SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

THE UNIVERSITY OF ADELAIDE AUSTRALIA
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Geochemical constraints in slag valorisation: The case of oxyanions and nanoparticles

Geert Cornelis, Tom Van Gerven, Carlo Vandecasteele, Jason. K. Kirby, Mike J. McLaughlin

centre
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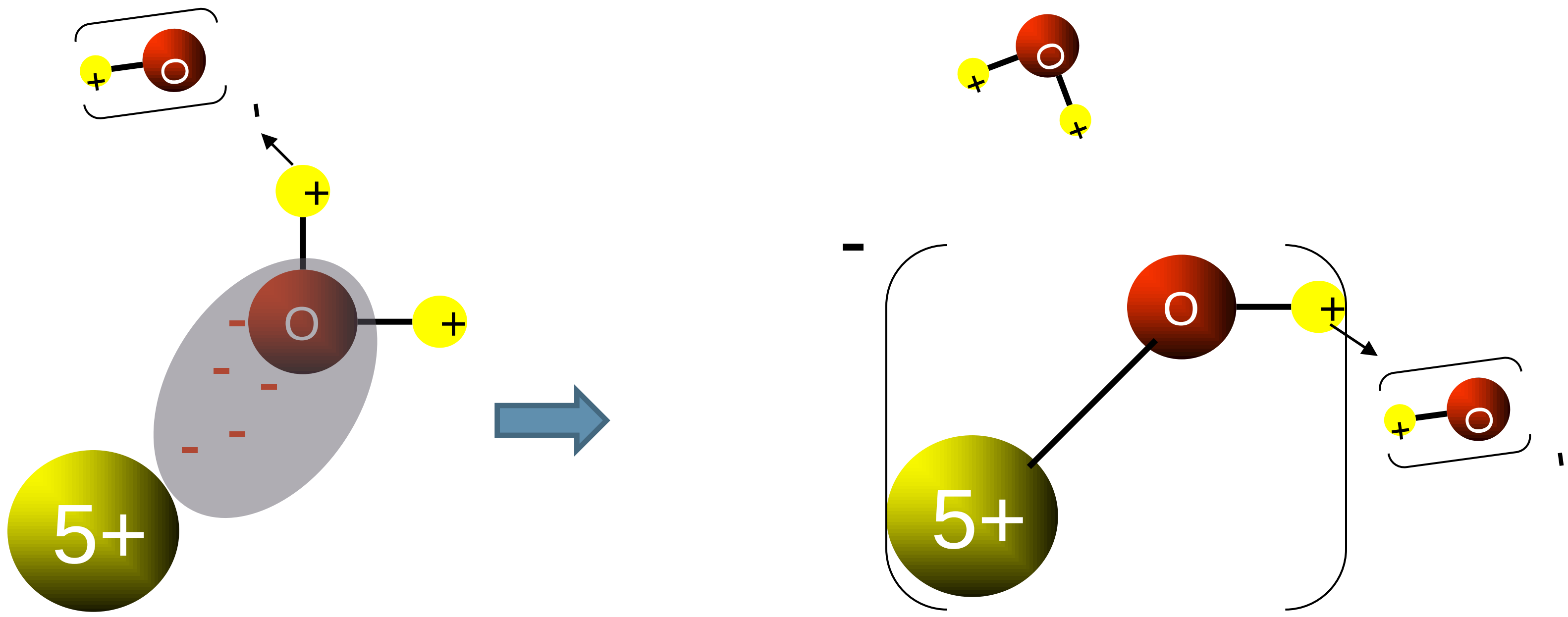
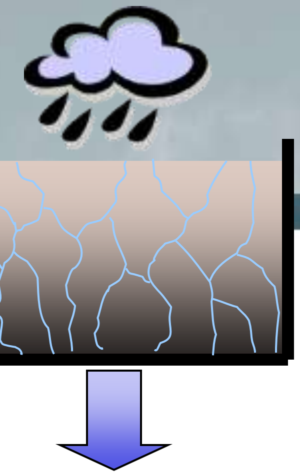
Oxyanions



Sb^{5+}, As^{5+} $Sb(OH)_6^-$, AsO_4^{3-}

Oxyanions



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Review

Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: A review

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Oxyanions

- Arsenic $As^{V}O_4^{3-}$, $As^{III}O_3^{3-}$
- Chromium $Cr^{VI}O_4^{2-}$, $Cr^{III}(OH)_3^{0}$
- Molybdenum $Mo^{VI}O_4^{2-}$
- Selenium $Se^{VI}O_4^{2-}$, $Se^{IV}O_3^{2-}$
- Antimony $Sb^{V}(OH)_6^{-}$, $Sb^{III}(OH)_3^{0}$
- Vanadium $V^{V}O_4^{3-}$, $V^{IV}O(OH)_2^{0}$, $V^{III}(OH)_3^{0}$
- Tungsten $W^{VI}O_4^{2-}$

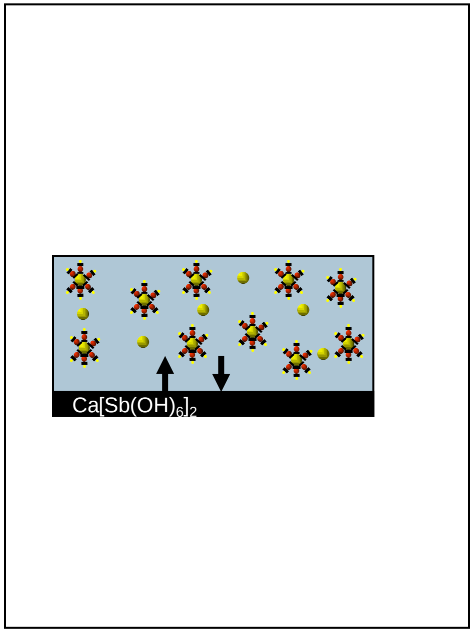
Oxyanions

- Have oxidation states that are oxyanionic
- Redox sensitive
- Enriched in many industrial wastes
- Legislation is recent for all except As and Cr

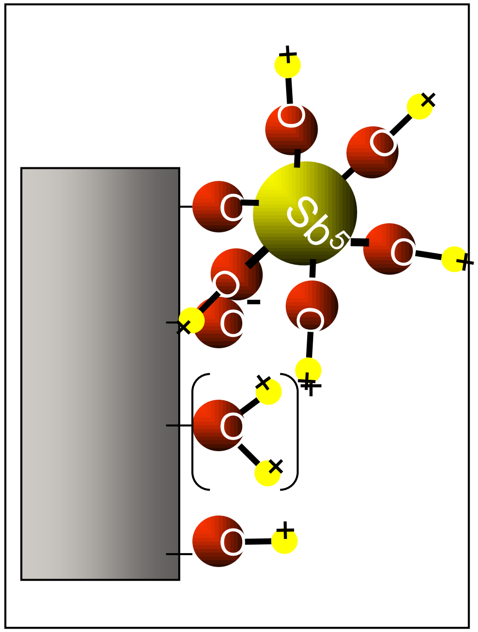
			MSWI residues			Fossil Fuel Combustion residues			Metallurgical slags		
Element	Lithosphere	Soils	Bottom ash	Fly ash	APC* residues	Coal bottom ash	Coal fly ash	FGD** ash	Blast furnace slag	Steel slag	Non-ferrous slags
As	5	1-50	0.1-200	40-300	20-500	0.02-200	2-400	0.8-50	<0.7	5	0.2 – 2
Cr	200	1-1000	20-3000	100-1000	70-700	0.2-6000	4-900	2-200	30	8000-30000	20-300
Mo	2	0.2-5	2-300	15-200	2-40	1-500	1-100	1-50	<6.0	20	3 – 50
Sb	0.2-0.5	-	10-400	300-1000	80-1000	NA	NA	NA	NA	NA	<0.1 – 0.3
Se	0.09	0.1-2	0.05-10	0.4-30	0.7-30	0.1-10	0.2-100	2-200	NA	NA	2 – 6
V	200	20-500	20-100	30-200	8-90	10-500	10-1000	8-400	400	1000-10000	40-400
W	-	-	30	NA	NA	NA	NA	NA	<13	400	0.4-3

