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

R. Fernández¹, U. Mäder² & J. Cuevas³

¹ Instituto de Ciencias de la Construcción Eduardo Torroja
   CSIC, Madrid, Spain
² Rock-Water Interaction group
   Institute of Geological Sciences
   University of Bern, Switzerland
³ Departamento de Geología y Geoquímica
   UAM, Madrid, Spain
Engineered multi-barrier system

- Radioactive Waste
- Steel Canister
- Compacted bentonite
- Concrete
- Host rock (clay)

Concrete - bentonite interface
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 ≤ 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 $90 \, ^\circ C$ (expected temperatures in a repository)
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]

MgCl_2, 1M

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

\[ Mg_{0.32}(Al_{1.545}Mg_{0.425})(Si_{3.86}Al_{0.145})O_{10}(OH)_2 \]
Experimental scheme

- **Synthetic alkaline solution (YCW or ECW)**
- **Compacted Mg-saturated FEBEX bentonite (1.65 g/cm³, dry density)**
- **MgCl₂ 0.6 M recirculation**
- **Teflon filter**

Diagram details:
- **21 mm**
- **Hyper-alkaline solution**
- **MgCl₂ 0.6 M**
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 $[\text{Na}^+, \text{K}^+, \text{Ca}^{+2}, \text{Mg}^{+2}]$

Cation exchange capacity

Mineralogy (XRD)

BET surface

SEM-EDX

S1

S2

S3

S4

S5

YCW: 60 ºC, 6 months

Mg-clay

Brucite
XRD at 60 °C, 6 months (section 1)

(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

K$_2$O (%) vs. µm

MgO (%) vs. µm

60 ºC
YCW: EDX profiles at 90 °C

MgO (%) vs. µm

K2O (%) vs. µm

- Mg6
- Mg12
- Mg18
- K6
- K12
- K18
- K18
- K60 24
YCW: scheme of reactivity at 60 ºC

Alkaline solution

Mg(OH)$_2$

Bentonite column
Multicomponent diffusion model: CrunchFlow

**Primary aquatic species**
- OH⁻
- Al³⁺
- Ca²⁺
- Cl⁻
- HCO₃⁻
- K⁺
- Mg²⁺
- Na⁺
- SiO₂(aq)
- SO₄²⁻
- Fe³⁺
- O₂(aq)

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

**Secondary aquatic species**
- H⁺, Al(OH)_2⁺, AlOH⁺², AlO₂⁻, CaSO₄(aq)
- CaCO₃(aq), CaHCO₃⁺, CaOH⁺, CaHSiO₃⁺, CO₃²⁻, CO₂(aq), FeOH⁺, FeSO₄(aq)
- H₂SiO₄⁻², HSiO₃⁻, KCl(aq), KSO₄⁻, KOH(aq), MgCl⁺, MgOH⁺, MgSO₄(aq), MgCO₃(aq)
- MgHCO₃⁺, NaCl(aq), NaSO₄⁻, NaHSiO₃(aq), NaOH(aq), NaCO₃, NaHCO₃(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

**Exchangeable cations**
- Mg²⁺, Ca²⁺, 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
- Reactive surface area of mineral
- Rate constant
- Species conc. affecting rate (e.g. pH)

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):

\[ J = -D \left( \frac{\partial x}{\partial C} \right); \quad D = D_{25} e^{\left( \frac{E_a}{RT} \right)} \]
Model: YCW 60 °C

Mineralogy - porosity

Distance from the interface (mm)

Volume (%)
Model: YCW 60 °C

Mineralogy - porosity

Distance from the interface (mm)

Volume (%)

Albite
Calcite
Cristobalite-α
Illite
K-Feldspar
Mg-montmor-FEBEX
Quartz
Brucite
Chlorite
C-S-H (0.8)
C-S-H (1.2)
C-S-H (1.6)
Ettringite
Gibbsite
Hydrotalcite
Phillipsite
Portlandite
Saponite-Mg
Talc
Tobermorite-11A

t = 30 days
Mineralogy - porosity

Model: YCW 60 °C

Distance from the interface (mm)

