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Designing a slag composition to optimize Tc-99 retention in oxidized grouts

Walt Kubilius, Fabienne Johnson, Christine Langton, Madison Caldwell

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Overview & Relevance

- **Technetium-99 eventually leaches out of cementitious waste forms.**
- **Waste forms rely on insoluble Tc(IV) which will convert to leachable TcO_4^- when oxidized in the future by the environment.**
- **Can grout waste forms be designed to bind/retain oxidized TcO_4^-?**

Some hydroxide compounds may retain TcO_4^- in their crystal structure

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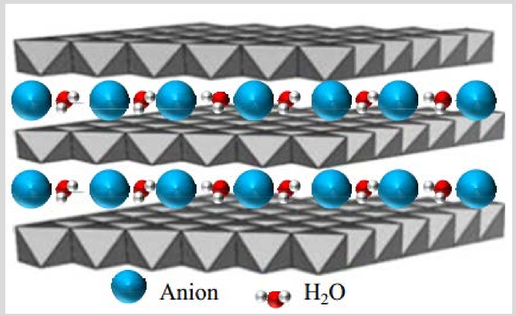
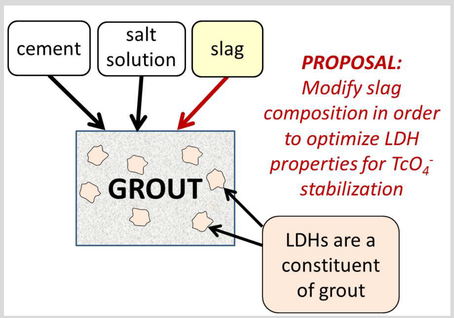
Layered Double Hydroxides (LDHs)

- LDHs have the brucite structure, $M^{2+}(OH)_2$, M^{2+} is a metal, with Al^{3+} substituting for some M atoms.
- This imparts a positive charge to the octahedral sheets, balanced by incorporation of anions (e.g. NO_3^-, OH^-, or TcO_4^-) within the interlayers.
- LDHs with M = Mg,Ca appear in cured grouts, including saltstone. They bind anions weakly.
- But Krumhansl etal (2006) and Pless (2007) found that LDHs with Cu or Zn as the divalent cation (instead of Mg or Ca) can strongly bind ReO_4^-, TcO_4^-, I^-, and IO_3^-, at near-neutral pH.

If saltstone-type grouts can be formulated to crystallize Cu- or Zn-LDHs, retention of Tc-99 or I-129 may be improved.

This project will test ReO_4^- (surrogate for TcO_4^-) sorption in saltstone-type grouts, using simulated slags of varying composition.





Approach

1: Synthesize LDHs of desired compositions

LDHs were easily synthesized at room temperature by mixing metal nitrates with NaOH, then washing & filtering the precipitate. Nominal compositions:

$Mg_6Al_2(OH)_{16}(NO_3)_2$
$Zn_6Al_2(OH)_{16}(NO_3)_2$
$Cu_6Al_2(OH)_{16}(NO_3)_2$

2: Test ReO_4^- sorption by LDH in aqueous solutions

Perrhenate (ReO_4^-) was used as a surrogate for TcO_4^-. ReO_4^-/LDH sorption tests were done with 7 days of contact on a shaker table. All work was conducted in oxidizing conditions, and mostly at pH=12 (appropriate for oxidized grout environments).

3: Make grouts spiked with Cu, Zn

Saltsone has three ingredients: portland cement, fly ash, and blast furnace slag (BFS). Two approaches were used to make grout:

1. Produce simulated BFS with desired compositions (Mg, Cu, or Zn-rich, and oxidizing).
2. Add Mg-, Cu-, or Zn-LDH directly to oxidized saltstone mix.

4: Test ReO_4^- sorption by grouts

Grouts were cured for 30 days, then ground to -100 mesh. They were put in contact with alkaline solutions simulating Saltstone pore-water. ReO_4^- /grout sorption tests were done with 7 days of contact on a shaker table.

