SAND2024-06781C

Evaluation of novel materials for anion sorption

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Annual Meeting of the Clay Minerals Society and Asian Clay Conference

Honolulu, Hawaii

June 3- June 6

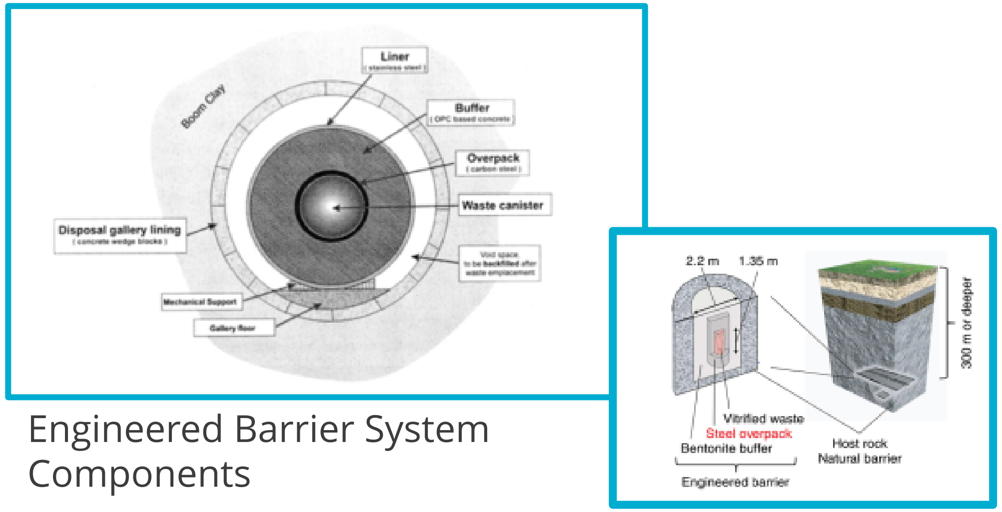
Spent Fuel and Waste Science and Technology (SFWST)

Outline

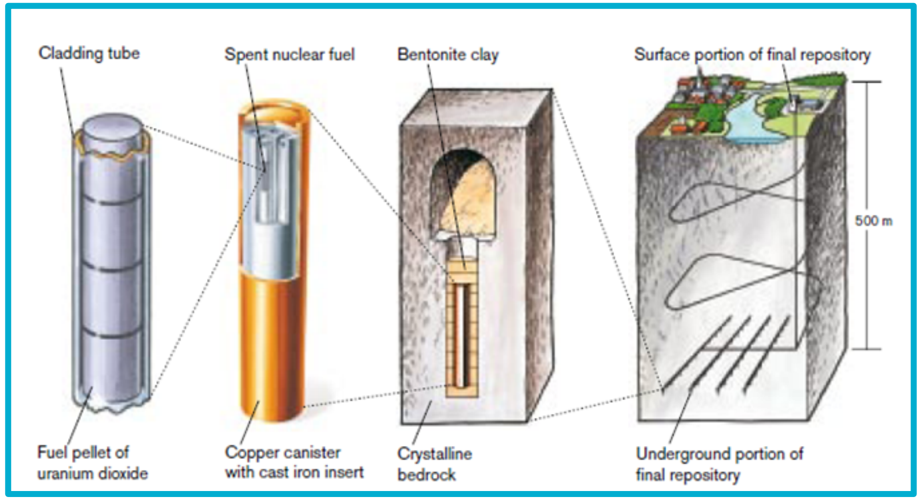
- Background and Motivation
- Synthesis and Characterization
- Metal Functionalization and Characterization
- Anion Sorption
- Molecular Modeling
- Summary and Future Work

Background and Motivation

- Deep geologic disposal concepts are based on a “multiple barrier system” to control radionuclide release
    - Waste package
    - Engineered barrier system
    - Host rock itself
- One of the main functions of the bentonite buffer and/or backfill in the engineered barrier system (EBS) is to capture and isolate cationic radionuclides in the near-field environment.



Engineered Barrier System Components



Mined repositories in crystalline rock (SKB 2011)

