Calcium antimonate precipitation in cementituous systems

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Introduction

Waste	Sb concentration range (mg/kg)	Reference
Coal Fly ash	6 -7	Miravet et al. (2006)
MSWI bottom ash	10 - 400	IAWG (1997)
MSWI APC residues	300 – 1000	IAWG (1997)
Non-ferrous metal APC-residues	162000 - 347000	Dutré et al. (1997)

Wastes that contain antimony are often processed in a cementituous 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 cementituous matrix

Although still a matter of debate, Sb is suspected to have toxic properties and is therefore regulated in many countries

Guideline	Leaching limit value (mg/kg)
EU Landfilling of **non-hazardous** wastes (L/S=10)	0.7
EU Landfilling of **hazardous** wastes (L/S=10)	5

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

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

- 3 different $logK_{sp}$ values for $Ca[Sb(OH)_6]_2$ (-12.55, -10.23, -10.98)
- Interaction of Sb(V) with common minerals?

➔ Limited understanding of the long-term behaviour of Sb in a cementituous or other alkaline matrix

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 cementituous matrix

Roméite has a structure similar to *pyrochlore*

Pyrochlore: $(Ca,Na)_2Nb_2O_6(O,OH,F)$

Roméite: $(Ca,Na)_2Sb_2O_6(O,OH,F)$

Perfect Roméite:
$Ca_2Sb_2O_7$

Calcium antimonate = **Roméite**

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

In a CaO-Sb_2O_5-H_2O system:

A=Ca

B=Sb(V)

X=O^{2-}

Y=O^{2-}, OH^- or H_2O

e.g. $Ca_2Sb_2O_7$

these indices indicate the possibility of vacancies

vacancies:

e.g. $Ca[Sb(OH)_6]_2 = (Ca_1[]_1)^A Sb_2^B O_6^X (H_2O)_6^Y$

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 [Ca^{2+}]:

➔ low A-site occupancy

High pH and/or high [Ca^{2+}]:

➔ High A-site occupancy

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

Variation in composition

Applied molar Ca:Sb ratio	pH during synthesis	Aging time	Structure (Rietveld)
1:2	~6	24h	Amorphous
1:2	~6	60d	Pyrochlore
0.66:2	12	14d	Pyrochlore
1:2	12	14d	Pyrochlore
2:2	12	14d	Pyrochlore
4:2	12	14d	Pyrochlore
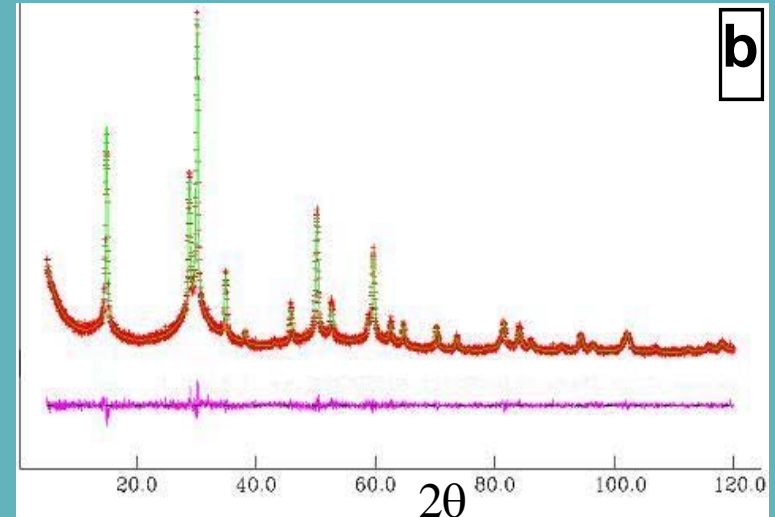
XRD + Rietveld fit of the roméite synthesized at pH 12 and at a total molar Ca:Sb ratio of 1:2

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

Variation in composition

Applied molar Ca:Sb ratio	pH during synthesis	Aging time	Formula (Rietveld analysis)	Ca:Sb (EDX)
1:2	~6	24h	$Ca[Sb(OH)_6]_2$ (based on EDX)	0.94:2
1:2	~6	60d	$Ca_{1.13}[]_{0.87}Sb_2O_6(OH)_{0.26}:0.74H_2O$	1.16:2
0.66:2	12	14d	$Ca_{1.46}[]_{0.54}Sb_2O_6(OH)_{0.92}:0.08H_2O$	1.31:2
1:2	12	14d	$Ca_{1.44}[]_{0.56}Sb_2O_6(OH)_{0.88}:0.12H_2O$	1.36:2
2:2	12	14d	$Ca_{1.55}[]_{0.45}Sb_2O_6(O_{0.10},(OH)_{0.90})$	1.38:2
4:2	12	14d	$Ca_{1.67}[]_{0.33}Sb_2O_6(O_{0.34},(OH)_{0.66})$	1.41:2