Cornelis et al. 2008a

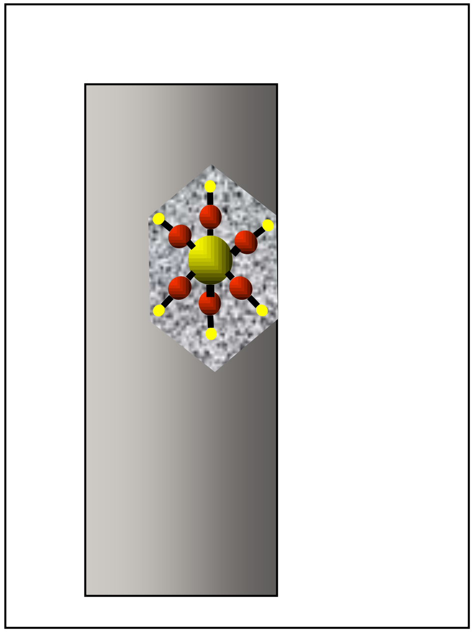
Solubility control



Precipitation

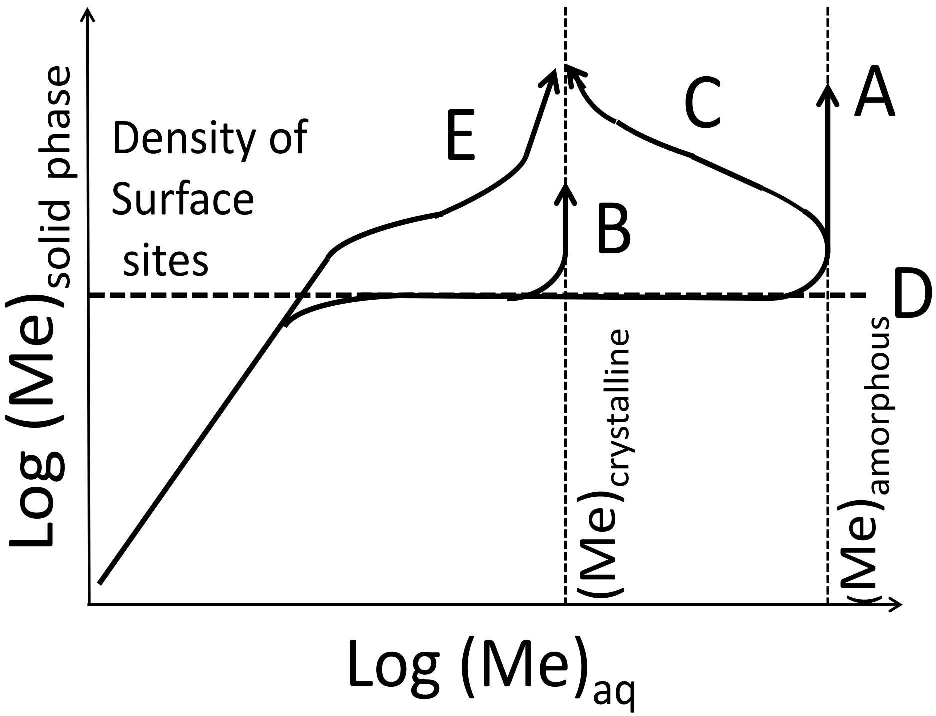


Adsorption



Solid solution

Solubility control

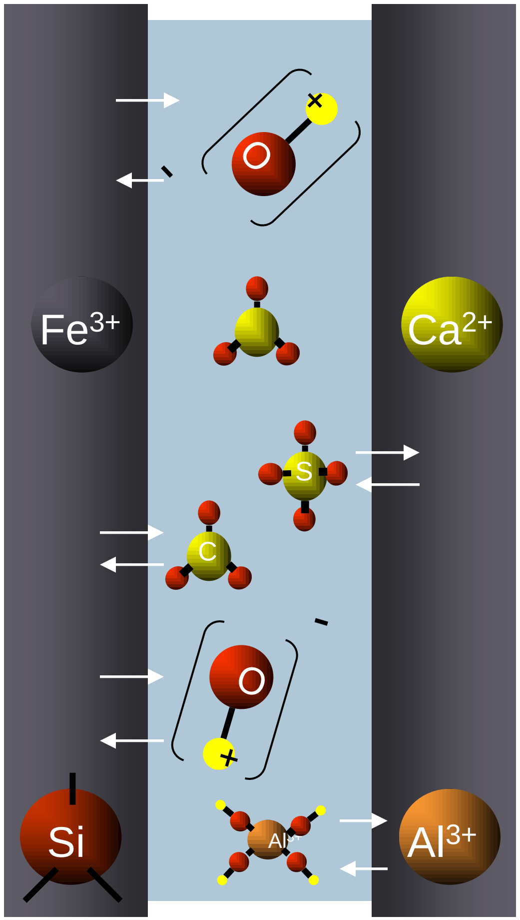


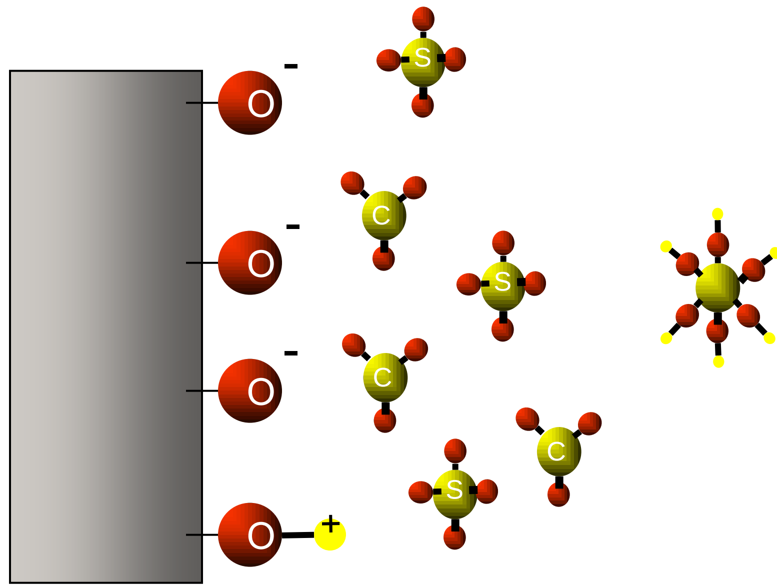
A. Precipitation of an amorphous compound
B. Precipitation of a crystalline compound
C. Ageing
D. Adsorption
E. Solid solution

Langmuir, 1997

Adsorption

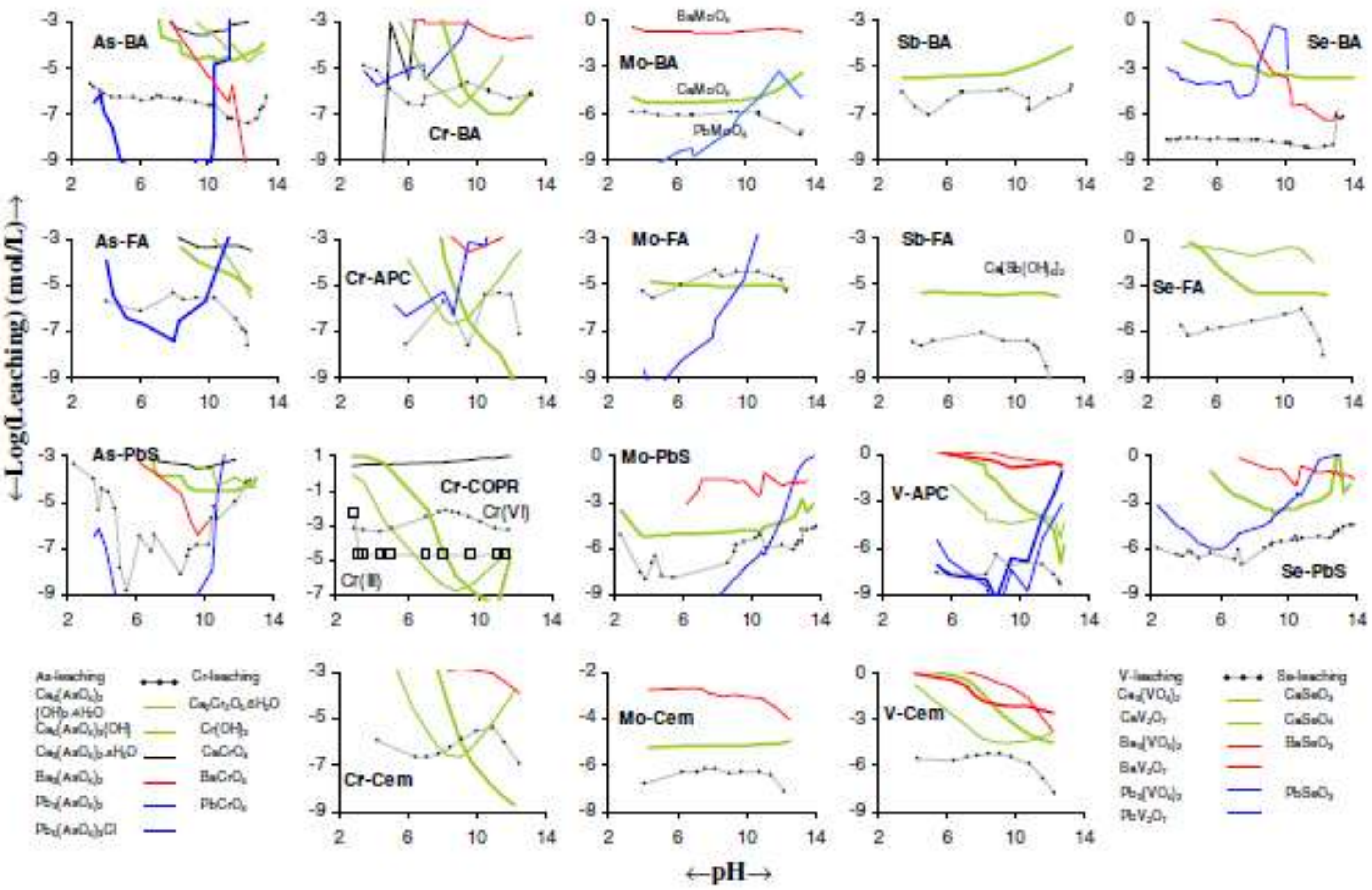
Alkaline waste porewaters





Adsorption

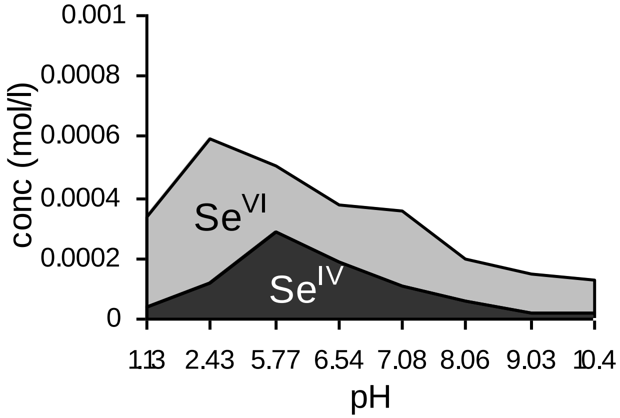
Precipiation



Cornelis et al. 2008a

Knowledge gaps

- No knowledge of the redox speciation
- Errors in thermodynamic database
- Insufficient knowledge of possible interactions

