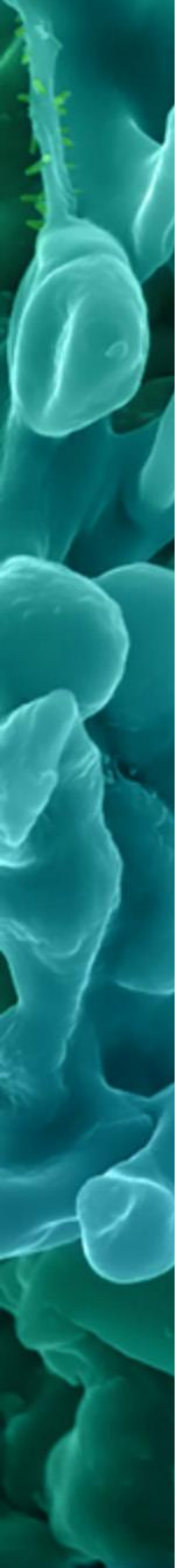

Synthesis and Characterization of Functionalized Organoclays for Use in a Radioactive Waste Repository

November 15, 2022

Carolyn Pearce[1], Nathalie Wall[2], Emily Maulden[2], Elizabeth Gager[2], Seaton Ullberg[2], An Ta[2], Juan Nino[2], Simon Phillpot[2], Maxime Pouvreau[1], Jim Szecsody[1]

[1]Pacific Northwest National Laboratory; [2]University of Florida

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NEUP Nuclear Energy University Program

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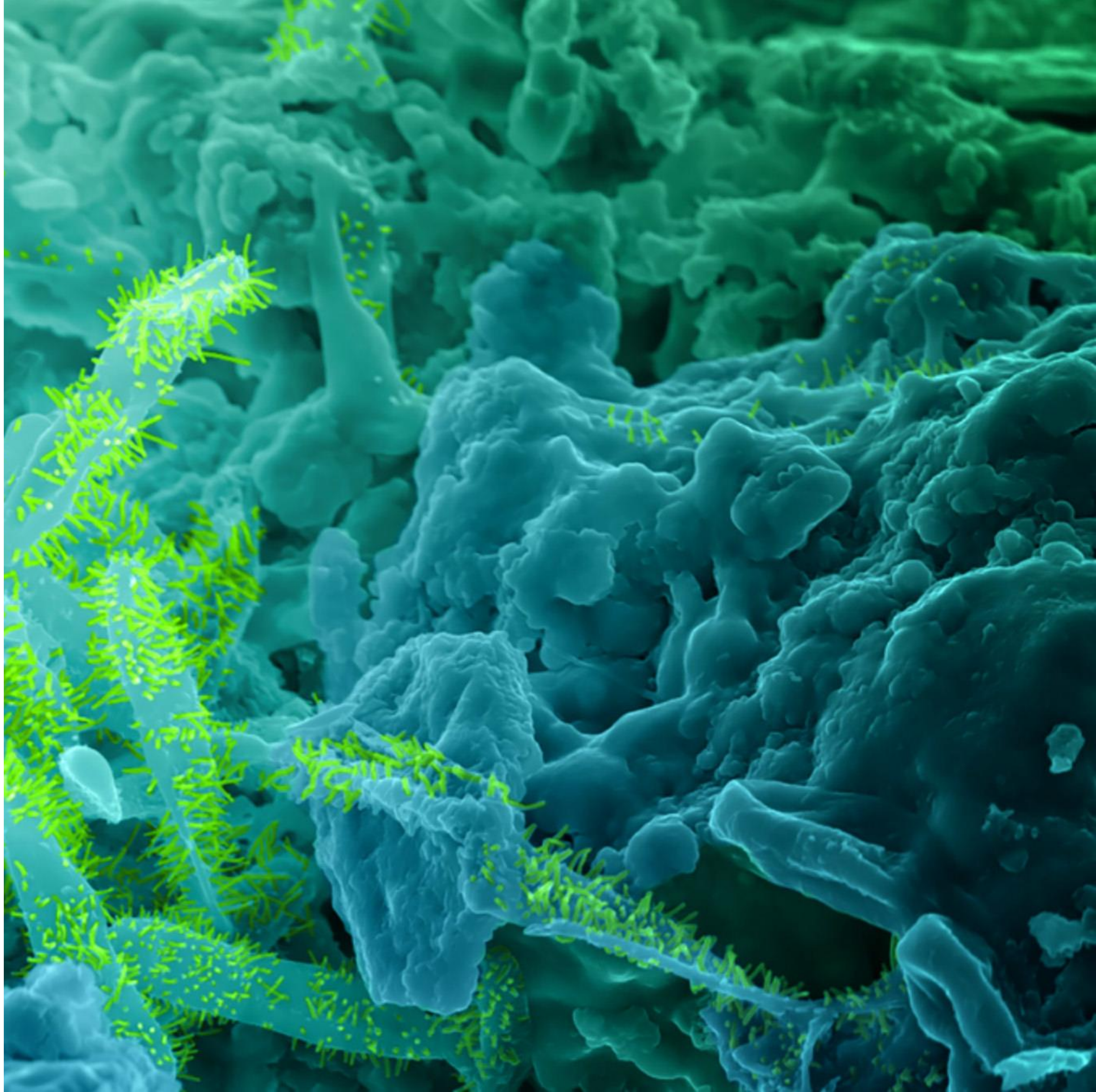
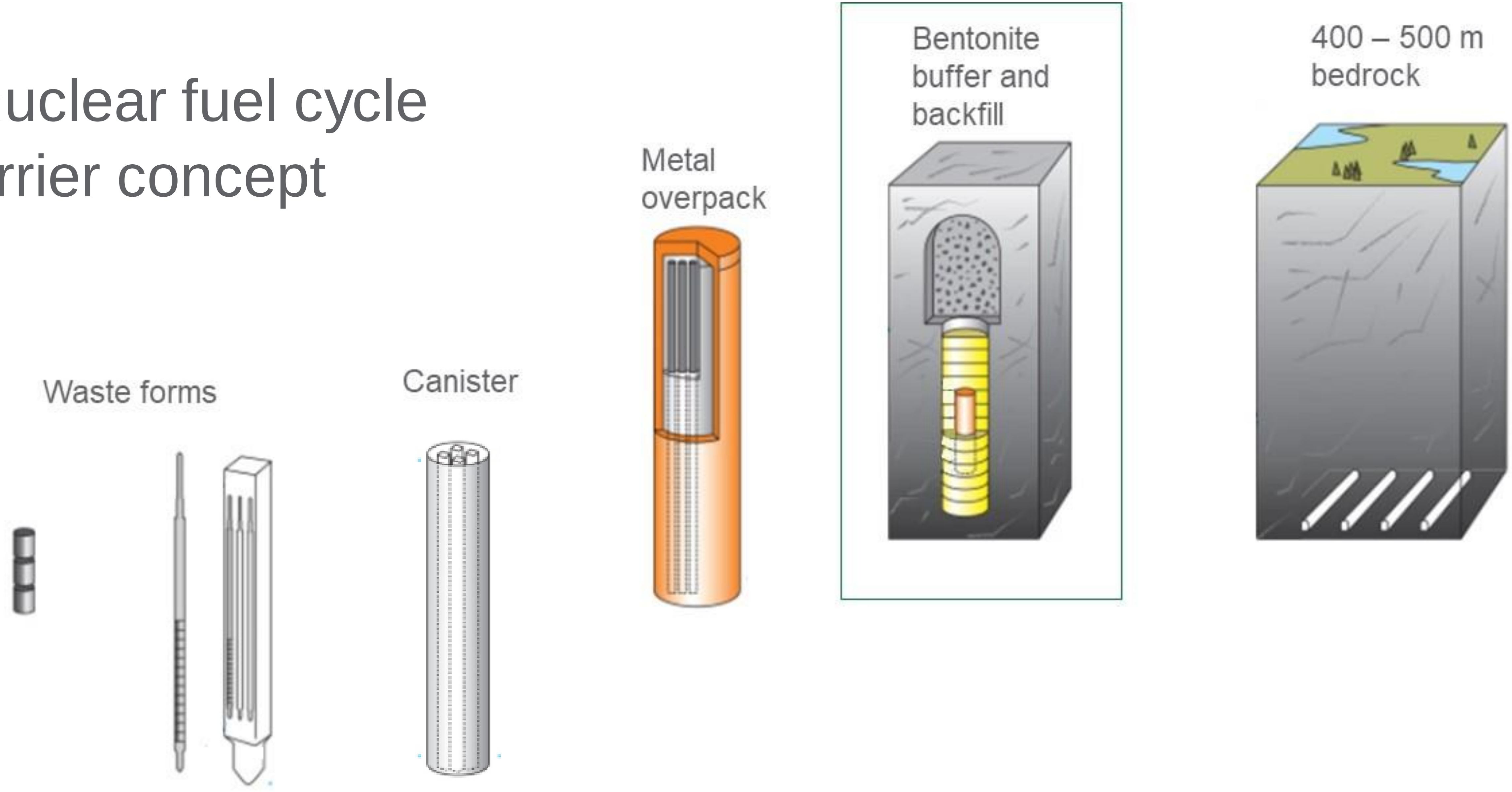


Radioactive waste repository

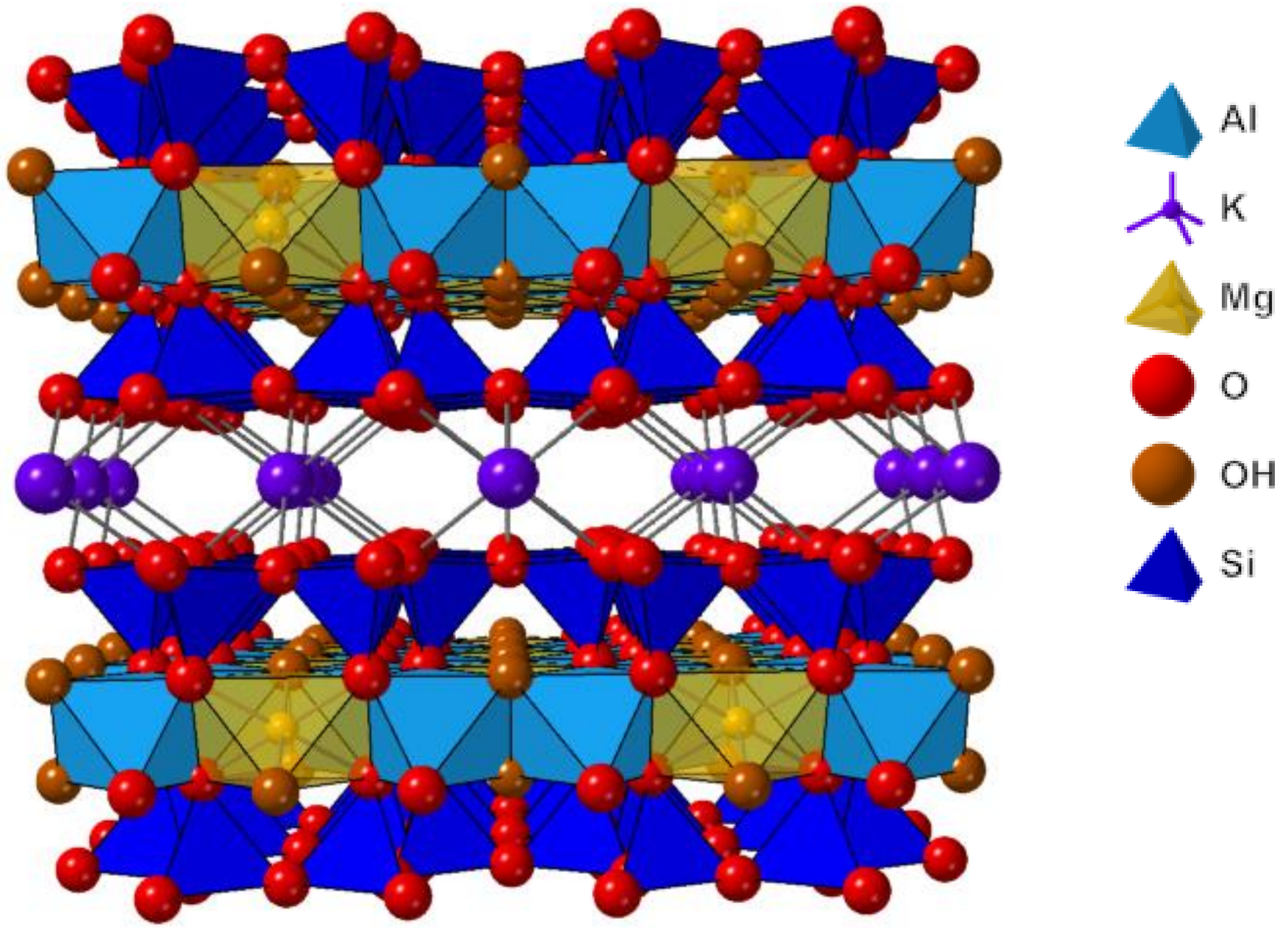
- End of nuclear fuel cycle
- Multi-barrier concept



Source: Posiva Oy; World Nuclear Association

Bentonite backfill to contain contaminants

- Bentonite Properties:
  - Montmorillonite (smectite)
  - Surface area
  - Permeability
  - Cost
  - Cation exchange capacity
  - Cation affinity