- 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 as a function of [Ca]
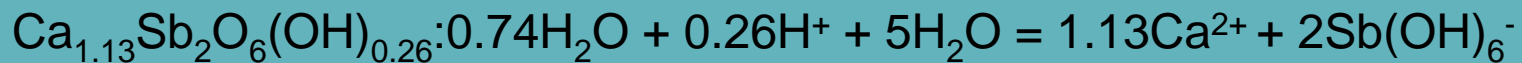($Ca_{1.13}Sb_2O_6(OH)_{0.26}$:0.74$H_2O$, synthesized at pH~6)
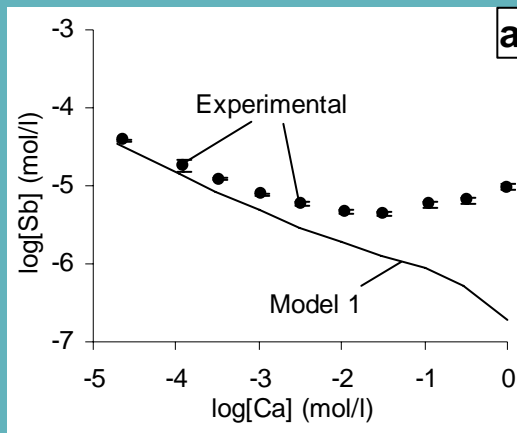
Sb in equilibrium with roméite as
a function of the applied [Ca] (as $Ca(NO_3)_2$)
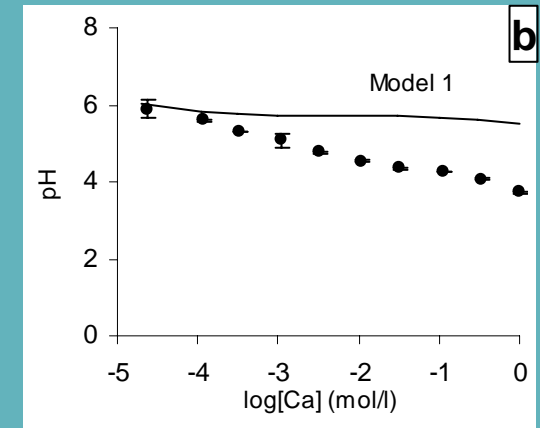
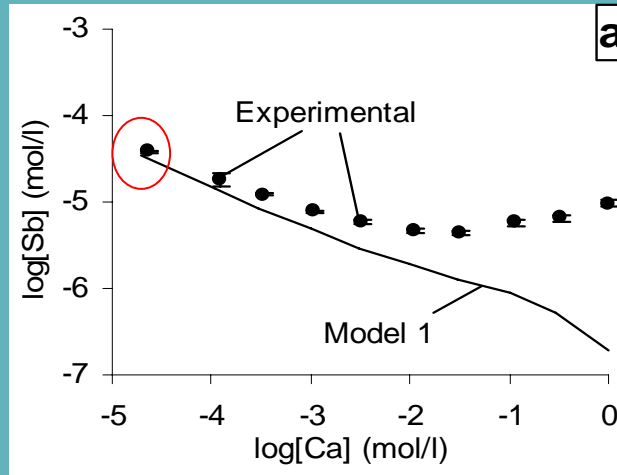*pH in equilibrium with roméite as*
a function of the applied [Ca] (as $Ca(NO_3)_2$)

