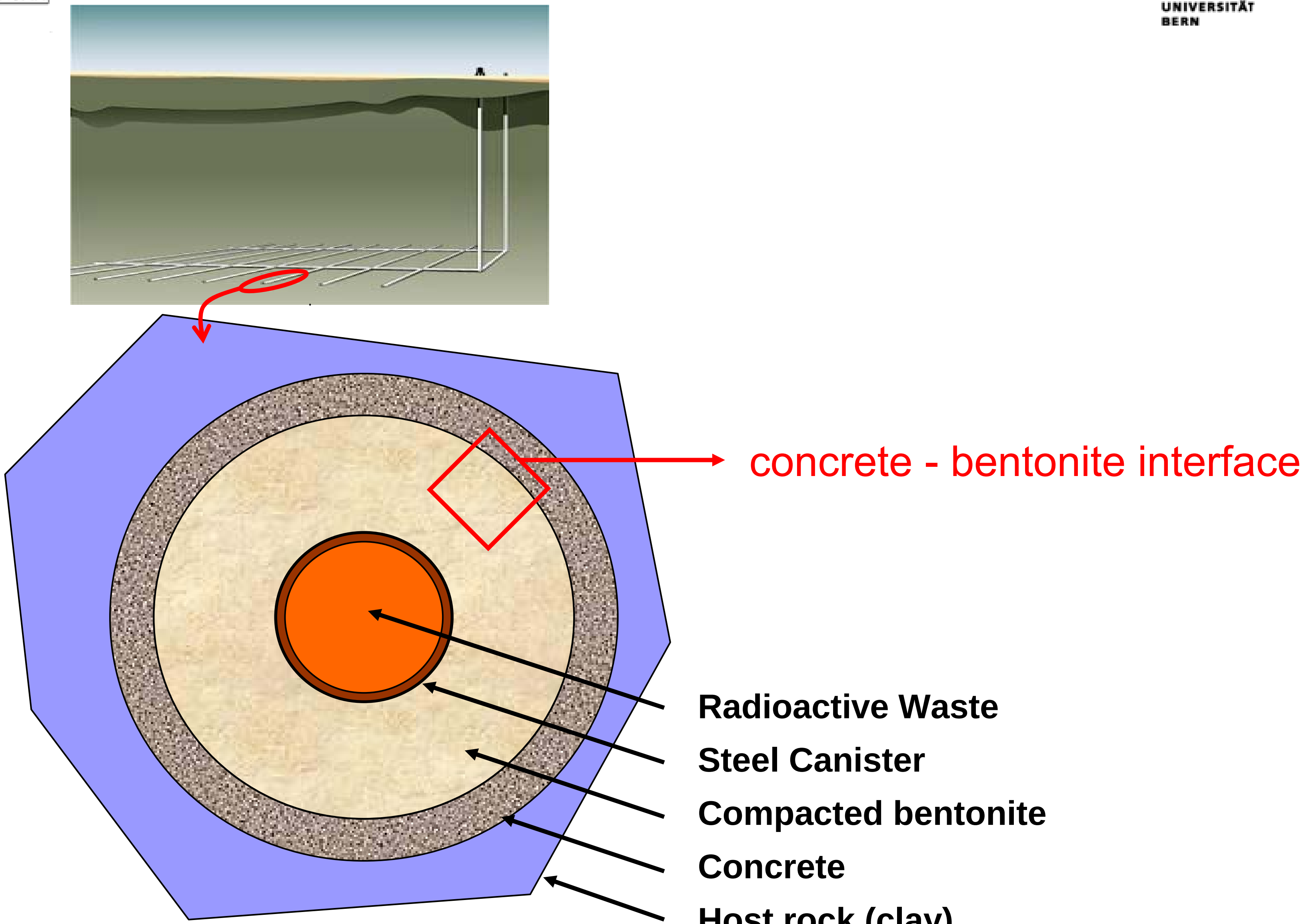
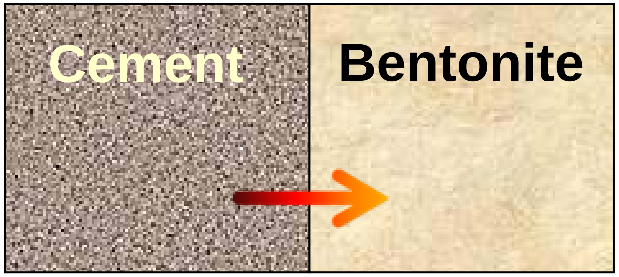
Engineered multi-barrier system



Antecedents



Cement porewater:

pH 13-14

K^+ (0.2 -0.5 M)

Na^+ (0.05 – 0.2 M)

Ca^{+2} (0.02 M)

OH^- (0.3 – 0.7 M)

- Montmorillonite dissolves under hyperalkaline conditions, precipitating zeolites and leaving a Mg-rich residual clay
- Bentonite buffer the hyperalkaline pH at the interface to pH $\leq$ 12.5 (portlandite control) and then to lower pH (C-S-H)
- Exchangeable Mg^{+2} precipitates as brucite [$Mg(OH)_2$] or magnesium silicate and/or hydrotalcite, depending on the temperature of reaction

Objectives

•Study the geochemical reactivity in the interface cement/bentonite for two types of cement porewater:

- YCW: K/Na-OH hyperalkaline solution, pH = 13.5
- ECW: $Ca(OH)_2$ alkaline solution, pH = 12.5

•Study the diffusive transport associated to the alkaline plume in compacted bentonite at T = 60 and 90 ºC (expected temperatures in a repository)

Laboratory experiments. Pre-treatment

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FEBEX bentonite

Mineralogical composition	(% wt.)
Smectite (montmorillonite)	92 ± 3
Quartz	2 ± 1
Plagioclase	2 ± 1
Cristobalite	2 ± 1
K-Feldspar	Traces
Tridymite	Traces
Calcite	Traces

Secondary minerals

↓ Brucite [$Mg(OH)_2$], Mg-silicates

+ Alkaline fluids

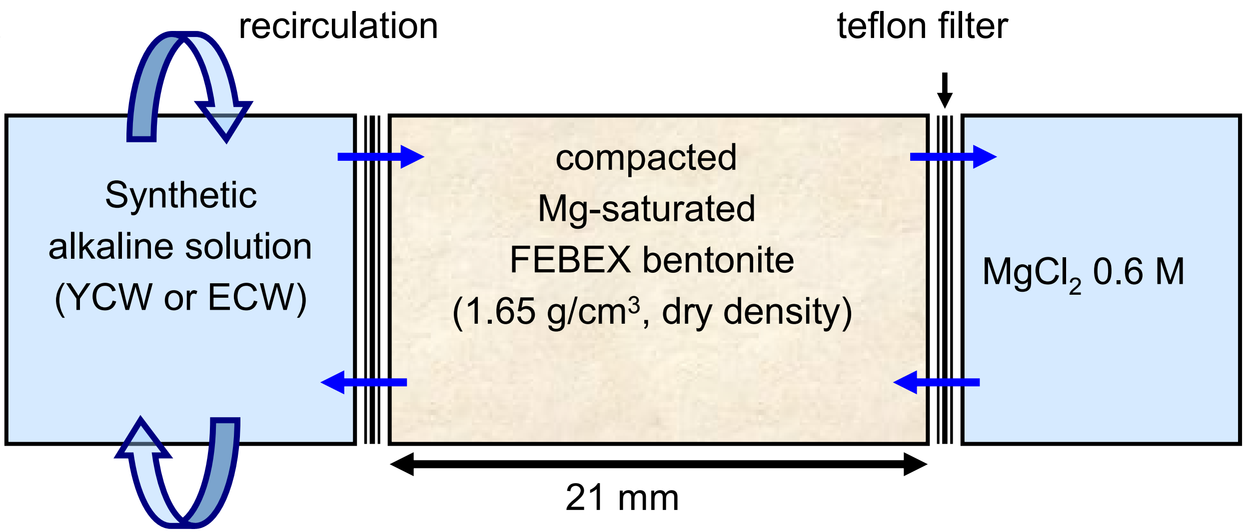
[NaOH, KOH, $Ca(OH)_2$]

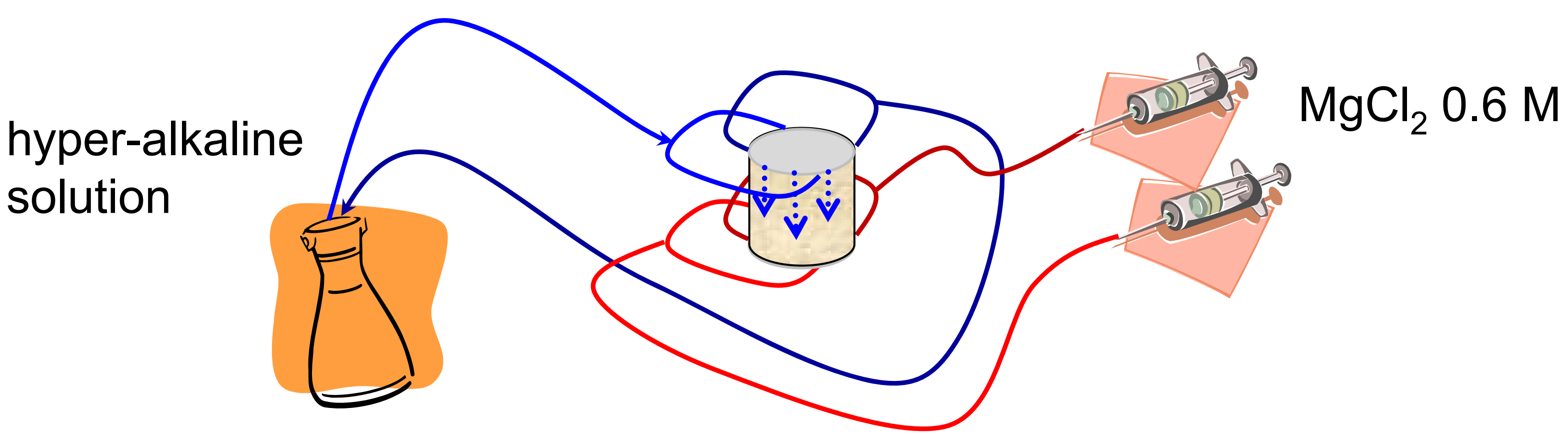
$K_{0.055}Na_{0.135}Ca_{0.125}Mg_{0.1}(Al_{1.545}Mg_{0.425})(Si_{3.86}Al_{0.145})O_{10}(OH)_2$

$MgCl_2$, 1M

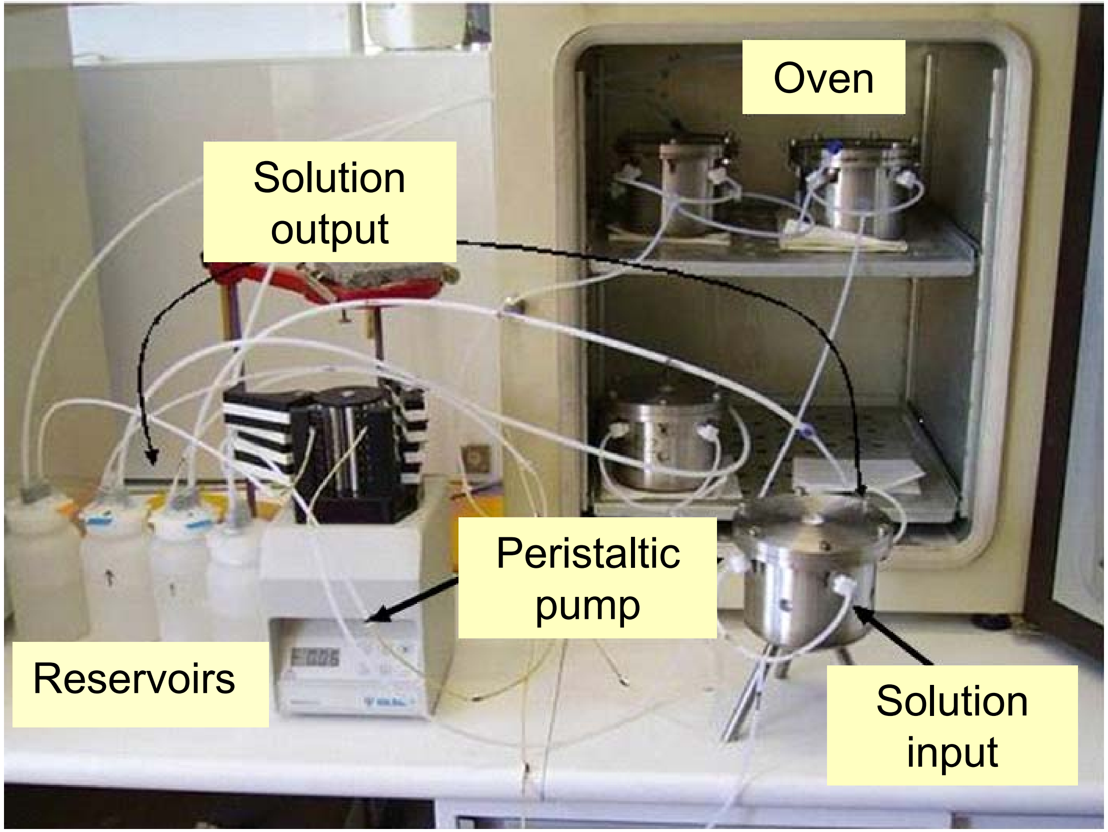
$Mg_{0.32}(Al_{1.545}Mg_{0.425})(Si_{3.86}Al_{0.145})O_{10}(OH)_2$

Experimental scheme





Experimental system



Experimental Conditions

Input alkaline solutions:

- YCW: K/Na-OH (pH=13.5)
- ECW: $Ca(OH)_2$ sat. (pH=12.5)

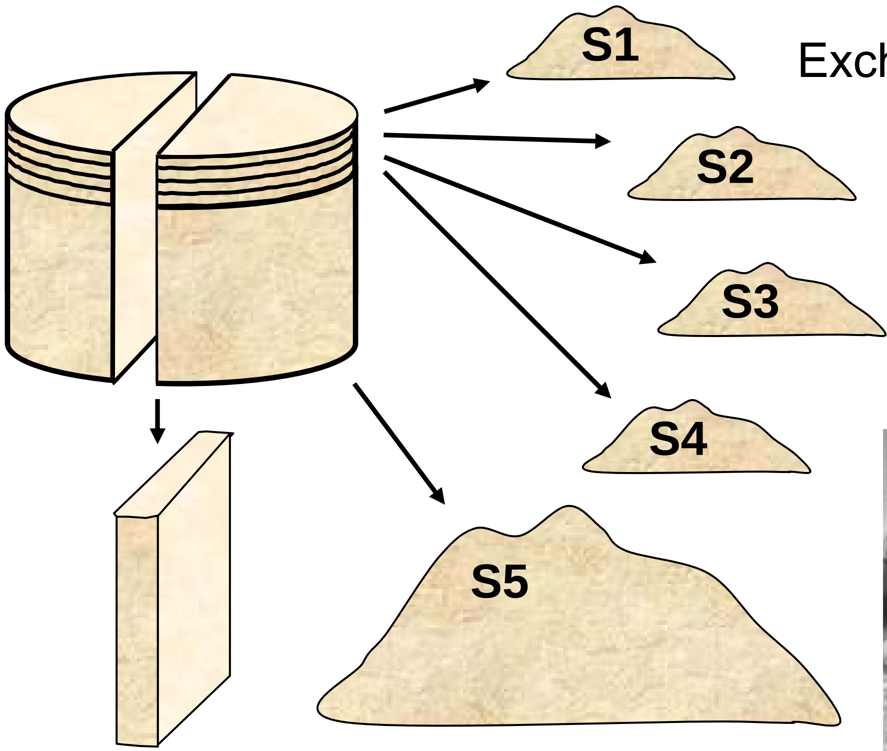
Temperatures:

- 60 and 90 ºC

Time:

- 6, 12 and 18/24 months

Analyses post-mortem



Exchangeable cations [Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}]

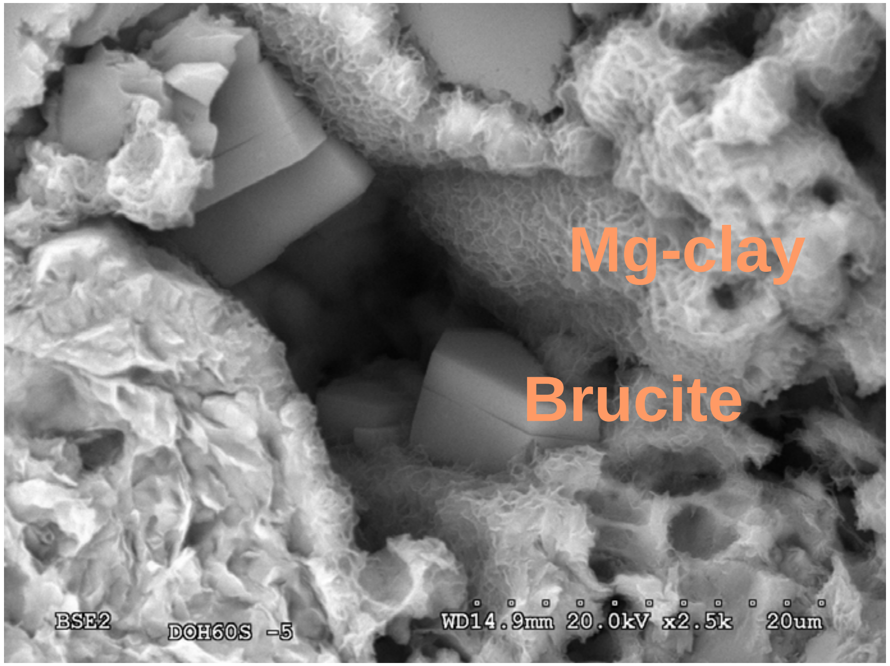
Cation exchange capacity

Mineralogy (XRD)

BET surface

SEM-EDX

YCW: 60 ºC, 6 months

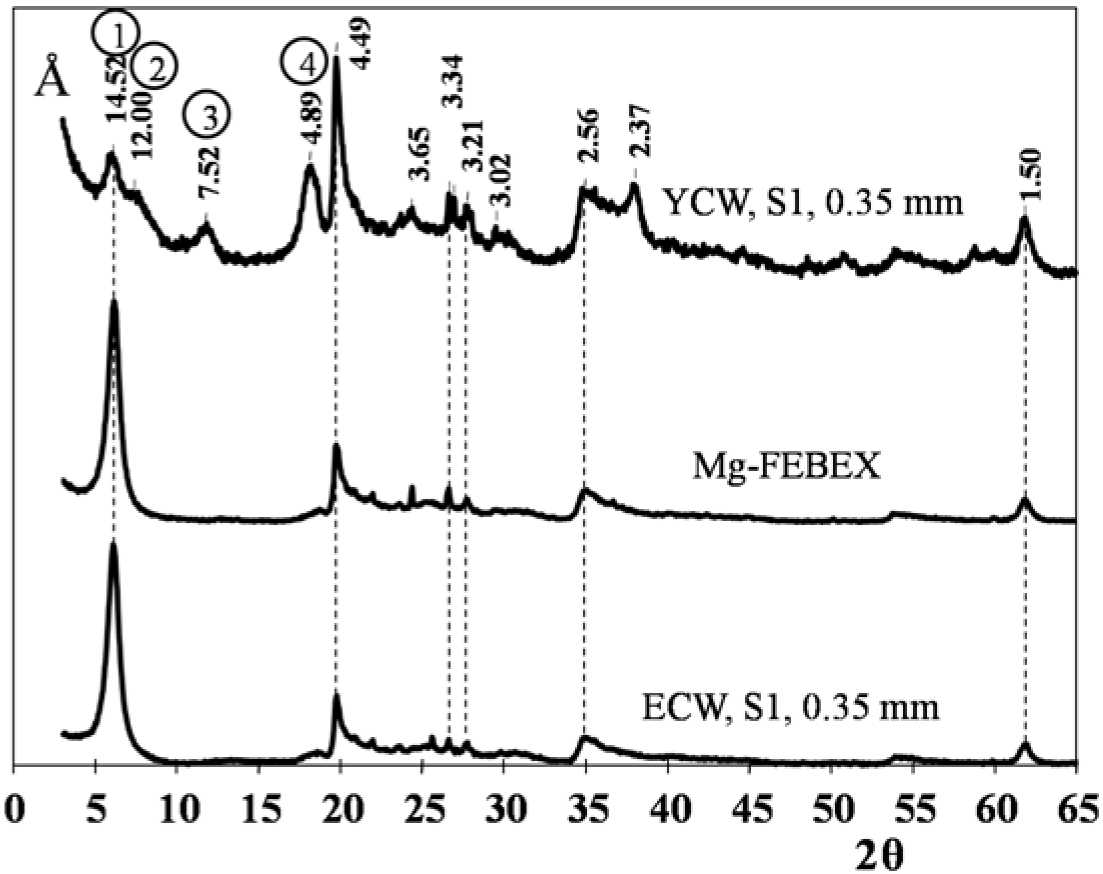


XRD at 60 ºC, 6 months (section 1)

K/Na-OH:

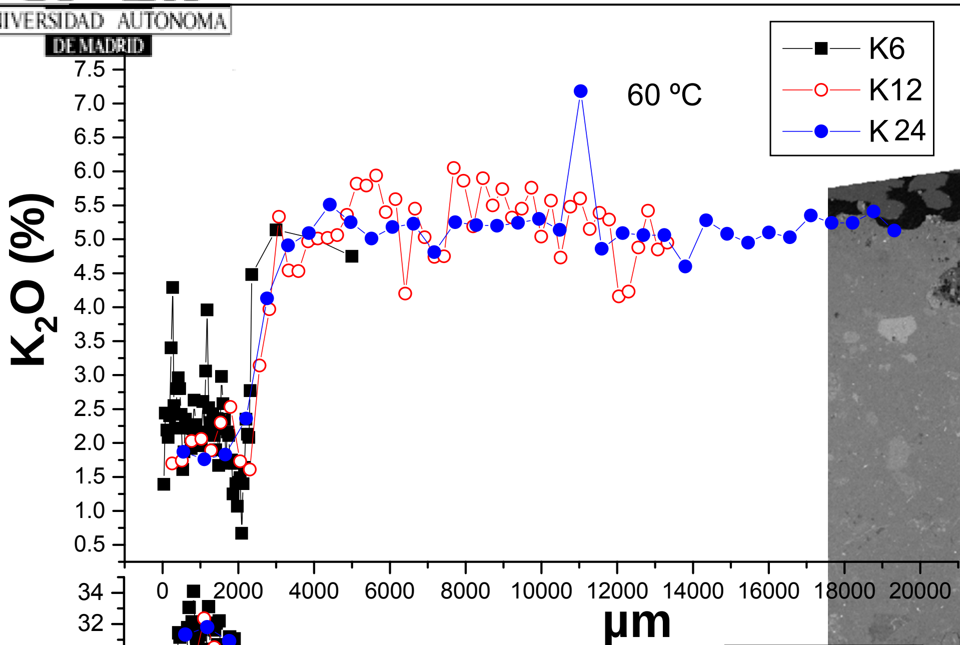
Reference:

Ca-OH:

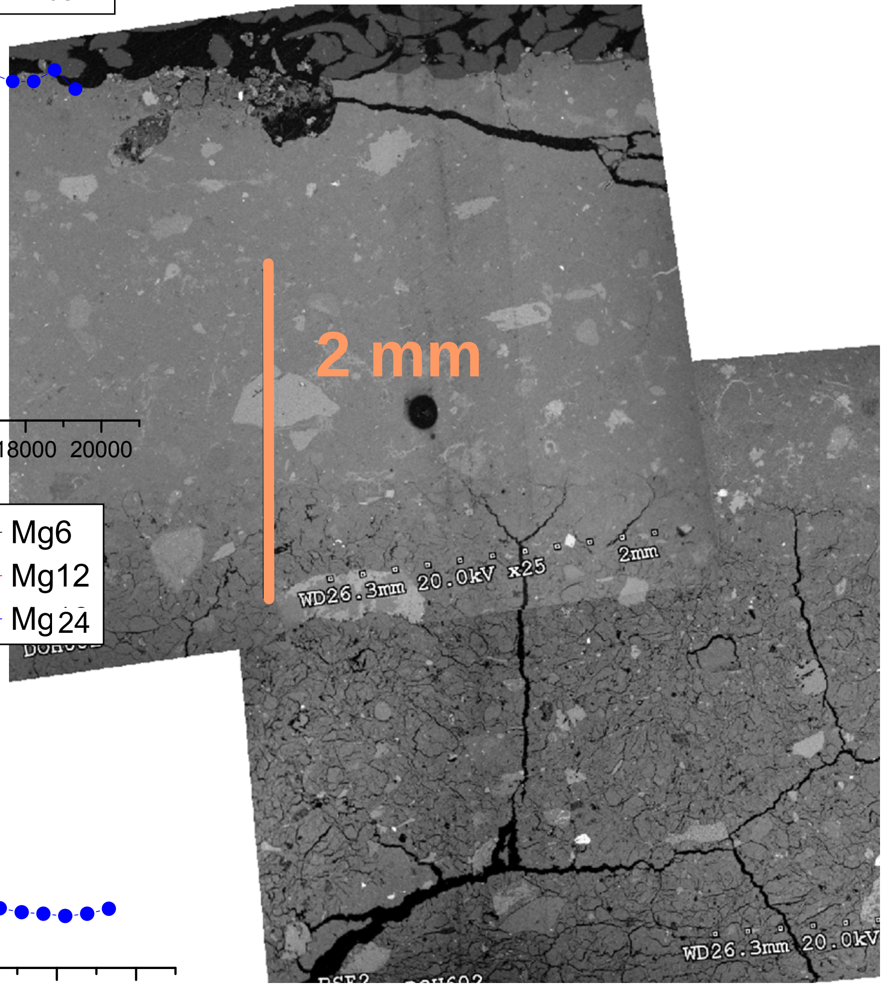


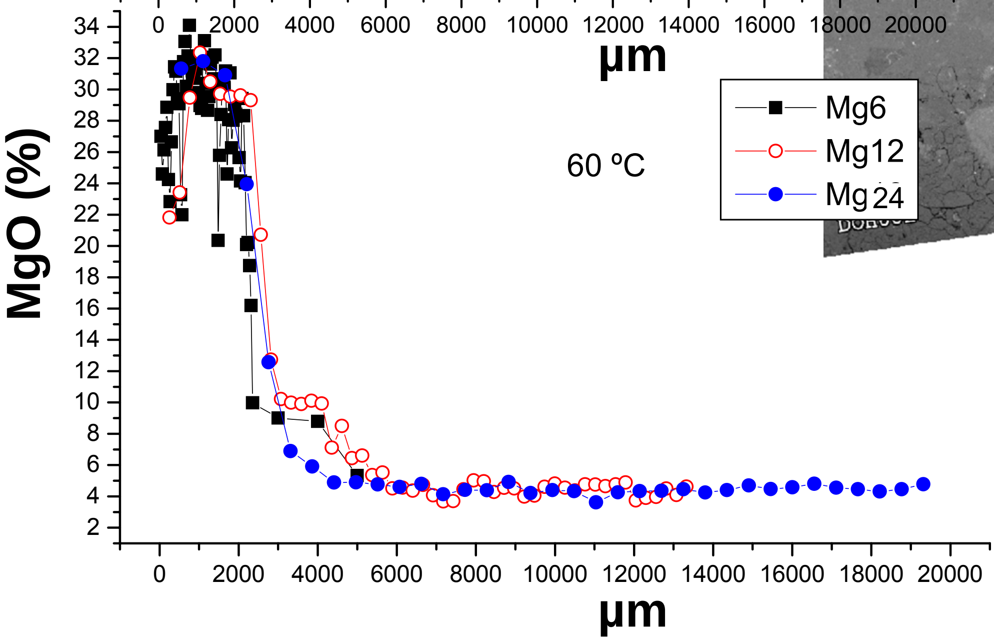
(1) divalent smectites
(2) monovalent smectites
(1) and (3) randomly interstratified trioctahedral chlorite/smectite,
(4) gibbsite [$Al(OH)_3$] and brucite [$Mg(OH)_2$]

