Calcium antimonate precipitation in cementitious systems

Geert Cornelis, Tom Van Gerven, Carlo Vandecasteele

Laboratory of Applied Physical Chemistry and Environmental Technology, K.U.Leuven
Wastes that contain antimony are often processed in a cementitious matrix:
- added to cement (Coal fly ash)
- replace gravel or sand in concrete production (MSWI bottom ash)
- solidified/stabilised (Hazardous wastes: MSWI or non-ferrous APC residues)

→ Sb is often found in a cementitious matrix

<table>
<thead>
<tr>
<th>Waste</th>
<th>Sb concentration range (mg/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Fly ash</td>
<td>6 -7</td>
<td>Miravet et al. (2006)</td>
</tr>
<tr>
<td>MSWI bottom ash</td>
<td>10 - 400</td>
<td>IAWG (1997)</td>
</tr>
<tr>
<td>MSWI APC residues</td>
<td>300 – 1000</td>
<td>IAWG (1997)</td>
</tr>
<tr>
<td>Non-ferrous metal APC-residues</td>
<td>162000 - 347000</td>
<td>Dutré et al. (1997)</td>
</tr>
</tbody>
</table>
Although still a matter of debate, Sb is suspected to have toxic properties and is therefore regulated in many countries.

<table>
<thead>
<tr>
<th>Guideline</th>
<th>Leaching limit value (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EU Landfilling of non-hazardous wastes (L/S=10)</td>
<td>0.7</td>
</tr>
<tr>
<td>EU Landfilling of hazardous wastes (L/S=10)</td>
<td>5</td>
</tr>
</tbody>
</table>

Incomplete knowledge on Sb toxicology has lead in the EU to low limit values, even lower than those of As.
Introduction

There is thus need to understand the geochemistry of antimony in alkaline matrices, but existing knowledge is limited:

- 3 different $\log K_{sp}$ values for $\text{Ca}[\text{Sb(OH)}_6]_2$ ($-12.55$, $-10.23$, $-10.98$)

- Interaction of Sb(V) with common minerals?

$\Rightarrow$ Limited understanding of the long-term behaviour of Sb in a cementitious or other alkaline matrix
Introduction

This presentation:

**Calcium antimonate precipitation**

- Sb(V) most abundant and most mobile oxidation state in solution: Sb(OH)$_6^-$
- Calcium antimonate most likely precipitate in a cementitious matrix
Calcium antimonate = Roméite

Roméite has a structure similar to pyrochlore

Pyrochlore: \((\text{Ca,Na})_2\text{Nb}_2\text{O}_6(\text{O,OH,F})\)
Roméite: \((\text{Ca,Na})_2\text{Sb}_2\text{O}_6(\text{O,OH,F})\)

*Perfect Roméite:*

\(\text{Ca}_2\text{Sb}_2\text{O}_7\)
Calcium antimonate = Roméite

General formula: $A_{2-m}B_2X_6Y_{1-n}\cdot pH_2O$

In a CaO-Sb$_2$O$_5$-H$_2$O system:
- $A$=Ca
- $B$=Sb(V)
- $X$=O$^{2-}$
- $Y$=O$^{2-}$, OH$^-$ or H$_2$O

- e.g. Ca$_2$Sb$_2$O$_7$

these indices indicate the possibility of vacancies
Calcium antimonate = Roméite

**vacancies:**

e.g. Ca[Sb(OH)$_6$]$_2$ = (Ca$_{1-\delta}$)$_{\delta}$Sb$_2$O$_6$X(H$_2$O)$_6^Y$

Especially the A and Y site can contain vacancies

⇒ Roméite has
a highly variable composition
The composition of pyrochlores depends on [Ca] and pH:

- Low pH and/or low $[\text{Ca}^{2+}]$: low A-site occupancy
- High pH and/or high $[\text{Ca}^{2+}]$: High A-site occupancy

Also true for roméite and what is the effect on solubility?
Variation in composition

