Chemical, spectroscopic, and *ab initio* modelling approach to interfacial reactivity applied to selenite ion retention by siderite

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Tutoring : M. L. Schlegel, P. Zeller, M. Descostes
The long-term high-level nuclear waste (HLW) storage

Introduction
Outline
Chemistry
XAS
Ab initio
Conclusions
Outlook

Nuclear spent fuel
High activity nuclear glass
High Level Waste
Iron canister
Storage in deep geological formation (Callovo-Oxfordian clay rock)
Evolution of an HLW storage (1)

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≈ 10 years
Aqueous resaturation

≈ 100 years
Canister corrosion

Siderite-containing corrosion layer

1 M.L. Schlegel et al. (2008), Appl. Geochem. 23 (9), 2619-2633
Siderite \((\text{Fe}^{II}\text{CO}_3)\) forms in the corrosion layer

Siderite **often controls redox** in anoxic natural environment

Thermodynamic predominance of aqueous (blue) and solid (yellow) iron species in the Fe-H\(_2\)O-CO\(_2\) system.

**Siderite crystallographic cells**

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Thesis defence – V. Badaut - 5 July, 2010
Evolution of an HLW storage (2)

≈ 10 years
Aqueous resaturation

≈ 100 years
Canister corrosion

≈ 1000 years
Radionuclide lixiviation and migration

Siderite-containing corrosion layer

79Se among other radionuclides
79Se is a long life radionuclide ($T_{1/2} \approx 10^5$ years) and should be lixiviated as selenite ($\text{SeO}_3^{2-}$).

Selenium: an important contributor to the potential radiotoxicity

Modelling of radionuclide migration through clay

- Soluble (mobile) as selenite ($\text{SeO}_3^{2-}$) and selenate ($\text{SeO}_4^{2-}$)
- Se(0,-II) forms sparingly soluble solid phases

Modelling did not take into account the canister corrosion layer
Possible selenium species in equilibrium with siderite:

From a thermodynamic point of view, selenite is unstable and should reduce as Se$^0$ or Fe$_x$Se$_y$. 

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**Objectives:**
- investigate siderite retention mechanism of selenite ion
- foresee long term behaviour

**Methods:**
1. Controlled environment chemistry of selenite retention by siderite
2. Spectroscopy (X-ray absorption spectroscopy)
3. Atomistic modelling (Density Functional Theory)  \[\text{Molecular scale}\]
Preparation of synthetic siderite suspensions

**Why synthetic siderite?**
- Siderite oxidation products (goethite, ferrihydrite) could compete with siderite for selenite retention
- Natural siderite sample rarely pure (Mg, Mn…)

Siderite synthesis in reducing glovebox
\[(H_2/CO_2/N_2 \ 5:10:8)\]

Precipitation from oversaturated solution
\[(0.3 \ M \ FeCl_2, \ 0.8 \ M \ NaHCO_3, \ 48 \ h)\]

**Crystalline siderite (XRD)**
intergrown 100 nm crystals

**Suspension in equilibrium with siderite:**
Wet crystals redissolved in \[C_{HCO_3^-} = 0.05 \ M, \ I = 0.1 M \ NaCl, \ C_s = 70 \ g/L.\]
> 48 h equilibration prior to use
Evolution of total aqueous selenium concentration with time:

With siderite

Without siderite (solution only)

\[
\text{n(Se) immobilized after 100h:} \quad >99 \% \quad \approx 30 \% \quad >99 \% \quad \approx 20 \%
\]

Siderite is mainly responsible of selenite removal

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Selenite reduction: formation of a new solid phase

Short time (6 h.)

Long time (10 d.)