YCW: SEM-EDX at 60 ºC

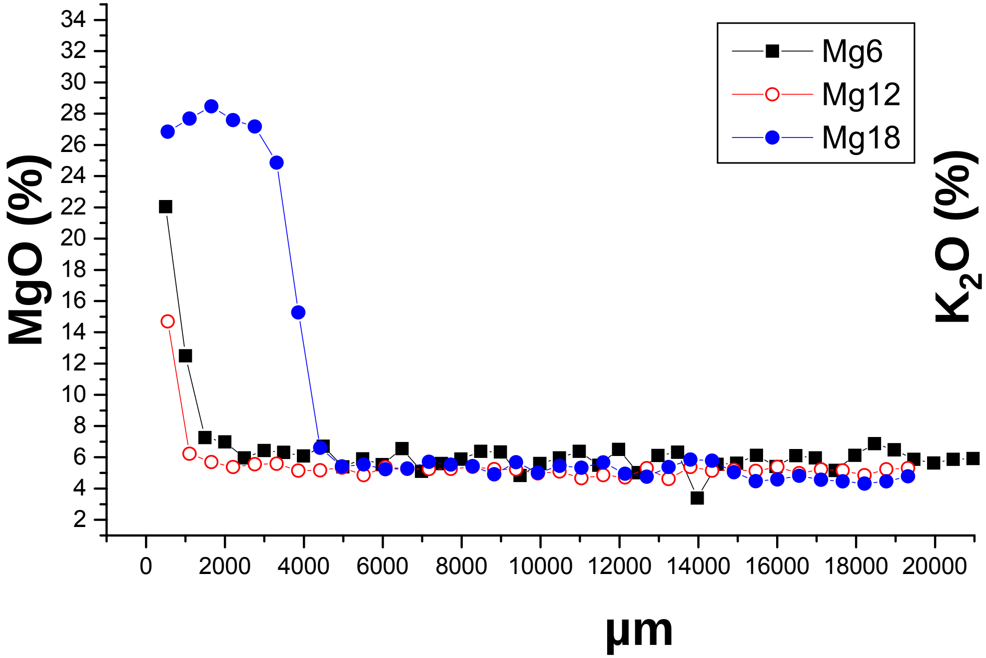


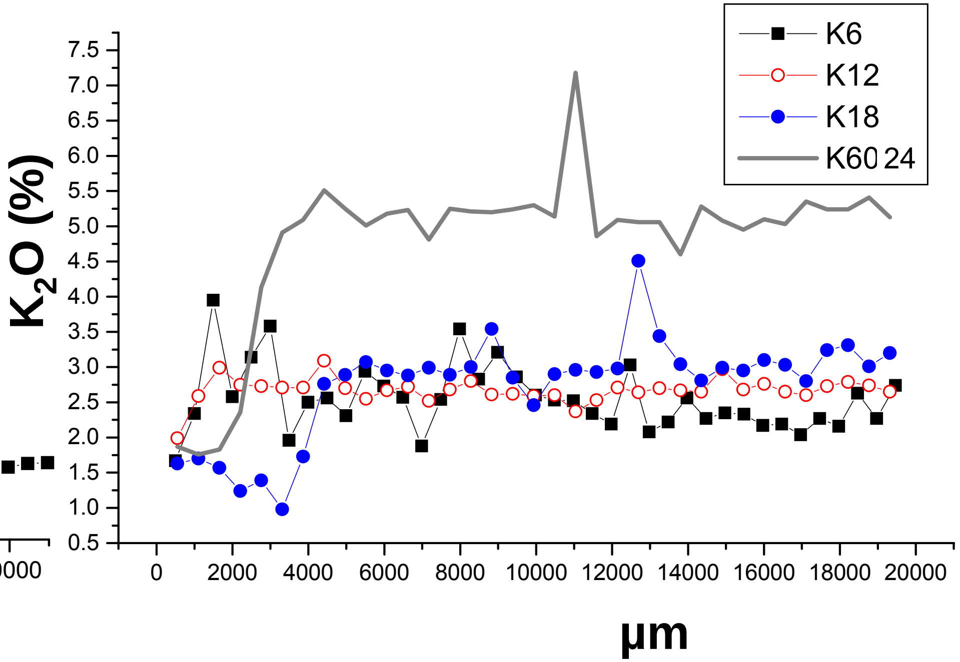
YCW , 60 ºC, 12 months



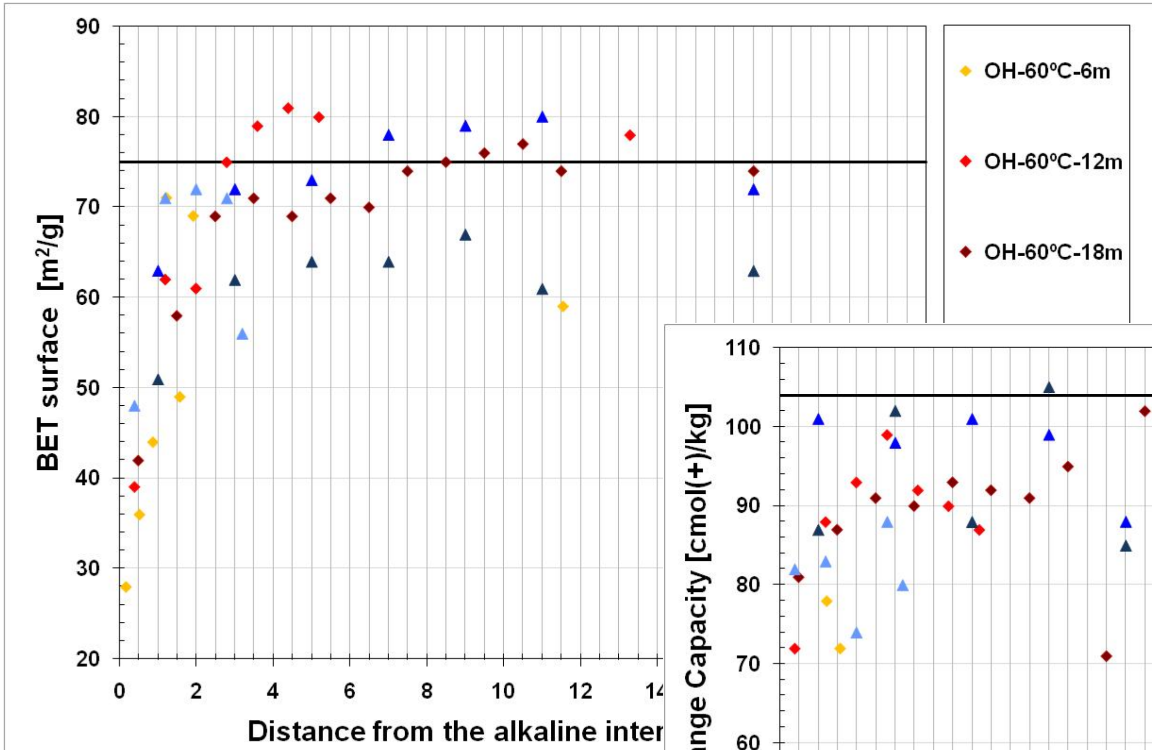


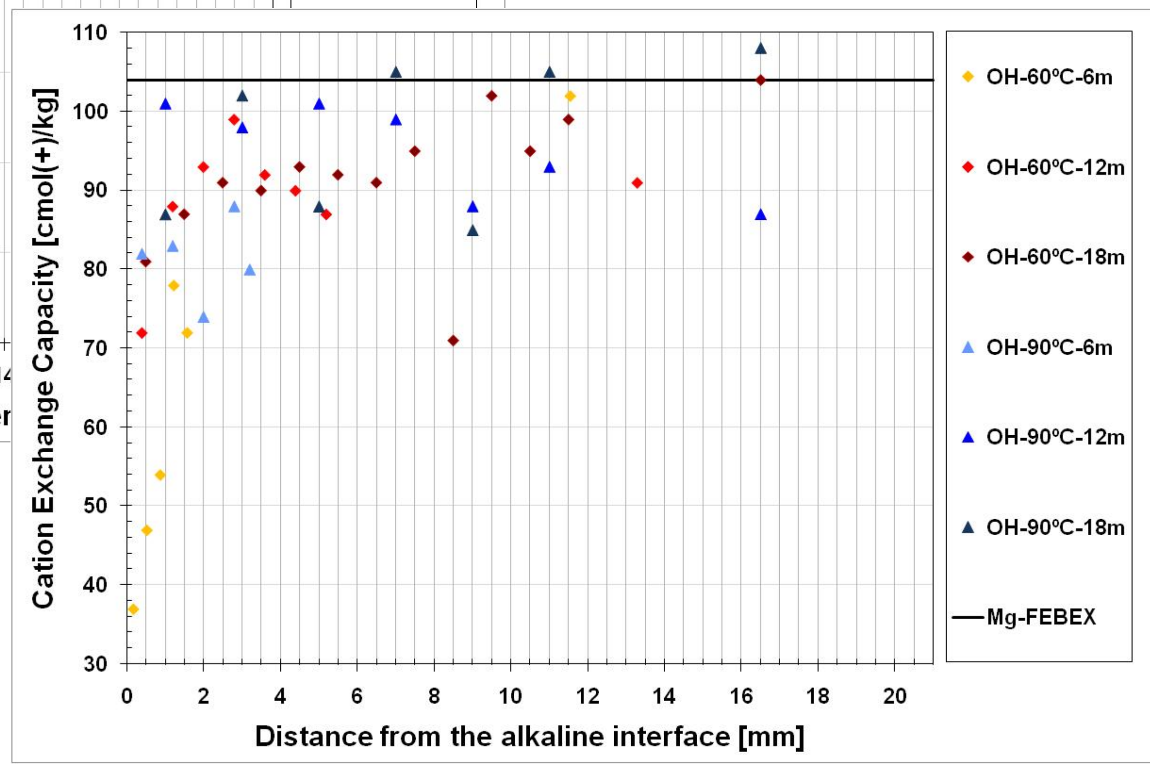
YCW: EDX profiles at 90 ºC



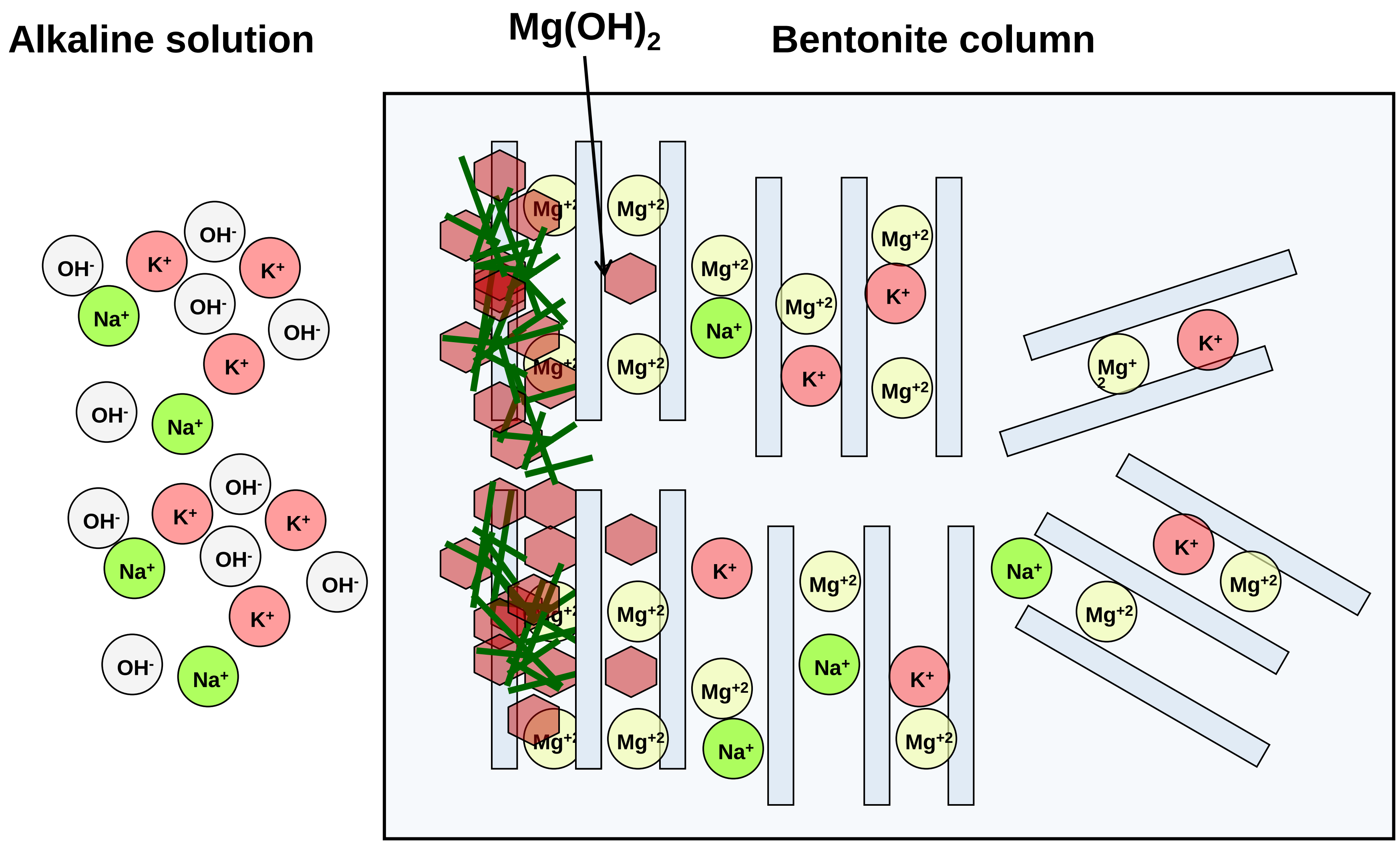


YCW: BET surface and CEC

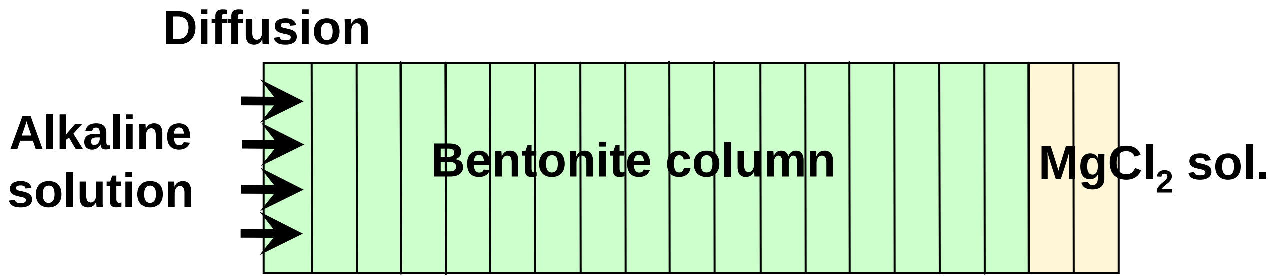




YCW: scheme of reactivity at 60 ºC



Multicomponent diffusion model: CrunchFlow



Secondary aqueous species

H^+, $Al(OH)_2^+$, $AlOH^{+2}$, AlO_2^-, $CaSO_{4(aq)}$, $CaCO_{3(aq)}$, $CaHCO_3^+$, $CaOH^+$, $CaHSiO_3^+$, CO_3^{-2}, $CO_{2(aq)}$, $FeOH^+$, $FeSO_{4(aq)}$, $H_2SiO_4^{-2}$, $HSiO_3^-$, $KCl_{(aq)}$, KSO_4^-, $KOH_{(aq)}$, $MgCl^+$, $MgOH^+$, $MgSO_{4(aq)}$, $MgCO_{3(aq)}$, $MgHCO_3^+$, $NaCl_{(aq)}$, $NaSO_4^-$, $NaHSiO_{3(aq)}$, $NaOH_{(aq)}$, $NaCO_3^-$, $NaHCO_{3(aq)}$

Secondary minerals

- Brucite
- Gibbsite
- Hydrotalcite
- Chlorite
- Saponite-Mg
- Talc
- Phillipsite
- C-S-H (0.8)
- C-S-H (1.2)
- C-S-H (1.6)
- Tobermorite-11Å
- Portlandite
- Ettringite

Primary aqueous species

- OH^-
- Al^{+3}
- Ca^{+2}
- Cl^-
- HCO_3^-
- K^+
- Mg^{+2}
- Na^+
- $SiO_{2(aq)}$
- SO_4^{-2}
- Fe^{+2}
- $O_{2(aq)}$

Primary minerals

- Albite
- Calcite
- Cristobalite-α
- K-Feldspar
- Illite
- Mg-Montmor-FEBEX
- Quartz

Exchangeable cations

Mg-Montmor-FEBEX $\rightleftharpoons$ Mg^{+2}, Ca^{+2}, K^+, Na^+

Fluid-Mineral Reaction Rate Laws

$$r_m = A_m k_m(T)\left(\prod_{i=1}^{N_c+N_x} a_i^n\right)\left[1-\left(\frac{Q_m}{K_m}\right)\right]$$

- n: experimentally determined number
- saturation state
- species conc. affecting rate (e.g. pH)
- reactive surface area of mineral
- rate constant

temperature dependence

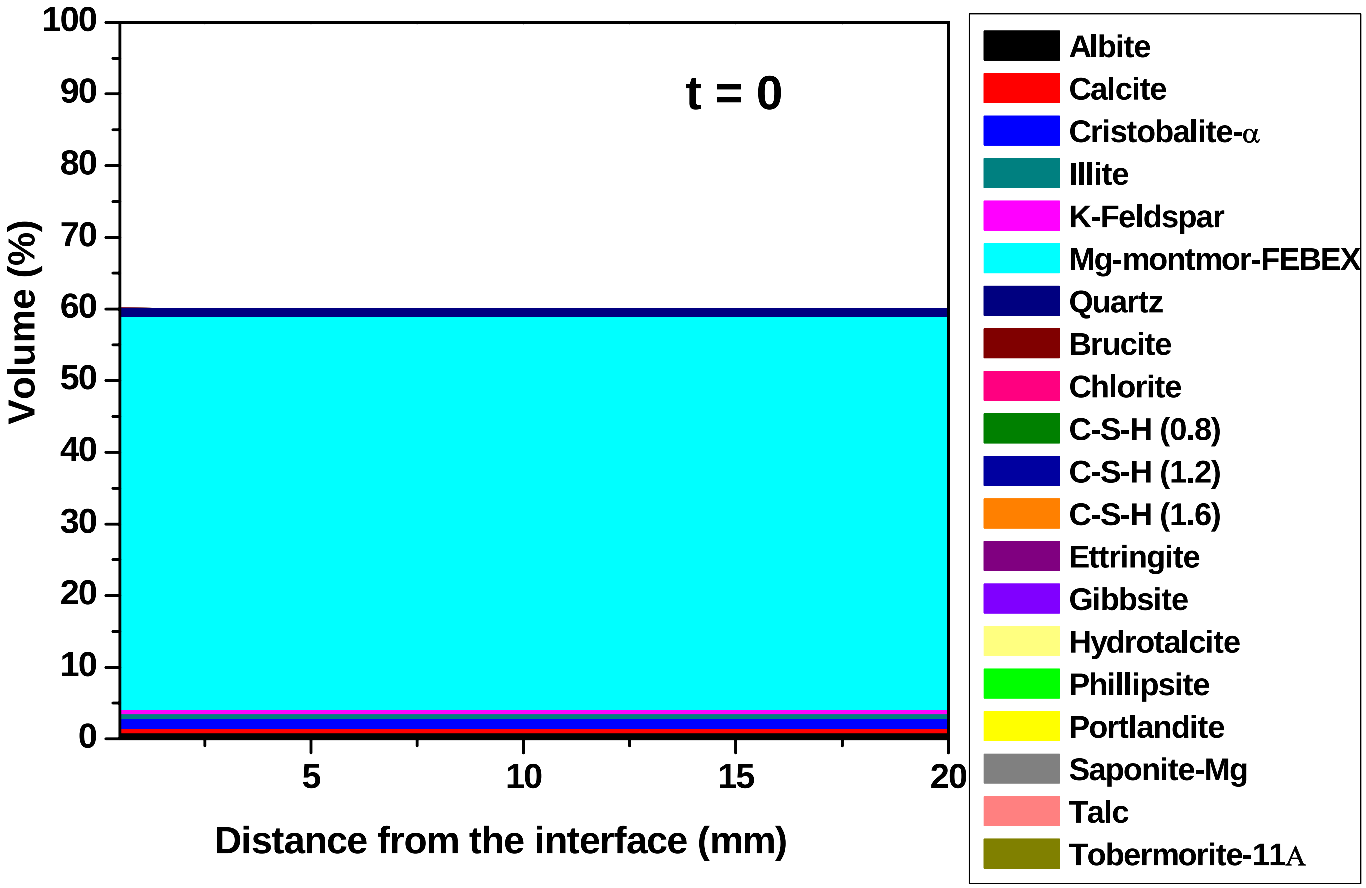
$$k = k_{25}\exp\left[\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right]$$