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+}, $CaCO_3$, $CaHCO_3^+$

$$Ca_{1.13}Sb_2O_6(OH)_{0.26}:0.74H_2O + 0.26H^+ + 5H_2O = 1.13Ca^{2+} + 2Sb(OH)_6^-$$

$$logK_{sp} = -12.7$$

Sb in equilibrium with roméite as a function of the applied [Ca] (as Ca(NO₃)₂)
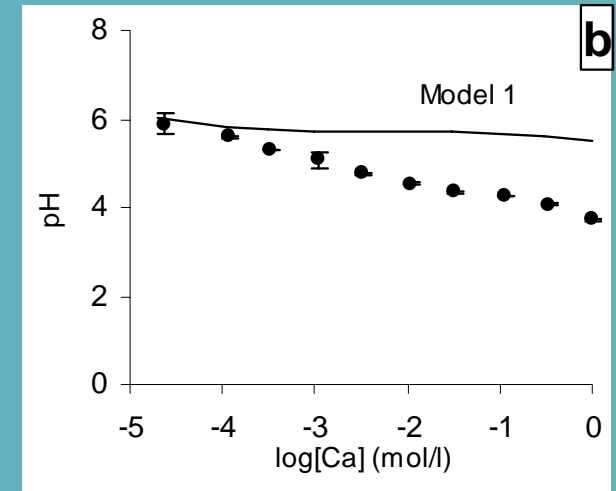
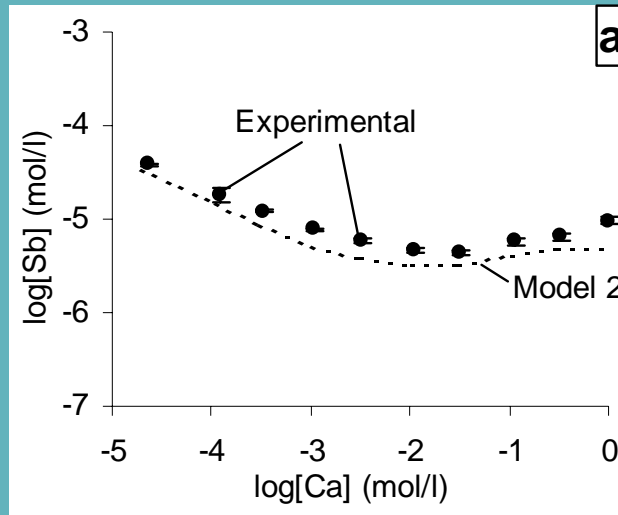*pH in equilibrium with roméite as a function of the applied [Ca] (as Ca(NO₃)₂)*

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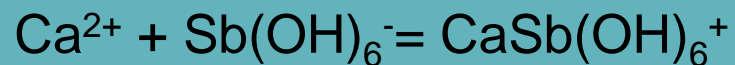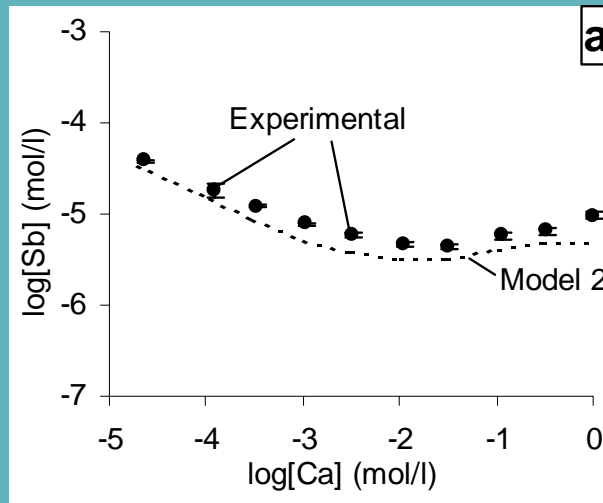- not the observed pH decline as a function of [Ca]

Solubility of roméite
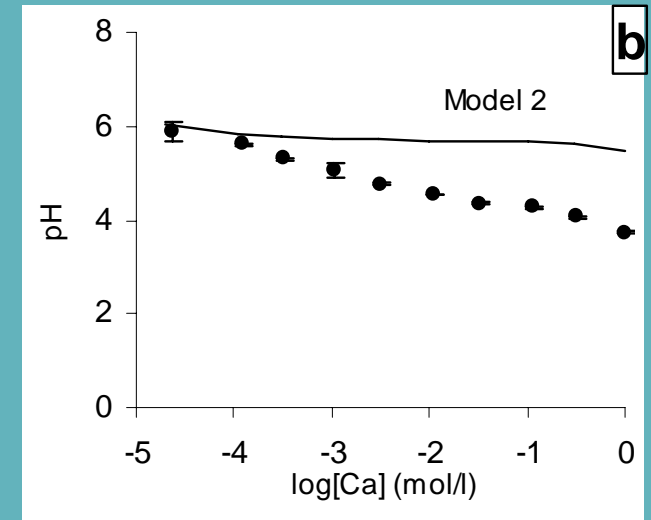
Sb in equilibrium with roméite as a function of the applied [Ca] (as $Ca(NO_3)_2$)

pH in equilibrium with roméite as a function of the applied [Ca] (as $Ca(NO_3)_2$,