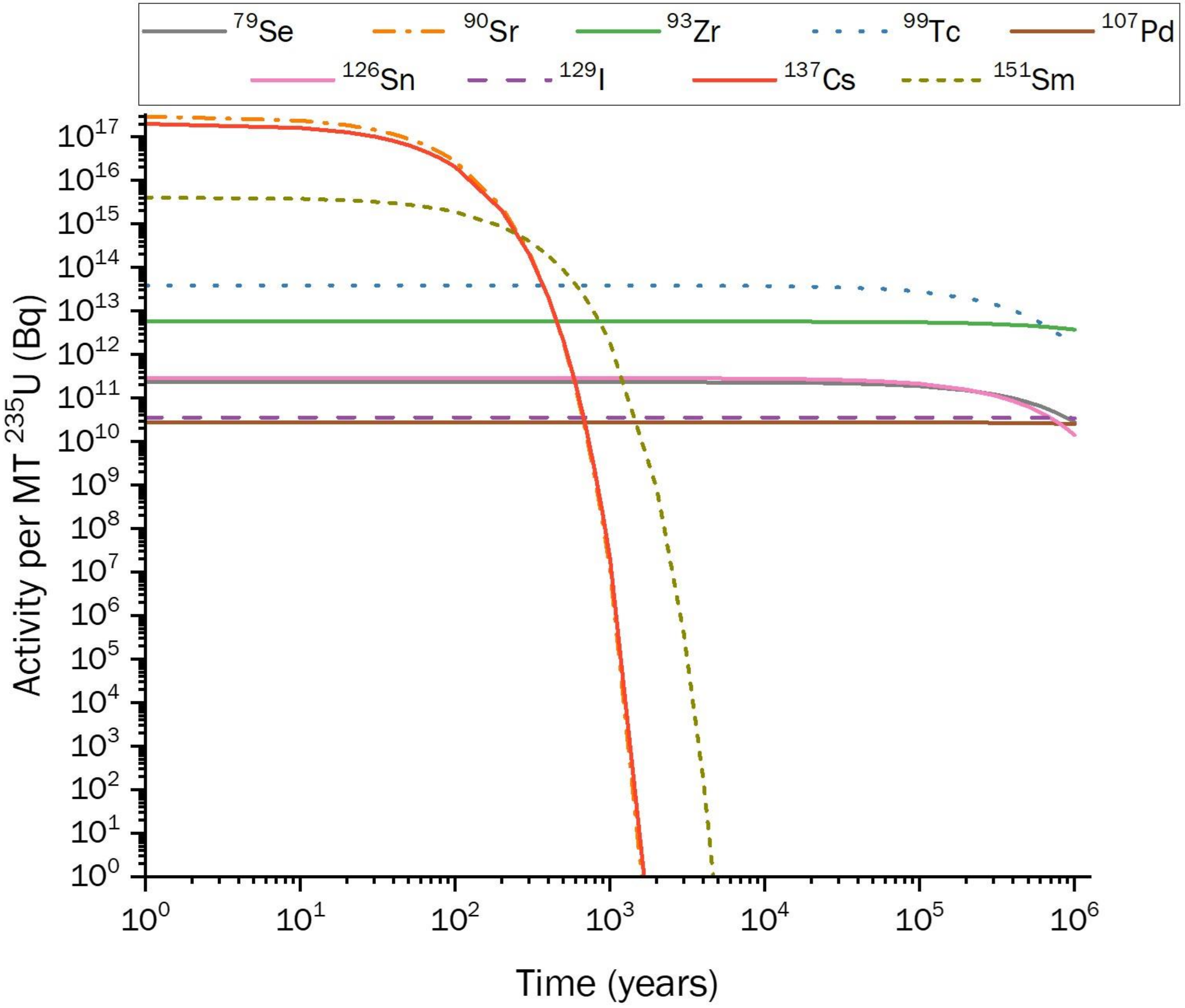


Yang, J.; et al Chemical Engineering Journal, 428, 2022 131333
Tspursky and Drits (1984) Clay Minerals 19:177-193

Problematic fission products

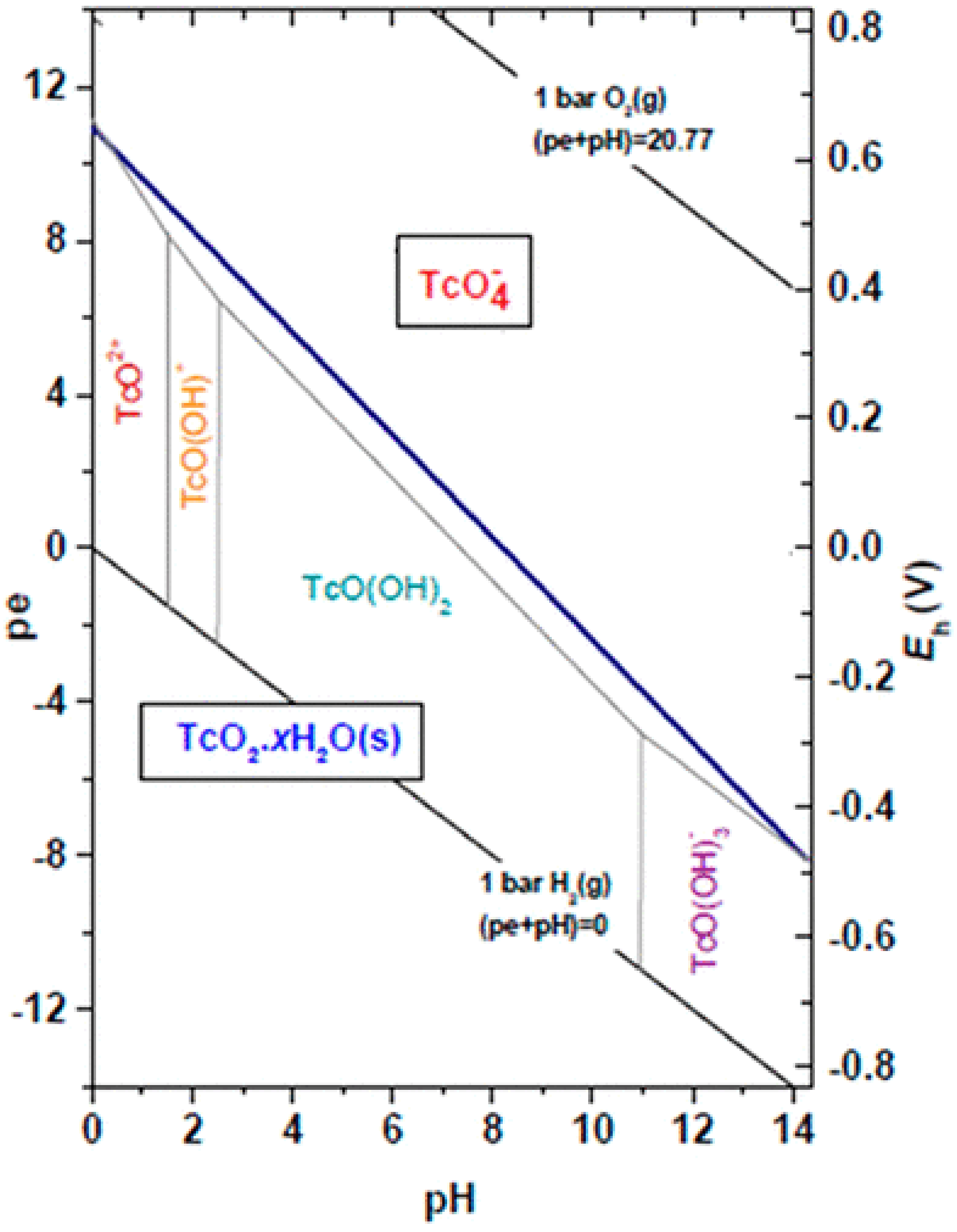
- Elements that exist as cations in the environment:
  - Sr-90
  - Zr-93
  - Pd-107
  - Sn-126
  - Cs-127
  - Sm-151

- Elements that exist as anions in the environment:
  - Se-79 ($t_{1/2}$ = 3.27 x 10^5 y)
  - Tc-99 ($t_{1/2}$ = 2.13 x 10^5 y)
  - I-129 ($t_{1/2}$ = 15.7 x 10^6 y)



ENDF/B-VIII.0 US Evaluated Nuclear Data Library, NNDC
Knolls Atomic Power Lab: Nuclides and Isotopes Chart of the Nuclides. 17th Ed., 2010, Bechtel Marine Propulsion Corp.

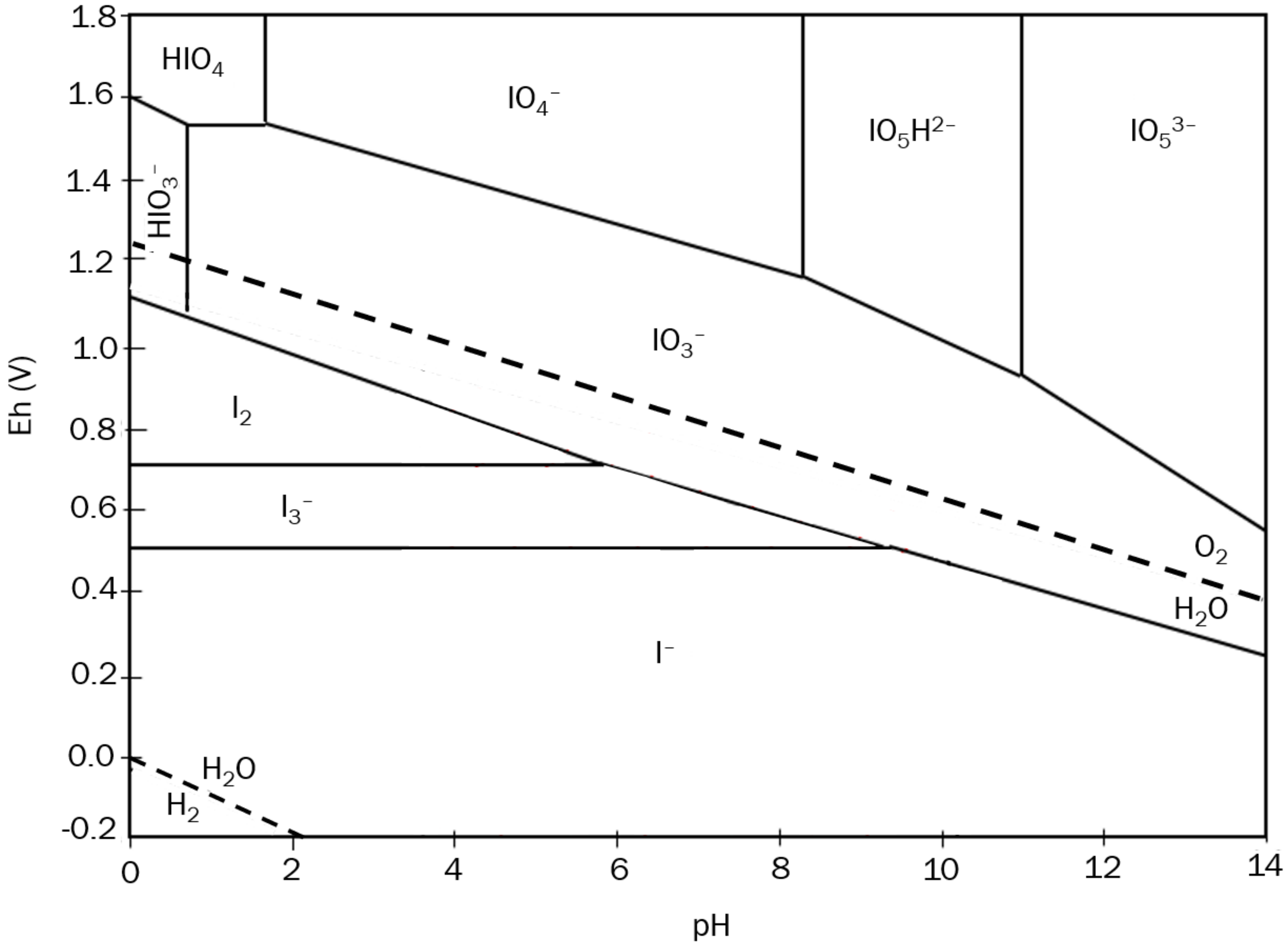
Technetium-99 chemistry



- $Tc^{VII}O_4^-$ is mobile in the subsurface environment
- $Tc^{VII}O_4^-$ can be reduced to produce relatively immobile and sparingly soluble Tc^{IV} species.
- Tc^{IV} solubility on the order of 10^{-9} M in water under near-neutral pH conditions.
- But complexing organic ligands can increase Tc^{IV} solubility.

Pearce et al. ACS Earth Space Chem. 2018, 2, 6, 532–547

Iodine-129 chemistry

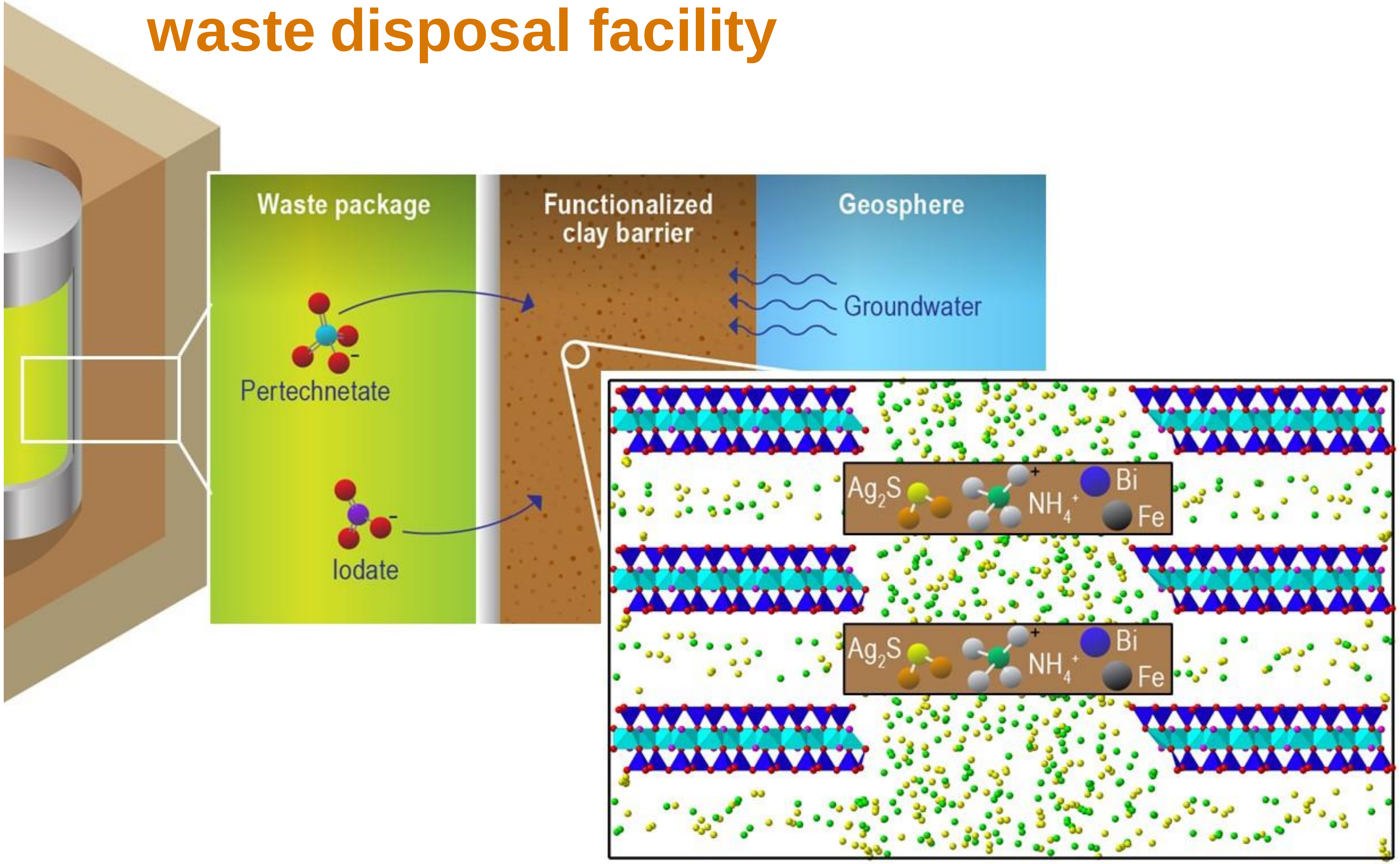


Conditions: 10^{-5} M I in water

- I^- and IO_3^- are dominant species in environment
- IO_3^- reduction to I^- can occur in sediments,
- I^- oxidation can occur abiotically under acidic conditions.