Background and Motivation

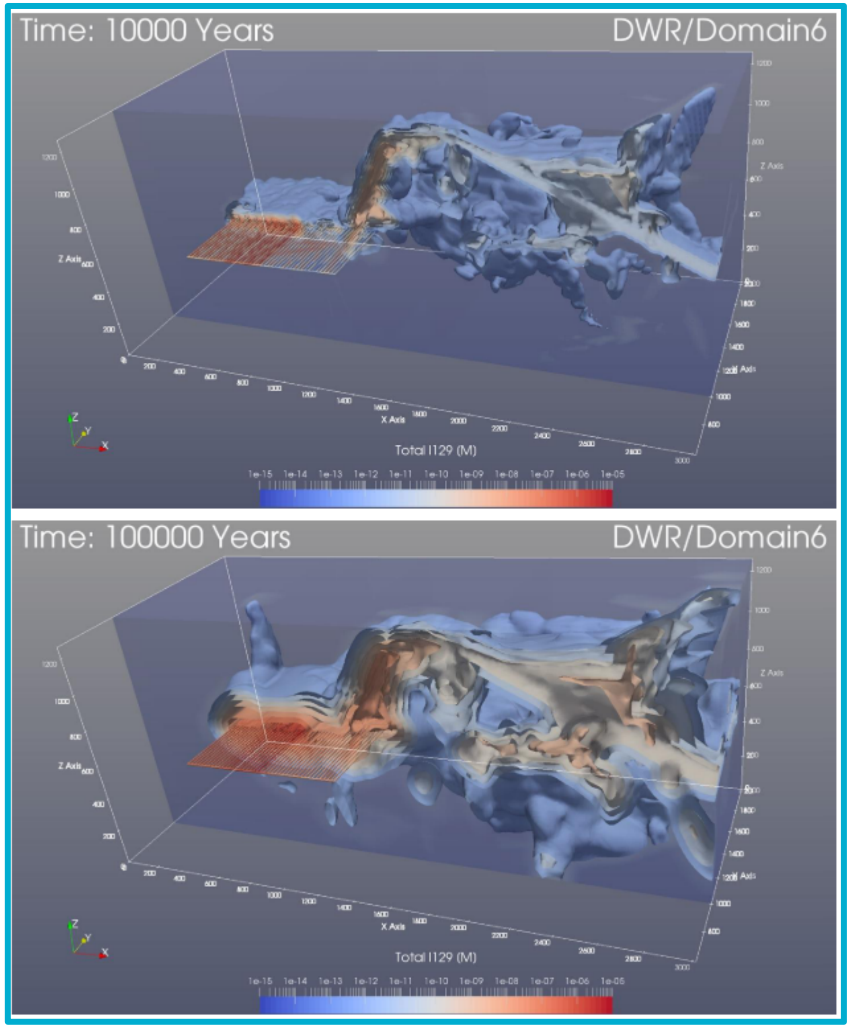
Iodide (I^-)

- Dose release in the safety case for the deep geologic repository is frequently driven by the release of anion species.
- More specifically the anionic species- ^{129}I due to long half life of 15.7 million years and mobility
- The DOE Hanford Site is another example of remediation issues particularly ^{129}I contamination in the subsurface from former plutonium production.

Moore et al. 2020

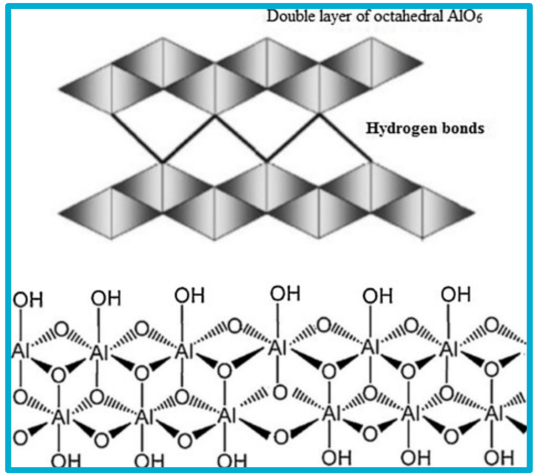
Performance Assessment (PA Models)

- Thermal-hydrological-chemical processes simulated via PFLOTRAN



Sevougian et al. 2016

Synthesis and Characterization



M.Mohammadi, et.al. (2021)

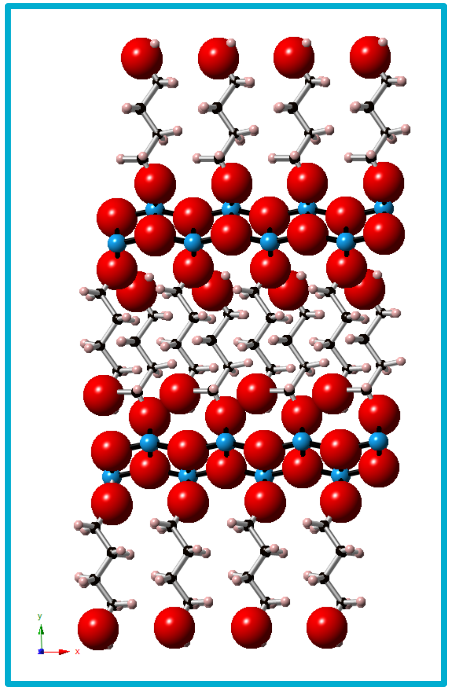
Boehmite

- Aluminum oxyhydroxide (γ-AlO(OH)): commercially used because of its high surface area as a catalyst support material or adsorbent.