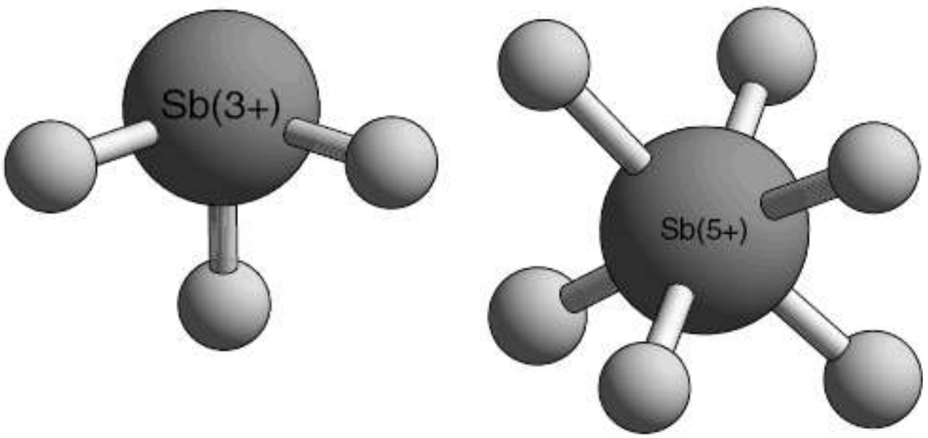


For example:
Se leaching from residue from physico-chemical treatment of wastewaters from Se production (Umicore)

Cornelis et al. 2008b, J. Hazard. Mat. 159, 271-279.

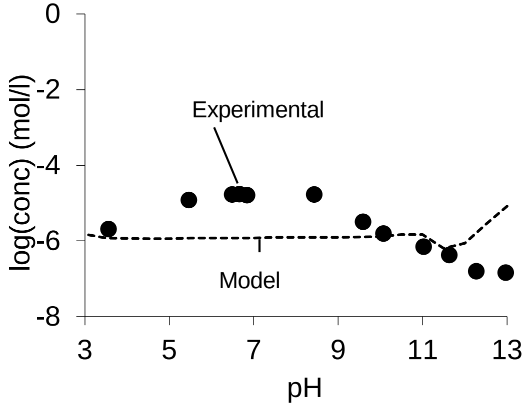
Most critical elements: Se, Mo, Sb, V, (W)

Antimony



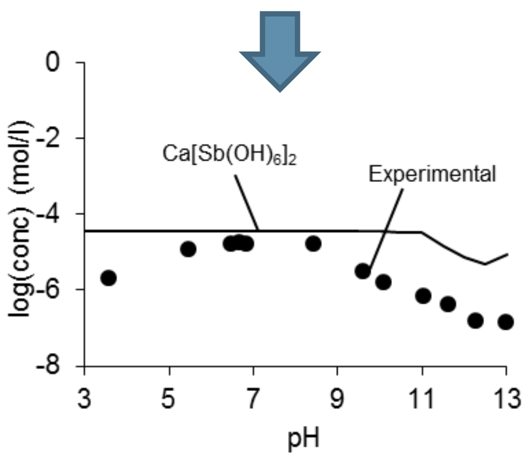
Antimony in OPC paste

$Ca^{2+} + Sb(OH)_6^- = Ca[Sb(OH)_6]_2$ $\log K_{sp} = 12.55$



$Ca^{2+} + Sb(OH)_6^- = CaSb(OH)_6^+$ $\log K_{ass} = 2.15$

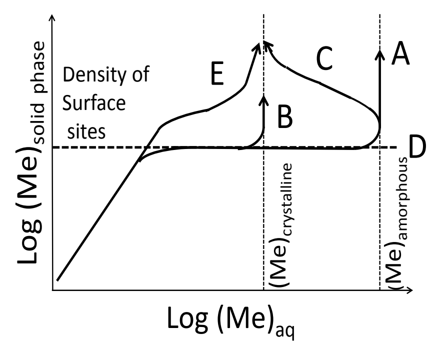
Cornelis et al., 2011. Appl. Geochem. 26, 809-817.



Sb leaching as a function of pH
in a 1000 mg kg^{-1} spiked OPC paste

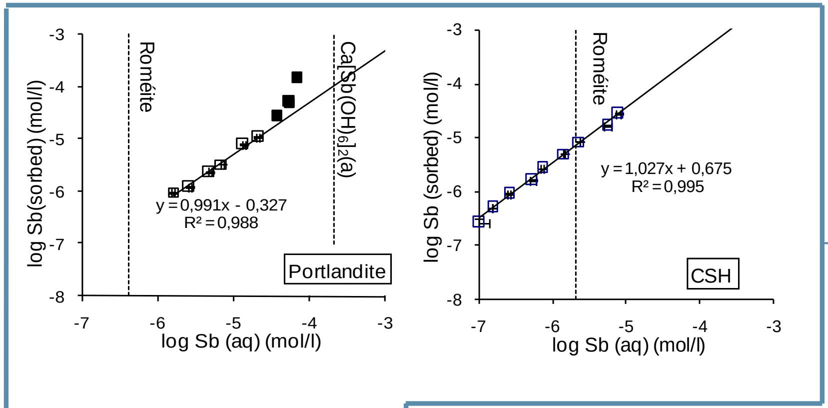
$Sb(OH)_6^-$ interaction with

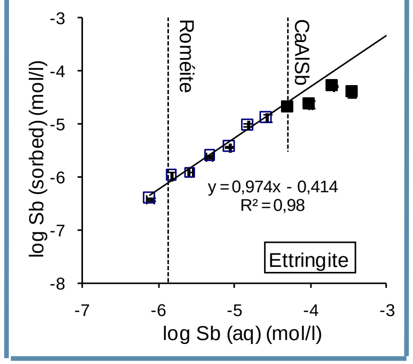
- CSH
- Monosulphate
- Portlandite
- Ettringite