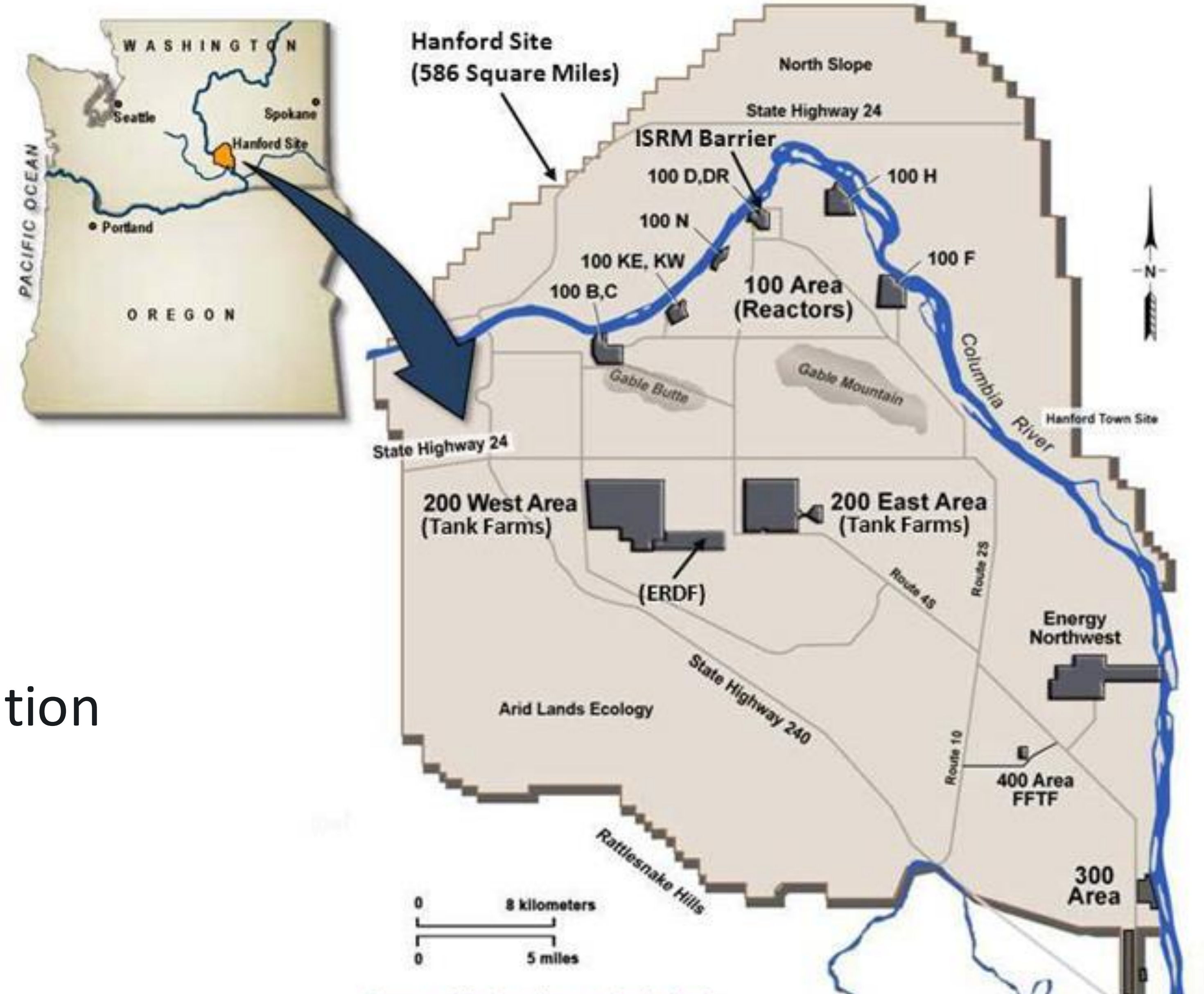
Fuge R (2013) Soils and Iodine Deficiency. In: Selinus O (ed) Essentials of Medical Geology: Revised Edition. Springer Netherlands, Dordrecht, pp 417-432.

Clay buffer functionalization to enhance sequestration of anionic radionuclides that have an increased risk of leaching out of a radioactive waste disposal facility



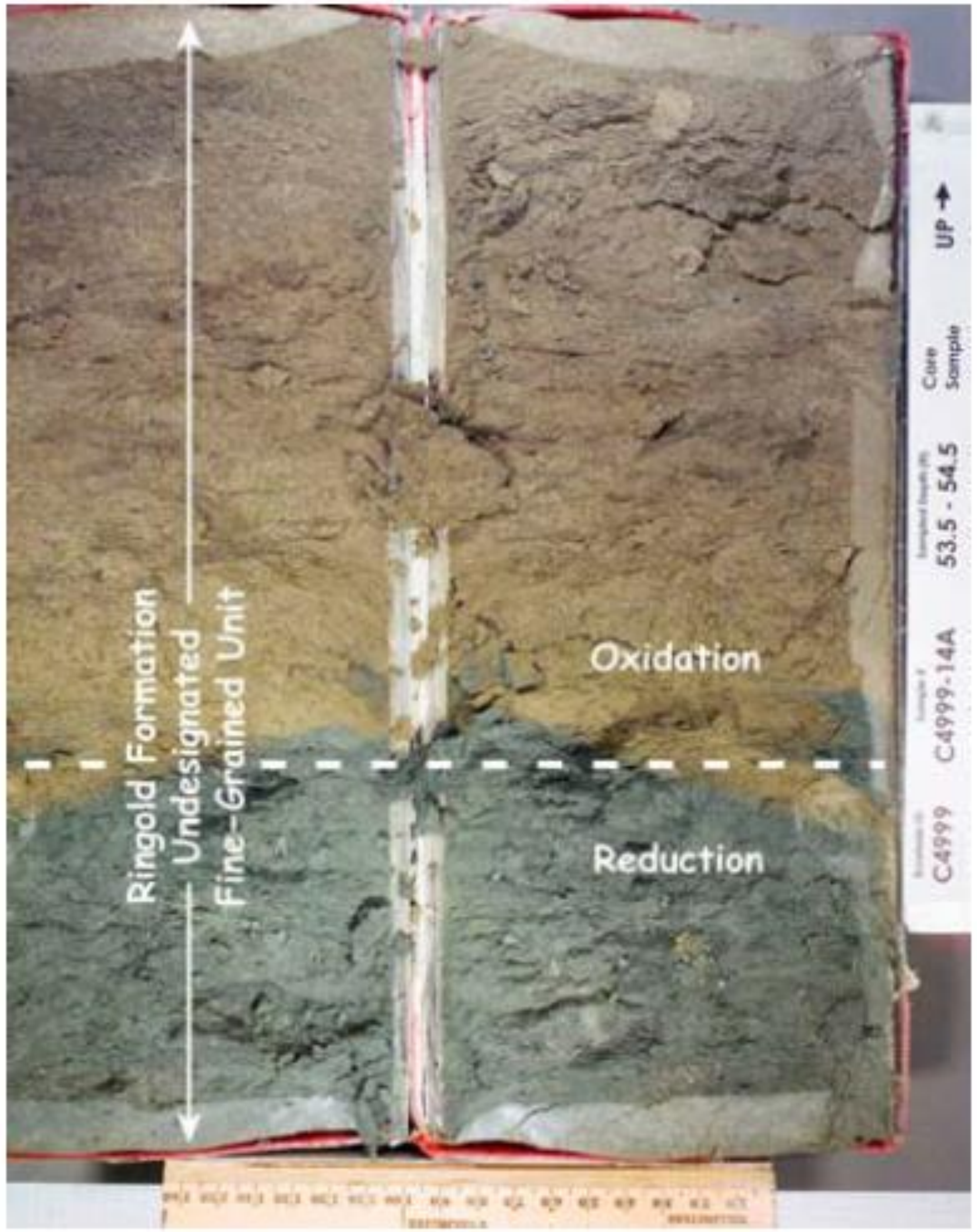
Inspiration from U.S. Department of Energy's Hanford Site in southeastern Washington State

- Metal Intercalation



Geographic location and principal facilities at the Hanford Site.

Redox transition zone sediments at Hanford site dominated by Fe-rich smectite



Mineralogic Characteristics:

Clay-sized fraction more than 84% Fe-rich montmorillonite (~1.3 mmol/g Fe)

Exchangeable (interlayer) cations: Ca^{2+}(67%), Mg^{2+}(21%), Na^{+}(7%), K^{+}(5%)

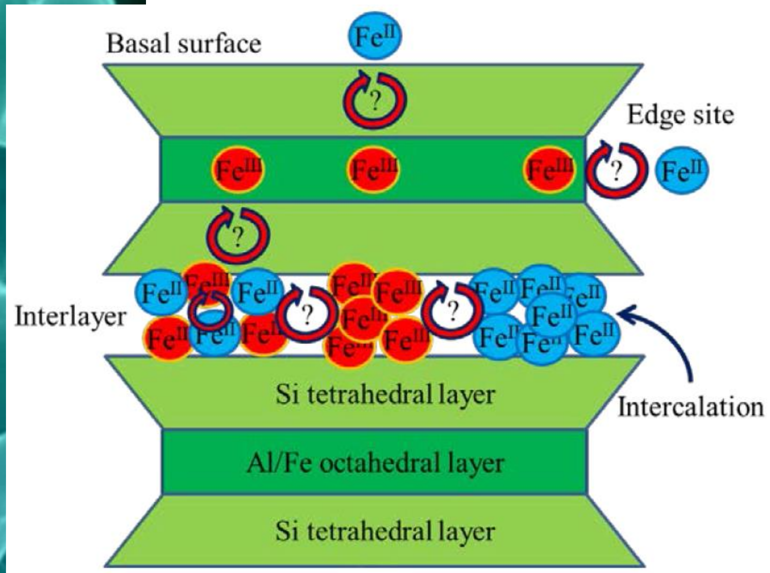
Oxidized: 4.6% Fe_{Tot} = Fe(II)

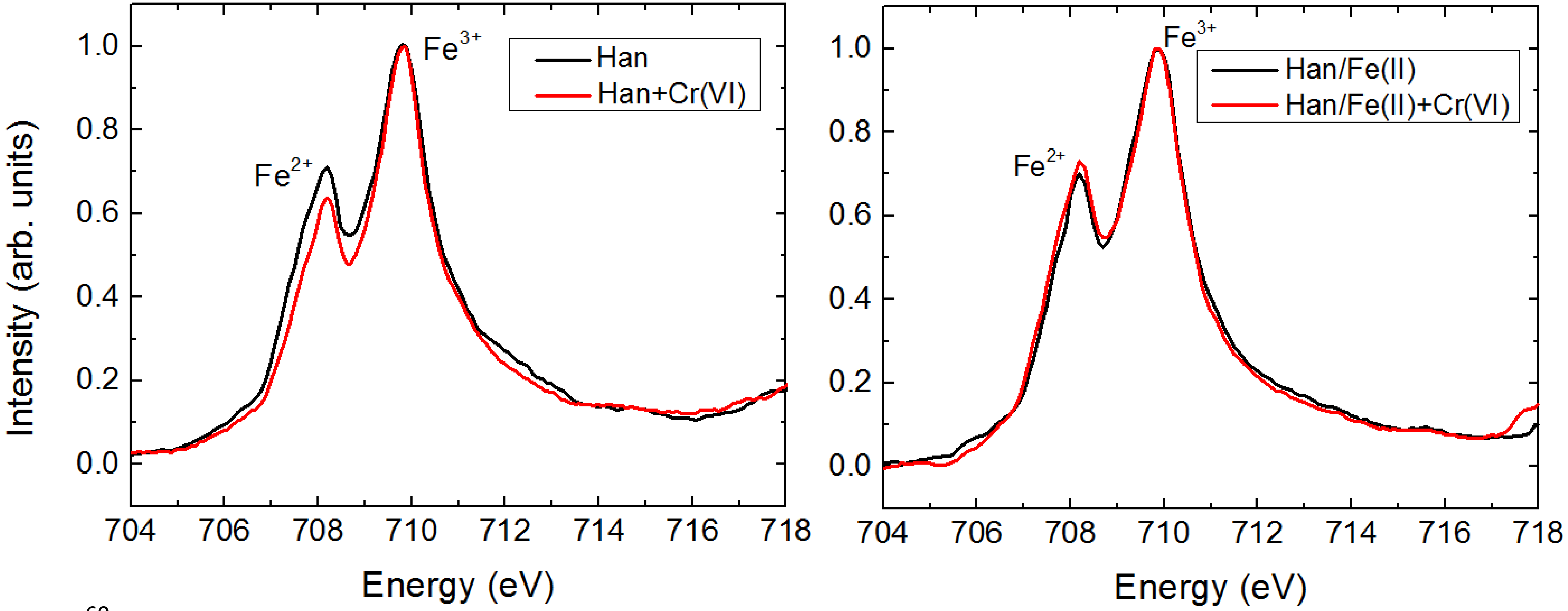
Reduced: 12.6% Fe_{Tot} = Fe(II)

Minor kaolinite, albite, quartz, anorthoclase, cristobalite, pyrite

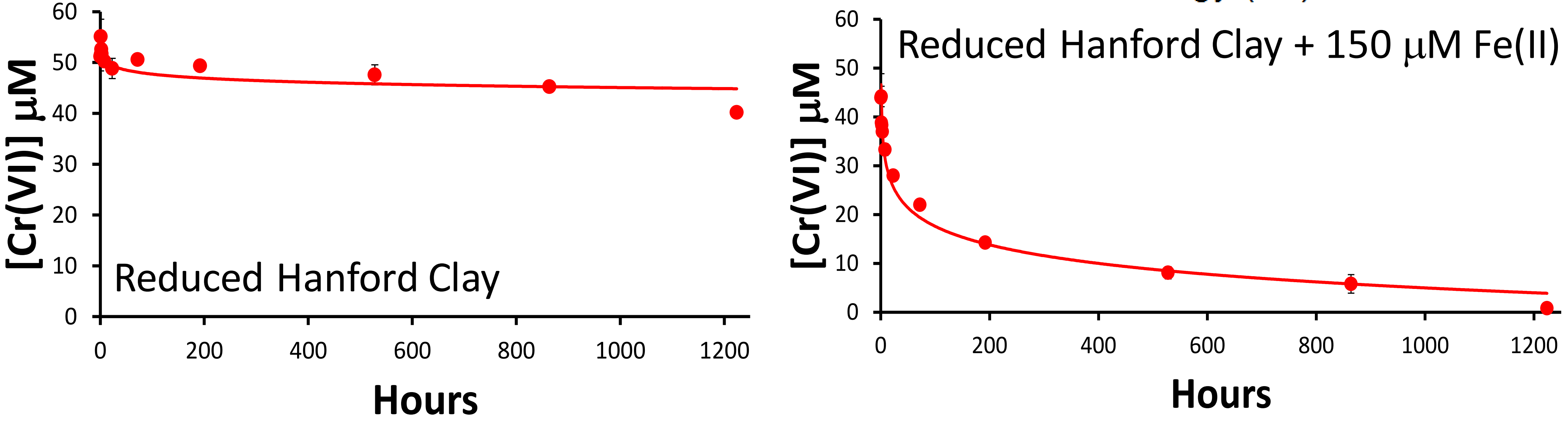
Qafoku et al. Environ Sci Technol. 2017 Aug 15;51(16):9042-9052.