EDX Spectroscopy

New selenium-bearing solid
- Unknown exact composition

SEM, Secondary electron x40000
Se Kα edge (12658 eV)

**Ex situ**
- Wet paste conditioning
- Frozen in N₂
- Measurements in cryostat (N₂/He)
  - Solid, low T.

**In situ**
- In electrochemistry cell
- Imposed redox potential ≈ siderite
- On-site selenite injection
  - Suspension, ambient T.
**In situ XANES characterization of selenite retention**

**In electrochemical cell:**

- Small currents – no electrochemical selenite reduction
- XANES: Se(IV) conversion to Se(≤0)
- EXAFS: poor signal/noise ratio caused by low selenium concentration

**Chemistry**

- E = - 0.25 mV/ENH, potentiostatic.
- Siderite suspension (70 g.L\(^{-1}\))
- 
  \[ [\text{Se}]_i = 1 \text{ mM} \]

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**Ex situ XAS: selenite reduction…**

**Without siderite**

(solution only)

- **Long time (40d)**
  - $\text{Se(IV)}$
- **Se(IV) species in the solid phase**

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\chi(E)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12620</td>
<td>0</td>
</tr>
<tr>
<td>12660</td>
<td>3</td>
</tr>
<tr>
<td>12700</td>
<td>0</td>
</tr>
</tbody>
</table>

- **HSeO$_3$ (aq.)**
- **[Se]$_i$ = 0.1 mM**
- **[Se]$_i$ = 1.0 mM**

**No reduction** of selenite after 40 days

Small photo-oxidation

(Se$^{IV}$ to Se$^{VI}$)

**With siderite**

- **Short time (5 h)**
  - Se(IV)
- **Long time (10 d)**
- **Se(IV) to Se(0) after 10 days**

**T = 5h: transient Se(IV) species in the solid phase**

**Total reduction**

Two different kinetics:

- Immobilization/reduction

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Thesis defence – V. Badaut - 5 July, 2010
Characterization of end product by *ex situ* EXAFS

### Introduction

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- *Ab initio*

### Chemistry

#### XAS

**Conclusions**

**Outlook**

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<table>
<thead>
<tr>
<th>$S_0^2$</th>
<th>N x type</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^{-1}$)</th>
<th>$\Delta E_0$ (eV)</th>
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<tbody>
<tr>
<td>0.98</td>
<td>2 x Se</td>
<td>2.35</td>
<td>0.001</td>
<td></td>
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<tr>
<td></td>
<td>4 x Se</td>
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<td>4 x Se</td>
<td>4.44</td>
<td>0.015</td>
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*Trigonal (grey) $\text{Se}^0$ ; R fact. = 0.4%*

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**Fourier transform of EXAFS signal**

**Amplitude**

**Imaginary part**
Characterization of end product by *ex situ* EXAFS

**EXAFS signal**

**Fourier transform of EXAFS signal**

**Trigonal (grey) $Se^0$ ; R fact. = 0.4 %**

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**Inter-chain interactions**

Poorly crystallized trigonal “grey” selenium
Characterization of intermediate Se(IV) species by \textit{ex situ} EXAFS

Se(IV) immobilized in the solid phase at short reaction time

Grey-Se$^0$ + SeO$_3$: R fact. = 6.5%

<table>
<thead>
<tr>
<th>Type</th>
<th>N x type</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^{-1}$)</th>
<th>$E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 % Se$^0$ (grey)</td>
<td>2 x Se</td>
<td>2.37</td>
<td>0.003</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>4 x Se</td>
<td>3.39</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 x Se</td>
<td>3.69</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>50 % SeO$_3$</td>
<td>3 x O</td>
<td>1.70</td>
<td>0.003</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>6 x O-O</td>
<td>3.14</td>
<td>0.008</td>
<td></td>
</tr>
</tbody>
</table>

Not conclusive enough to point to a specific structural model

Intermediate Se(IV) solid species not identified
Some hypotheses on the reaction pathway

Transient Se(IV) species in the solid phase not identified

Nevertheless, hypotheses can be made about the transition state(s):

\[
4 \text{Fe}^{II} + \text{Se}^{IV} \rightarrow 4 \text{Fe}^{III} + \text{Se}^{0}
\]