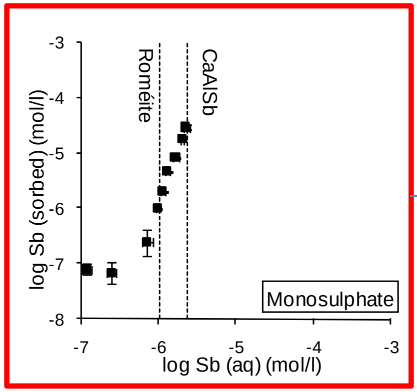
Antimony in OPC paste

- Adsorption isotherms

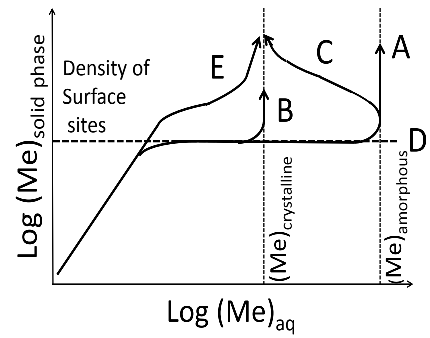




Surface Adsorption

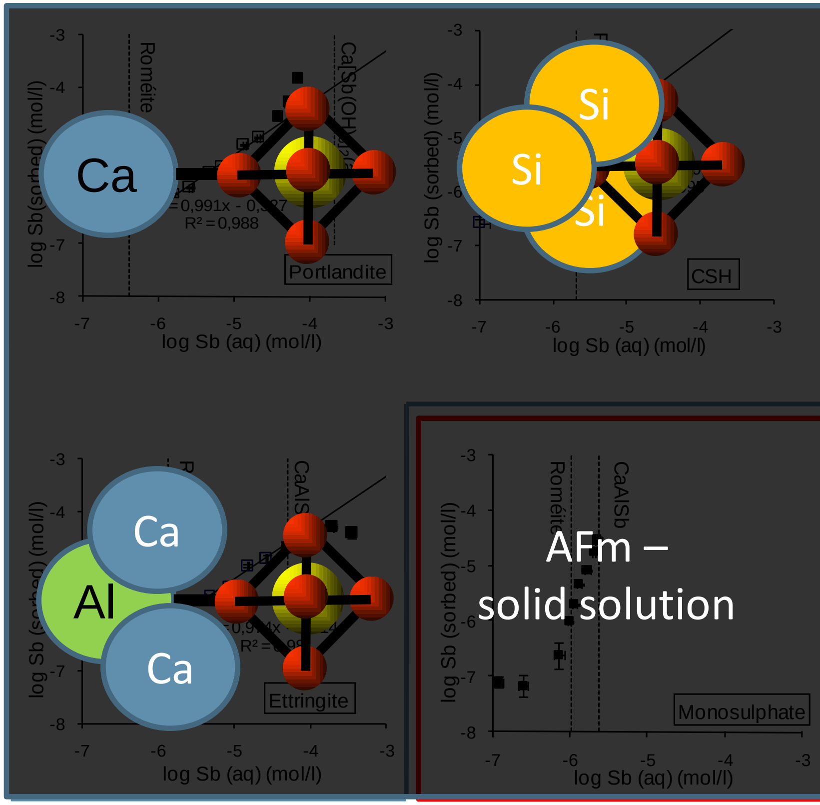


Solid solution formation

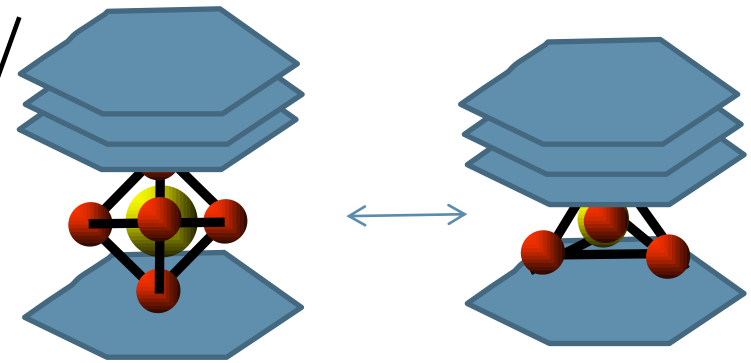


Antimony in OPC paste

- Sb K-edge EXAFS

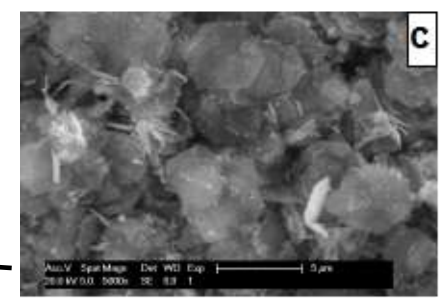


Afm phases: Stacked $Ca_4Al_2(OH)_{12}^+$ layers



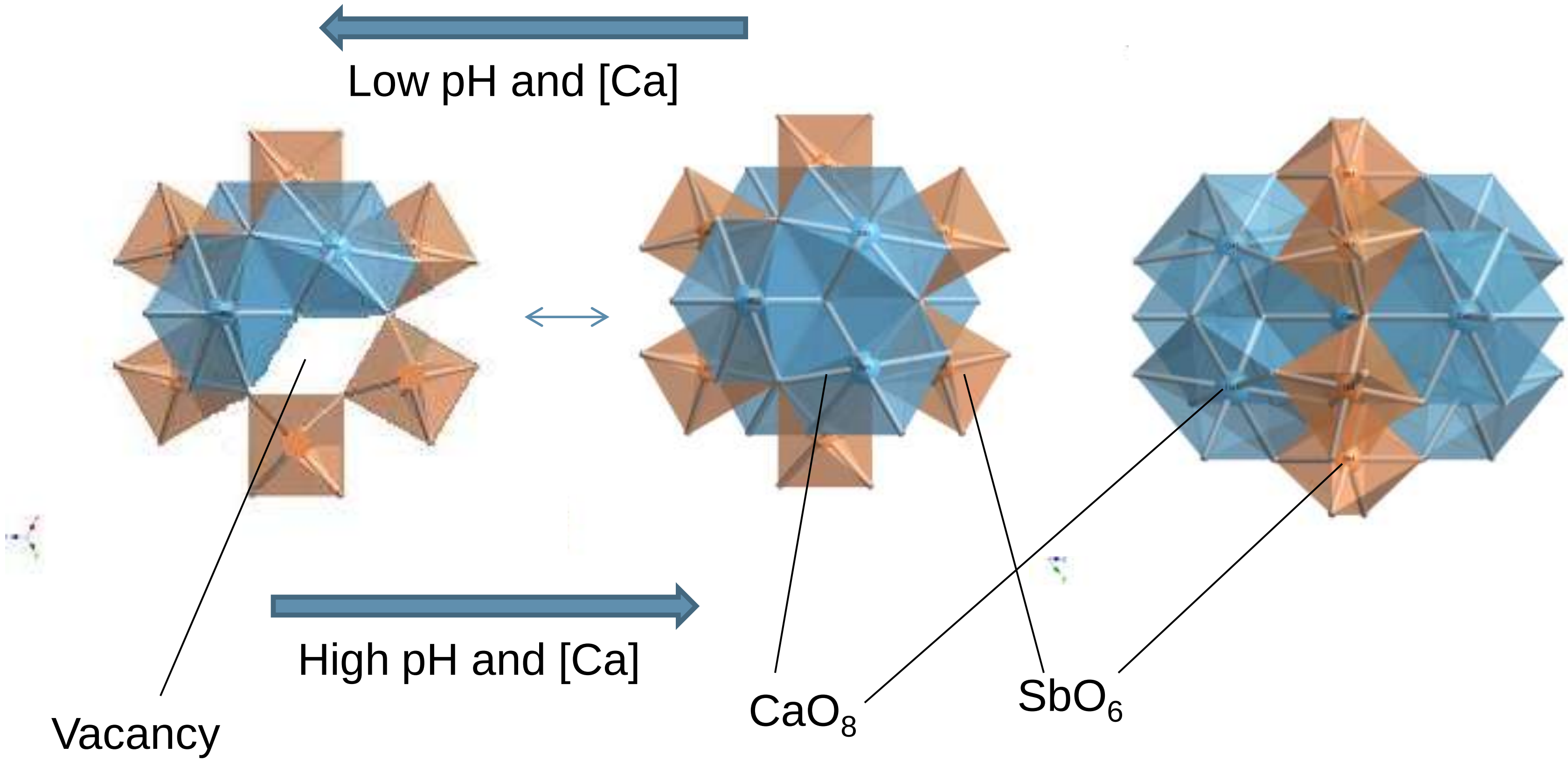
$Ca_4Al_2[Sb(OH)_6]_2(OH)_{12}.3H_2O$ $\log K_{sp} = 65.4$

$\leftrightarrow Ca_4Al_2(SO_4)(OH)_{12}.26H_2O$



Romeite - structure

Calcium antimonate = Romeite

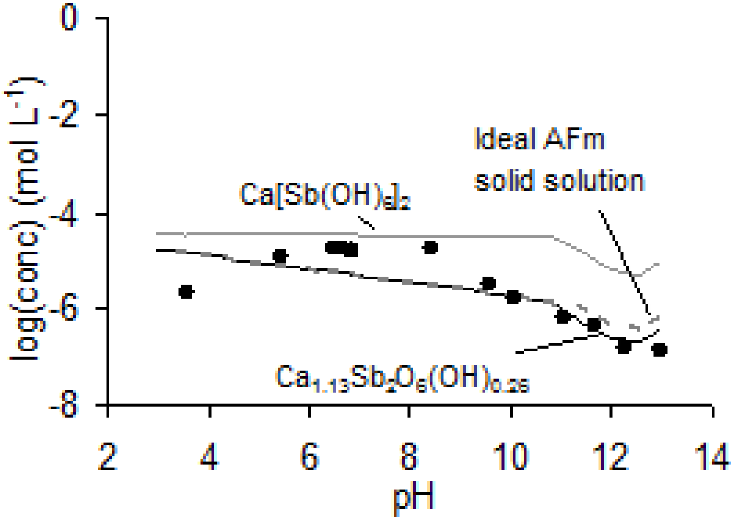


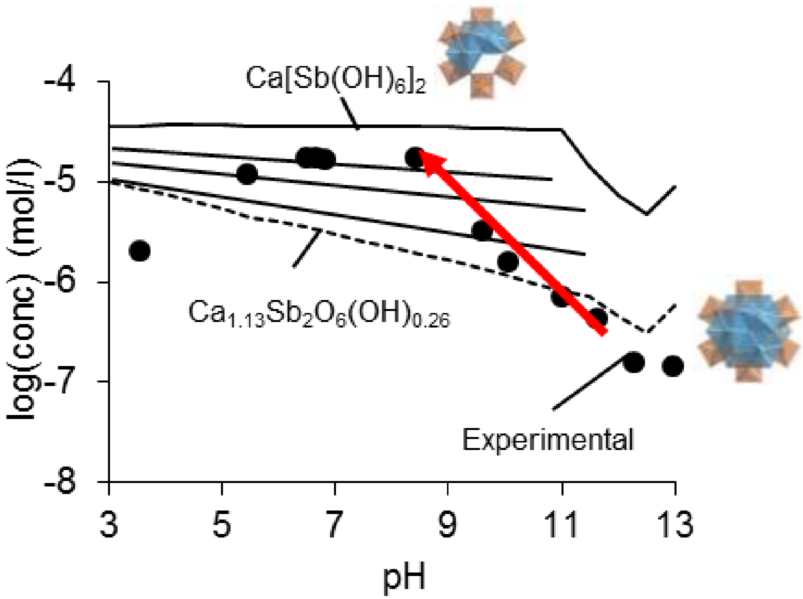
XRD + Rietveld analysis
EXAFS analysis

Cornelis et al., 2011. Appl geochem 26: 809-817.