Glycoboehmite (GB)

- Aluminum oxyhydroxide boehmite synthesis using a glycothermal reaction in 1,4-butanediol
    - Under synthesis conditions the atomic structure of the boehmite phase is altered by chemisorption of the glycol solvent in place of interlayer hydroxyl groups

M. Inoue, Y. Kondo, and T. Inui, (1988)
M. Inoue, (2004)



Bell, N. et. al. (2021)

Diol content

Comparison of atom ratios from XPS and hypothetical diol loading a site substitution of 0.15 (C4H8OH) is the best match to XPS and C content (combustion)

XPS data

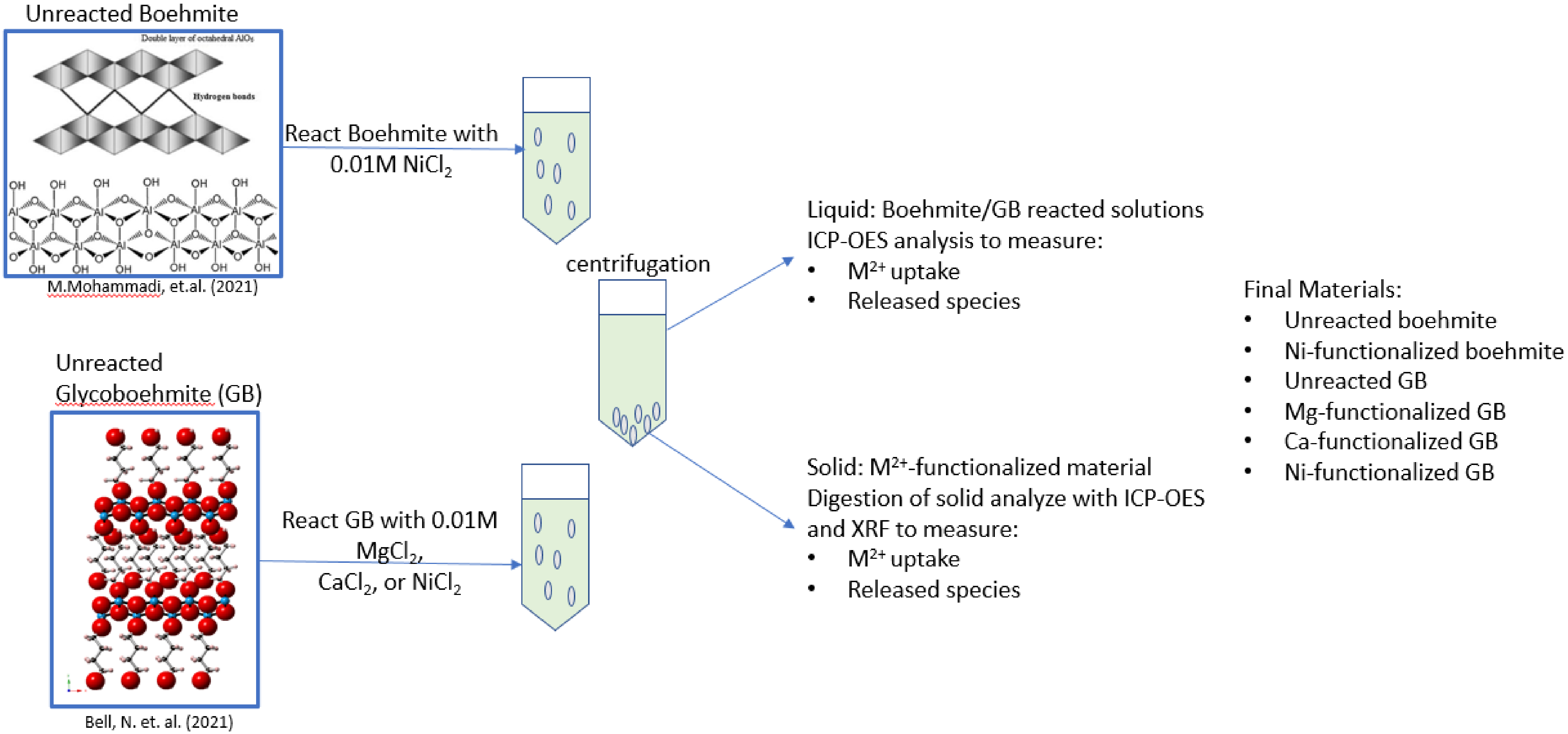
Combustion analysis

	mol %Al	mol% C	mol% O	mol% K[a]	wt% C
XPS	24.95	16.46	58.33	0.26	13.4[b]
AlOOH	33.33	0.00	66.67		
AlOOH $(C_4H_8OH)_{0.10}$	28.49	11.40	59.83	0.28	7.11
AlOOH $(C_4H_8OH)_{0.15}$	**26.60**	**15.96**	**57.18**	**0.27**	**10.12**
AlOOH $(C_4H_8OH)_{0.20}$	24.94	19.95	54.86	0.25	12.85
AlOOH $(C_4H_8OH)_{0.25}$	23.47	23.47	52.82	0.23	15.32
AlOOH $(C_4H_8OH)_{0.30}$	22.17	26.61	51.00	0.22	17.58

Hypothetical values

[a] Based on 0.01 K per AlOOH formula unit for hypothetical formulas. [b] Average weight % C from two combustion samples (Galbraith Laboratories, Inc.)