$Fe(II)_{Oct}$ reduces Cr(VI) at edges, resupplied with electrons from Fe(II) in clay particle interiors

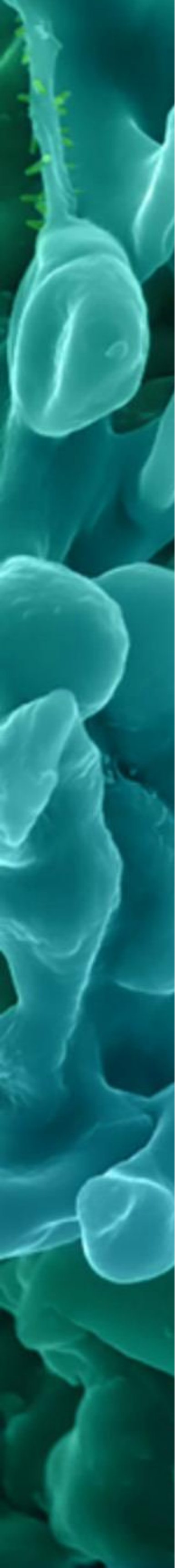




- At Hanford, structural Fe(II) is a strong enough reductant to reduce anionic $Cr(VI)O_2^{2-}$; reduction is enhanced when aqueous Fe(II) is available



Qafoku et al. Environ Sci Technol. 2017 Aug 15;51(16):9042-9052.



Inspiration from U.S. Department of Energy's Savannah River Site

- Organoclays

Journal of Environmental Radioactivity
Volume 136, October 2014, Pages 56-63

Aqueous ^{99}Tc, ^{129}I and ^{137}Cs removal from contaminated groundwater and sediments using highly effective low-cost sorbents

Dien Li, Daniel I. Kaplan, Anna S. Knox, Kimberly P. Crapse, David P. Diprete

Savannah River National Laboratory, Aiken, SC 29808, United States

Received 27 January 2014, Revised 13 May 2014, Accepted 14 May 2014, Available online 4 June 2014.

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https://doi.org/10.1016/j.jenvrad.2014.05.010

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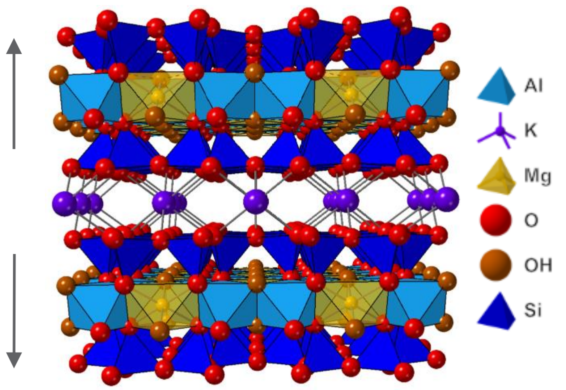
Highlights

- Two organoclays are effective sorbents for TcO_4^-, I^-, and Cs^+.
- The binding of TcO_4^-, I^-, and Cs^+ onto the two organoclays were largely irreversible.
- 0.5 wt% organoclays removed TcO_4^- leached from a contaminated sediment.
- Other sorbents were identified having Tc K_d values under oxidizing conditions.

Goal of this research



- Synthesize and functionalize clays
  - Metal intercalation
  - Organic intercalation
  - Metal intercalation of organoclays
- Characterize functionalized clays
  - XRD
  - Zetapotential and carbon content
- Investigate Tc and I retention by functionalized clay

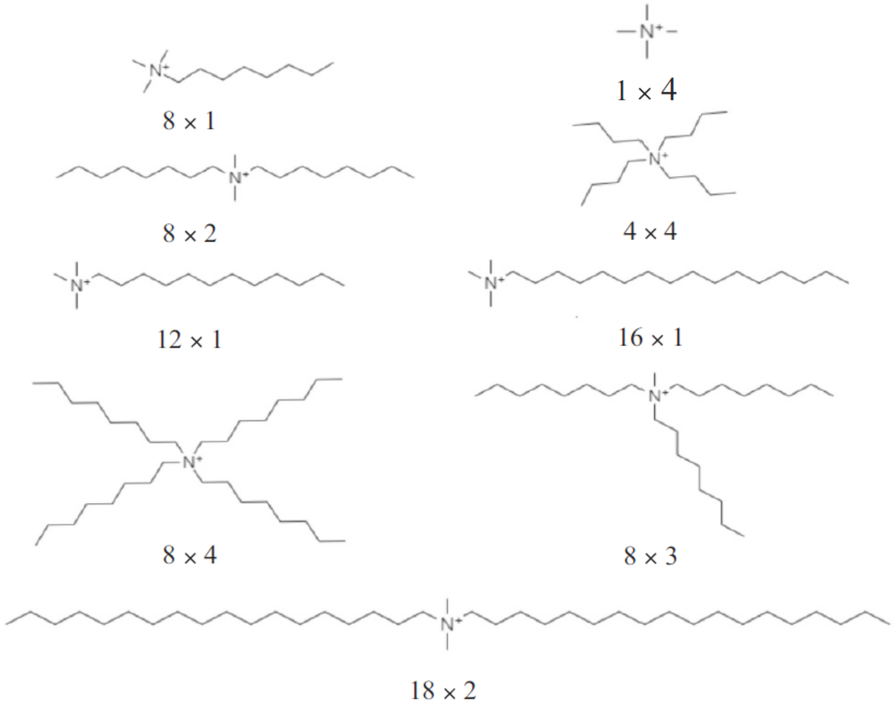
Clay Synthesis and Functionalization

Metal Intercalation

- Clays have been synthesized with chlorides of Fe, Ag, Bi, Cu, and Zr
  - $FeCl_2$ absorbs water and is multivalent
  - AgCl does not enter interlayer
  - $BiCl_3$ forms $BiClO_3$
  - $CuCl_2$ is multivalent
  - $ZrOCl_2$ polymerizes

Maulden et al. Applied Clay Science (2023) 233, 106828

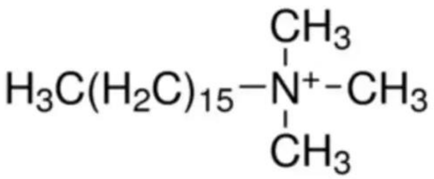
Clay Synthesis and Functionalization



Organic Intercalation

Na-SWy-Montmorillonite

3 mmol



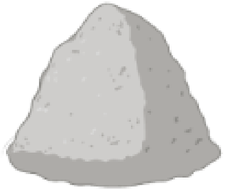
150 mL DIW; 2 g clay

60 °C; 24 h

$EtOH/H_2O$

Atmospheric conditions

16 x 1-SWy-Montmorillonite



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Clay Synthesis and Functionalization

16 × 1

Metal Intercalation of organoclays

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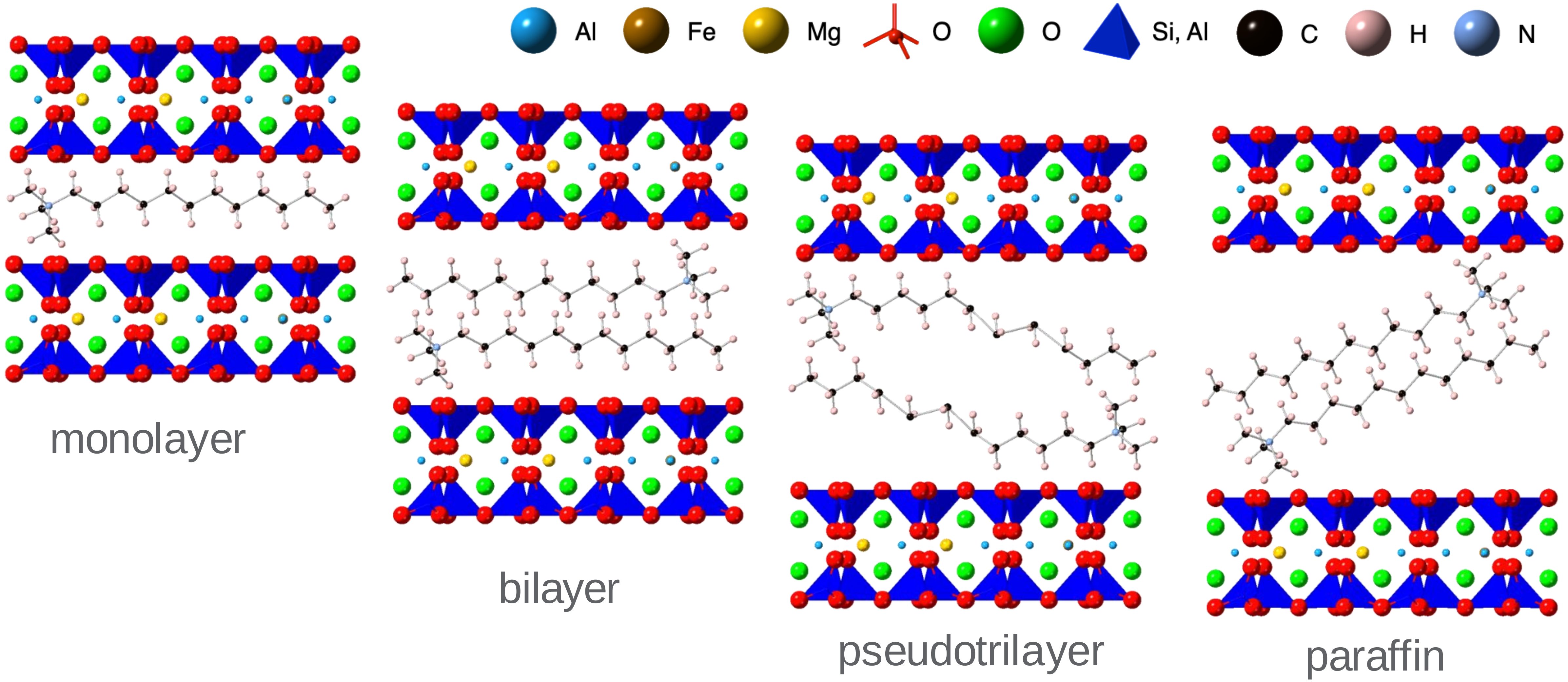
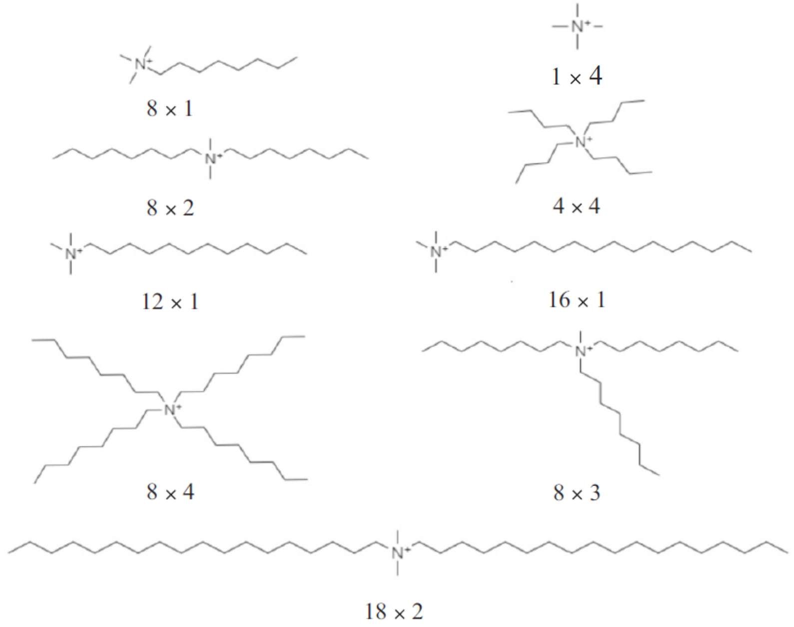
Functionalized Clay Characterization

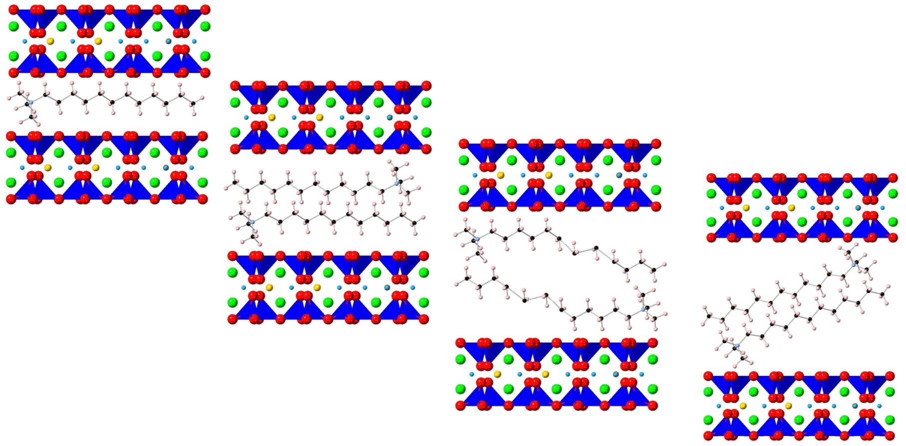
Potential arrangement of 16 x 1 quaternary amine in clay interlayer