Antimony in OPC paste

pH – dependent leaching





$Ca[Sb(OH)_6]_2 = Ca^{2+} + 2\ Sb(OH)_6^-$

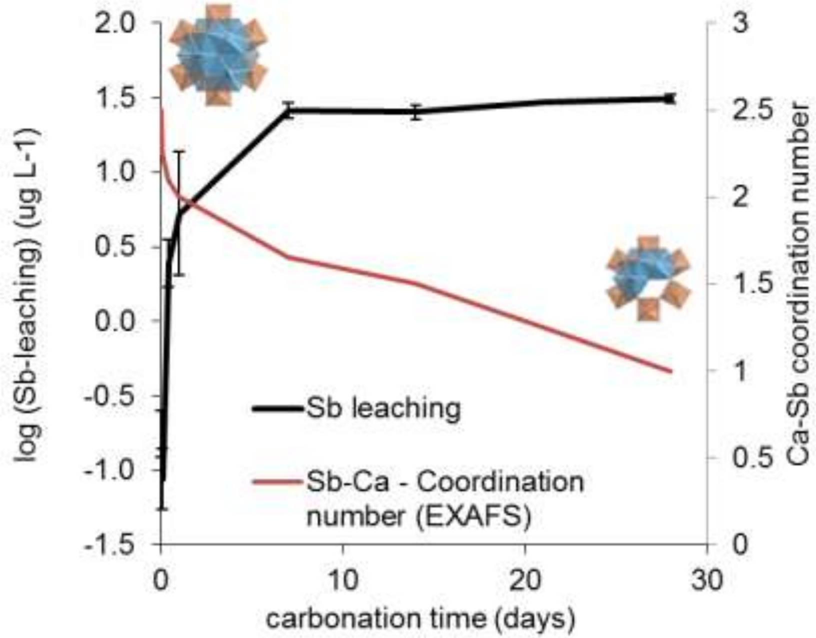
$\log K_{sp} = 12.55$

$Ca_{1.13}Sb_2O_6(OH)_{0.47} \cdot xH_2O$ **$+ 0.47H^+$** $= 1.13\ Ca^{2+} + 2\ Sb(OH)_6^- + xH_2O$

$\log K_{sp} = -12.50$

Antimony in OPC paste

Carbonation dependent leaching



Carbonation:

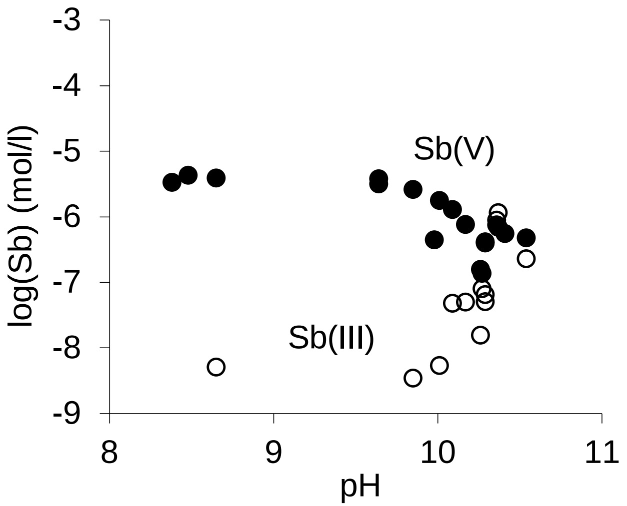
- [Ca] decreases
- pH decreases

➔ Composition of rometie changes

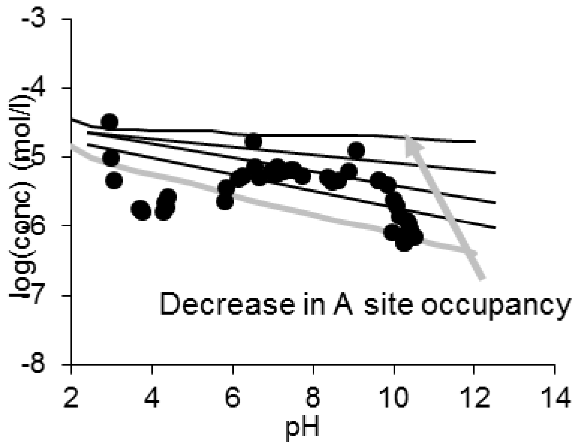
➔ Sb becomes more soluble

Antimony in bottom ash

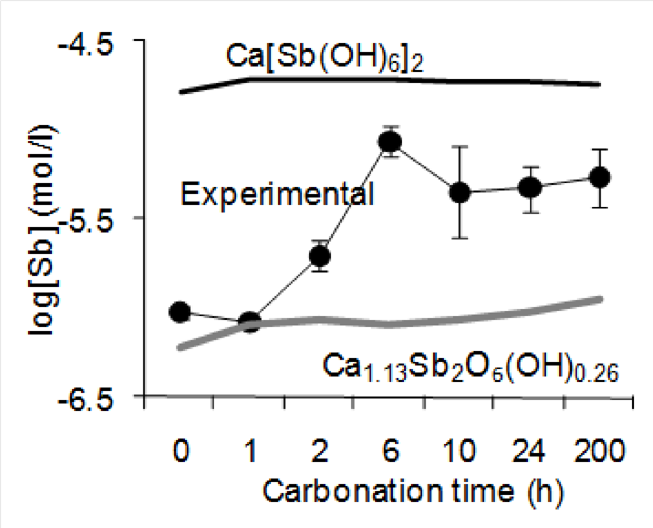
HPLC-ICP-MS



pH-dependent leaching



Carbonation -dependent leaching



Importance of precipitation

Element	Oxidation state	Mechanism
As	V	**Calcium arsenate precipitation**
	III	**Calcium arsenite precipitation**
Cr	VI	solid solution formation with AFt phases
	III	**$Ca_2Cr_2O_5$ precipitation**
Mo	VI	**$CaMoO_4$ precipitation,** solid solution formation with AFm-phases
Se	VI	solid solution formation with AFt phases
	IV	**$CaSeO_3$ precipitation** Adsorption to CSH
Sb	V	**Calcium antimonate precipitation**
	III	**Sb_2O_3 precipitation**, adsorption to oxides, **spinels**
V	V	**$Pb_2(VO_4)_3$ or $Ca_3(VO_4)_2$ precipitation**
	III	**$V(OH)_3$ precipitation or contained in spinels**
W	VI	**$CaWO_4$ precipitation**
	III	**Contained in spinels**

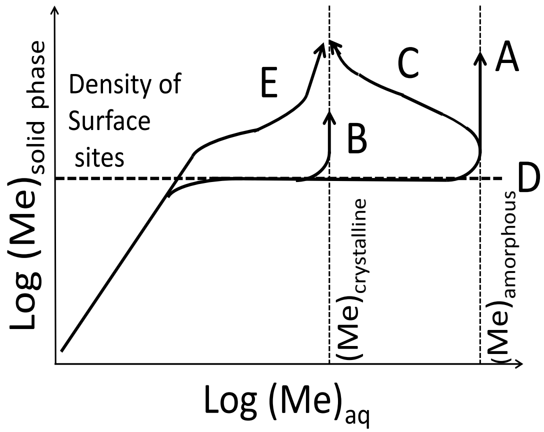
Solubility control by

- Calcium metalates
- Spinels for +III states

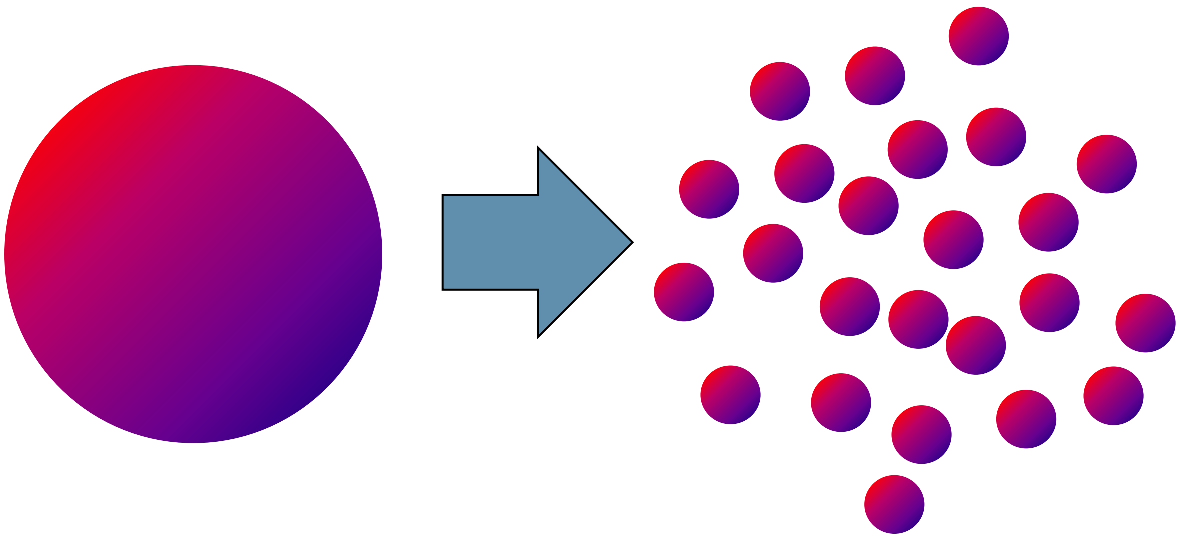
Reduced states generally have lower solubilities