Transfer of four \(3d\) electrons from siderite Fe\(^{II}\) ions to each selenite ion

1. Basolo conjecture\(^1\): No more than two electrons can be transferred at once.

\[\text{Transition state of intermediate oxidation state}\]

2. Direct bonding between selenite and Fe(II) ions: Highest probability at the interface.

\[\text{Surface complexation}\]

\(\text{Ab initio}\) modelling of selenite surface complexes on siderite surface

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DFT modelling of siderite surface complexes: subsystems

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Using the crystallographic symmetry operations and the primitive cell:

**Structures & Energies:** OK. But...

- Experimentally, siderite is insulating
- Incorrect description of the last \((3d^6)\) electron?

**Fe\(^{2+}\) (PDOS)**

- Fermi level DOS \(\neq 0\) → **Metallic**?

**Band structure**

- Band sticking near Fermi level
  - caused by **ground state degeneracy**
  - causing « metallic » DOS
  - however, **band dispersion \(\neq\) metal**

- This electron is responsible of siderite redox!
Symmetry constraints are reduced when building surfaces

With $R\bar{3}c$ symmetry operations applied on electronic density:

Without any applied symmetry operations (P1):

Bulk FeCO$_3$: numerical symmetry effects
Symmetry constraints are reduced when building surfaces

Iron 3d orbitals (electronic isodensity surfaces)

Without any applied symmetry operations (P1):
Bulk FeCO₃: numerical symmetry effects

Symmetry constraints are reduced when building surfaces

Iron 3d orbitals (electronic isodensity surfaces)

Without any applied symmetry operations (P1):

- Electronic symmetry breaking: density symmetry ≠ crystal symmetry
- SCF & geometry optimization convergence issues
- Heavy calculations
- Results are not reproducible
- But there is a (null) gap…

Several almost degenerate pseudo-ground states, causing the convergence issues

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Bulk FeCO$_3$: numerical symmetry independent DFT ground state

The translation operations of the primitive cell are not compatible with the symmetry of the ground state electronic density

DFT ground state: P2$_1$/a cell

- Orbital ordering incompatible with the primitive cell (2 Fe/cell)
- Energy stabilization (3 kJ.mol$^{-1}$)
- Fewer convergence issues
- Insulating
- Minor atomic position differences (<0.01 Å)
Retention studies on siderite surfaces

On the (10\overline{1}4) perfect surface:
- Non-polar
- Perfect cleavage plane (as in other carbonates)

Using magnesite (MgCO\textsubscript{3}) as a calculation intermediate
- Isomorphic with siderite
- In our DFT modelling, ΔV(siderite-magnesite) < 1%
- Fewer electrons = quick & easy calculations

1. Speed up the calculation
   1. Magnesite geometry optimization
   2. Mg\textsuperscript{2+}/Fe\textsuperscript{2+} substitution
   3. Geometry optimization continuation

2. Direct identification of \textit{d} electron effects on chemistry
**H$_2$O retention on siderite/magnesite (1014) perfect surface**

Energies expressed as: 

$$E_{\text{surface-bond}} = E_{\text{bonded}} - (E_{\text{surface}} + E_{\text{molecule}})$$

Fe: $-75$ kJ mol$^{-1}$  
Mg: $-78$ kJ mol$^{-1}$

Ab initio
H₂O retention on siderite/magnesite (10\bar{1}4) perfect surface

Energies expressed as:

\[ E_{\text{surface-bond}} = E_{\text{bonded}} - (E_{\text{surface}} + E_{\text{molecule}}) \]

\[ \text{s-MCO}_3 + \text{H}_2\text{O} \rightarrow \text{s-MCO}_3 \]

Fe: -75 kJ.mol\(^{-1}\)
Mg: -78 kJ.mol\(^{-1}\)

\[ \text{OH}_2 \quad \text{H-bond} \]