<table>
<thead>
<tr>
<th>Applied molar Ca:Sb ratio</th>
<th>pH during synthesis</th>
<th>Aging time</th>
<th>Structure (Rietveld)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>~6</td>
<td>24h</td>
<td>Amorphous</td>
</tr>
<tr>
<td>1:2</td>
<td>~6</td>
<td>60d</td>
<td>Pyrochlore</td>
</tr>
<tr>
<td>0.66:2</td>
<td>12</td>
<td>14d</td>
<td>Pyrochlore</td>
</tr>
<tr>
<td>1:2</td>
<td>12</td>
<td>14d</td>
<td>Pyrochlore</td>
</tr>
<tr>
<td>2:2</td>
<td>12</td>
<td>14d</td>
<td>Pyrochlore</td>
</tr>
<tr>
<td>4:2</td>
<td>12</td>
<td>14d</td>
<td>Pyrochlore</td>
</tr>
</tbody>
</table>

XRD + Rietveld fit of the roméite synthesized at pH 12 and at a total molar Ca:Sb ratio of 1:2

Calcium antimonates obtained are indeed roméite (pyrochlore structure) except the first one which is amorphous.
Variation in composition

<table>
<thead>
<tr>
<th>Applied molar Ca:Sb ratio</th>
<th>pH during synthesis</th>
<th>Aging time</th>
<th>Formula (Rietveld analysis)</th>
<th>Ca:Sb (EDX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>~6</td>
<td>24h</td>
<td>Ca[Sb(OH)₆]₂ (based on EDX)</td>
<td>0.94:2</td>
</tr>
<tr>
<td>1:2</td>
<td>~6</td>
<td>60d</td>
<td>Ca₁.₁₃[Sb₂O₆(OH)₀.₈₇]·0.₉₄H₂O</td>
<td>1.16:2</td>
</tr>
<tr>
<td>0.66:2</td>
<td>12</td>
<td>14d</td>
<td>Ca₁.₄₆[Sb₂O₆(OH)₀.₅₄]·0.₀₈H₂O</td>
<td>1.31:2</td>
</tr>
<tr>
<td>1:2</td>
<td>12</td>
<td>14d</td>
<td>Ca₁.₄₄[Sb₂O₆(OH)₀.₅₆]·0.₁₂H₂O</td>
<td>1.36:2</td>
</tr>
<tr>
<td>2:2</td>
<td>12</td>
<td>14d</td>
<td>Ca₁.₅₅[Sb₂O₆(OH)₀.₄₅]·0.₁₀(OH)₀.₉₀</td>
<td>1.38:2</td>
</tr>
<tr>
<td>4:2</td>
<td>12</td>
<td>14d</td>
<td>Ca₁.₆₇[Sb₂O₆(OH)₀.₃₃]·0.₆₆</td>
<td>1.41:2</td>
</tr>
</tbody>
</table>

- Products obtained show variable composition
- The molar Ca:Sb ratio of synthesis products increases as the pH and Ca:Sb ratio applied during synthesis increase
- However, Ca:Sb ratio in synthesis product increases more slowly
Solubility of roméite

Solubility of roméite as a function of [Ca]
(Ca$_{1.13}$Sb$_2$O$_6$(OH)$_{0.26}$:0.74H$_2$O, synthesized at pH~6)

Model 1: congruent dissolution; equilibrium with atm. CO$_2$, formation of HCO$_3^-$, and CO$_3^{2-}$
and equilibria between Sb(OH)$_6^{-}$, Sb(OH)$_5$, CaOH$^+$, Ca$^{2+}$, CaCO$_3$, CaHCO$_3^+$

Ca$_{1.13}$Sb$_2$O$_6$(OH)$_{0.26}$:0.74H$_2$O + 0.26H$^+$ + 5H$_2$O = 1.13Ca$^{2+}$ + 2Sb(OH)$_6^-$

log$K_{sp}$ = -12.7
Solubility of roméite

- Model 1 only adequately predicts Sb conc. in solution at \((\text{Ca})<0.01 \text{ mol/l}\)
- not the observed pH decline as a function of \([\text{Ca}]\)

\[ \text{pH in equilibrium with roméite as a function of the applied } [\text{Ca}] \text{ (as } \text{Ca(NO}_3\text{)}_2) \]

\[ \text{Sb in equilibrium with roméite as a function of the applied } [\text{Ca}] \text{ (as } \text{Ca(NO}_3\text{)}_2) \]
Solubility of roméite