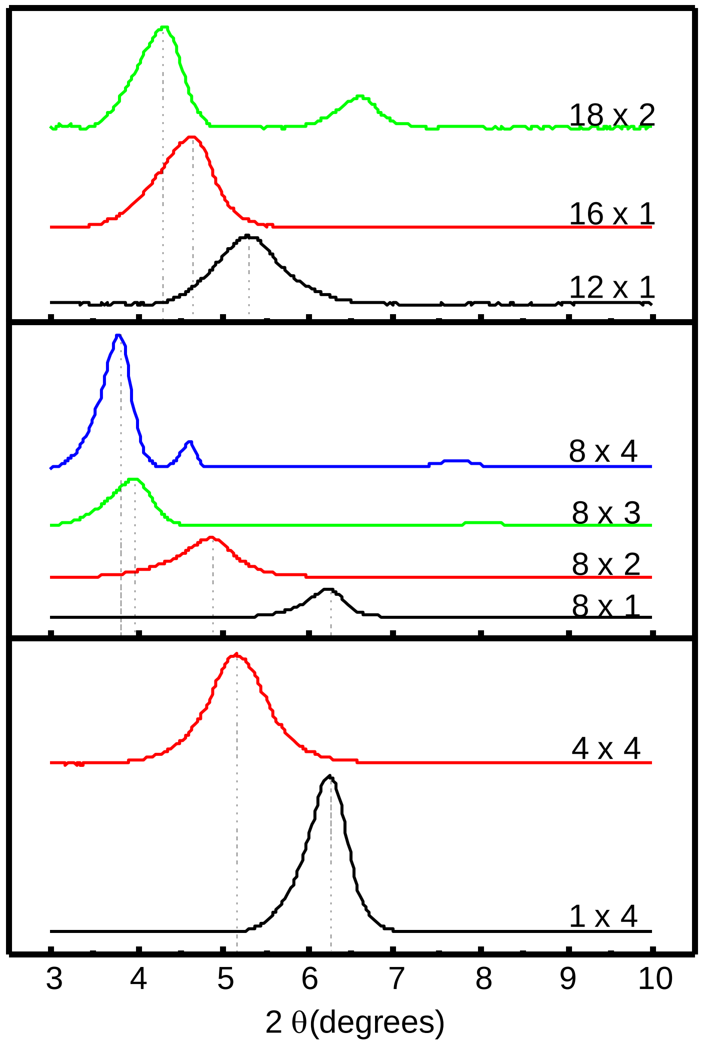


Functionalized Clay Characterization

X-ray Diffraction







Ammonium size	d(001) (nm)
SWy	1.45
1 x 4	1.42
4 x 4	1.72
8 x 1	1.42
12 x 1	1.70
8 x 2	1.83
16 x 1	1.93
8 x 3	2.25
8 x 4	2.34, 1.91
18 x 2	2.07

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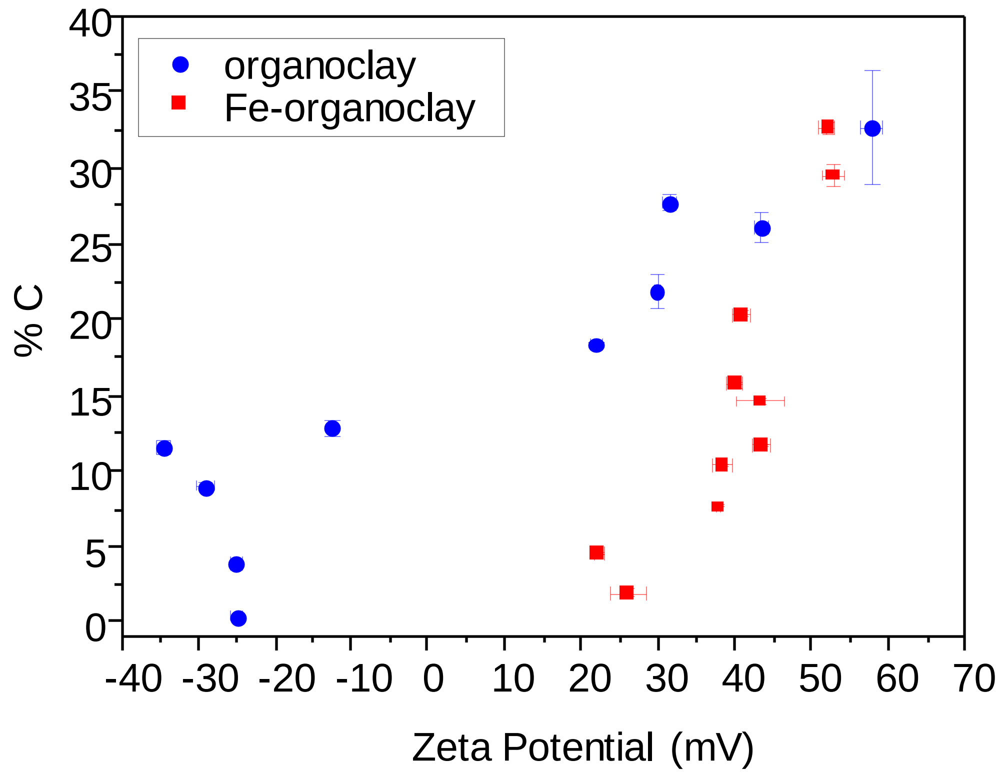
Functionalized Clay Characterization

Zeta Potential and carbon content

	organoclay		Fe organoclay	
Ammonium size	ζ (mV)	% C	ζ (mV)	% C
SWy	-25.0 ± 0.8	0.38 ± 0.05	26 ± 2	1.8 ± 0.2
1 x 4	-25.1 ± 0.7	3.78 ± 0.02	22.2 ± 0.7	4.5 ± 0.1
4 x 4	-34.5 ± 0.9	11.6 ± 0.4	38 ± 1	10.3 ± 0.2
8 x 1	-29 ± 1	9.0 ± 0.2	37.9 ± 0.4	7.6 ± 0.1
12 x 1	-12.6 ± 0.3	13.0 ± 0.5	44 ± 1	11.7 ± 0.1
8 x 2	32 ± 1	27.7 ± 0.6	43 ± 3	14.6 ± 0.1
16 x 1	21.9 ± 0.7	18.40 ± 0.02	40 ± 1	15.7 ± 0.1
8 x 3	29.9 ± 0.4	22 ± 1	41 ± 1	20.3 ± 0.2
8 x 4	58 ± 1	33 ± 4	53 ± 1	29.5 ± 0.7
18 x 2	43.5 ± 0.9	26 ± 1	52 ± 1	32.7 ± 0.4



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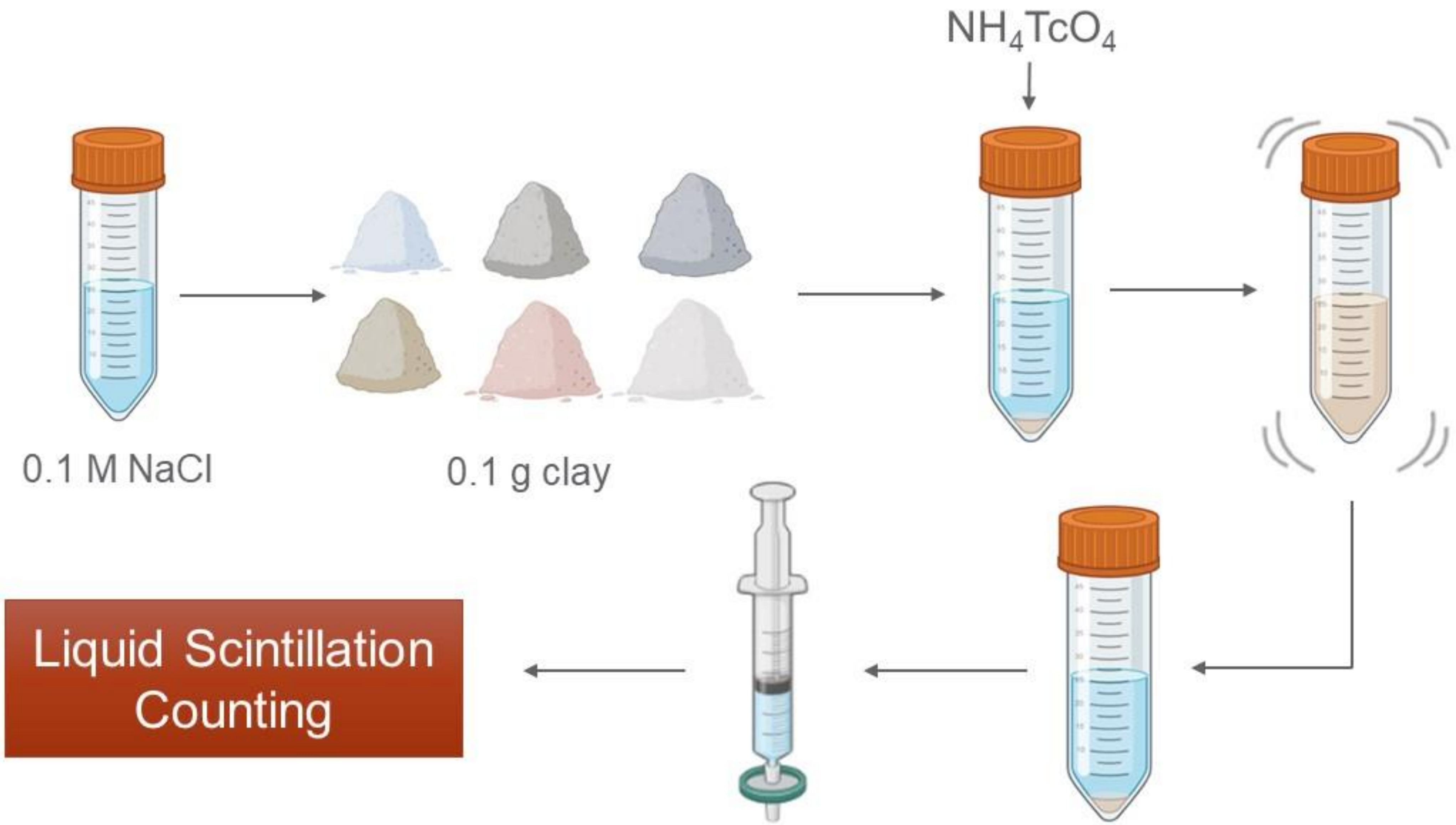
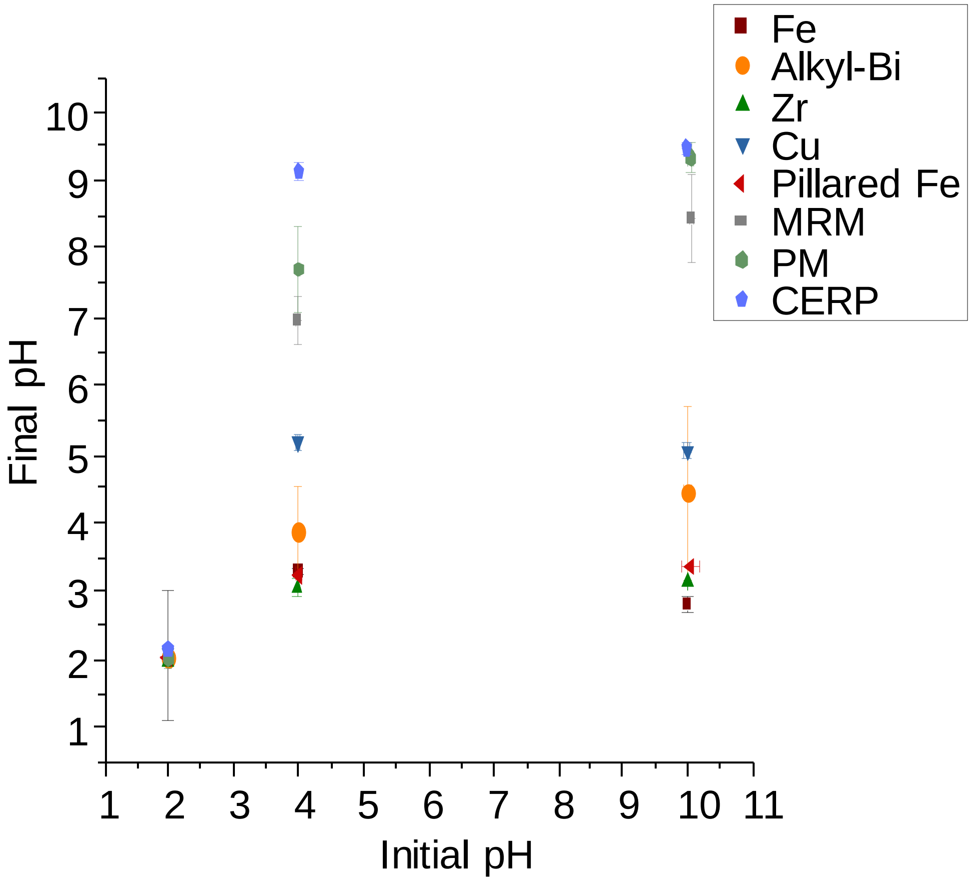
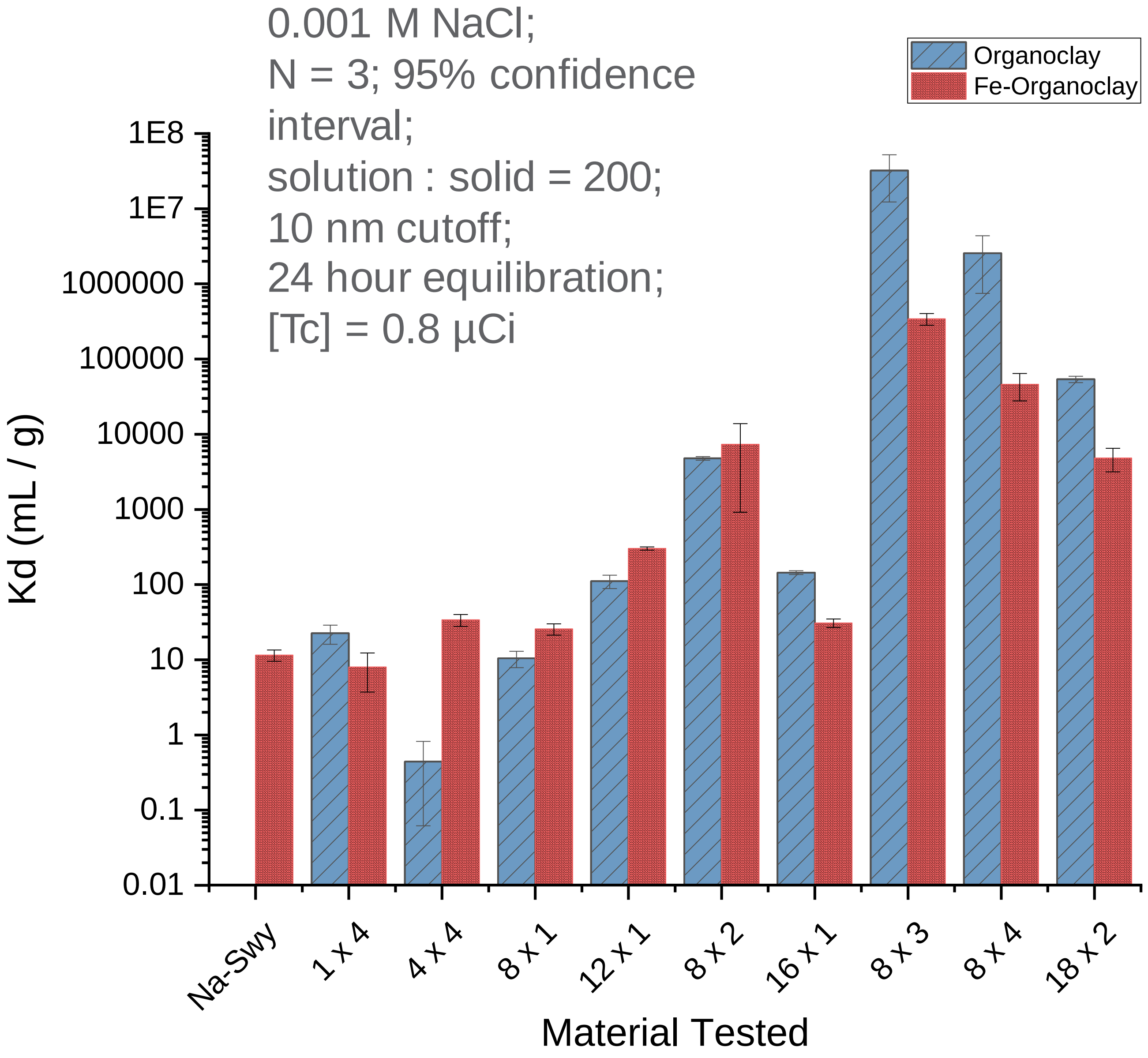
Tc and I Retention by Functionalized Clay