Volume (%) 0 10 20 30 40 50 60 70 80 90 100

Albite
Calcite
Cristobalite-α
Illite
K-Feldspar
Mg-montmor-FEBEX
Quartz
Brucite
Chlorite
C-S-H (0.8)
C-S-H (1.2)
C-S-H (1.6)
Ettringite
Gibbsite
Hydrotalcite
Phillipsite
Portlandite
Saponite-Mg
Talc
Tobermorite-11A

t = 60 days

14/10/2008

Le Croisic
Mineralogy - porosity

$t = 120$ days

- Albite
- Calcite
- Cristobalite-α
- Illite
- K-Feldspar
- Mg-montmor-FEBEX
- Quartz
- Brucite
- Chlorite
- C-S-H (0.8)
- C-S-H (1.2)
- C-S-H (1.6)
- Ettringite
- Gibbsite
- Hydrotalcite
- Phillipsite
- Portlandite
- Saponite-Mg
- Talc
- Tobermorite-11A
Mineralogy - porosity

$t = 150$ days

Distance from the interface (mm)

Volume (%)
Mineralogy - porosity

Distance from the interface (mm)

Volume (%)

- Albite
- Calcite
- Cristobalite-α
- Illite
- K-Feldspar
- Mg-montmor-FEBEX
- Quartz
- Brucite
- Chlorite
- C-S-H (0.8)
- C-S-H (1.2)
- C-S-H (1.6)
- Ettringite
- Gibbsite
- Hydrotalcite
- Phillipsite
- Portlandite
- Saponite-Mg
- Talc
- Tobermorite-11A

$t = 180$ days
Model: YCW 60 ºC

Mineralogy - porosity

Distance from the interface (mm) vs. Volume (%)

- Albite
- Calcite
- Cristobalite-α
- Illite
- K-Feldspar
- Mg-montmor-FEBEX
- Quartz
- Brucite
- Chlorite
- C-S-H (0.8)
- C-S-H (1.2)
- C-S-H (1.6)
- Ettringite
- Gibbsite
- Hydrotalcite
- Phillipsite
- Portlandite
- Saponite-Mg
- Talc
- Tobermanite-11A

t = 210 days
Model: YCW 60 °C

Mineralogy - porosity

t = 240 days

Distance from the interface (mm)

Volume (%)

Albite
Calcite
Cristobalite-α
Illite
K-Feldspar
Mg-montmor-FEBEX
Quartz
Brucite
Chlorite
C-S-H (0.8)
C-S-H (1.2)
C-S-H (1.6)
Ettringite
Gibbsite
Hydrotalcite
Phillipsite
Portlandite
Saponite-Mg
Talc
Tobermorite-11A
Model: YCW 60 °C

Mineralogy - porosity

Distance from the interface (mm)

Volume (%)
Mineralogy - porosity

Model: YCW 60 °C

Distance from the interface (mm)

Volume (%)

Albite
Calcite
Cristobalite-α
Illite
K-Feldspar
Mg-montmor-FEBEX
Quartz
Brucite
Chlorite
C-S-H (0.8)
C-S-H (1.2)
C-S-H (1.6)
Ettringite
Gibbsite
Hydrotalcite
Phillipsite
Portlandite
Saponite-Mg
Talc
Tobermorite-11A

t = 300 days
Model: YCW 60 °C

Mineralogy - porosity

Distance from the interface (mm)

Volume (%)

- Albite
- Calcite
- Cristobalite-α
- Illite
- K-Feldspar
- Mg-montmor-FEBEX
- Quartz
- Brucite
- Chlorite
- C-S-H (0.8)
- C-S-H (1.2)
- C-S-H (1.6)
- Ettringite
- Gibbsite
- Hydrotalcite
- Phillipsite
- Portlandite
- Saponite-Mg
- Talc
- Tobermorite-11A

t = 330 days
Mineralogy - porosity

Distance from the interface (mm)

Volume (%)
Mineralogy - porosity

t = 540 days

Distance from the interface (mm)

Volume (%)
Mineralogy - porosity

$t = 720$ days

Distance from the interface (mm)

Volume (%)
Cation exchange distribution

Model: YCW 60 °C

14/10/2008
Le Croisic
Cation exchange distribution

- Na+ (540 days)
- K+ (540 days)
- Mg+2 (540 days)
- Ca+2 (540 days)
- CEC (540 days)
- Na+ (360 days)
- K+ (360 days)
- Mg+2 (360 days)
- Ca+2 (360 days)
- CEC (360 days)
Mineralogy - porosity

Model: ECW $[\text{Ca(OH)}_2]$ 60 ºC

$t = 720$ days

Distance from the interface (mm)

Volume (%)
Cation exchange distribution

Distance (cm)

meq/100 g solid

0 20 40 60 80 100

0 5 10 15 20

Na+ (720 days)
K+ (720 days)
Mg+2 (720 days)
Ca+2 (720 days)
CEC (720 days)
Conclusions

- 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).

- Quantitative 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.