Diffusion (1st Fick law):

$$J = -D\left(\frac{\partial x}{\partial C}\right); \quad D = D_{25}e^{\left(E_a/RT\right)}$$

Model: YCW 60 ºC

Mineralogy - porosity



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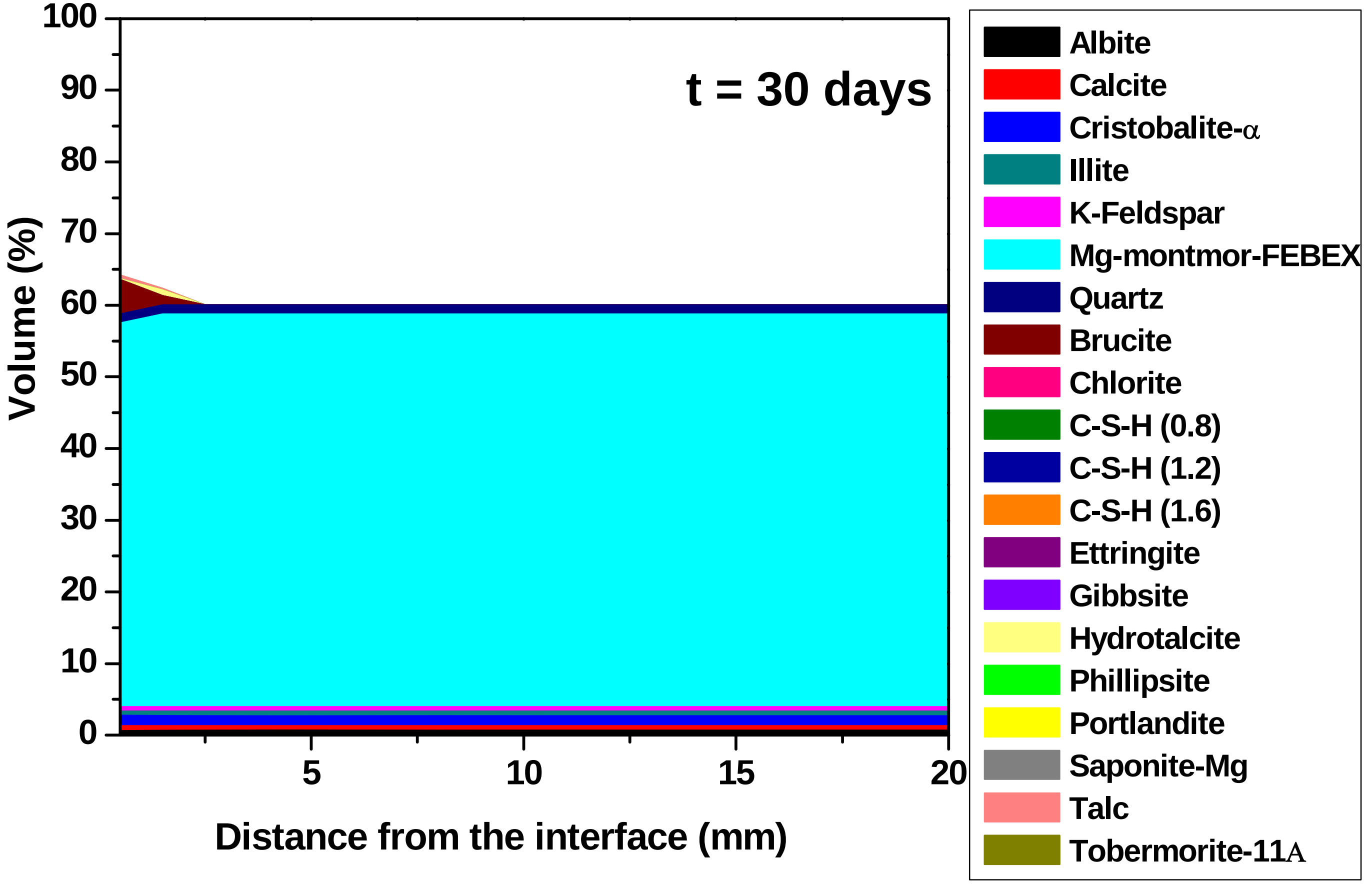
Mineralogy - porosity



Model: YCW 60 ºC

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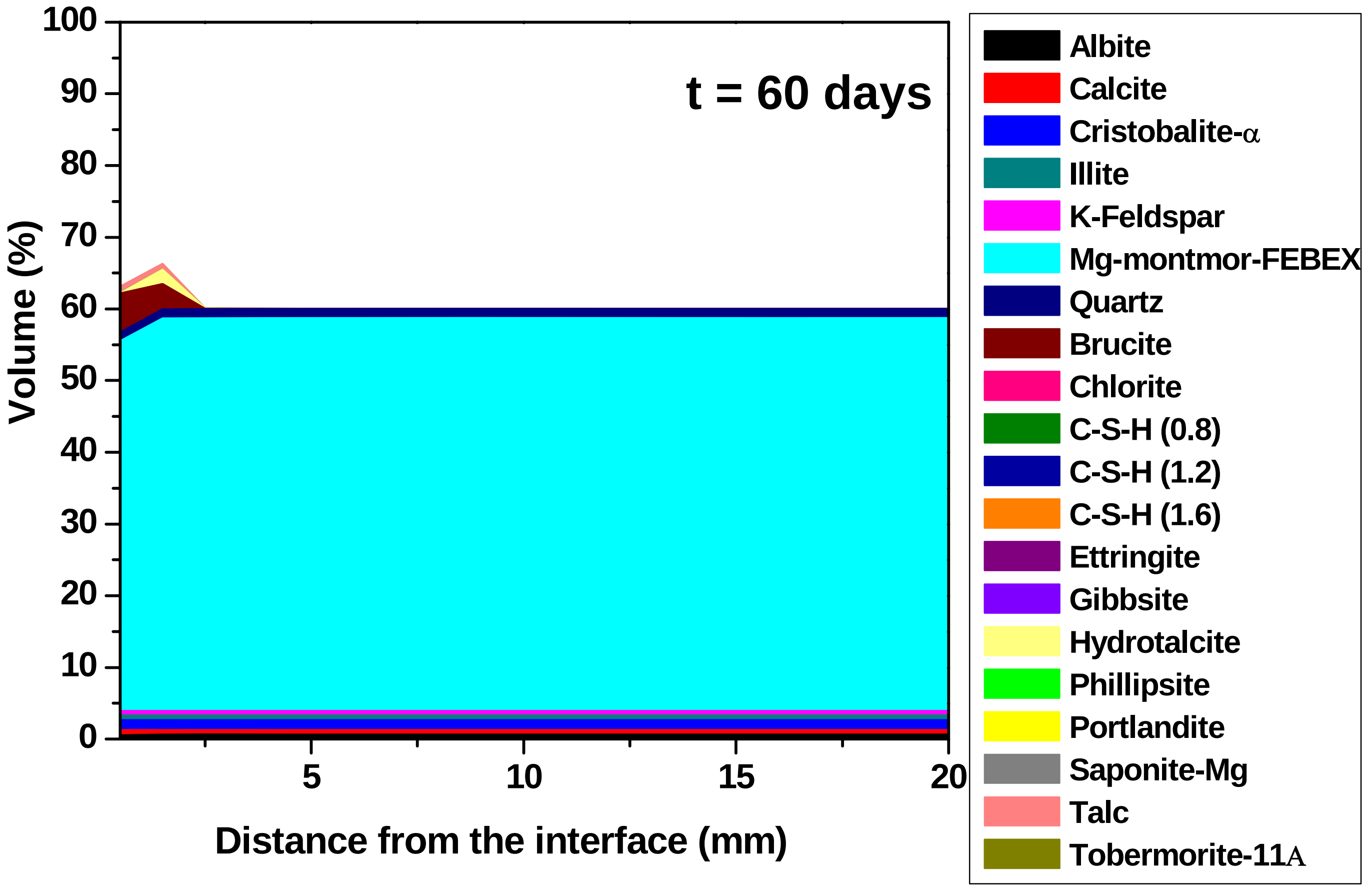
Mineralogy - porosity



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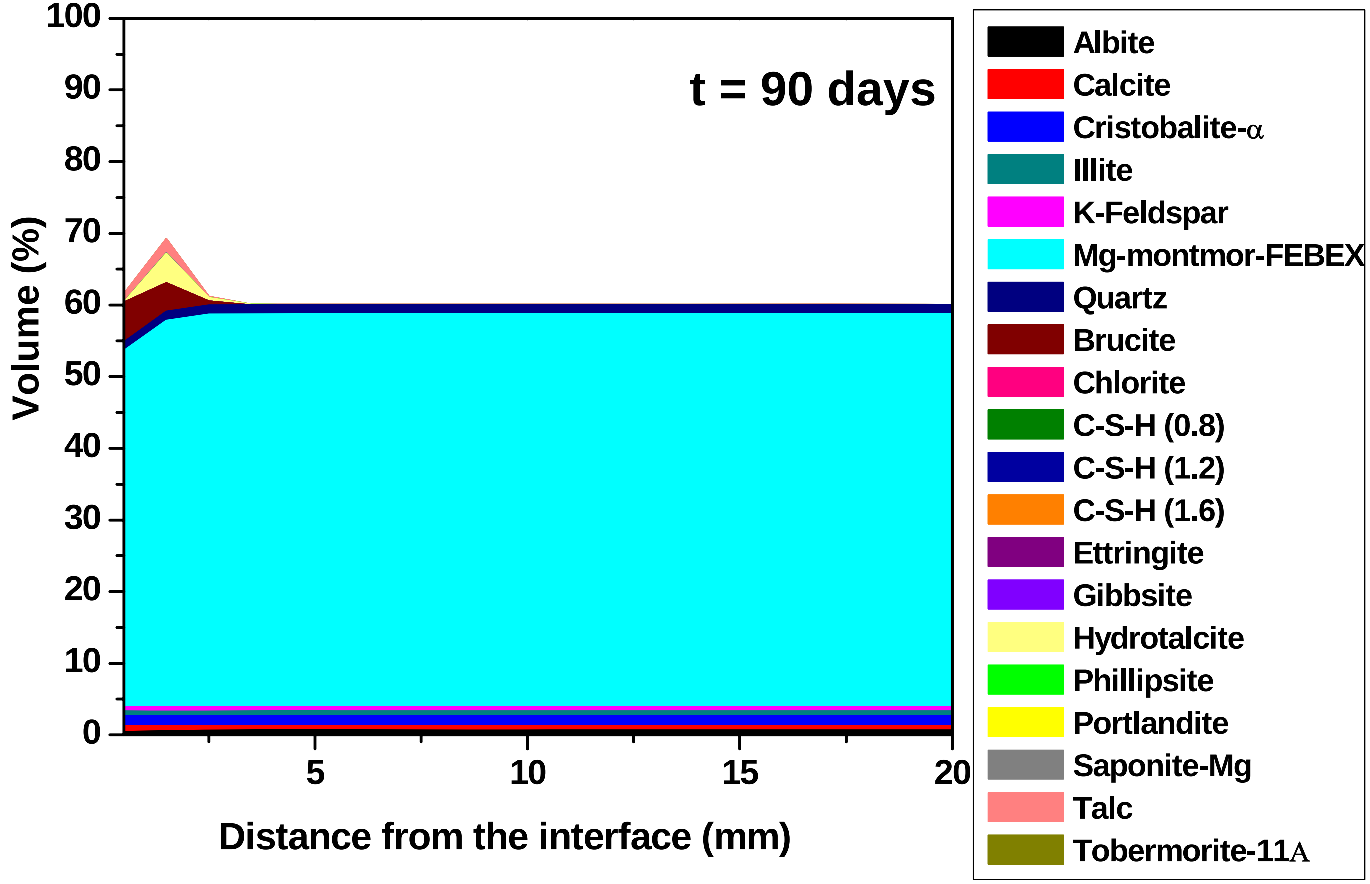
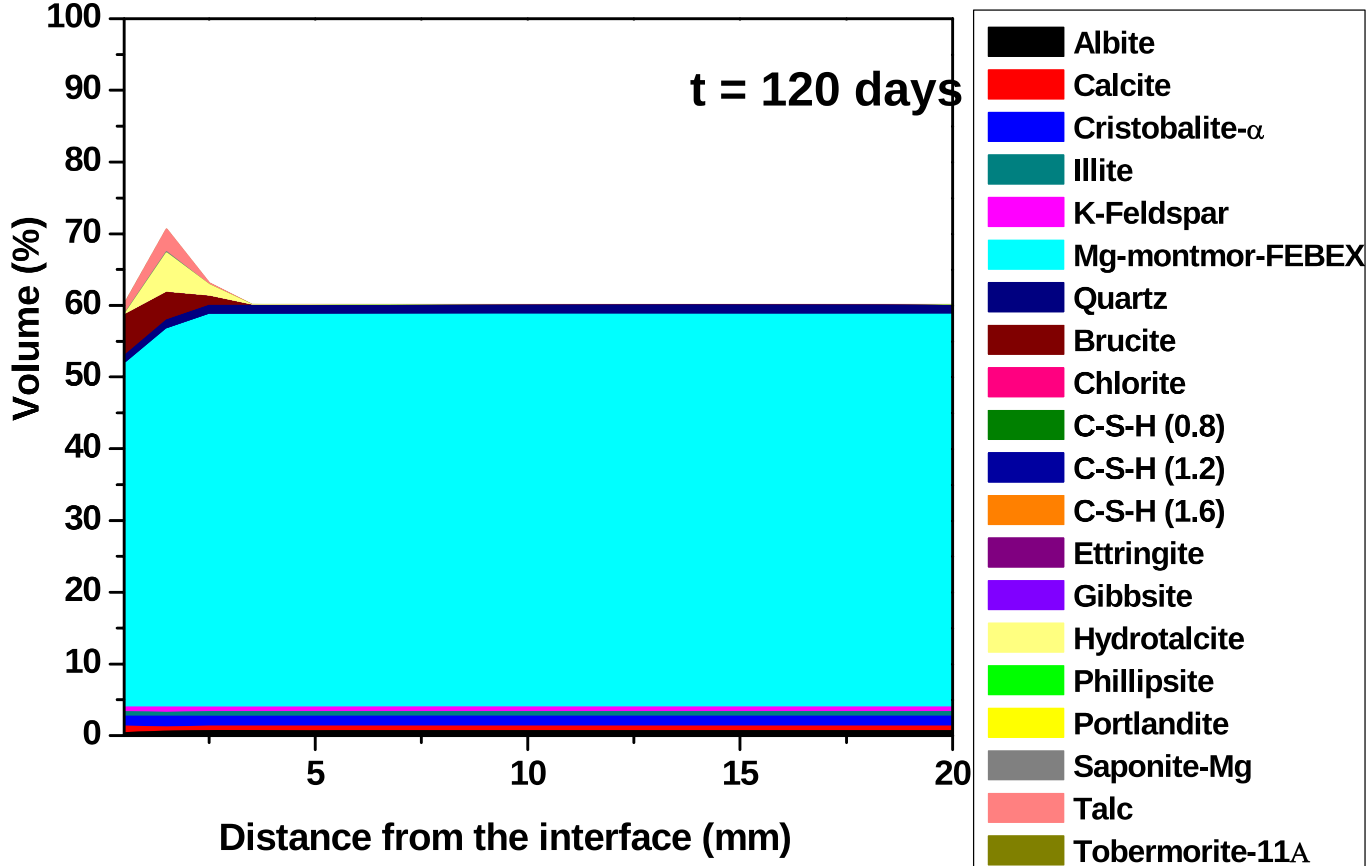
Mineralogy - porosity