Tc Retention





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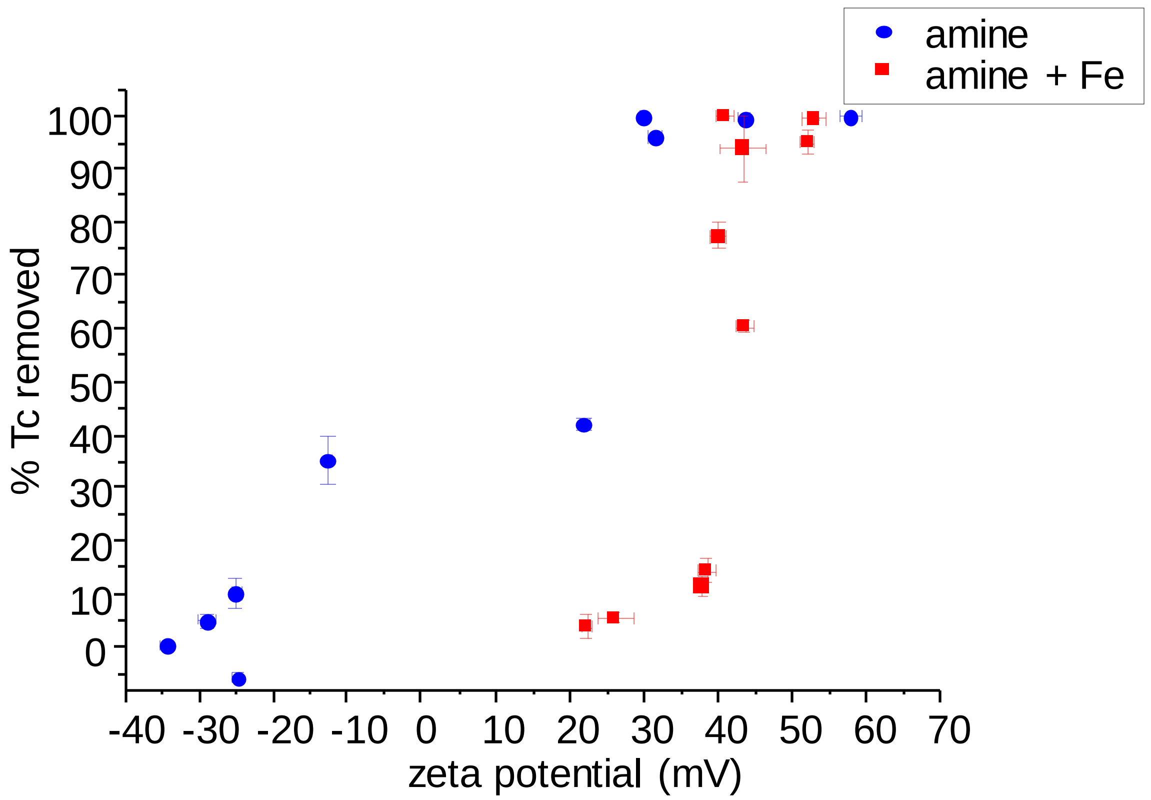
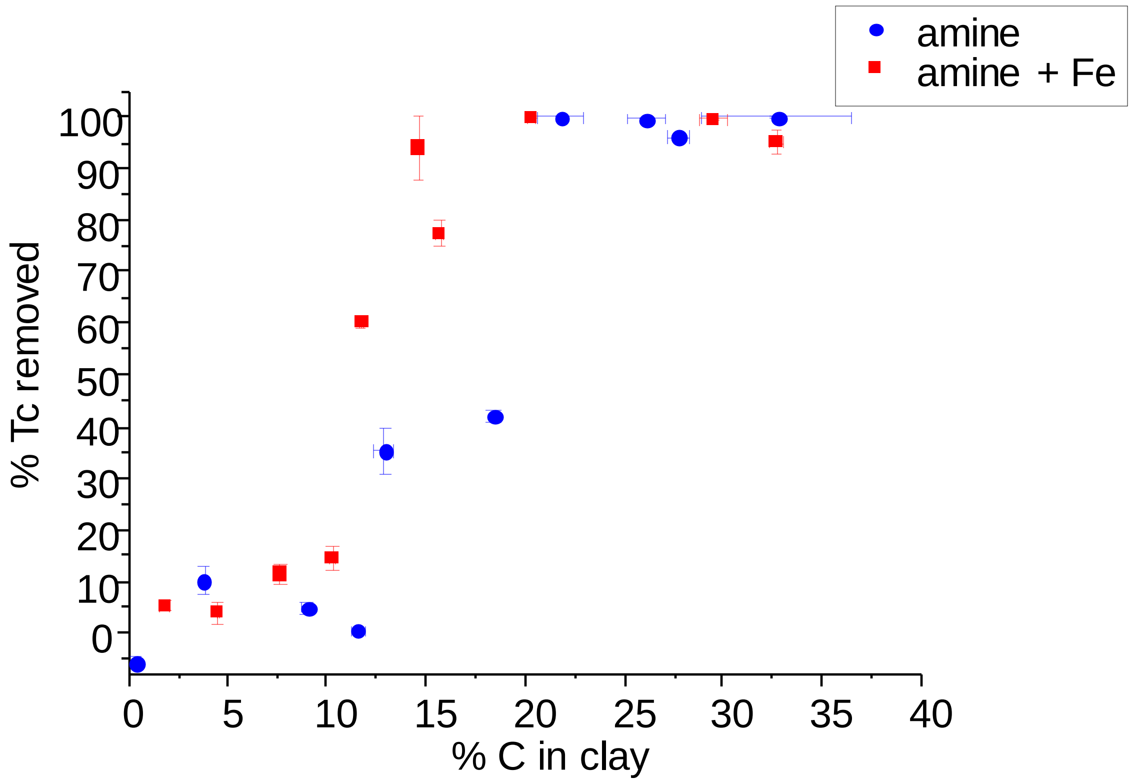
Correlating Tc Retention with Clay Properties





0.1 g clay, 20 mL 0.001 M NaCl, N = 3, 95% confidence interval, 25°C, particle cutoff = 10 nm

Functionalization of Clay: Organometallic Clay

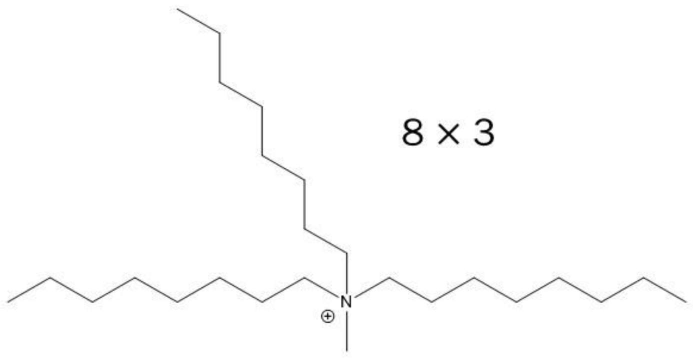
Organoclay

- 1 × 4
- 3 × 4
- 4 × 4
- 5 × 4
- 8 × 1
- 9 × 1
- 8 × 2
- 8 × 3
- 8 × 4
- 12 × 1
- 16 × 1
- 18 × 2

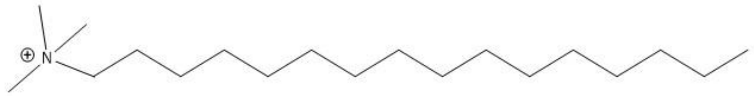
Inorganic clay

- Fe
- Cu
- Zr
- Bi

8 × 3



16 × 1

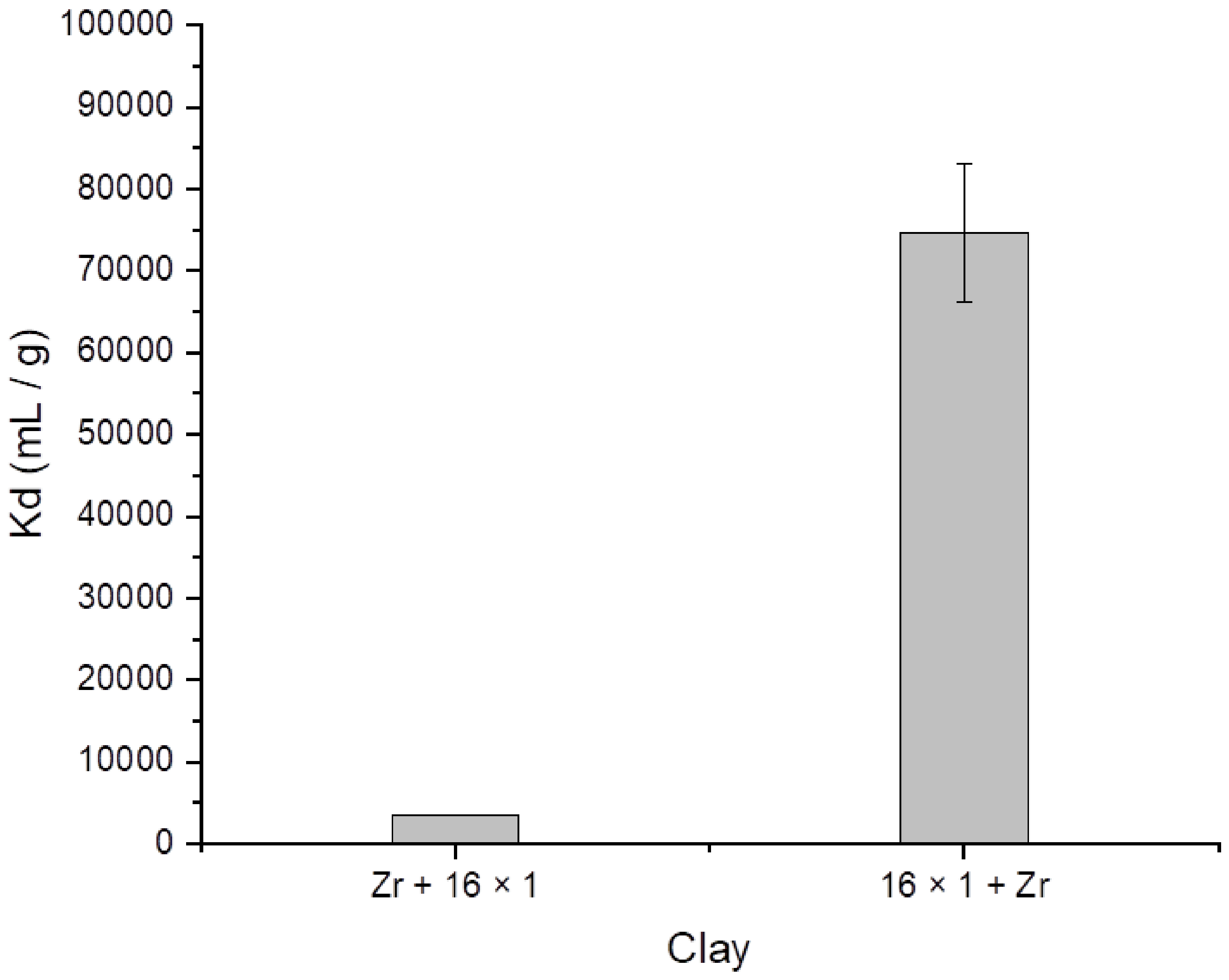


Organometallic clay

- 1 × 4 + Fe
- 4 × 4 + Fe
- 8 × 1 + Fe
- 8 × 2 + Fe
- 8 × 3 + Fe
- 8 × 4 + Fe
- 12 × 1 + Fe
- 16 × 1 + Fe
- 18 × 2 + Fe
- 16 × 1 + Cu
- 16 × 1 + Zr
- 16 × 1 + Bi
- Cu + 16 × 1
- Zr + 16 × 1

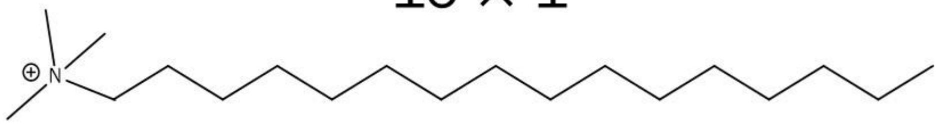
Effect of Clay Synthesis Conditions on Tc Retention

0.1 g clay;
20 mL 0.001 M NaCl;
N = 3; Error = 95% CI;
24 hours;
25°C;
[Tc] = 0.8 µCi;
Particle Cutoff = 10 nm