Technical Progress (Accomplishments)

LDH synthesis

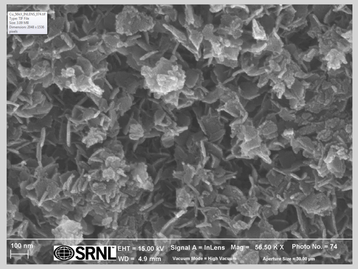
1. SORPTION EXPERIMENTS WITH PURE LDHs were encouraging. Copper-LDH and calcined Mg-LDH showed very strong sorption of ReO_4^- at pH 12,; K_ds exceeded 200 mL/g for both compositions. However, sorption was strongly reduced in the presence of 0.1M nitrate or 0.1M nitrite.

ReO_4^- SORPTION COEFFICIENTS (mL/g) for various LDHs in aqueous solutions

sorption test liquid	Mg-LDH	Zn-LDH	Cu-LDH	calcined Mg-LDH	calcined Zn-LDH
0.01M NaOH, 0.01M NaReO4	18	14	353	226	0
0.01M NaOH, 0.0001M NaReO4			265	217	0
0.1M NO2, 0.01 M NaReO4			44	22	
0.1M NO3, 0.01M NaReO4			45	23	

2. HOWEVER, when Cu-LDH and calcined Mg-LDH were incorporated into grouts, sorption of ReO_4^- was low, with K_ds near 1 mL/g in all samples, even in the absence of nitrate or nitrite. This was true for grouts made with Cu-rich slags, as well as for LDH amendment into the saltstone mix. The reason is not known.

Preparation of simulated Blast Furnace Slag



SEM image of Cu-Layer Double Hydroxide

ReO_4^- SORPTION COEFFICIENTS (mL/g) for LDH-containing grouts in aqueous settings.

grout mixture solid	grout mixture liquid	sorption liquid	Kd (mL/g)
10 OPC, 45 FA, 45 Mg-BFS[1]	Tank 50 simulant	pore water simulant	0
10 OPC, 45 FA, 45 Zn-BFS[2]	Tank 50 simulant	pore water simulant	1
10 OPC, 45 FA, 45 Cu-BFS[3]	Tank 50 simulant	pore water simulant	0
9 OPC, 39 FA, 39 Mg-BFS, 13 MgLDH	Tank 50 simulant	pore water simulant	0
9 OPC, 39 FA, 39 Mg-BFS, 13 calcined MgLDH	Tank 50 simulant	pore water simulant	0
9 OPC, 39 FA, 39 Mg-BFS, 13 CuLDH	Tank 50 simulant	pore water simulant	1

Tank 50 simulant is approx comp. of Tank 50 supernate.
Pore water simulant models comp. of Saltstone porewater.

grout mixture solid	grout mixture Liquid	sorption liquid	Kd (mL/g)
10 OPC, 45 FA, 45 Mg-BFS[1]	zero nitrate	aged pore water simulant	1
10 OPC, 45 FA, 45 Zn-BFS[2]	zero nitrate	aged pore water simulant	1
10 OPC, 45 FA, 45 Cu-BFS[3]	zero nitrate	aged pore water simulant	1
9 OPC, 39 FA, 39 Mg-BFS, 13 MgLDH	zero nitrate	aged pore water simulant	1
9 OPC, 39 FA, 39 Mg-BFS, 13 calcined MgLDH	zero nitrate	aged pore water simulant	1
9 OPC, 39 FA, 39 Mg-BFS, 13 CuLDH	zero nitrate	aged pore water simulant	1

"Zero nitrate" = Tank 50 simulant without NO3, NO2, SO4.
"Aged porewater" simulates saltstone porewater after nitrate leaches out. It is 0.01M NaOH, 0.005M Ca(OH)2.

Remaining Challenges and Barriers

The dramatic contrast between very strong sorption of ReO_4^- by Cu-LDH and calcined Mg-LDH in aqueous solution, and very poor sorption by grouts is not understood.

Proposed Future Work

In view of the importance in improving long-term Tc-99 retention in grout wasteforms, and the promise shown by certain Layered Double Hydroxide compounds in retaining ReO_4^-, studies should be continued to determine whether retention behavior could be improved in grouts.

Project Summary

- Layered Double Hydroxides (LDHs) of various compositions were synthesized at room temperature.
- Aqueous sorption experiments showed that Cu-LDH and calcined Mg-LDH sorbed ReO_4^- very well in alkaline aqueous solutions.
- Sorption ability was lessened in 0.1M NO_3 or 0.1M NO_2 solutions.
- Grouts containing the same LDHs did not sorb ReO_4^- in alkaline solutions.

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