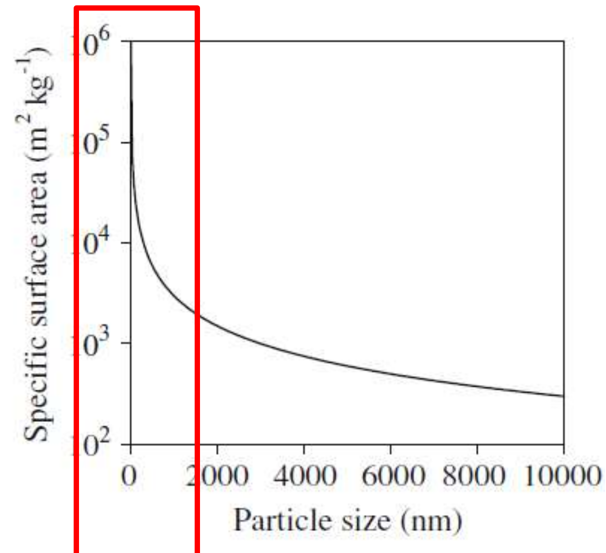
What can be done?

- pH and Ca-concentration needs to be high
- Ageing
  Slow cooling may e.g. Improve Cr^{III}, V^{III}, Sb^{III} uptake in spinels
- Reduction to less soluble species
- In some cases accelerated carbonation combined with neoformation of iron oxides



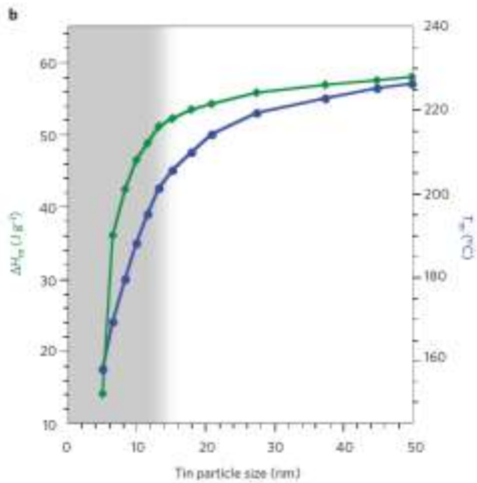
Nanoparticles





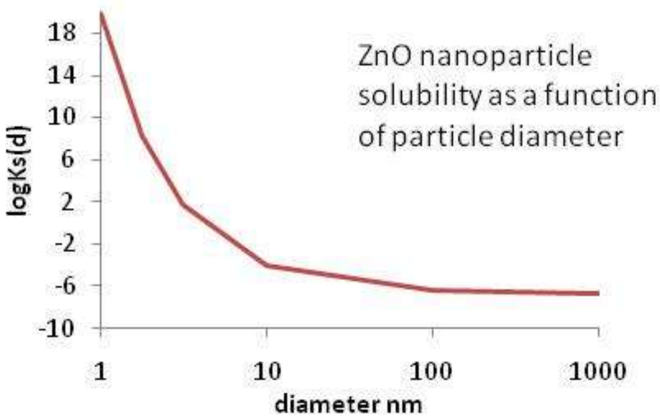
Nanoparticles: ”having at least one dimension less than 100 nm”

Nanoparticles

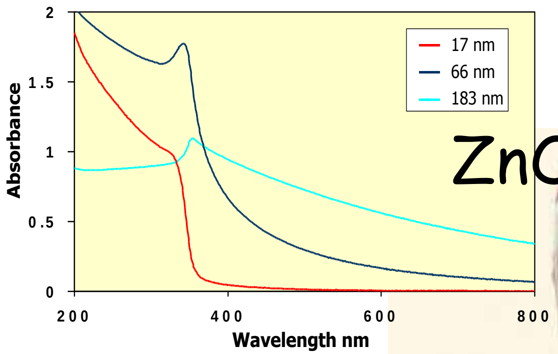


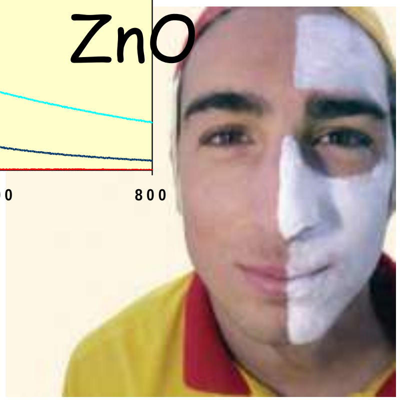
Heat of fusion (ΔH_m) and melting point of Sn nanoparticles

(Auffan et al., 2009
Nature Nanotechnol. 4, 634-641)



Gold nanoparticles of different size



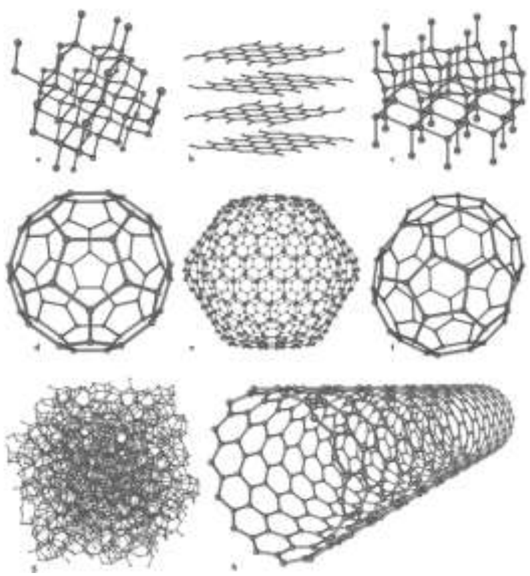


UV absorption by ZnO nanoparticles of different size

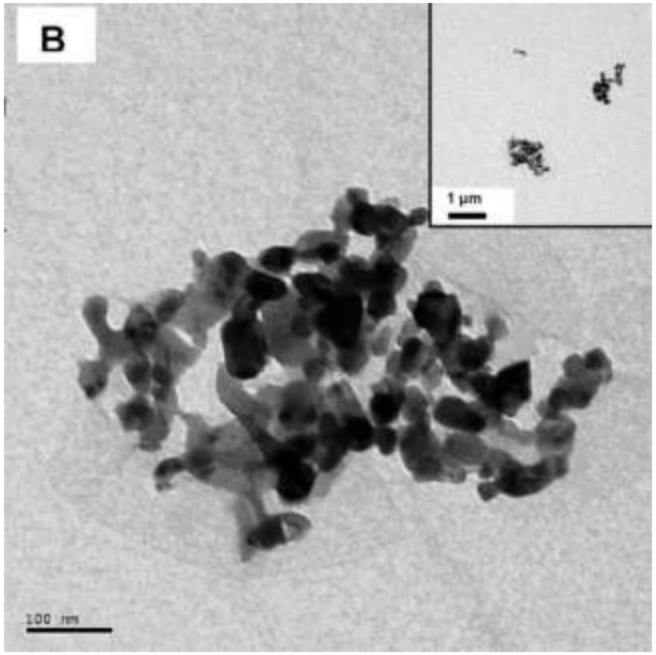
Nanoparticles today

Nanoparticles today

Carbon allotropes



Metal and metal oxides



Environmental applications

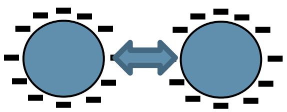
- High strength cements using Carbon nanotubes, SiO_2, Cr_2O_3, TiO_2 nanoparticles
- Fe^0 nanoparticles reducing solubility of CrO_4^{2-}, AsO_4^{3-}, organohalogens, ...
- Films of SiO_2 and TiO_2 nanoparticles on slags

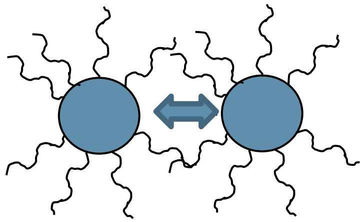
➔ Interest in:

Geochemistry of nanoparticles

Environmental fate and effect of nanoparticles

Aggregation

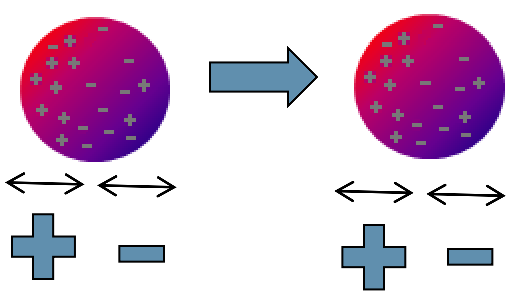




Repulsive electrostatic and steric forces

Vs.