Metal Functionalization



Unreacted Boehmite

M.Mohammadi, et.al. (2021)

React Boehmite with 0.01M $NiCl_2$

Unreacted Glycoboehmite (GB)

Bell, N. et. al. (2021)

React GB with 0.01M $MgCl_2$, $CaCl_2$, or $NiCl_2$

centrifugation

Liquid: Boehmite/GB reacted solutions ICP-OES analysis to measure:

- M^{2+} uptake
- Released species

Solid: M^{2+}-functionalized material Digestion of solid analyze with ICP-OES and XRF to measure:

- M^{2+} uptake
- Released species

Final Materials:

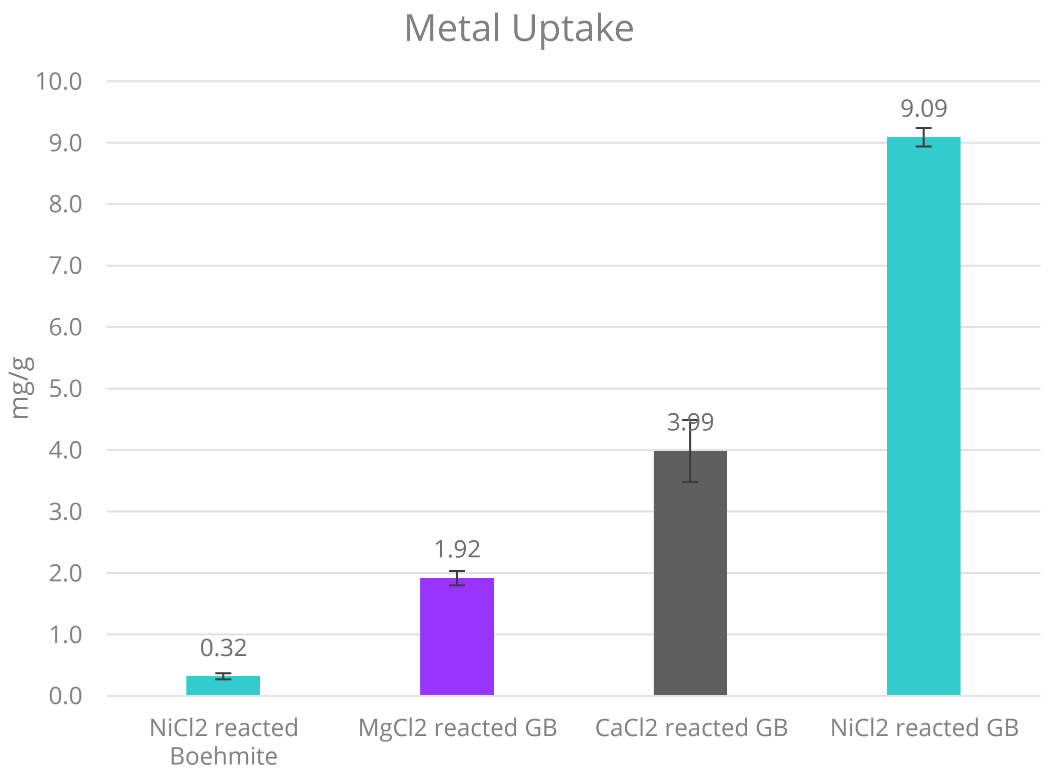
- Unreacted boehmite
- Ni-functionalized boehmite
- Unreacted GB
- Mg-functionalized GB
- Ca-functionalized GB
- Ni-functionalized GB