Fe: +150 kJ.mol\(^{-1}\)

\[ \text{OH} \quad \text{s-MCO}_3 \]

\[ \text{HOH} \quad \text{H-bond} \]

Mg: -17 kJ.mol\(^{-1}\)
Fe: \approx -20 kJ.mol\(^{-1}\)

\[ E_{\text{surface-bond}} (\equiv \text{Mg-OH}_2) = -61 \text{ kJ.mol}^{-1} \approx E_{\text{hydration}} \]

In both cases:
- Bonding between H₂O and surface through M-O
- Same as with other carbonates (e.g. calcite\(^{(1)}\))
- Structural agreement with modelling studies\(^{(2)}\), \(^{(3)}\), \(^{(4)}\)

WRIGHT et al. \(^{(4)}\): \( E_{\text{hydration}}(\text{MgCO}_3) = -60.7 \text{ kJ.mol}^{-1} \)

**O₂ retention on siderite/magnesite (1014) perfect surface**

\[
s\text{MCO}_3 + O_2 \rightarrow \text{s-MCO}_3 \quad \text{Fe: } -50 \text{ kJ.mol}^{-1} \\
\text{Mg: } +115 \text{ kJ.mol}^{-1}
\]

\[
\text{O}_2 \rightarrow \text{s-MCO}_3 \quad \text{Fe: } -70 \text{ kJ.mol}^{-1} \\
\text{Mg: } +215 \text{ kJ.mol}^{-1}
\]

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**O₂ retention on siderite/magnesite (10\bar{1}4) perfect surface**

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\text{Mg: } +215 \text{ kJ.mol}^{-1}
\]

**Different behaviours:**
- In magnesite, no bonding
- In siderite, dissociative sorption is favoured

**Ab initio**

<table>
<thead>
<tr>
<th></th>
<th>Fe BVM charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure surface</td>
<td>2,0</td>
</tr>
<tr>
<td>\text{≡Fe-O}_2 bond</td>
<td>2,4</td>
</tr>
<tr>
<td>\text{≡Fe-O} bond</td>
<td>3,2</td>
</tr>
</tbody>
</table>

In presence of oxygen, siderite oxidizes/magnesite does not.
DFT results in agreement with elementary chemistry
Selenite surface complexes on magnesite: (1) without $\text{H}_2\text{O}$

SeO$_3^{2-}$ $\rightleftharpoons$ 2 $\text{H}^+$ added for neutrality

Case 1: Surface anion substitution
$E_{\text{bonding}}(\text{AS}) = -17 \text{kJ.mol}^{-1}$

Case 2: Bidentate surface complex
$E_{\text{bond}}(\text{BSC}) = -48 \text{kJ.mol}^{-1}$

Is BSC the most stable?
Selenite surface complexes on magnesite perfect surface. (1) without $\text{H}_2\text{O}$

**Selenite surface complexes on magnesite:**

$\text{SeO}_3^{2-} \iff 2 \text{H}^+$ added for neutrality

**Case 1: Surface anion substitution**

$E_{\text{bonding}}(\text{AS}) = -17 \text{ kJ.mol}^{-1}$

Overcoming an activation barrier

$E_{\text{bonding}}(\text{BSC'}) = -63 \text{ kJ.mol}^{-1}$

\[
\text{CO}_3^{2-} + 2 \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

**Case 2: Bidentate surface complex**

$E_{\text{bond}}(\text{BSC}) = -48 \text{ kJ.mol}^{-1}$

Overcoming an activation barrier

$E_{\text{bonding}}(\text{AS'}) = -51 \text{ kJ.mol}^{-1}$

\[
\text{SeO}_3^{2-} + 2 \text{H}^+ \rightarrow \text{SeO}_2 + \text{H}_2\text{O}
\]

$\iff$ Hydration should stabilize selenite/carbonate anions
Selenite surface complex on magnesite perfect surface. (1) with H$_2$O

Hydrated selenite surface complexes: which one is the most stable?