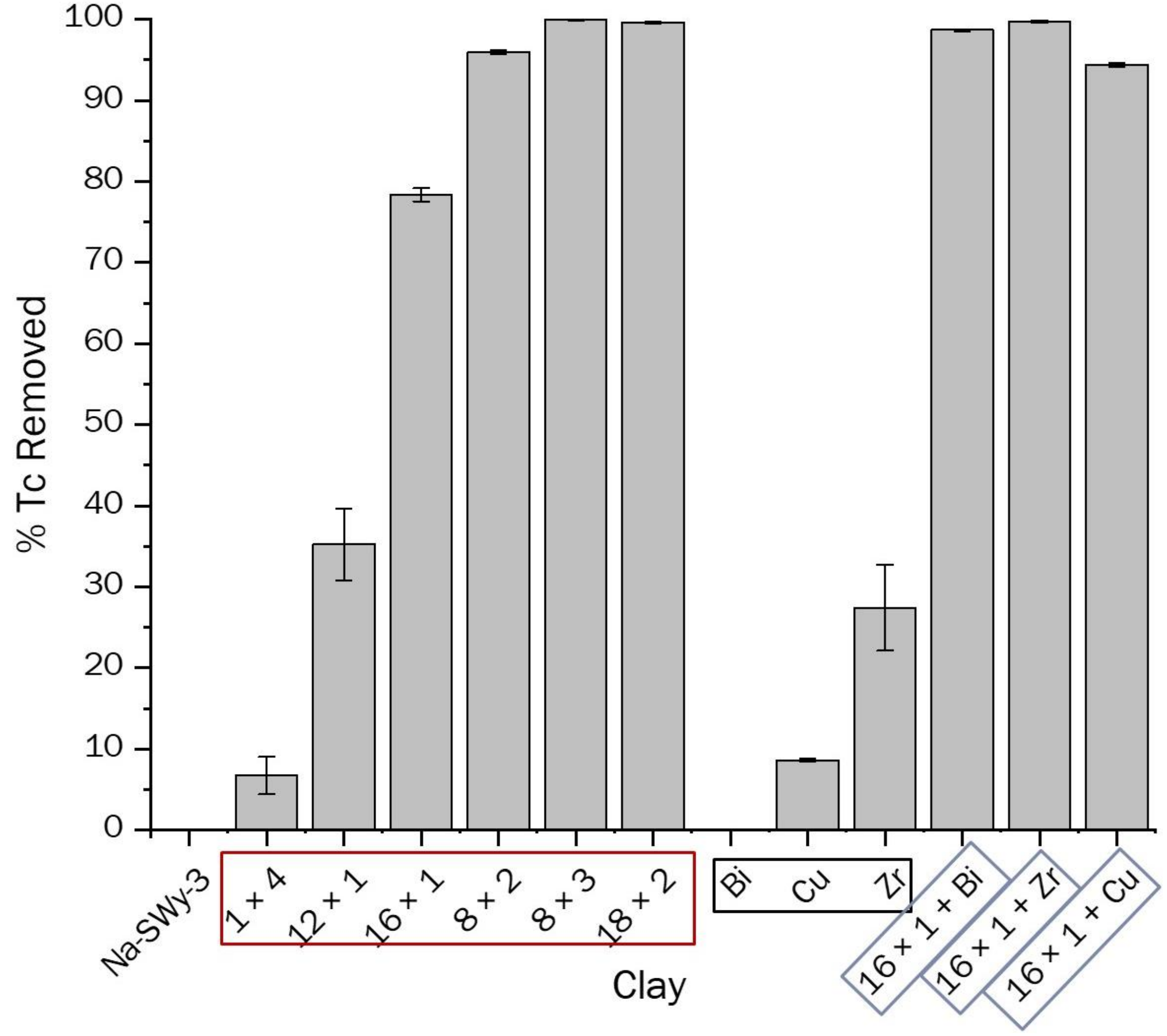


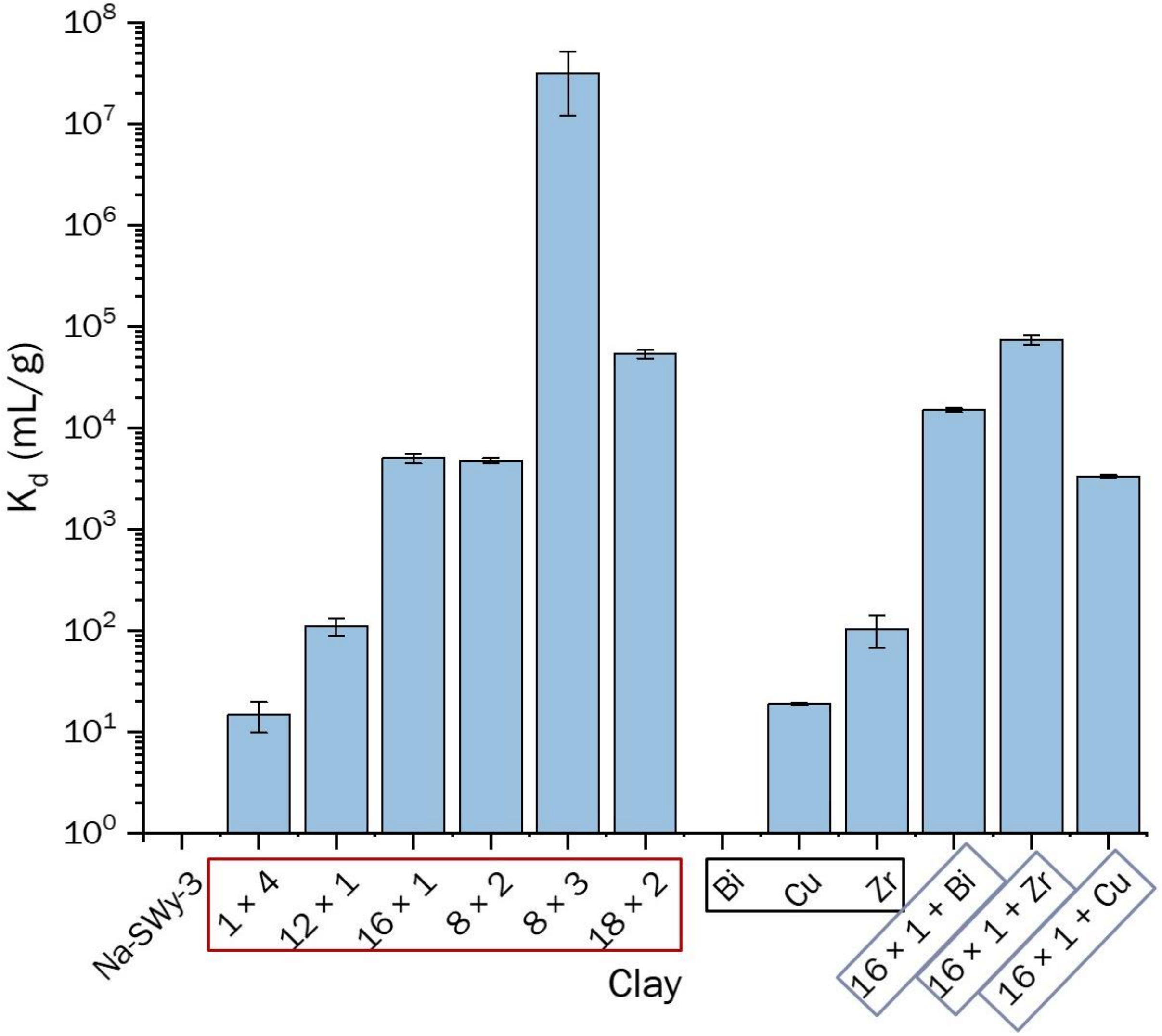
TcO_4^- Uptake

16 × 1



$$K_d = \frac{\frac{[Tc]_{sorbed}}{g}}{\frac{[Tc]_{aqueous}}{mL}}$$

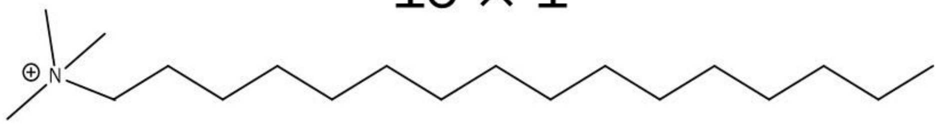




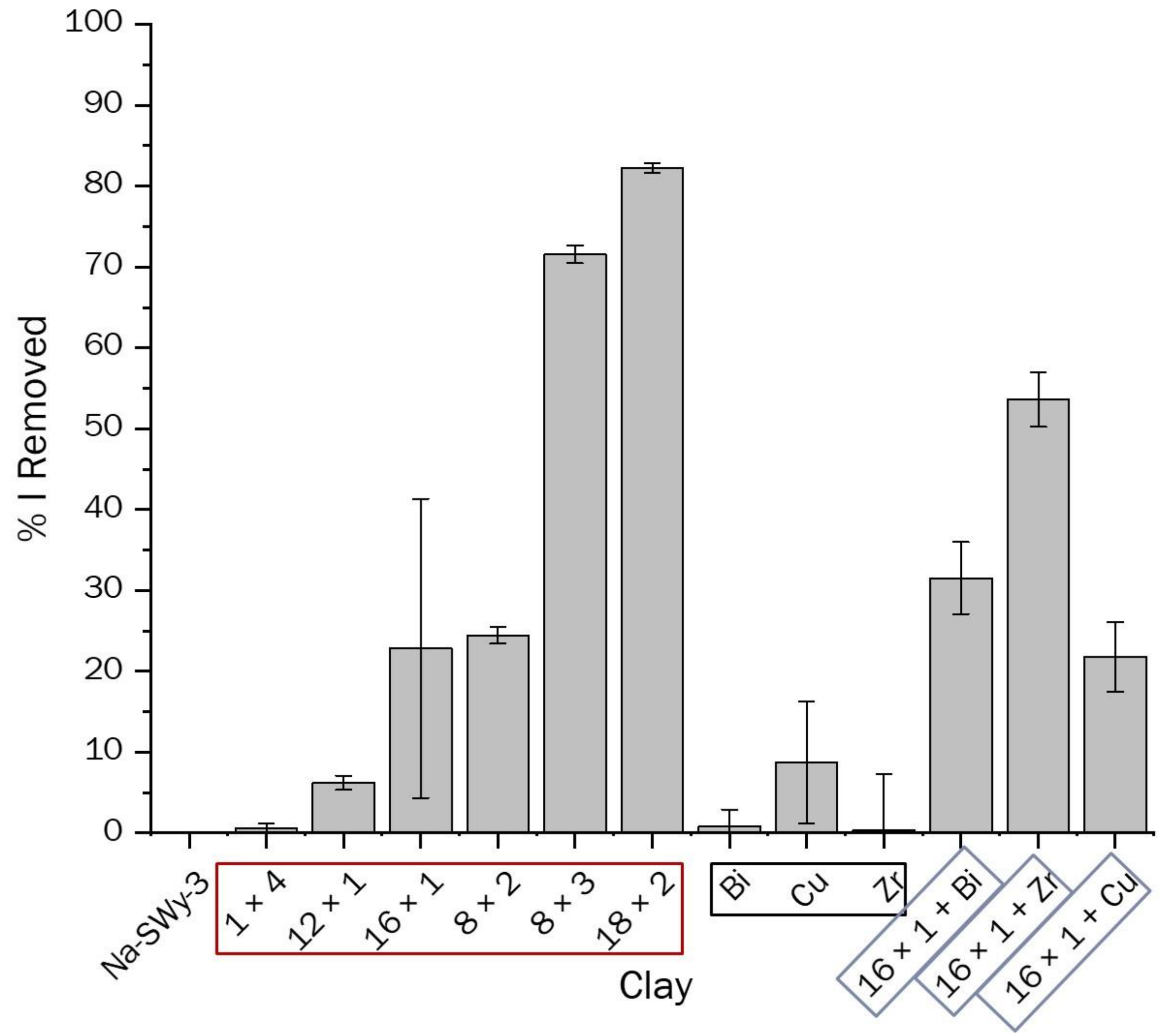
Conditions: 0.001 M NaCl; solution : solid ratio = 200; ~10 nm cutoff; 24-hour shaking; [Tc] = 0.8μCi; N = 3; 95% confidence interval

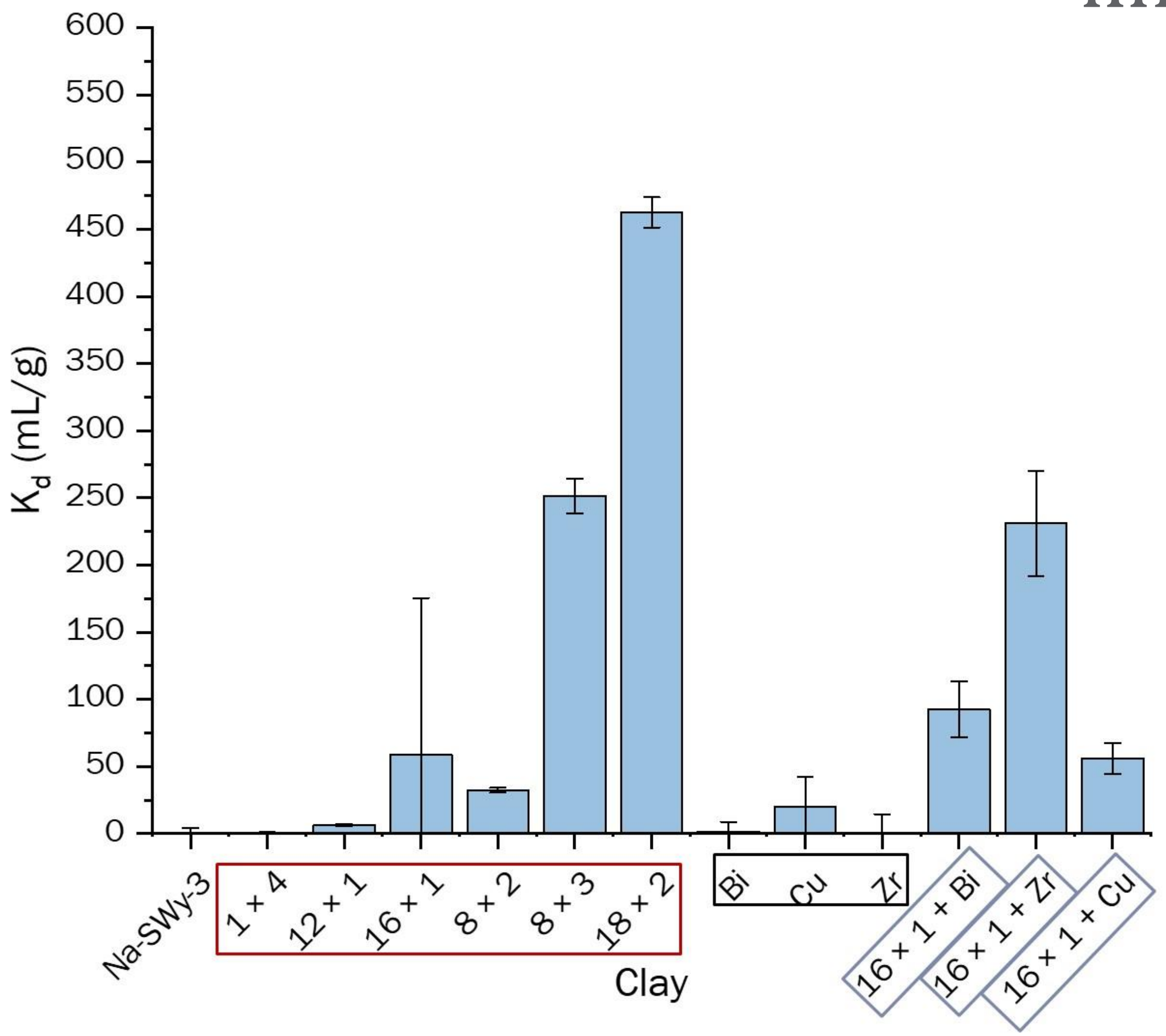
I^- Uptake

16 × 1

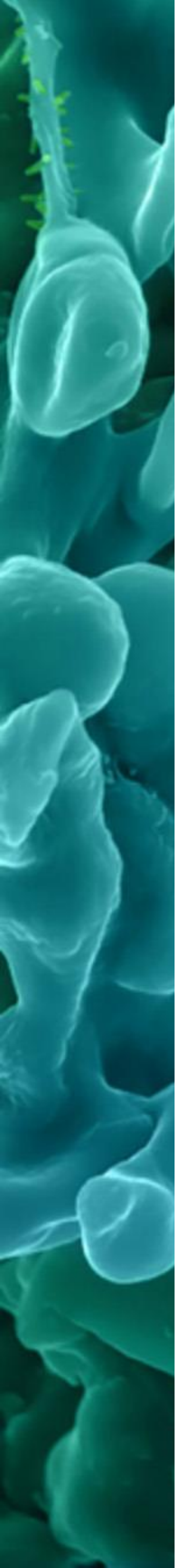


$$K_d = \frac{\frac{[I]_{sorbed}}{g}}{\frac{[I]_{aqueous}}{mL}}$$



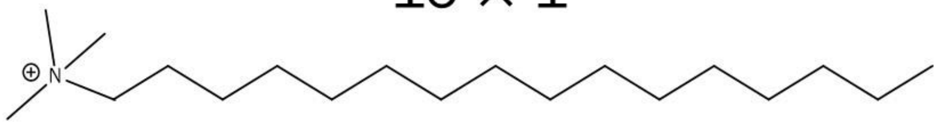


Conditions: 0.001 M NaCl; solution : solid ratio = 200; ~10 nm cutoff; 24-hour shaking; [I] = 0.9nCi; N = 3; 95% confidence interval