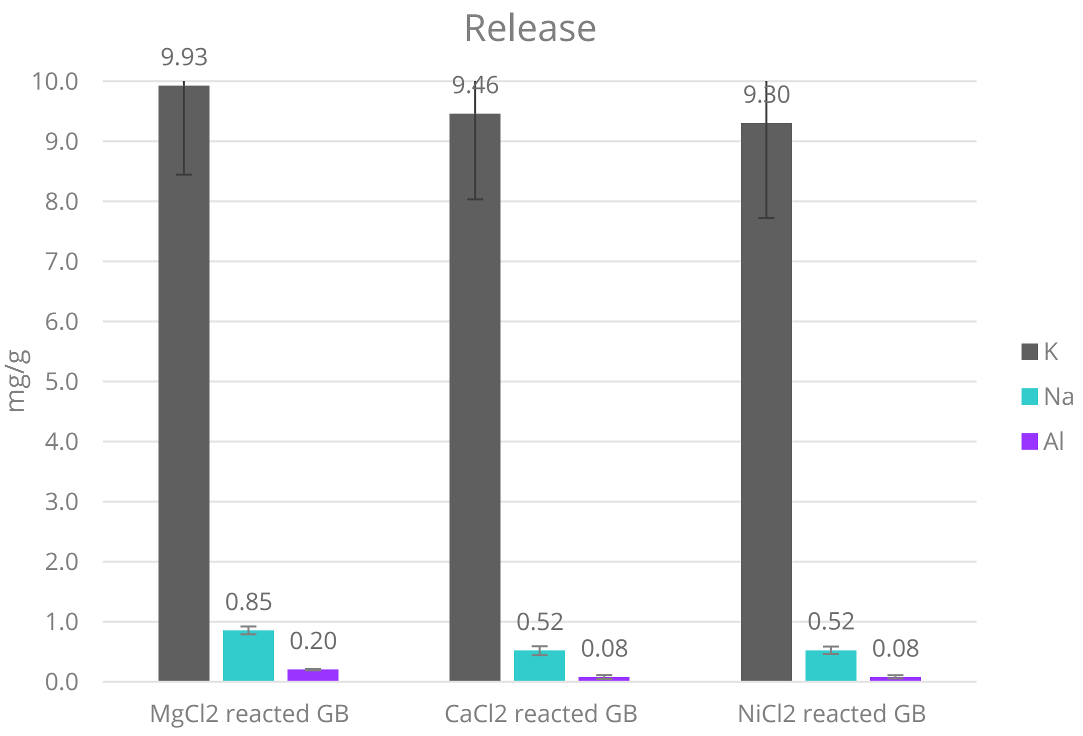
Modified material characterization

Liquid analysis using ICP-OES (metal uptake and release)

- GB has a greater capacity for Ni^{2+} that either Mg^{2+} and Ca^{2+}
- GB significantly great uptake of Ni^{2+} compared to boehmite

- The same amount of K^+ is released when reacted with either $MgCl_2$, $CaCl_2$, and $NiCl_2$