$\text{Sb in equilibrium with roméite as a function of the applied } [\text{Ca}] \text{ (as } \text{Ca(NO}_3\text{)}_2\text{)}$

Model 2: $\text{Model 1 + ion association:}$

$\text{Ca}^{2+} + \text{Sb(OH)}_6^{-} = \text{CaSb(OH)}_6^+$

fitted $\log K_{\text{ass}} = 2.15$

$p\text{H in equilibrium with roméite as a function of the applied } [\text{Ca}] \text{ (as } \text{Ca(NO}_3\text{)}_2\text{)}$
Solubility of roméite

- Better prediction of Sb conc. at [Ca] > 0.01mol/l. Assumption of CaSb(OH)$_6^+$ association is likely
- Model does not predict observed pH decline as a function of [Ca]

**Sb in equilibrium with roméite as a function of the applied [Ca] (as Ca(NO$_3$)$_2$)**

**pH in equilibrium with roméite as a function of the applied [Ca] (as Ca(NO$_3$)$_2$)**
Solubility of roméite

Model 3: Model 2 + precipitation of 2nd romeite \( \text{Ca}_2\text{Sb}_2\text{O}_7 \) is allowed

\[
\text{Ca}_2\text{Sb}_2\text{O}_7 + 2\text{H}^+ + 5\text{H}_2\text{O} = 2\text{Ca}^{2+} + 2\text{Sb(OH)}_6^- 
\]

fitted \( \log K_{sp} = -6.7 \)

Sb in equilibrium with roméite as a function of the applied \([\text{Ca}]\) (as \( \text{Ca(NO}_3)_2 \))

\( \text{pH} \) in equilibrium with roméite as a function of the applied \([\text{Ca}]\) (as \( \text{Ca(NO}_3)_2 \))
Solubility of roméite

Model 3 explains the Sb conc. in solution and the pH-decline: as $[\text{Ca}]$ increases $\text{Ca}_{1.13}\text{Sb}_2\text{O}_6(\text{OH})_{0.26} \cdot 0.74\text{H}_2\text{O}$ dissolves in favour of $\text{Ca}_2\text{Sb}_2\text{O}_7$ and more $\text{H}^+$ is set free.

However, a fitted $\log K_{sp} = -6.7$ for $\text{Ca}_2\text{Sb}_2\text{O}_7$ was not yet confirmed experimentally.

Sb in equilibrium with roméite as a function of the applied $[\text{Ca}]$ (as $\text{Ca(NO}_3\text{)}_2$)

pH in equilibrium with roméite as a function of the applied $[\text{Ca}]$ (as $\text{Ca(NO}_3\text{)}_2$)
Sb leaching in cement pastes

- OPC paste spiked with 300 mg/kg Sb(V)
- 28 days hydration
- Leaching of Sb as a function of pH: max. at pH=7, min. at pH=13
Sb leaching in cement pastes

- Modelling with PHREEQC
- \( \text{Ca}[\text{Sb(OH)}_6]_2 \ \log K_{sp} = -12.55 \) (Johnson et al., 2005)
- Overestimation of Sb leaching at high pH
- Leaching close to equilibrium with \( \text{Ca}[\text{Sb(OH)}_6]_2 \) at pH<9
Sb leaching in cement pastes

- At pH>11 concentration of Sb is close to equilibrium with $\text{Ca}_{1.13}\text{Sb}_2\text{O}_6(\text{OH})_{0.26}\cdot0.74\text{H}_2\text{O}$
- Sb leaching at 9<pH<11?
Sb leaching in cement pastes

- A site occupancy of romeites decreases with pH
- Romeites with lower A-site occupancy cause higher Sb concentrations

![Graph showing the relationship between pH and Sb leaching](image)

Decrease Ca-occupancy of calcium antimonate
Conclusions

- Calcium antimonate = roméite that equilibrates with pore solutions by 3 simultaneously occurring equilibria:
  - Dissolution
  - Change of the A-site (and Y-site) occupancy as a function of pH and Ca-activity
  - CaSb(OH)$_6^+$ formation