Model: YCW 60 ºC

Mineralogy - porosity



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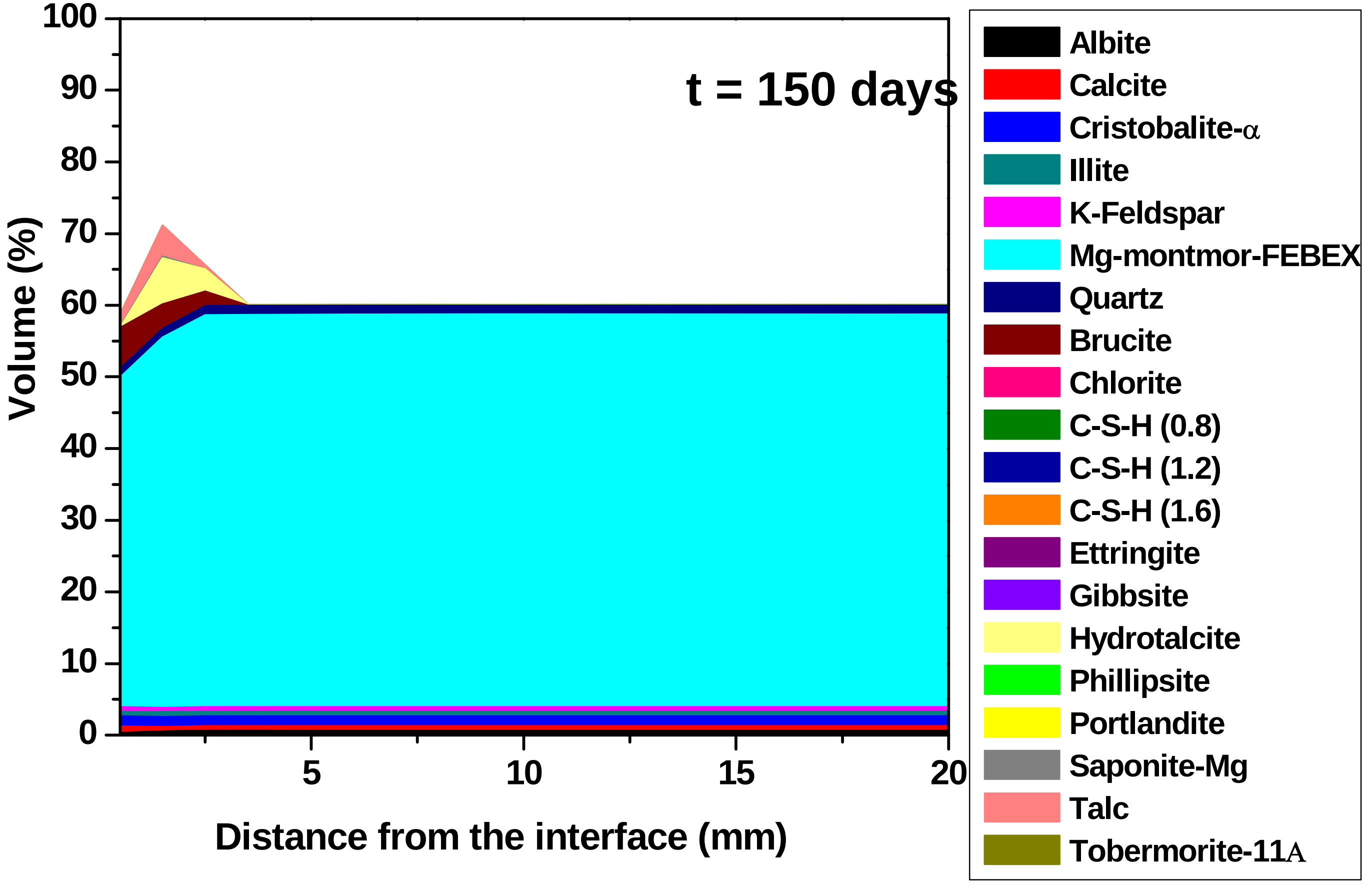
Mineralogy - porosity



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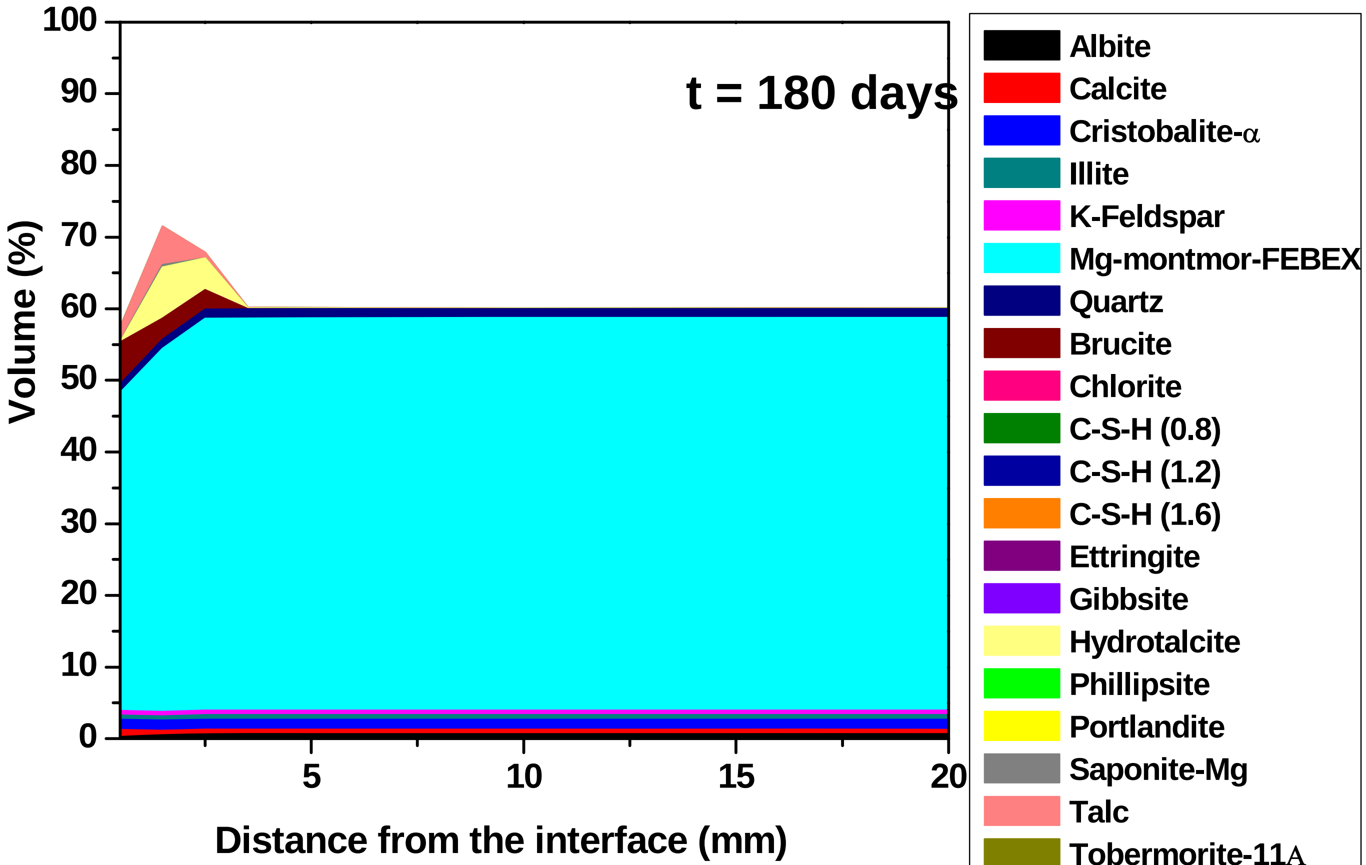
Mineralogy - porosity



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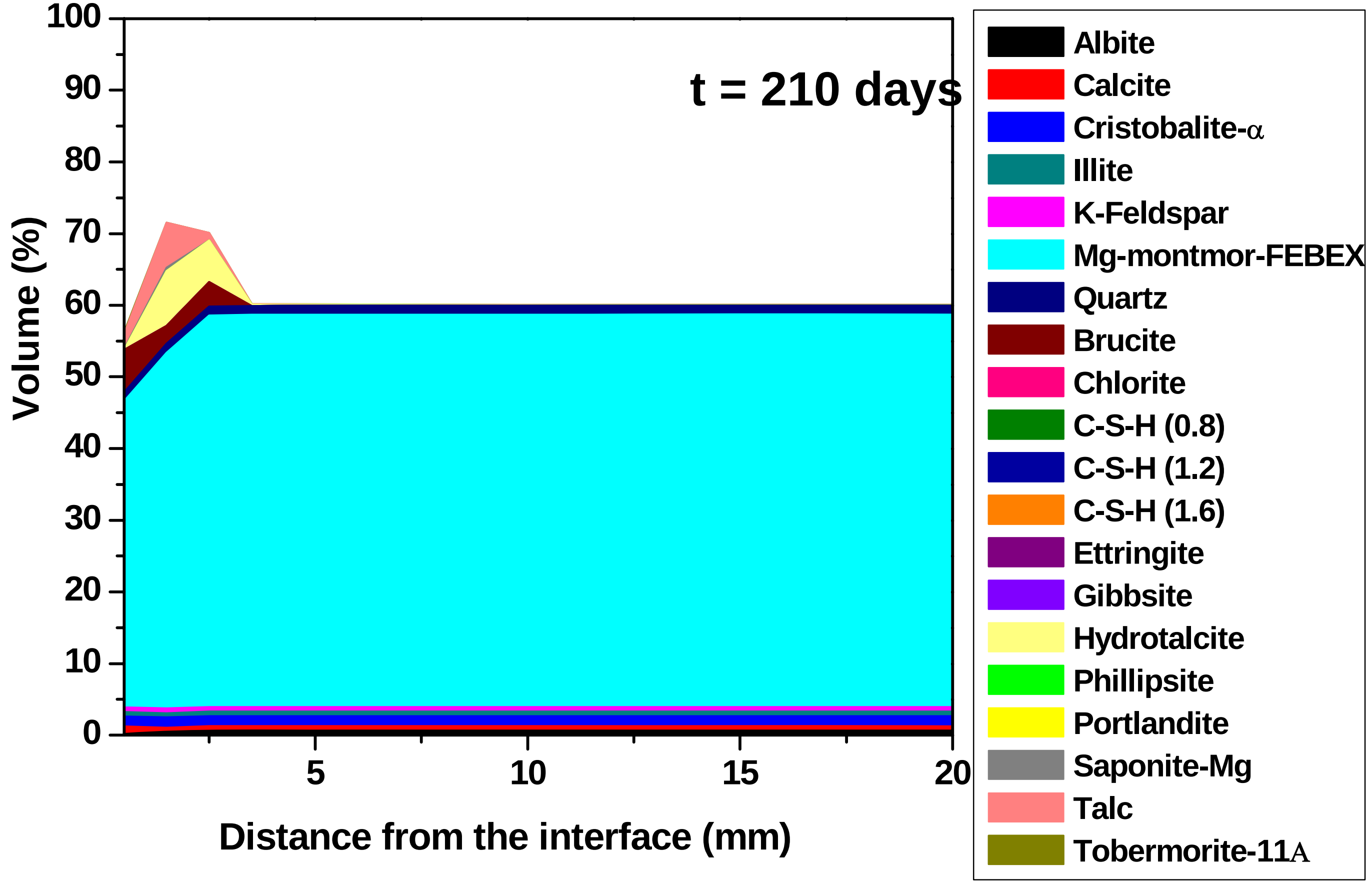

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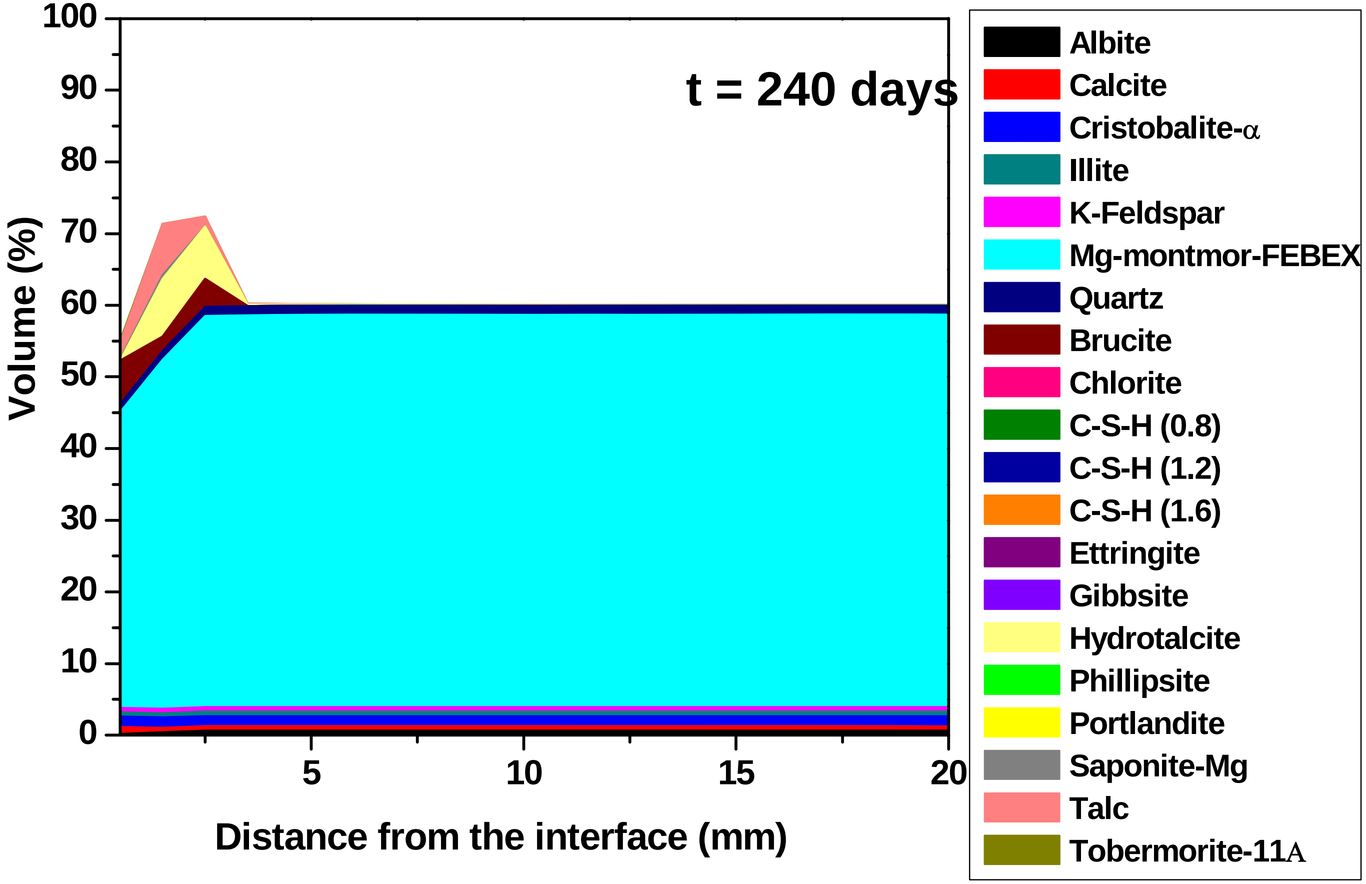