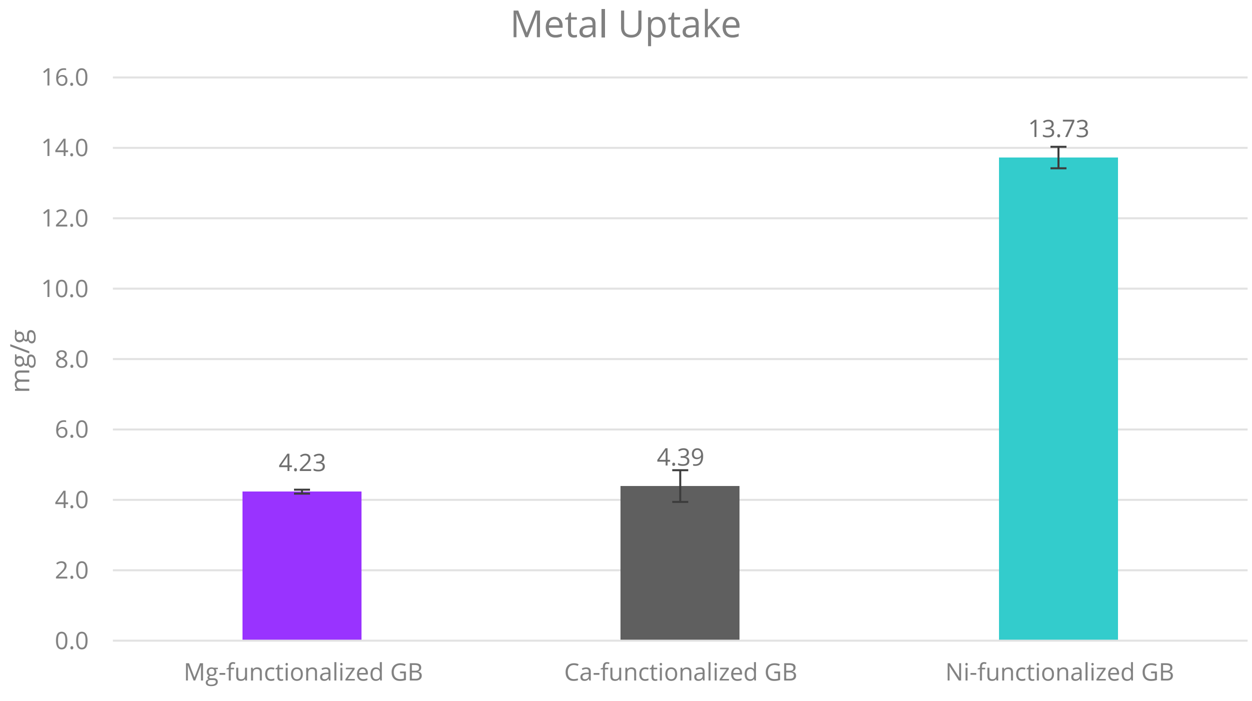


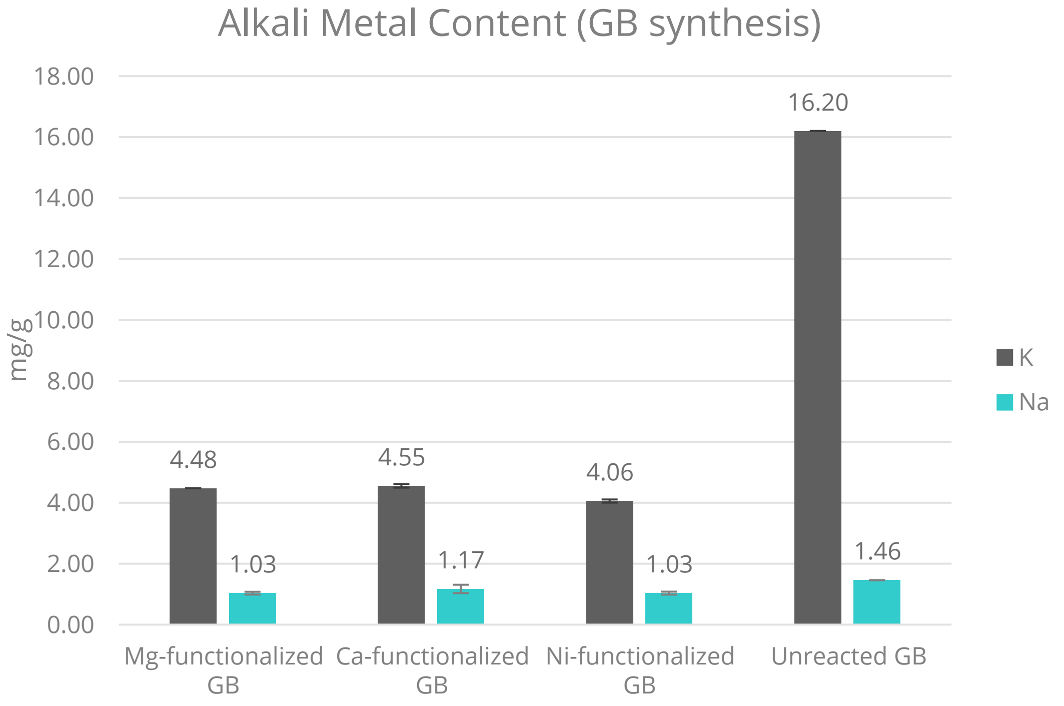


Modified material characterization

Solid material acid digestion then liquid analysis using ICP-OES (metal uptake and release)

- Similar results to liquid analysis
  - Ni^{2+} uptake significantly higher than Mg^{2+} and Ca^{2+} by GB
  - K^+ release is similar when GB reacted with $MgCl_2$, $CaCl_2$, and $NiCl_2$





Metal Composition by X-ray Fluorescence

XRF of GB and metal functionalized GB (metal uptake and release)

- Conclusion: Third method shows same trend as above two elemental methods:
  - Metal uptake trend: $Ni^{2+} > Ca^{2+} > Mg^{2+}$
  - K^+ similar release in all reacted materials