Attractive Van der Waals



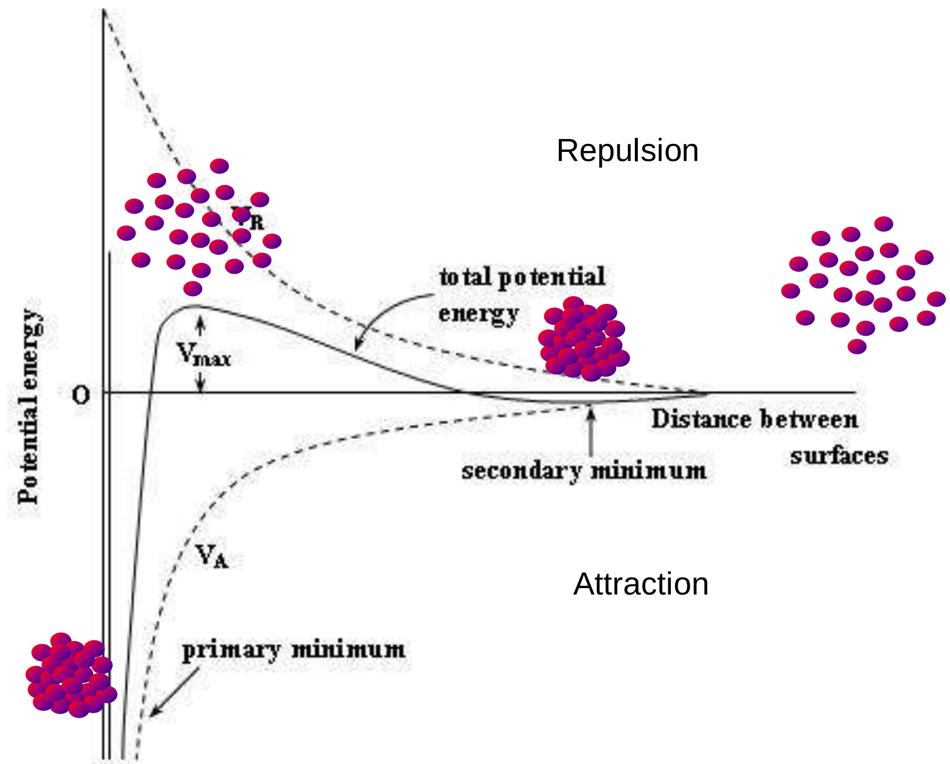
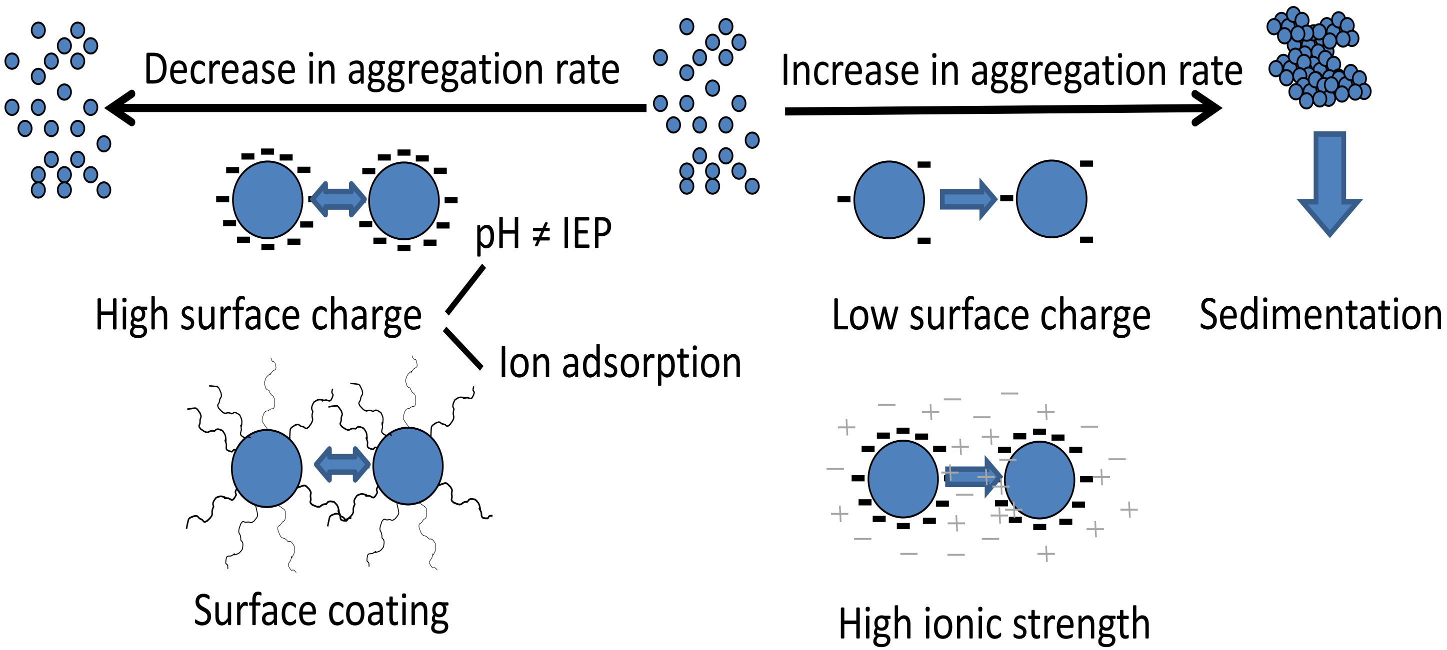
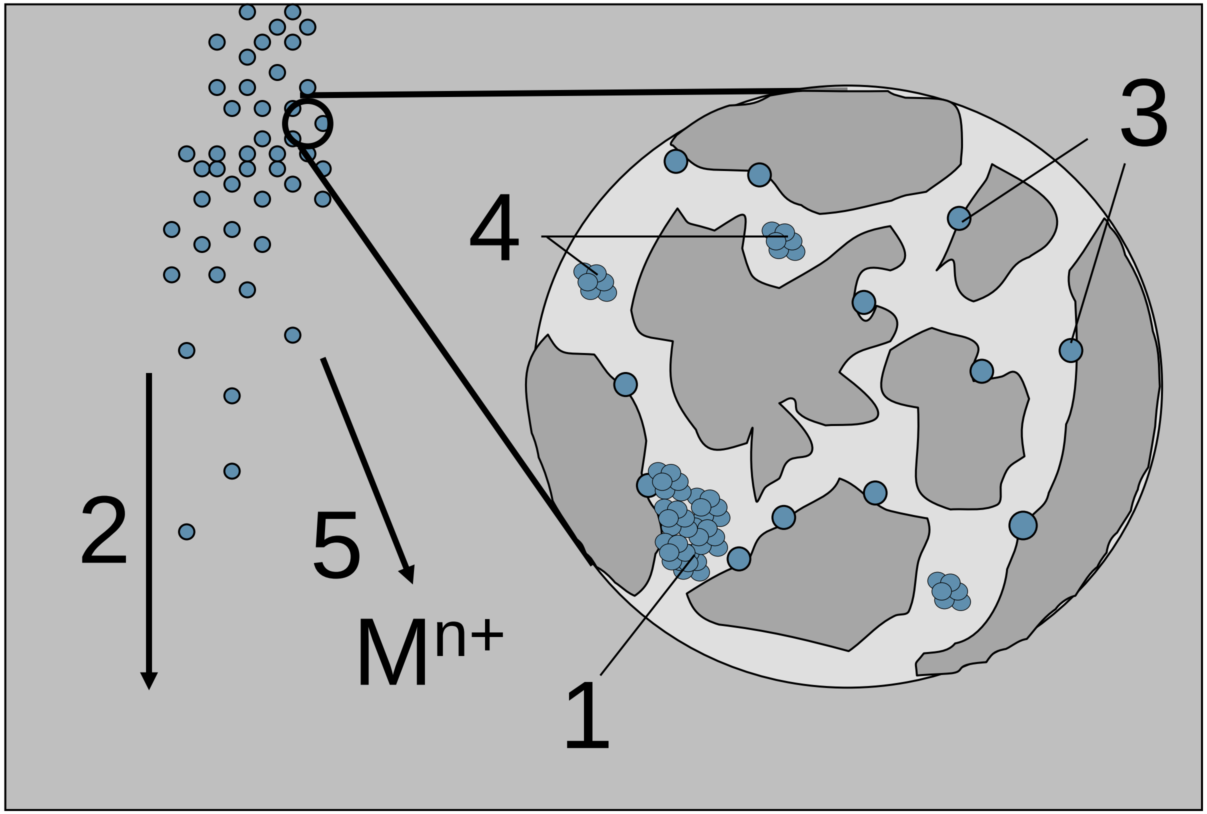