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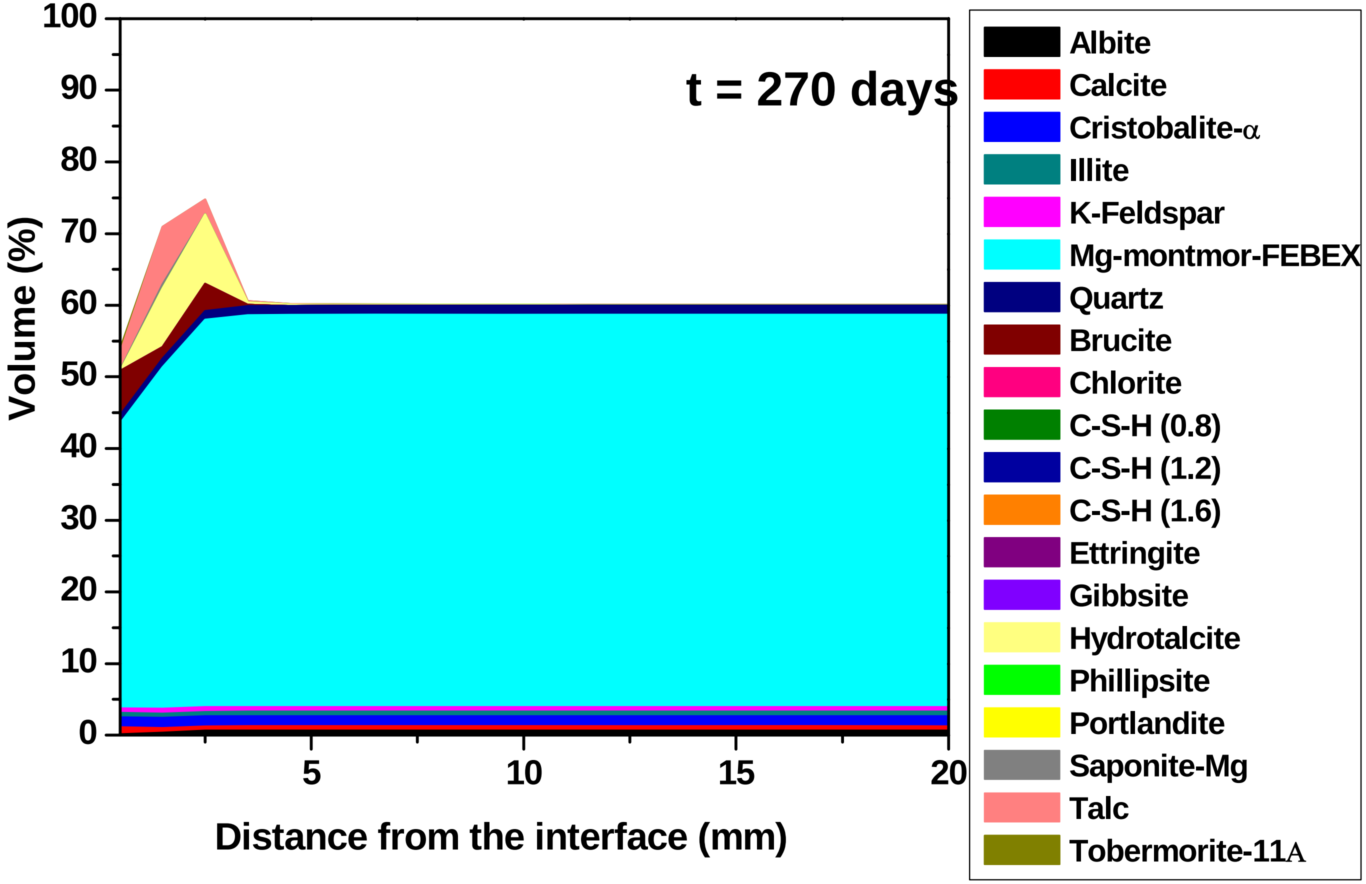

Model: YCW 60 ºC

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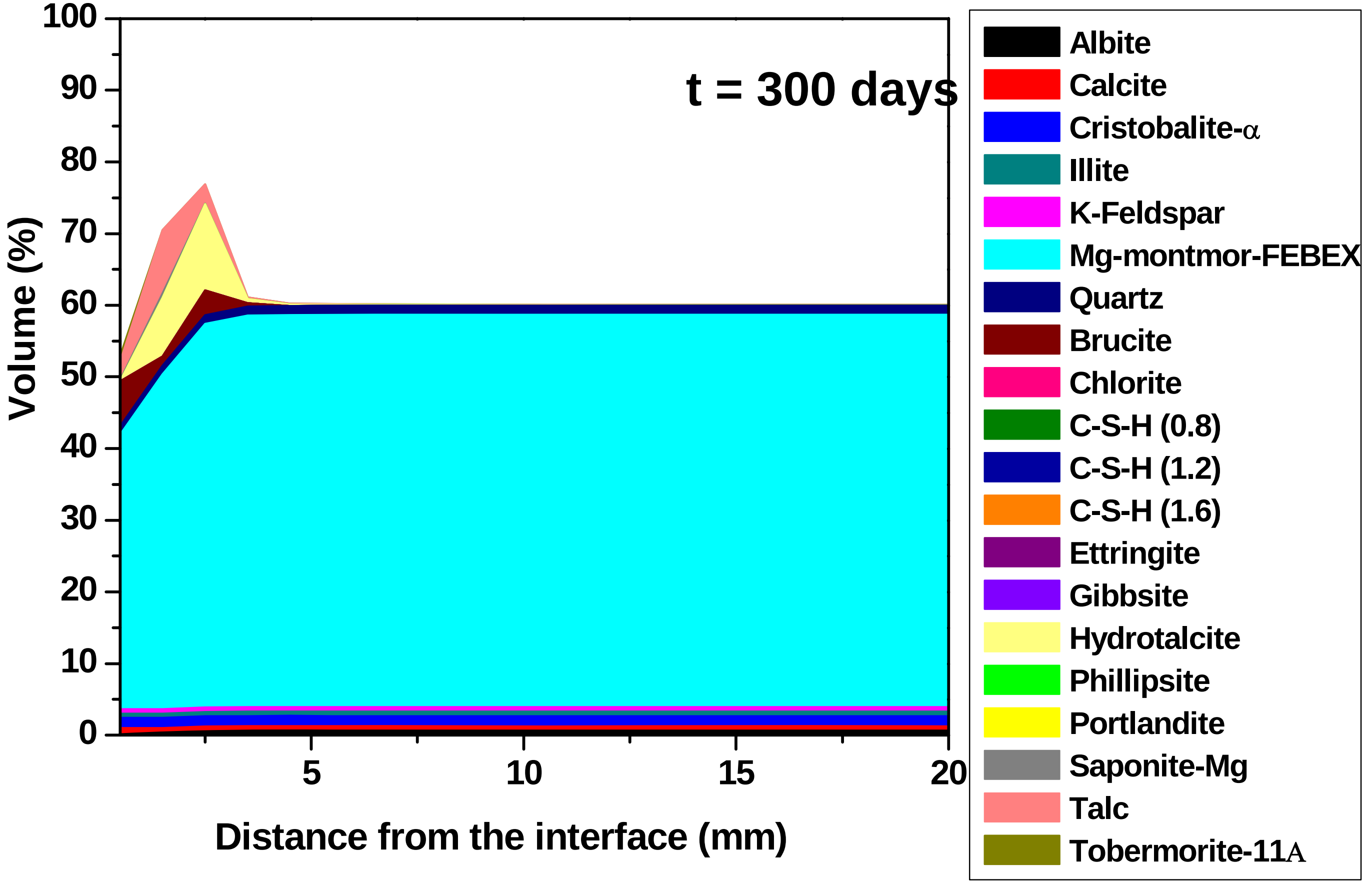
Mineralogy - porosity



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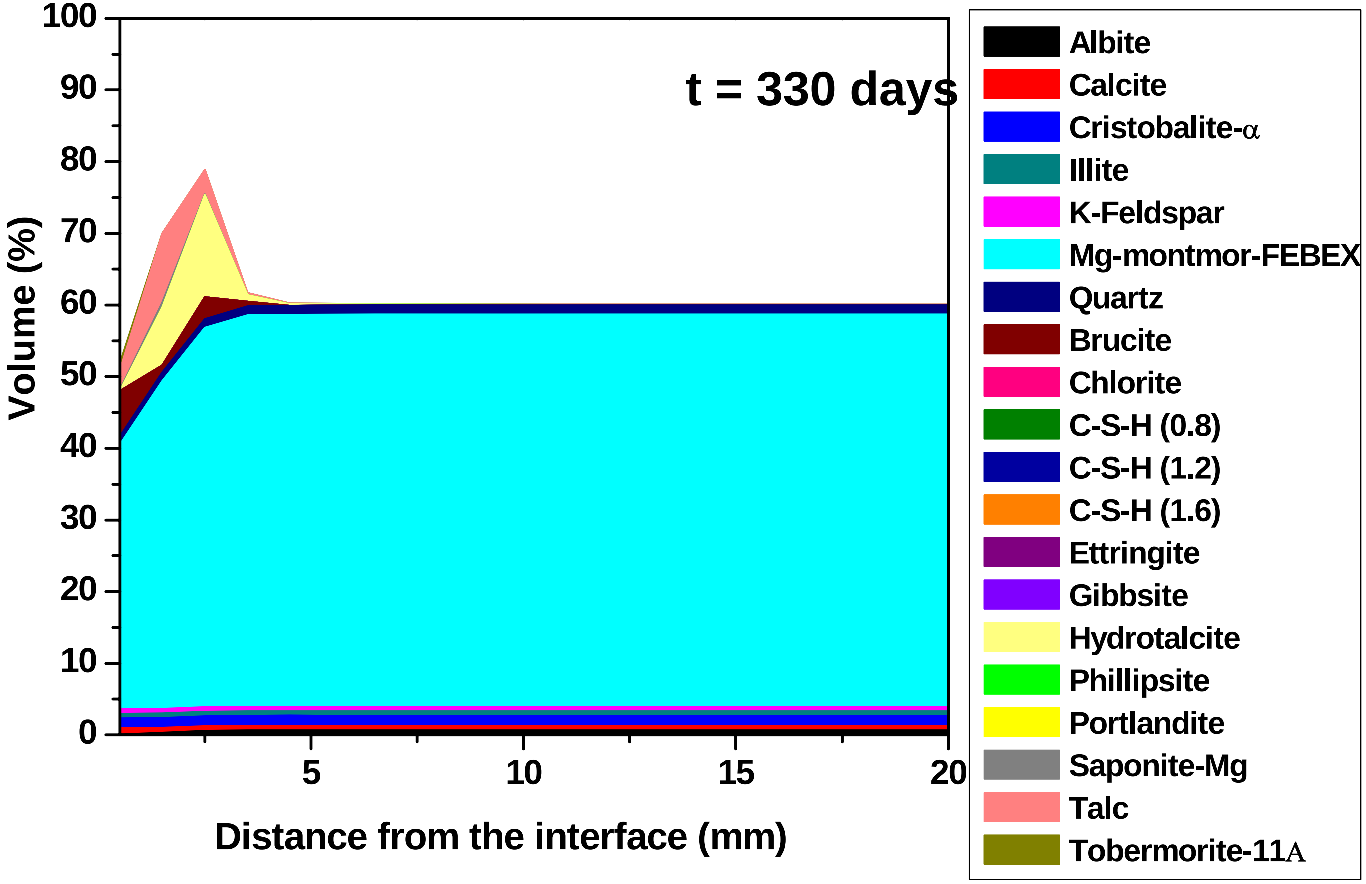
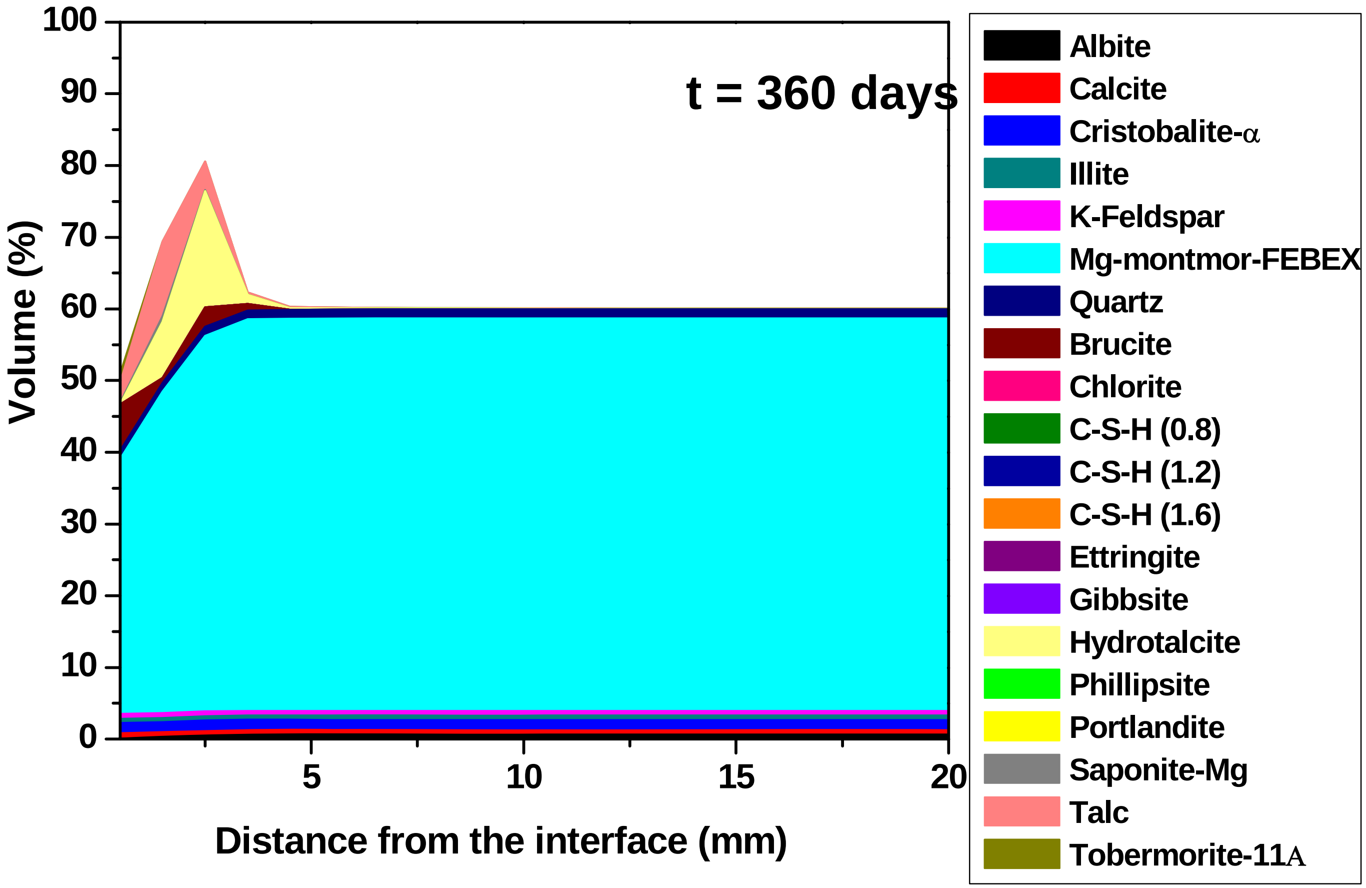
Mineralogy - porosity