Model 2: Model 1 + ion association:
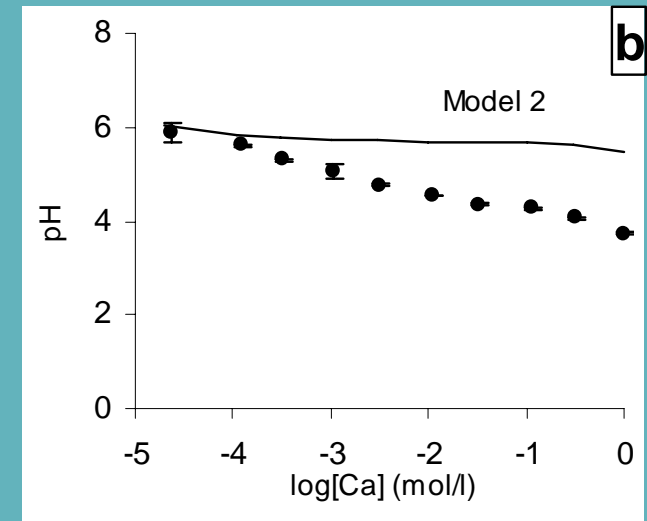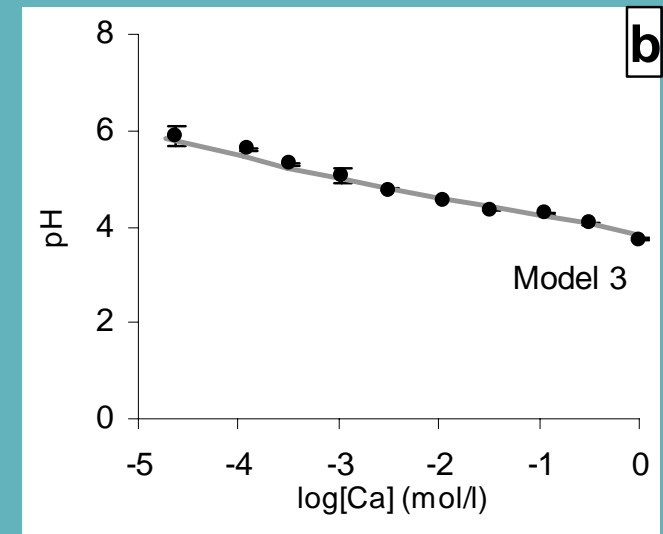
$$Ca^{2+} + Sb(OH)_6^- = CaSb(OH)_6^+$$

fitted $logK_{ass} = 2.15$

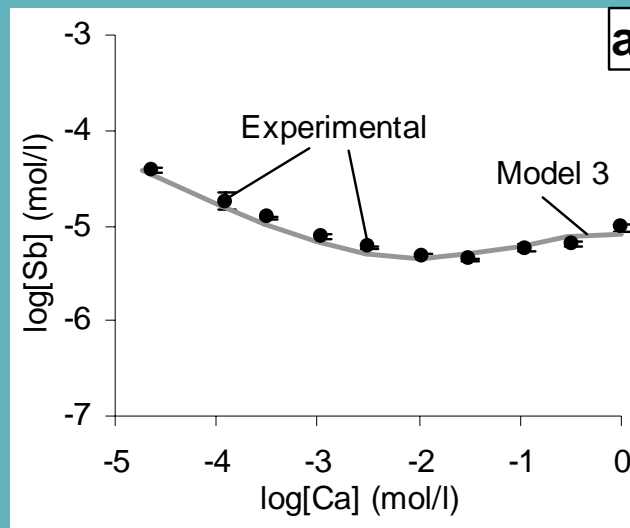Sb in equilibrium with roméite as
a function of the applied [Ca] (as $Ca(NO_3)_2$)

pH in equilibrium with roméite as
a function of the applied [Ca] (as $Ca(NO_3)_2$)

- Better prediction of Sb conc. at [Ca]> 0.01mol/l. Assumption of $CaSb(OH)_6^+$ assocation 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(NO₃)₂)

pH in equilibrium with roméite as a function of the applied [Ca] (as Ca(NO₃)₂)