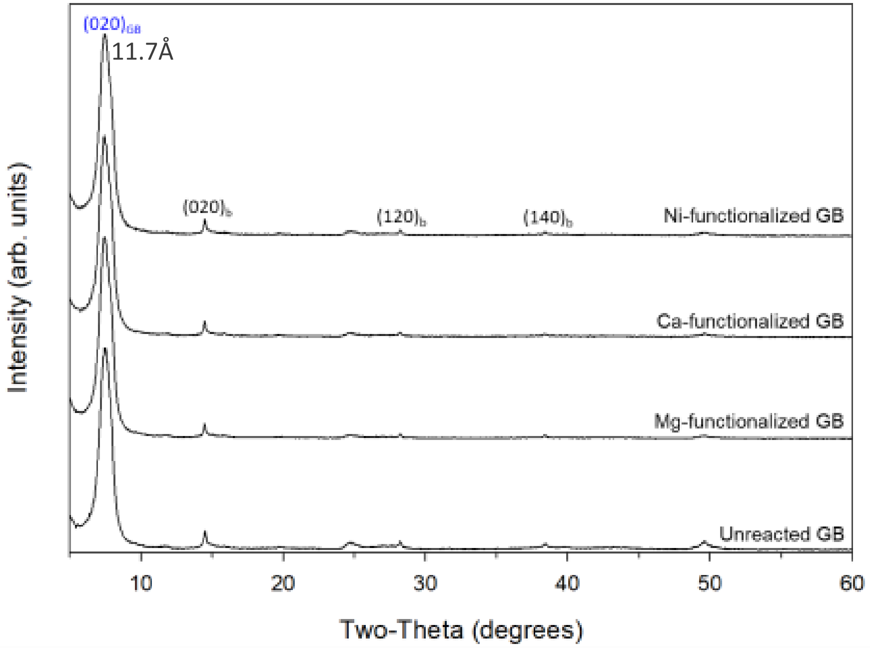
	Mole percent elemental species					
GB Material	Al	Cl	K	Ca	Mg	Ni
Unreacted GB	94.96	0.06	**5.64**	0.00	0.00	0.00
Mg-functionalized GB	96.21	2.07	1.24	0.02	**0.44**	0.00
Ca-functionalized GB	94.58	2.07	1.24	**2.10**	0.00	0.00
Ni-functionalized GB	93.92	2.84	0.85	0.00	0.00	**2.38**

*Cl^- from reaction step (chloride salts)

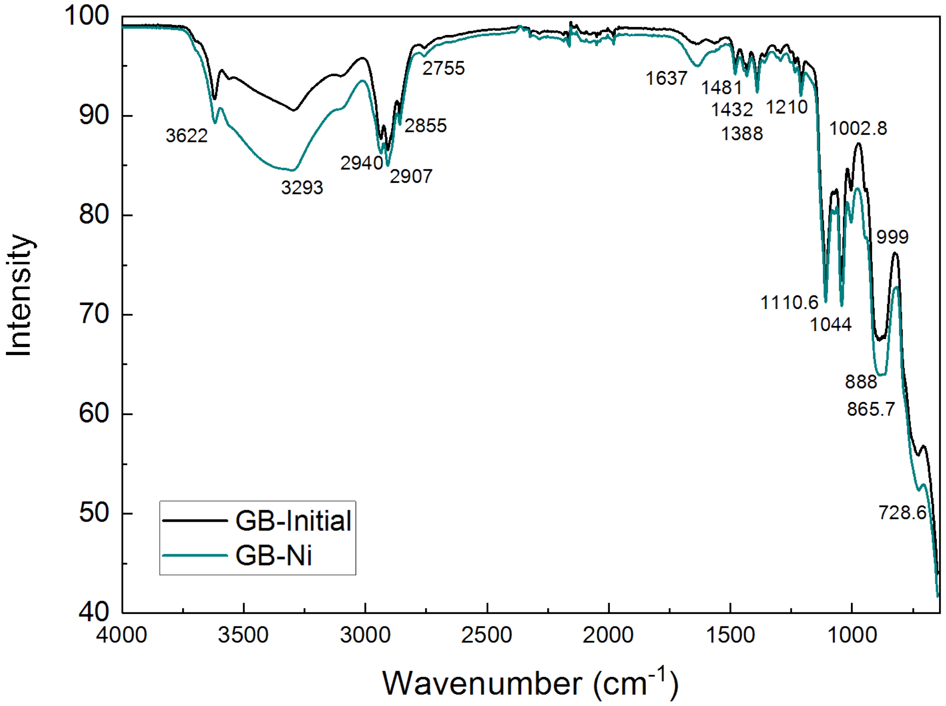
Structural Analysis

XRD and FTIR show no structural change when GB functionalized with divalent metals

- Little to no change in the $(020)_{GB}$ peak location for all functionalized materials when compared to unreacted GB
- Interlayer spacing for dry GB powders is dictated by the incorporation of the organic glycol molecule regardless of cation present



- GB and Ni-functionalized GB appear unchanged in FTIR peak location and intensity



Anion Sorption

Iodide/pH adjusted

- Sorption Reactors
  - 0.1g of material
  - 7.425 mL deionized water
    - pH adjusted to 7(+/-0.5) using KOH or HNO3
  - 0.075 mL 1000ppm I^- standard (final I^- concentration 10ppm)
    - pH adjusted to 7(+/-0.5) using KOH or HNO3 before I- addition
- Analyze I- concentration using Ion Chromatography (IC)

Arsenate

- Sorption Reactors
  - 0.1g of material
  - 19.9 mL deionized water
  - 0.1 mL 0.01M sodium arsenate (final arsenic concentration 3.75ppm)
- Analyze arsenic at the 188nm wavelength using Inductively Coupled Plasma- Optical Emission Spectra (ICP-OES)