Model: YCW 60 ºC

Mineralogy - porosity



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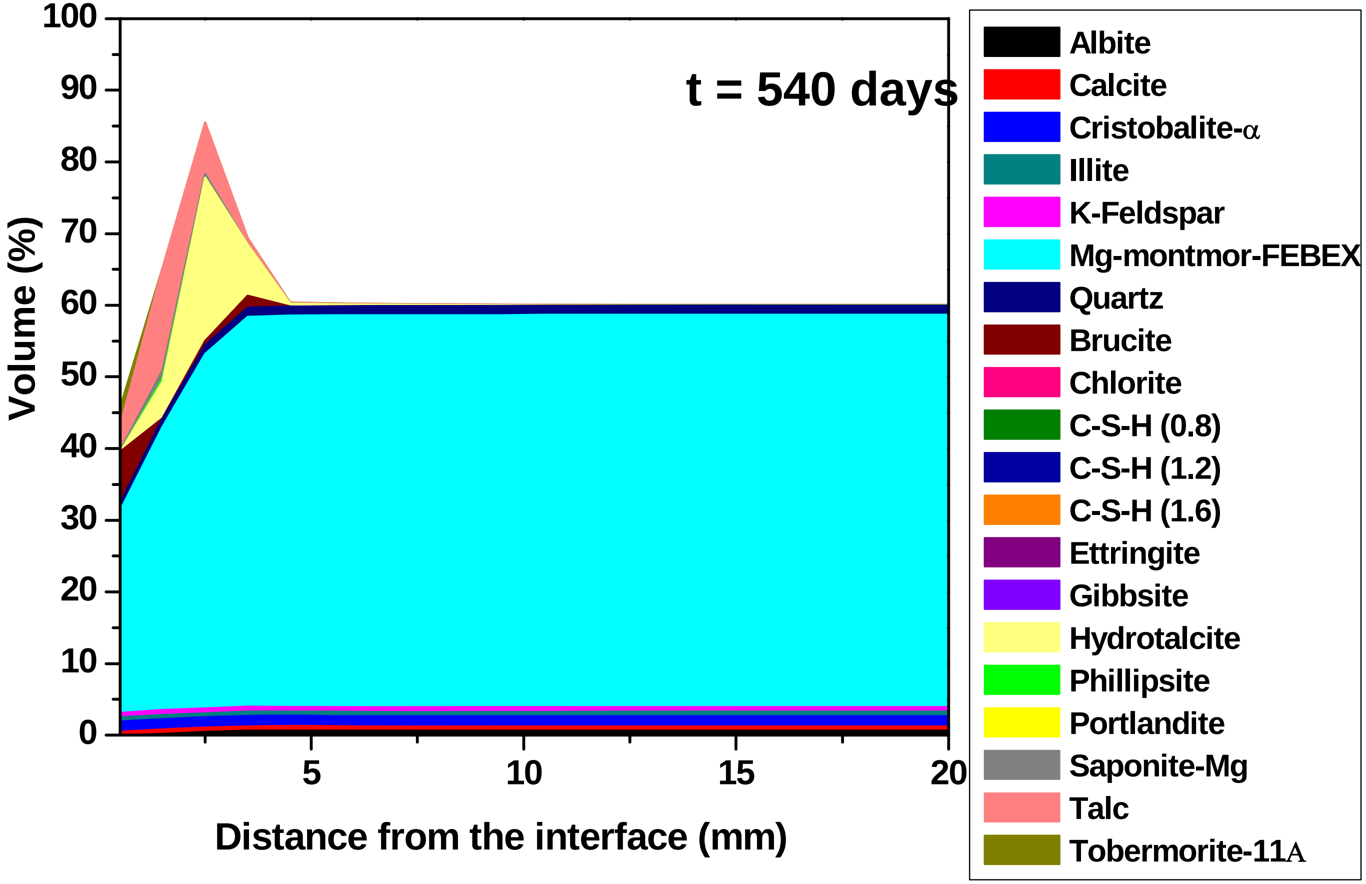
Mineralogy - porosity



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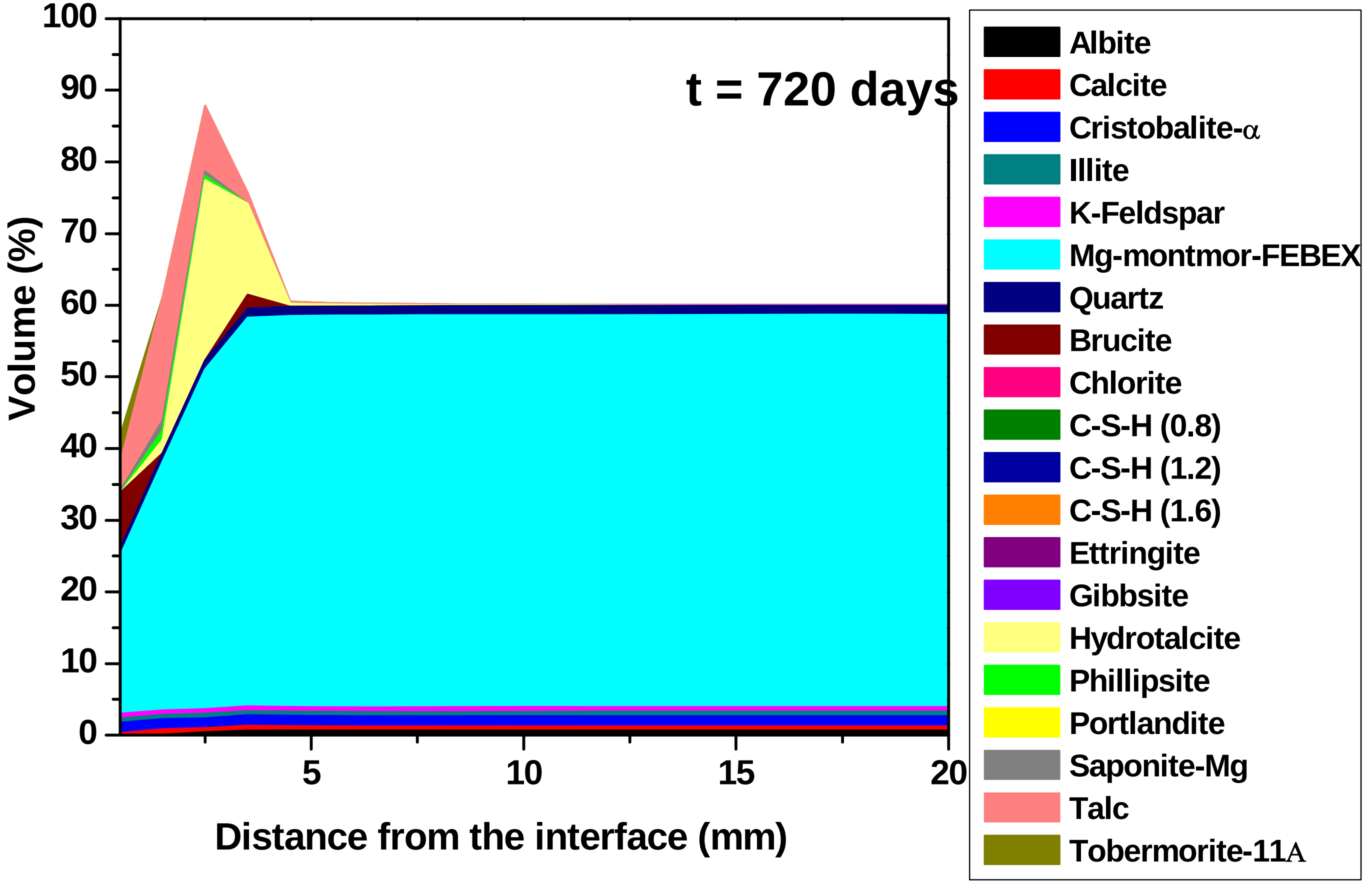

Model: YCW 60 ºC

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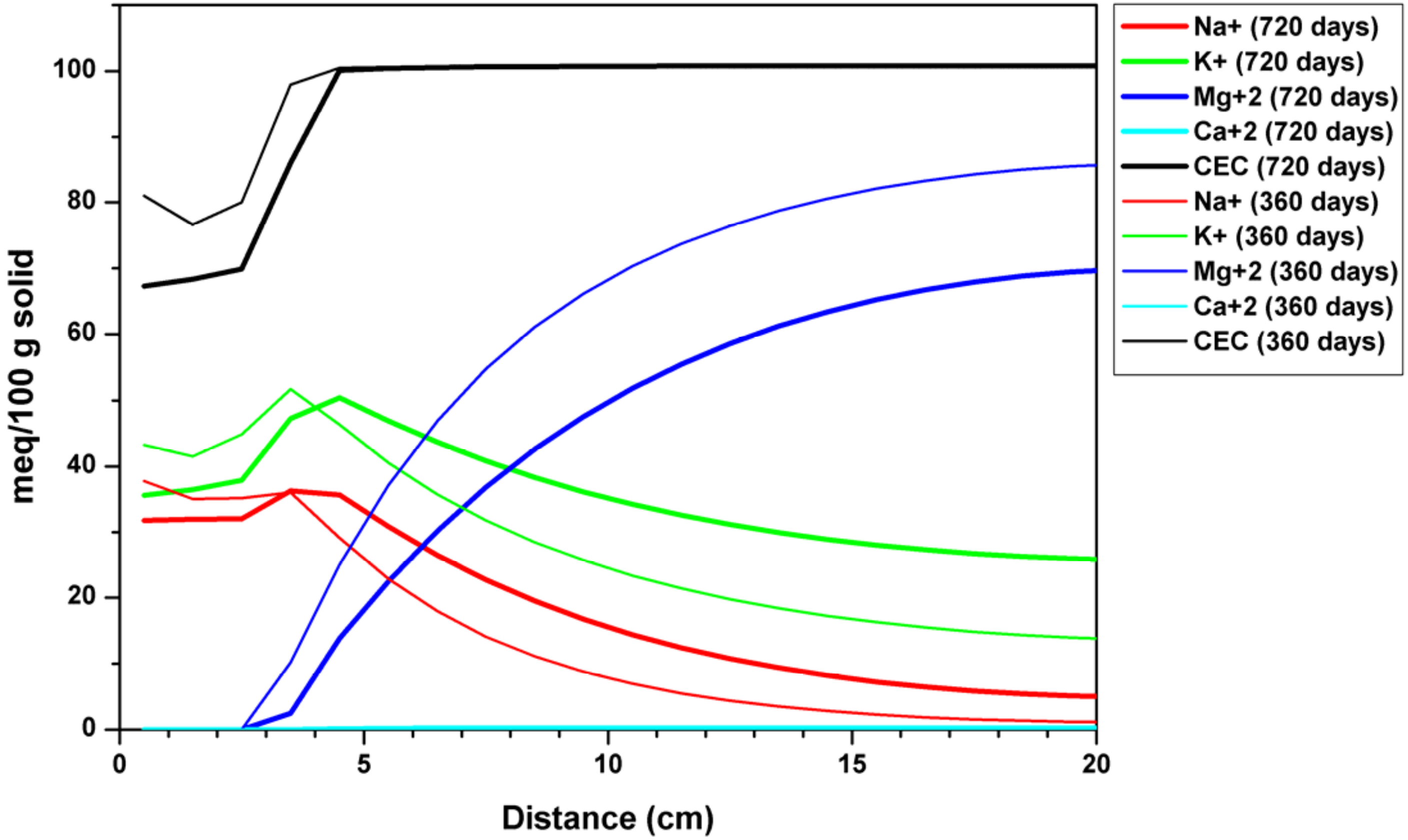
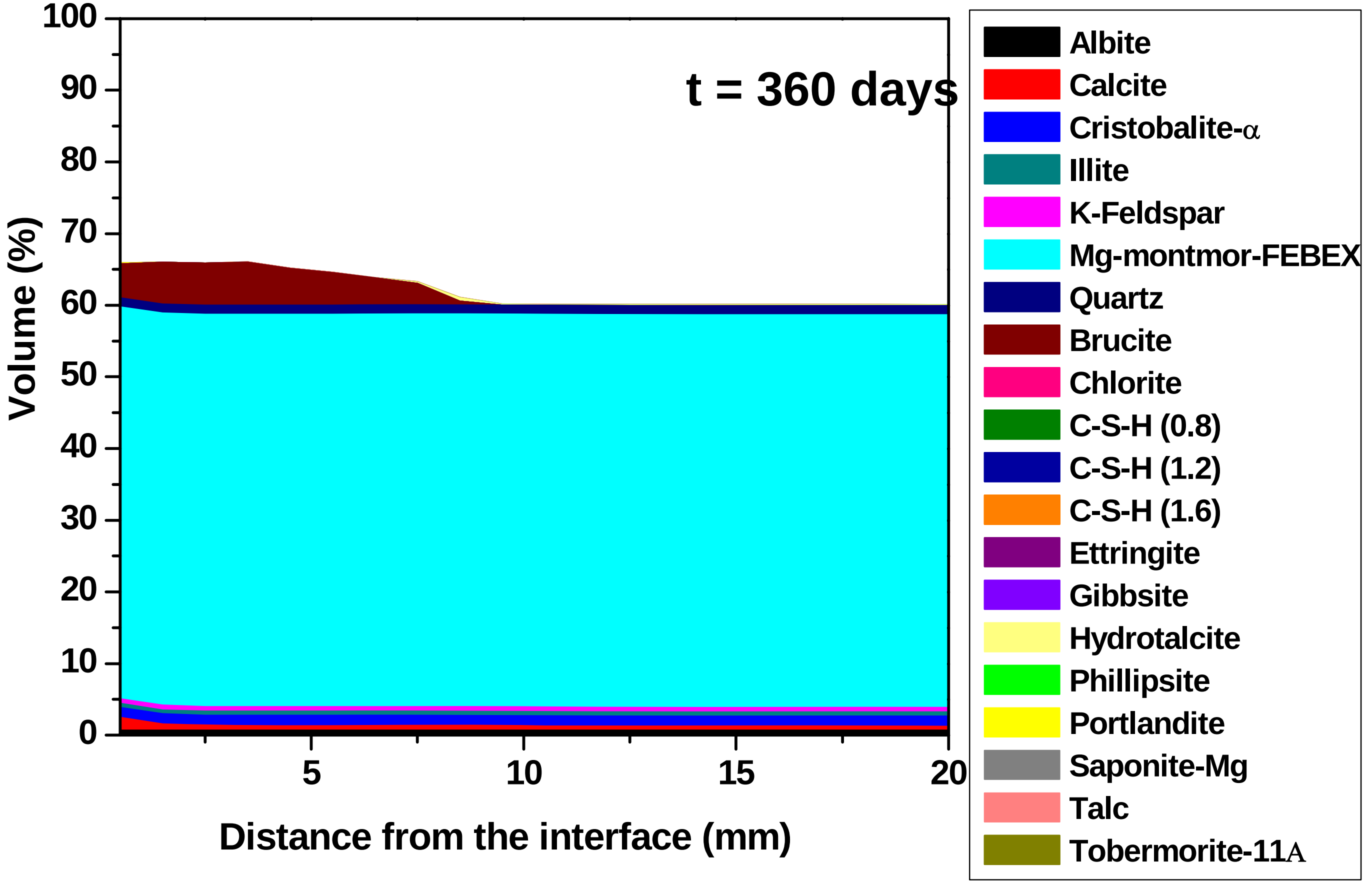
Cation exchange distribution