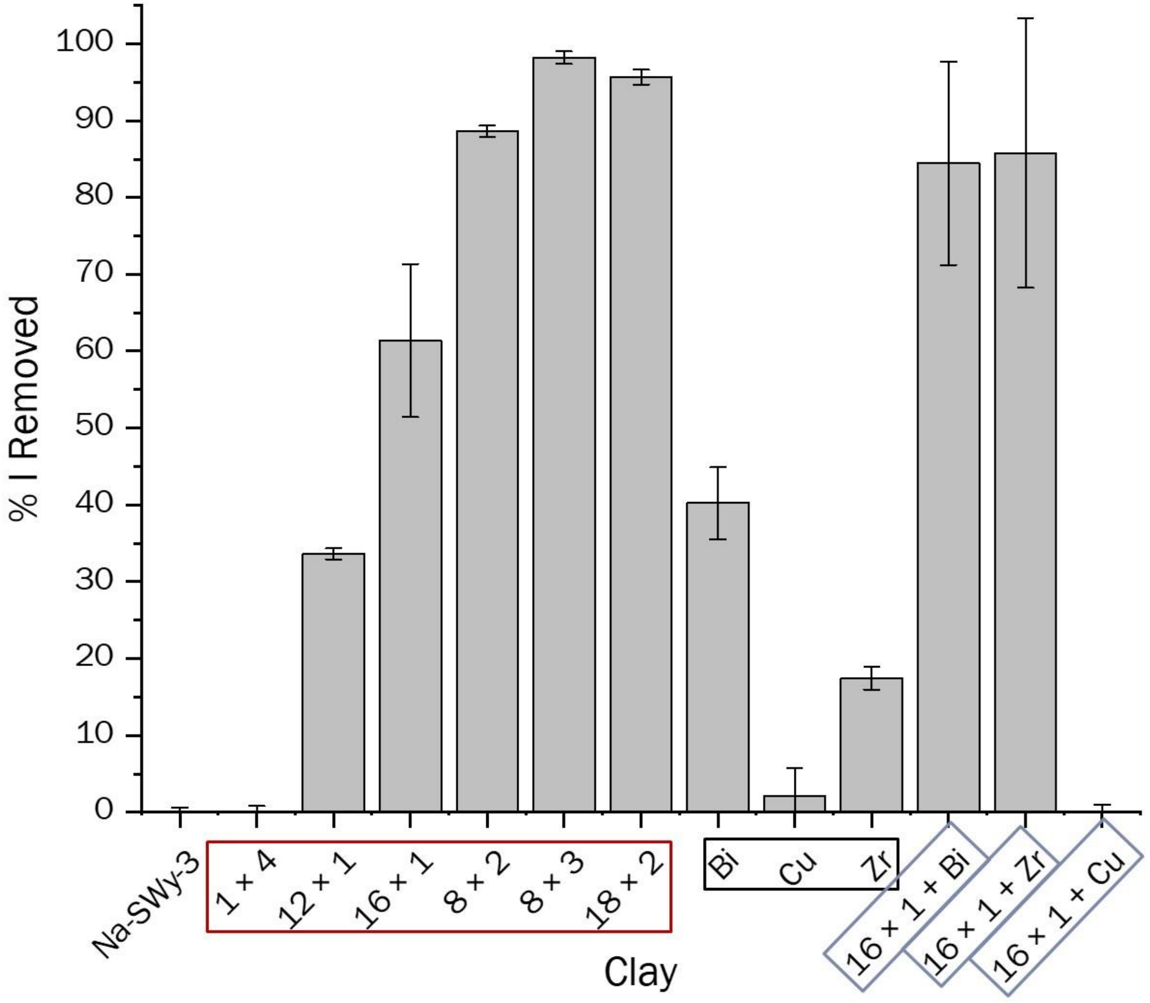


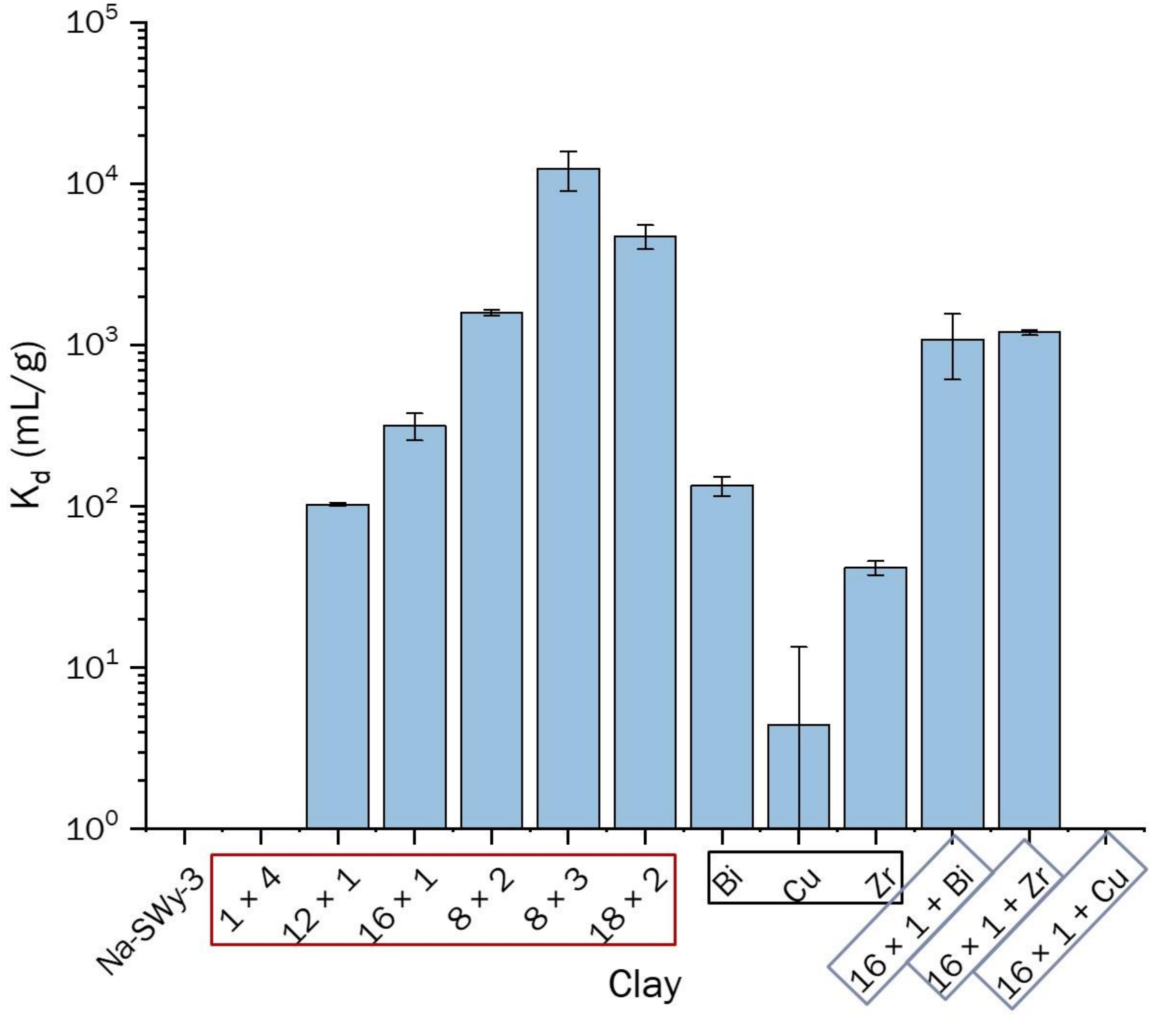
IO_3^- Uptake

16 × 1



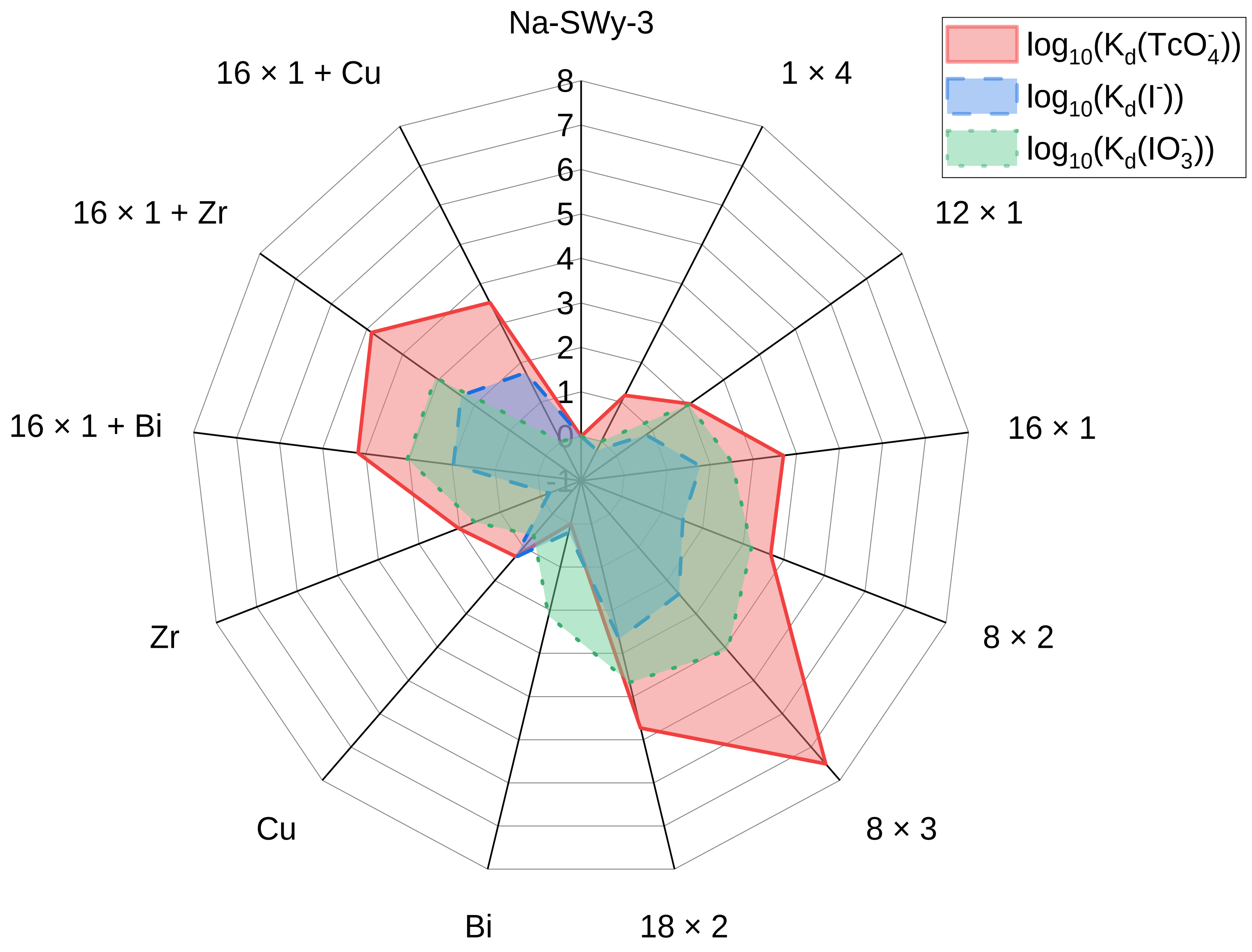
$$K_d = \frac{\frac{[I]_{sorbed}}{g}}{\frac{[I]_{aqueous}}{mL}}$$





Conditions: 0.001 M NaCl; solution : solid ratio = 200; ~10 nm cutoff; 24-hour shaking; [I] = 0.9nCi; N = 3; 95% confidence interval

Comparison of I^-, IO_3^- and TcO_4^- Retention

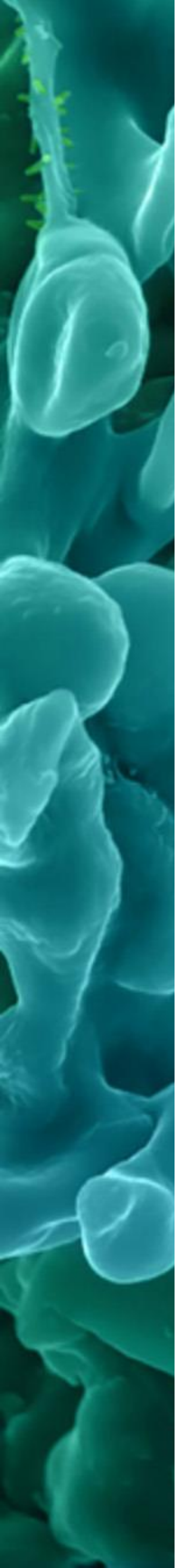


Conclusions

- Tc and I radioisotopes of concern for nuclear waste management
- Synthesize functionalized clay: intercalation of metal and alkylammonium
- Functionalized clay characterization:
  - XRD → increased basal spacing
  - Surface area decrease with % C
  - Zeta potential increase with % C
- Orientation → MD and DFT calculations
- Tc retention improves with inclusion of large alkylammonium and Fe
- Order of addition alkylammonium/metal is important
- Best sorption: TcO_4^- on 8x3 organoclay, I^- on 18x2 organoclay, IO_3^- on 8x3 organoclay

Acknowledgements

- U.S. Department of Energy (DOE)
  - Nuclear Energy University Program (NEUP)
  - Grant DE-NE0008952, Project 20-19198



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Thank you