Outer-sphere complex

Monodentate inner-sphere complex

Bidentate inner-sphere complex

Surface anion substitution

$\Delta E$ (kJ.mol$^{-1}$) 16 0 128 152

H C O Se Mg
Selenite surface complex on magnesite perfect surface. (1) with \( \text{H}_2\text{O} \)

**Hydrated selenite surface complexes: which one is the most stable?**

<table>
<thead>
<tr>
<th>Outer-sphere complex</th>
<th>Monodentate inner-sphere complex</th>
<th>Bidentate inner-sphere complex</th>
<th>Surface anion substitution</th>
</tr>
</thead>
</table>

\[
\Delta E \text{ (kJ.mol}^{-1}\text{)} \quad 16 \quad \text{0} \quad 128
\]

After moving one \( \text{H}_2\text{O} \) and geometry optimization:

\[\Delta E = 25 \text{ kJ.mol}^{-1}\]

Which one is the most stable?

Extremely constrained water network. Representativity of a single calculation?

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Conclusions
Conclusions

Quantitative retention and reduction of selenite by siderite:

- retention is quantitative for $t > 24$ h
- reduction is quantitative for $t < 10$ j

\{ Distinct kinetics \\

- Reduction product is identified as **poorly crystallized trigonal Se$^0$ (grey)**
- Intermediate Se(IV) solid species were **observed but not characterized**


DFT ground state of siderite:

- DFT ground state electronic density is not compatible with crystalline symmetry
- New primitive cell with orbital ordering

Oral communication at Réunion générale du GDR-DFT++ (2009).

DFT modelling of properties on siderite surfaces:

- Simple surface phenomenon correctly described (water retention, oxydation)
- First selenite retention study *on magnesite* showed hydration is needed for ion stability

  Long way to go for surface complexes modelling on *siderite*
Selenite contribution to repository radiotoxicity should be low
immobilized as sparingly soluble Se\(^0\) in the canister’s corrosion layer

To confirm it:
Could these results be extrapolated to lower selenium concentration?

Role of surface defects on reactivity?

Effect of competing ions?

(DFT)
Passage from static 0 K results to macroscopic repository conditions?
Thanks to:
M. Ruffoni, M. Vacari (BM29, ESRF)
S. Belin, E. Fonda (SAMBA, SOLEIL)
H. Badji, C. Blanc, L. Salmon (LRSI, CEA)
J-L. Flèche and all the team (LM2T, CEA)
B. Grenut (L3MR, CEA)

Support from GDR PARIS & GDR DFT ++

L’association MAIOT

&

Les amis et la famille pour leur soutien
Crystal Field Theory applied to siderite

- Hexagonal crystal (R3c, 167), rhomboedral primitive cell
- Octaedral FeO$_6$ compressed along (111) → $C_{3i}$

State degeneracy of free Fe$^{2+}$ in siderite crystal field

Without CSO, ground state degeneracy

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1 Kanamori, J. Progress of Theoretical Physics. 1958, 20 (6), 890 – 908
Population of the $d$ states of $\text{Fe}^{2+}$:

State degeneracy of the $\text{Fe}^{2+}$ $d$ states in the crystal field

$\text{Fe}^{2+}$ population $(3d^6 \ 4s^0)$

Last occupied level: *ion degeneracy*
Fermi level band structure

- Good energetic agreement between DFT-GGA and crystal field theory
- Siderite Fundamental state degeneracy in DFT is caused by the monoelectronic states degeneracy in Fe$^{2+}$ (⇒ metallic ?)

$^1$Yi-Yang, Z. & Chung-Hao, Y. Phys. Rev. B. 1993, 47 (9), 5451 - 5454
- Fermi level: iron 3d states
- Flat bands: localized states – ionic type
- In blue and red: projection of the d states of majority spins and minority spins of the iron on a localized basis set