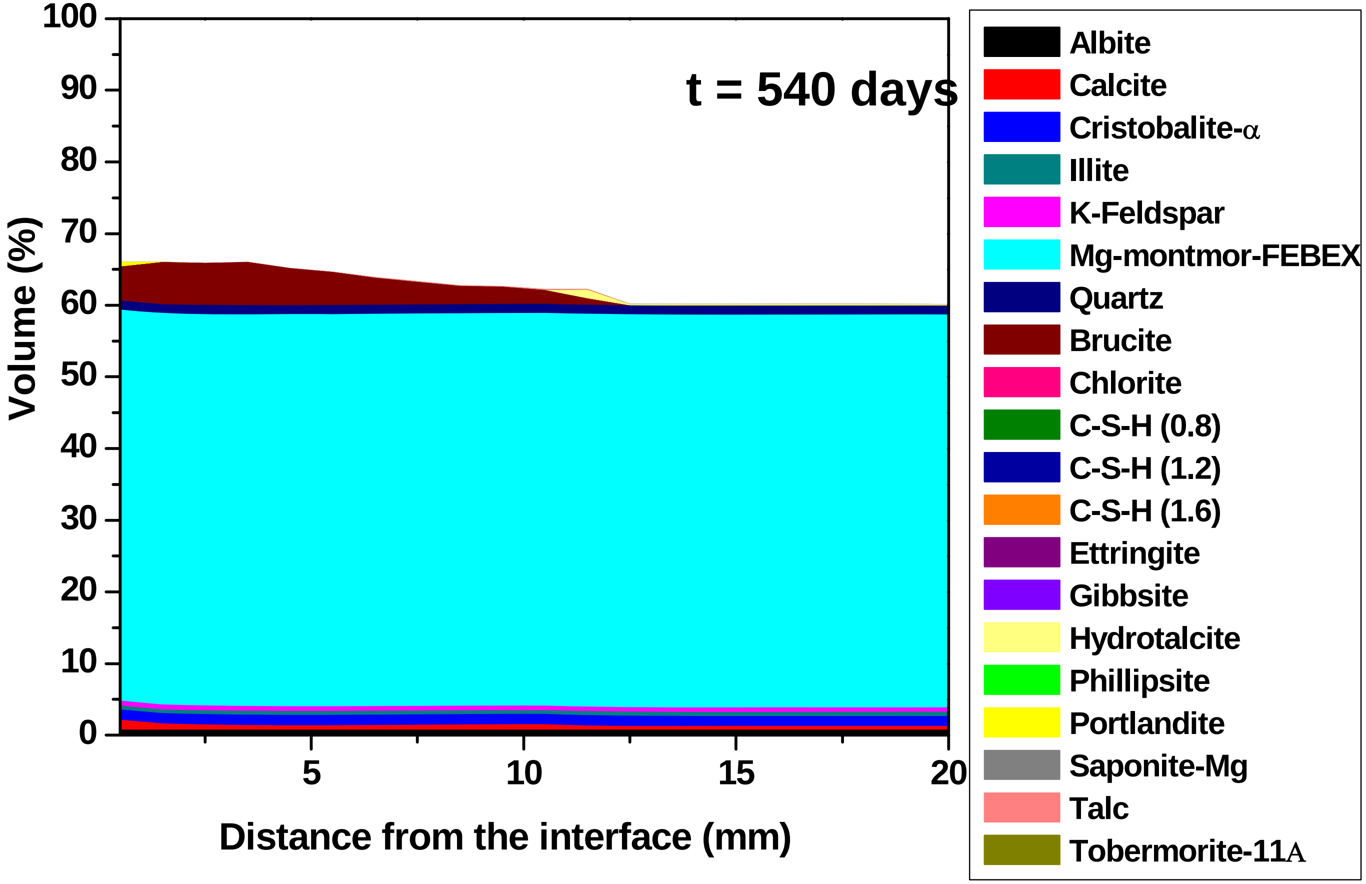


Mineralogy - porosity



Model: YCW 90 ºC

Mineralogy - porosity



Model: YCW 90 ºC

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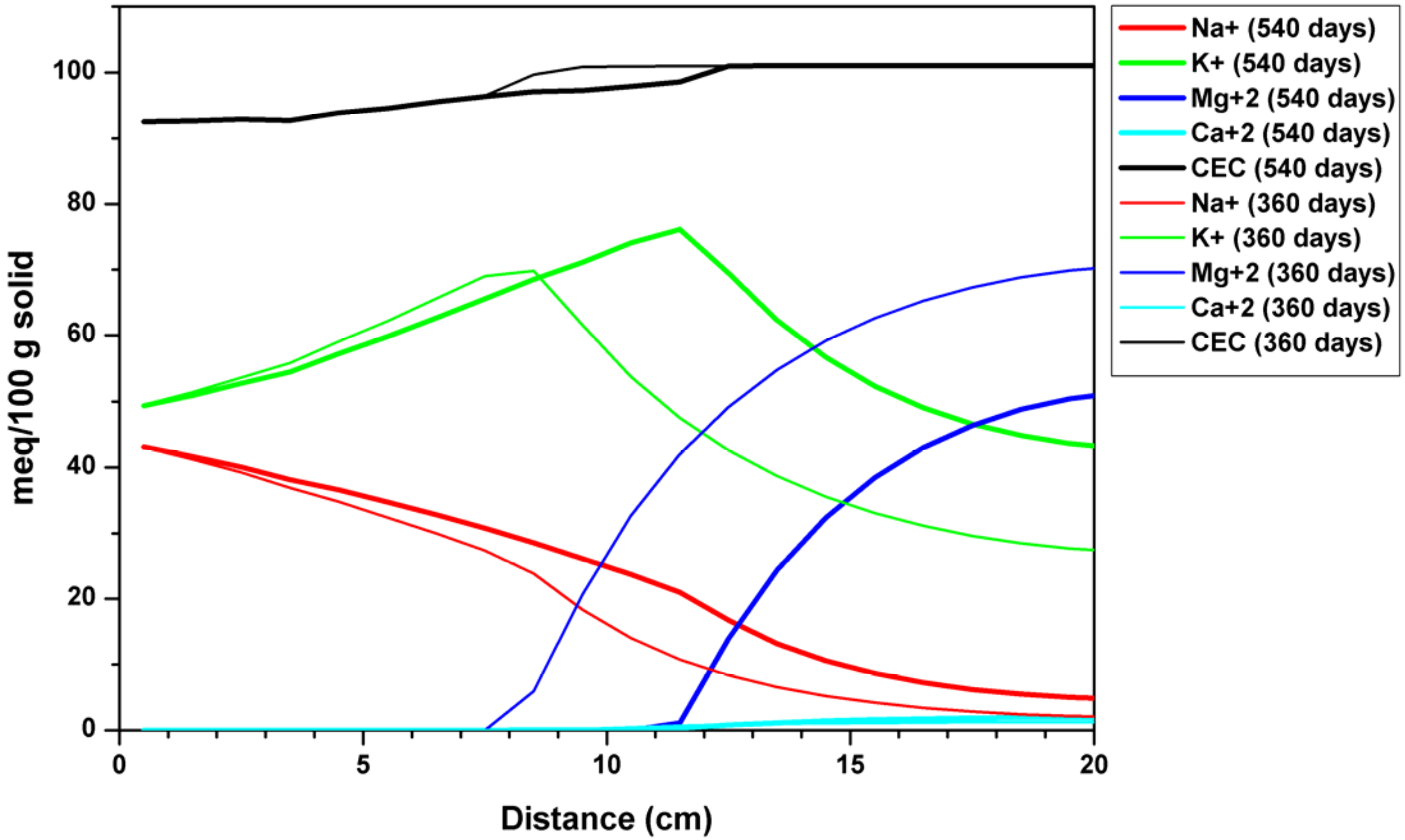
Cation exchange distribution



Model: ECW [$Ca(OH)_2$] 60 ºC

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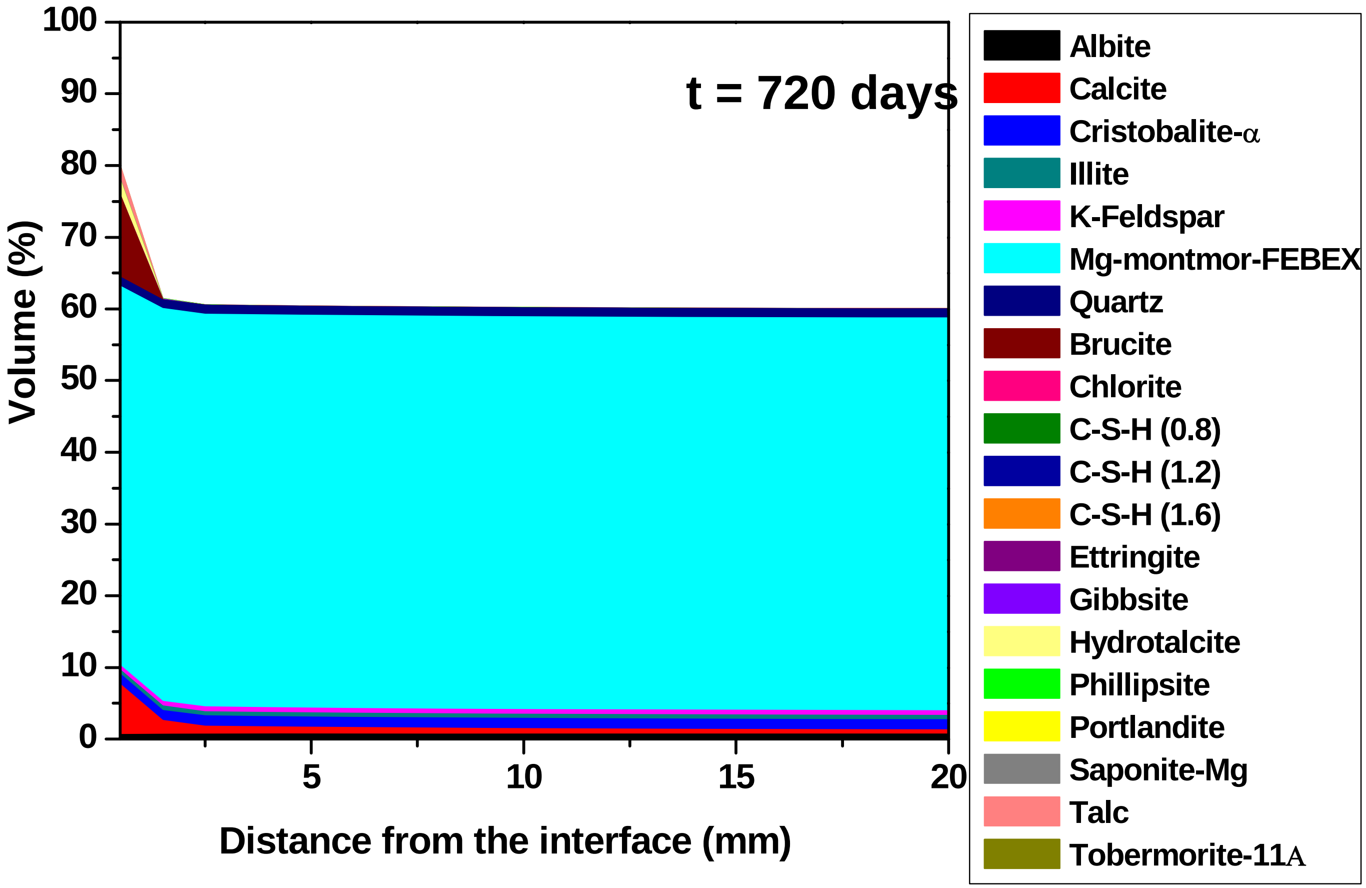
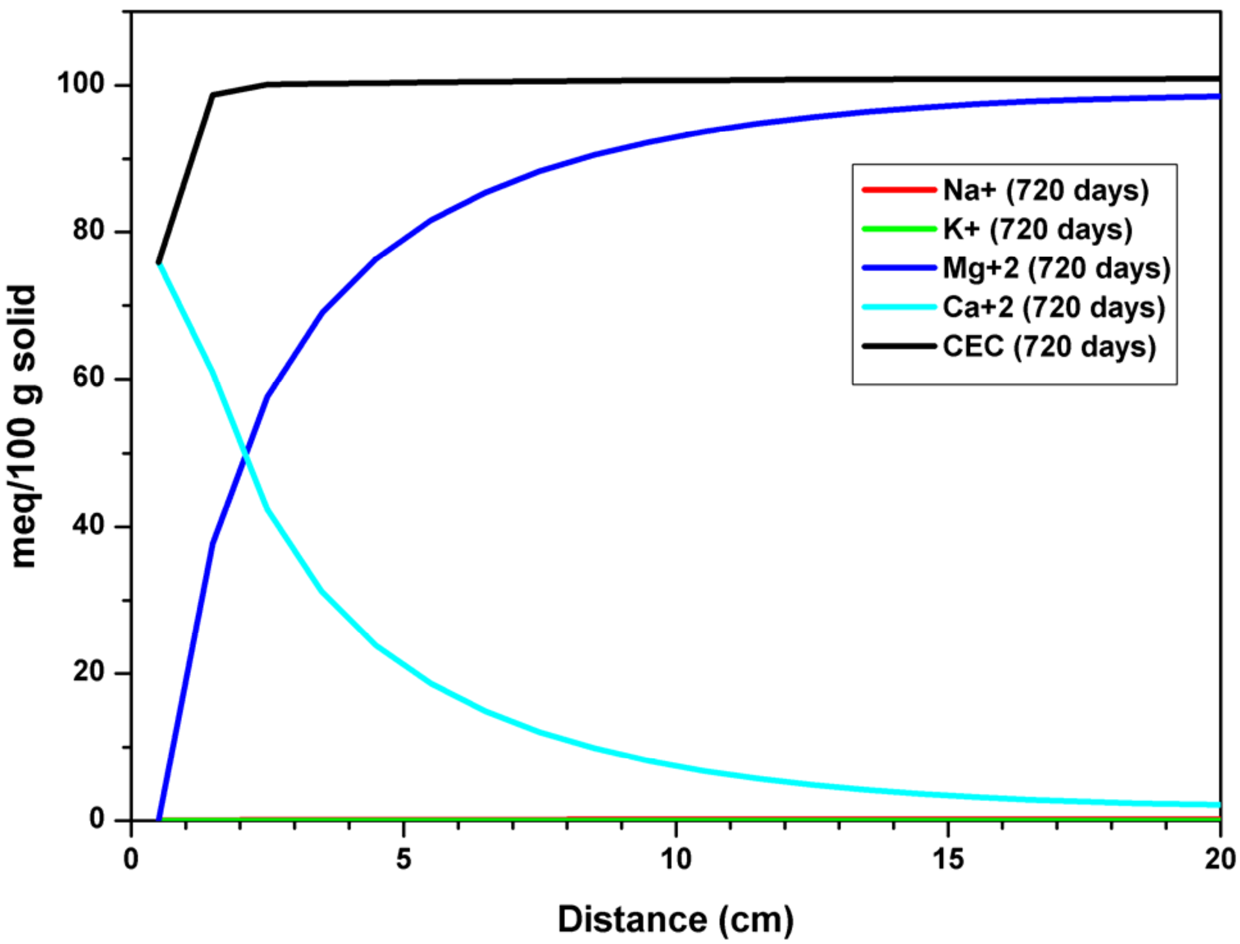
Mineralogy - porosity



Model: ECW 60 ºC

Cation exchange distribution



Conclusions

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- The Mg-saturation was an efficient method to detect the spatial region altered by the alkaline reaction in bentonite

- Dissolution of montmorillonite (and precipitation of secondary minerals) is activated with pH (significantly at pH > 12).

- Quantitave mineralogical transformations are observed in a thickness < 5 mm. Exchange reactions affect the whole column of bentonite.

- The ECW ($Ca(OH)_2$ solution) produce minor mineralogical changes but still have influence on the cation exchange distribution.

- Models confirm mineralogical alteration and cation exchange in the same thickness as in the experiment, however, the complexity of the system cannot be modelled and results need interpretation.