Figure 2.16

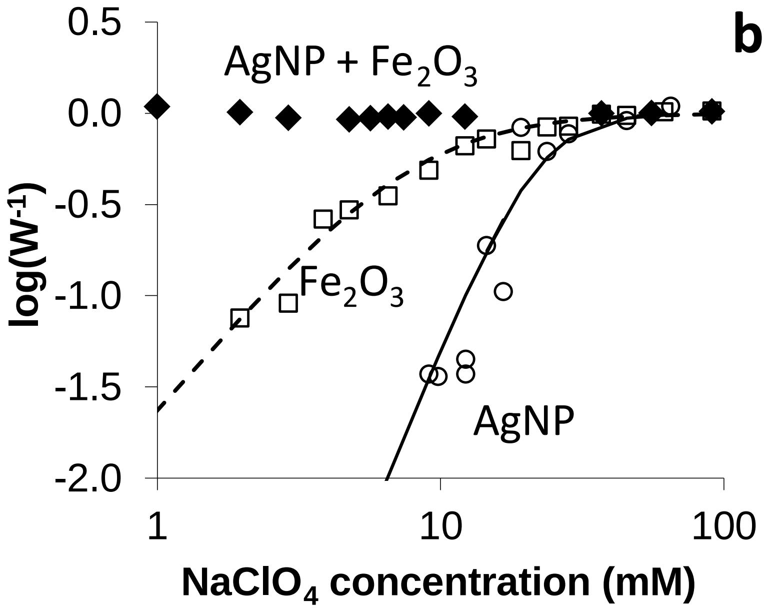
Aggregation

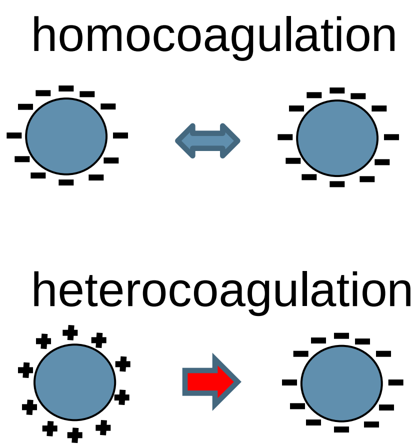


Fate in solid matrices



Fate in solid matrices

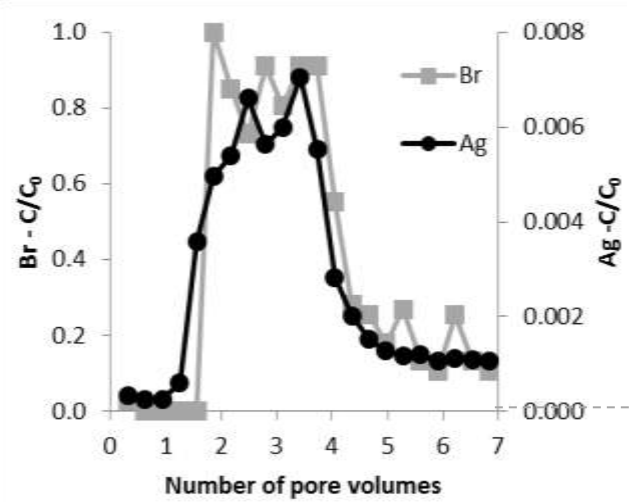


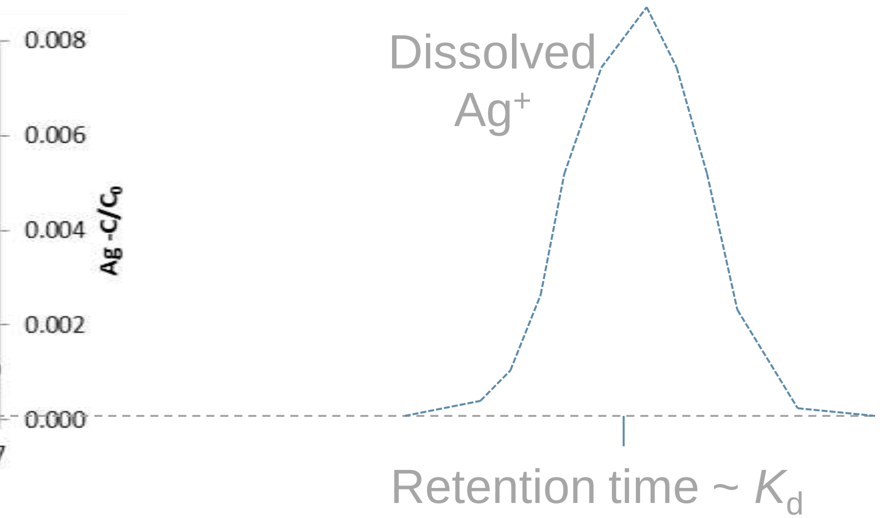


Cornelis et al., 2011. Environ. Sci. Technol. 45, 2777-2782.

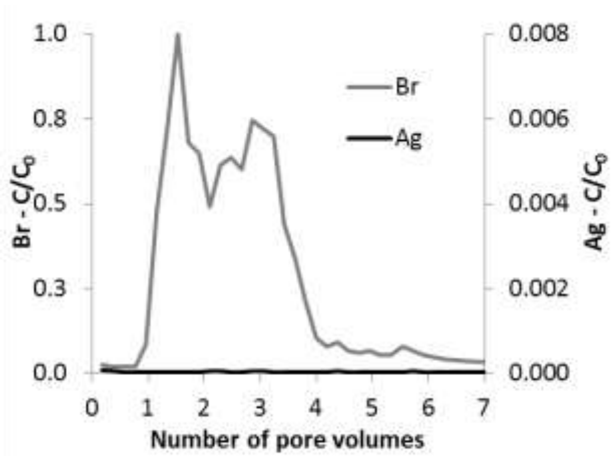
Fate in solid matrices

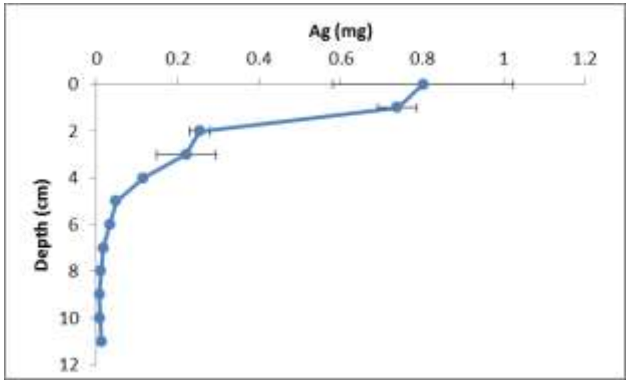
Sandy soil:



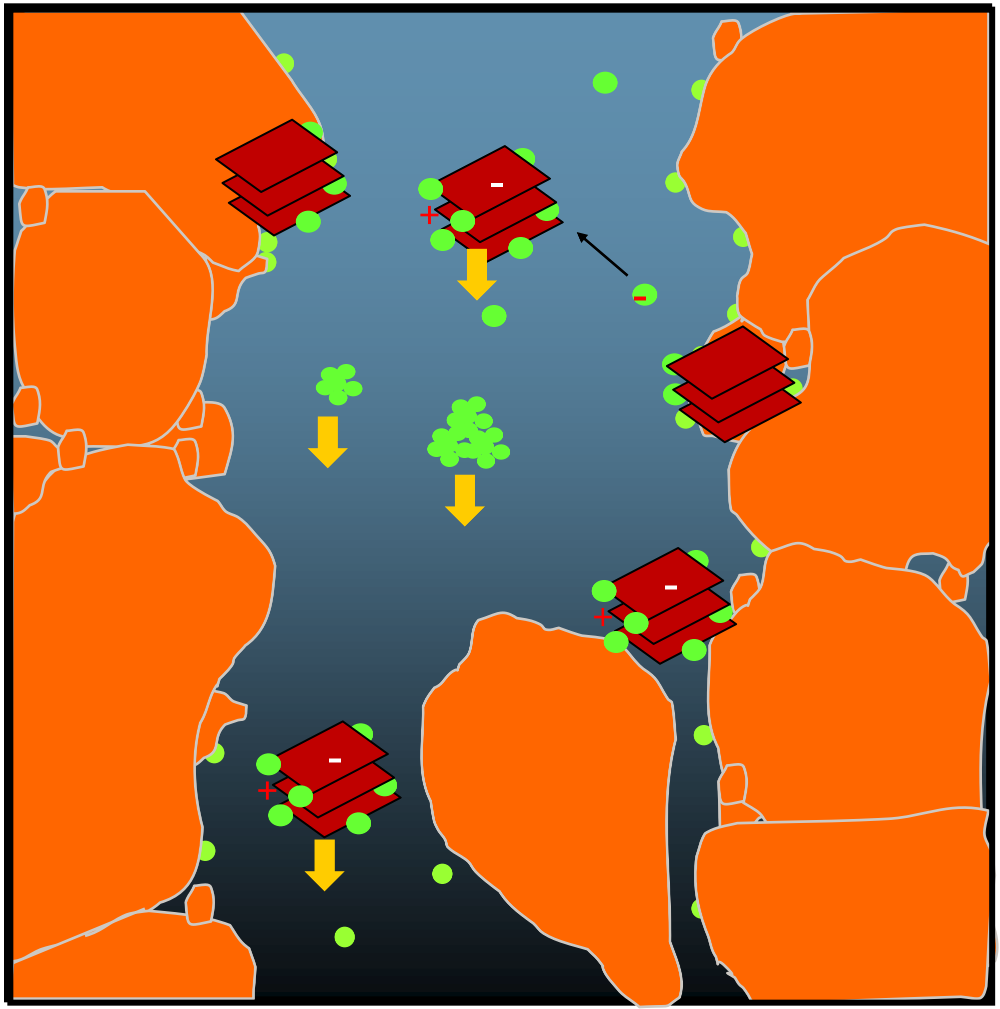


Clayey soil:





Fate in solid matrices



Colloid mediated
Nanoparticle
transport

Nanoparticles in slags/wastes ?

- High pH
  - High negative nanoparticle charge → stability
  - Most NP have coatings → stability
- Ionic strength high
  - 70 – 200 mM whereas critical coagulation concentrations are generally < 100 mM → Aggregation

Acknowledgments

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