Model 3: Model 2 + precipitation of 2nd romeite $Ca_2Sb_2O_7$ is allowed
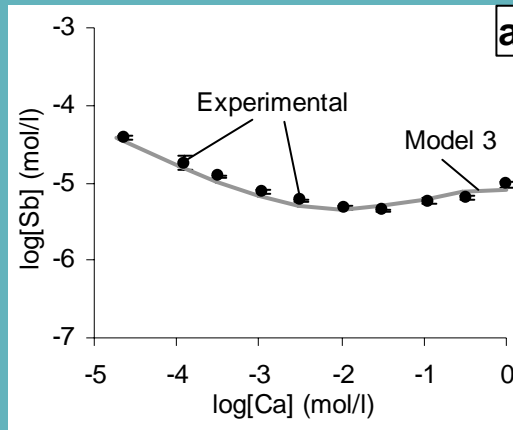
$$Ca_2Sb_2O_7 + 2H^+ + 5H_2O = 2Ca^{2+} + 2Sb(OH)_6^-$$

fitted $logK_{sp} = -6.7$
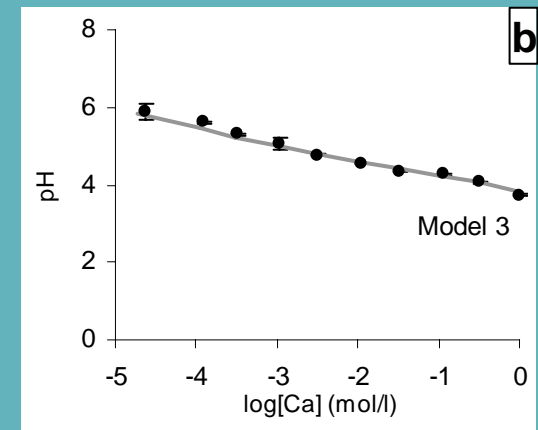
Solubility of roméite

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 $Ca(NO_3)_2$)

