MONTMORILLONITE COLLOID SIZE HETEROGENEITY EFFECTS ON: I. STABILITY, II. RADIONUCLIDES SORPTION III. SORPTION REVERSIBILITY

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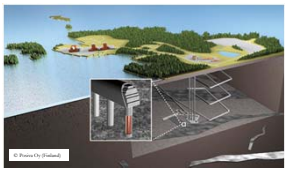
Deep nuclear waste disposal



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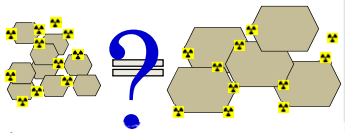
Glaciation cycles

= Potential release of clay colloids, acting as radionuclide carriers under favorable physico-chemical conditions → Colloidal mobility depends on their stability and size →



Are the smaller clay colloids miniatures of the bigger ones?

EXPERIMENTAL

Material

Unpurified MX80 bentonite (Volclay Ltd.), purified fulvic acids (FA) from Gorleben site, Lower Saxony, Germany

Contact solution

Synthetic carbonated ground water (SGW, glacial melt water type) containing Na^+ (28.4 mg/L), Ca^{2+} (1.5 mg/L), F^- (2.8 mg/L), Cl^- (2.6 mg/L), SO_4^{2-} (4.1 mg/L); HCO_3^-: 10^{-3} M. Initial pH: 8.4. IS: 1.3 10^{-3} M.

Characterization

Photon Correlation Spectroscopy (PCS), Flow Field-Flow Fractionation (AsFlFFF), XRD, SEM-EDX, ICP-OES/MS.

COLLOID FRACTIONATION, SIZE AND STABILITY [2]

Suspension (i^{th} supernatant)	Separation by sedimentation (S) or centrifugation (C)	Mean size from 1:PCS[c] 2: AsFlFFF[d] in nm	Edge sites (mmol/kg)
S0	S (3 days)	1: ~ 692 2: ~229 (35%)	11.2
S1	C: 30' at 313 x g	1: ~610 2: ~198 (62%)	17.8
S2	C: 1h at 700 x g	1: ~337 2: ~189 (77 %)	33.5
S3	C: 4h at 1.200 x g	1: ~ 186 2: ~151 (88%)	67.0
S3.5	C: 30' at 26.000 x g	1: ~ 172 2: ~84 (>90%)	64.7
$S3.5^{UC}$	C: 30'at 26.000 x g[a]	1: ~ 167 2: ~95 (>95%)	67.9
$S3.5^{UC, FA}$	C: 30' at 26.000 x g[b]	1: ~ 143 2: ~124 (87 %)	89.5

Table 1: Sequential clay fractionation protocol, mean clay colloidal sizes obtained and total amount of edges sites (Al-OH+Si-OH groups) calculated acc. to [1]. S0 is the initial suspension: 10 g/L raw MX80 in SGW. a: one step centrifugation of S0; **b:** one step centrifugation of S0 containing in addition 11.8 mg.L^{-1} FA; **c:** suspensions diluted to 10 mg.L^{-1}, measured 10 times during 5 sec, 5 times, mean values reported; **d:** peak maximum position and colloidal recovery.

- The fractionated clay suspensions present broad clay aggregate (nano-)size distributions (see AsFlFFF and ICP-MS results in [2]),
- Larger colloidal mean sizes than expected are obtained, nevertheless,
- The mean size of the clay aggregates decreases with the number of centrifugation steps (Table 1), so
- The fractionation protocol is successful.

→ The total amount of edge sites is found to increase by a factor 6 from the largest to the smallest colloidal fractions.

→ Presence of FA during the fractionation protocol increases the amount of collected clay colloids.

→ No difference in stability in 0.01 M up to 3 M ionic strength (IS) is evidenced between the different clay suspensions.

[1] Tournassat, C. et al. (2003), Am. Min. 88: 1989–1995

[2] Norrfors et al., Applied Clay Science, 114(2015)179-189

RADIONUCLIDE (RN) BATCH SORPTION AND SORPTION REVERSIBILITY

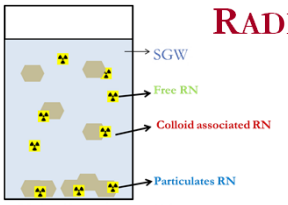


Fig.1: Schematic figure for distribution of RNs in sorption expt.

- [MontM] = 20 mg/L
- [RN]: 10^{-8}M ^{232}Th(IV); $5{\cdot}10^{-9}$M ^{99}Tc(VII); 10^{-8}M ^{233}U(VI); 10^{-8}M ^{237}Np(V); $2{\cdot}10^{-9}$M ^{242}Pu(IV)
- Sorption contact time: 3 days, 2 weeks, 1 and 6 months
- pH: 8.4 to 9.3
- $Eh_{(after\ 1\ y\ CT)}$: - 191 to -216 mV

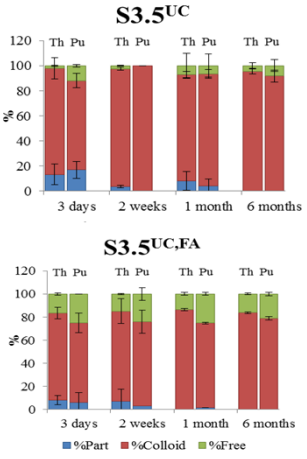


Fig. 2: Distribution of Th(IV) and Pu(IV) at varying sorption times. %Part: RNs associated to (clay) particulates (bigger clay size fraction, RN precipitates), %Colloid: RNs associated to clay colloids, %Free: RNs fraction remaining free (and/or complexed by FA if present)

- U(VI), Np(V) and Tc(VII) do not sorb onto the clay colloids under the present chemical conditions, whichever suspension tested
- Th(IV) and Pu(IV) sorb strongly (95% and 90% respectively) onto the montmorillonite colloids. They remain sorbed to larger colloids which sediment with time
- If FA are present initially, the amount of Pu and Th associated with clay aggregates is significantly decreased
- The mean colloid size does not affect the uptake of RNs significantly

→ **Conclusion: Smaller clay colloids seem to be miniatures of bigger ones**

IMPLICATION:
An "average K_D" can be used in reactive transport modeling for all colloidal sizes

[3] Norrfors et al., Applied Clay Science, 2016, In Press

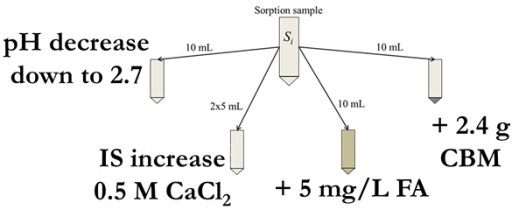


Fig.3: Schematic figure of the reversibility expt. Desorption time: 1 week and 1 year

- Sorption of $U(VI)_{pH7.5}$ and Th(IV) is partly reversible at lower pH in all suspensions; Pu(IV) sorption does not appear reversible even at pH 2.7
- All clay colloids agglomerate at 0.5 M $CaCl_2$ IS. Th and Pu remain sorbed onto the sedimented clay particles
- FA added after a certain sorption contact time results in a reversible uptake of Th and Pu up to 10% and 20%, respectively
- Np(V), U(VI) and Tc(VII) are reduced and sorbed onto the crushed bedrock material (CBM)

IMPLICATION:
RN sorption reversibility is not guaranteed and is dependent of geochemical parameters (i.e. pH, IS, competing ligands, ...)

[4] Norrfors et al., Applied Clay Science, 2016, in prep.

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