- Model 3 explains the Sb conc. in solution and the pH-decline: as [Ca] increases $Ca_{1.13}Sb_2O_6(OH)_{0.26}:0.74H_2O$ dissolves in favour of $Ca_2Sb_2O_7$ and more H^+ is set free
- However, a fitted $logK_{sp}=-6.7$ for $Ca_2Sb_2O_7$ was not yet confirmed experimentally
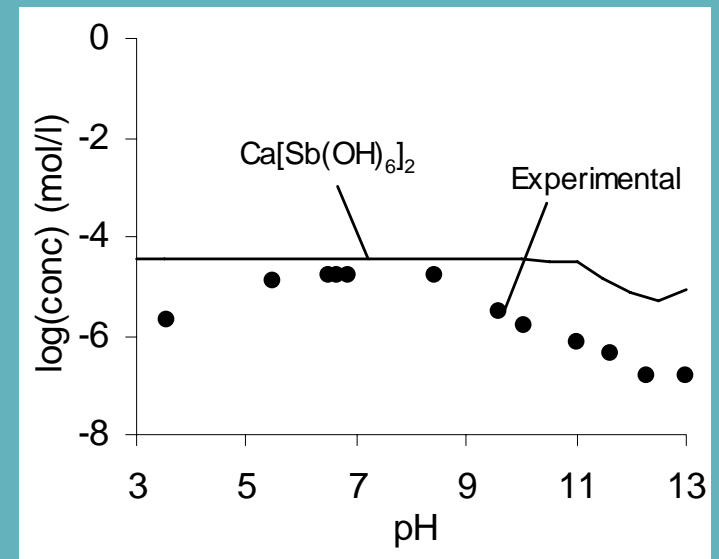
- OPC paste spiked with 300 mg/kg Sb(V)
- 28 days hydration
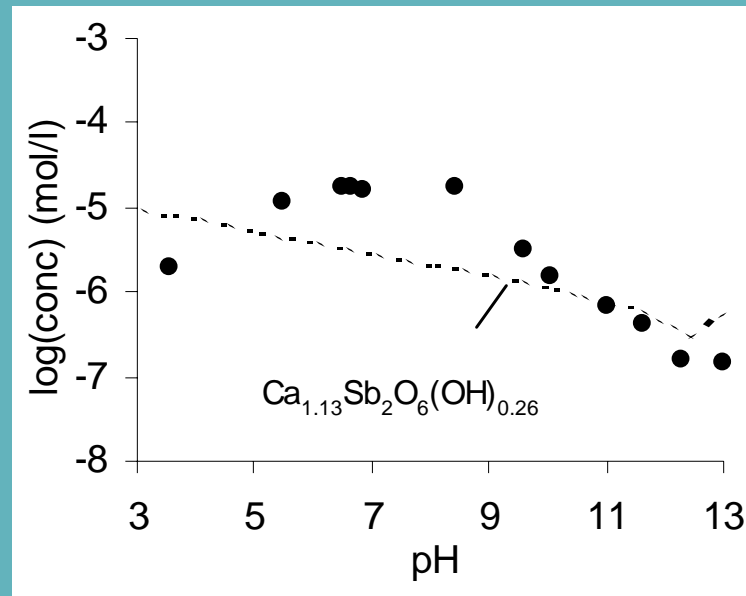- Leaching of Sb as a function of pH: max. at pH=7, min. at pH=13
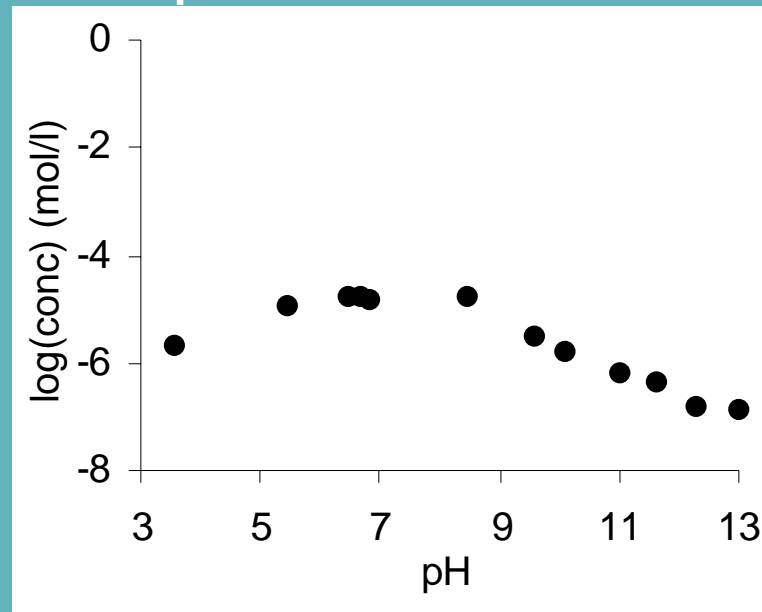
- Modelling with PHREEQC
- $Ca[Sb(OH)_6]_2$ $logK_{sp}$=-12.55 (Johnson et al., 2005)
- Overestimation of Sb leaching at high pH
- Leaching close to equilibrium with $Ca[Sb(OH)_6]_2$ at pH<9
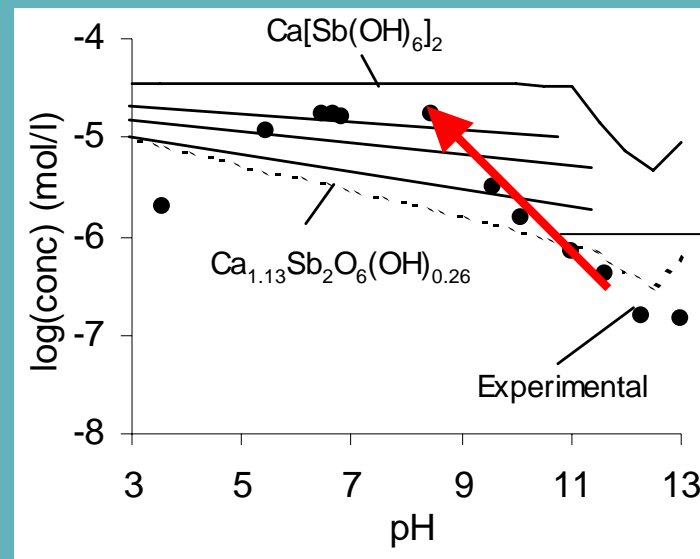
Sb leaching in cement pastes

- At pH>11 concentration of Sb is close to equilibrium with $Ca_{1.13}Sb_2O_6(OH)_{0.26}:0.74H_2O$
- Sb leaching at 9<pH<11?

$Ca_{1.13}Sb_2O_6(OH)_{0.26}$

Sb leaching in cement pastes

- A site occupancy of romeites decreases with pH

- Romeites with lower A-site occupancy cause higher Sb concentrations

Decrease Ca-occupancy of calcium antimonate

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