Calculate the K_d value

Solid: liquid partitioning coefficient (mL/g)

$$K_d = (C_1-C_f)/C_f*S$$

C_1= initial aqueous anion concentration (mg/L)

C_f= final aqueous anion concentration (mg/L)

S= solid: solution ratio (g/mL)

I^- and AsO_4^{3-} Sorption (surface area)

No pH adjustment:

- K_D for arsenate and iodide increases significantly when GB is functionalized with Ni^{2+} (~45 times)
- Mg^{2+} and Ca^{2+} doesn't influence I^- sorption like Ni^{2+} does
- pH remains high resulting in low sorption- while the pH in the Ni-functionalized reactor is much lower

pH adjustment:

- I^- K_D is much higher in Ni-functionalized GB compared to unreacted GB
- KD for iodide increase a small amount when comparing boehmite and Ni-functionalized boehmite
- pH adjustment in the Ni-functionalized GB showed a higher K_D for I^- than the un-adjusted pH reactors

	No pH adjustment			**pH adjustment**	
GB material	Iodide K_D	Arsenate K_D	Final pH	Iodide K_D	Final pH
Mg-functionalized GB	1.63		9.67		
Ca-functionalized GB	0.85		9.80		
Ni-functionalized GB	43.07	6427	6.28	60.85	6.42
Unreacted GB	0	135	9.67	13.23	7.96
Ni-functionalized boehmite				29.06	6.56
Unreacted boehmite				21.37	7.24

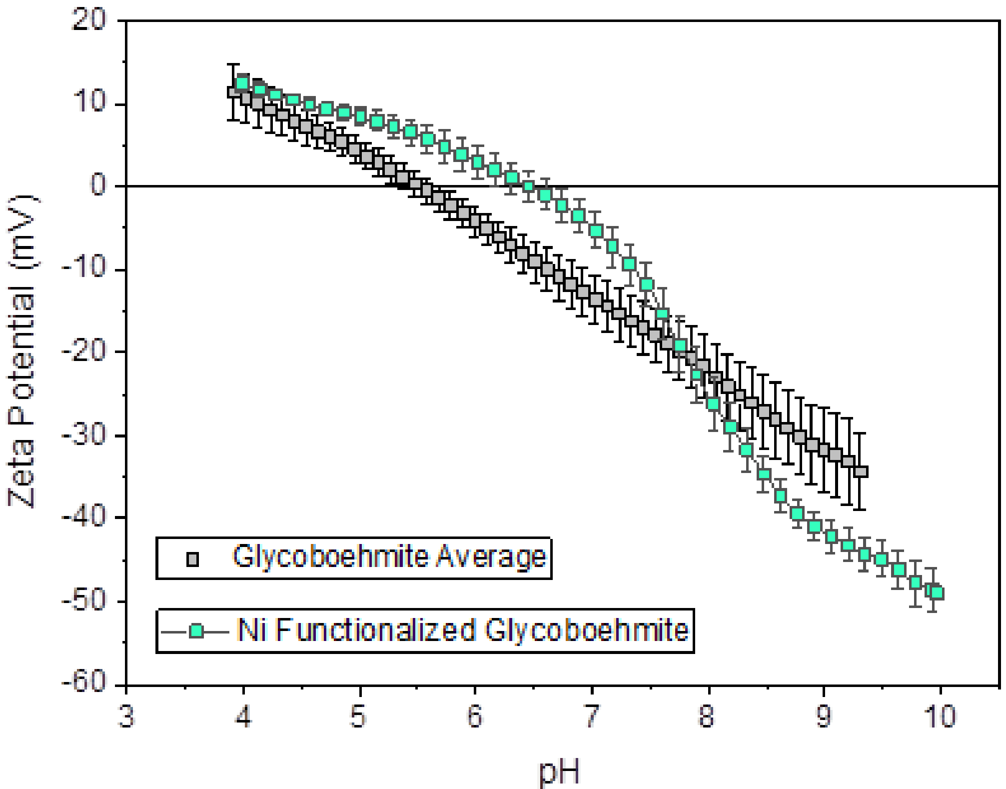
Surface area, Ni^{2+} uptake, and I^- sorption

- Boehmite has a much higher surface area than GB
- When surface area is considered GB has a 12 times higher affinity for Ni^{2+} than boehmite does
- Ni-functionalized GB has a 5 times higher I^- k_D than Ni-functionalized GB when normalized by surface area

Material	BET surface area (m^2/g)	Ni^{2+} uptake (mg/g)	I^- sorption (KD) (pH adjusted)
Unreacted boehmite	297.5	0.32	21.37
Ni-functionalized boehmite	285.4		29.06
Unreacted GB	122.7	9.09	13.23
Ni-functionalized GB	119.7		60.85

Surface charging behavior- Zeta Potential

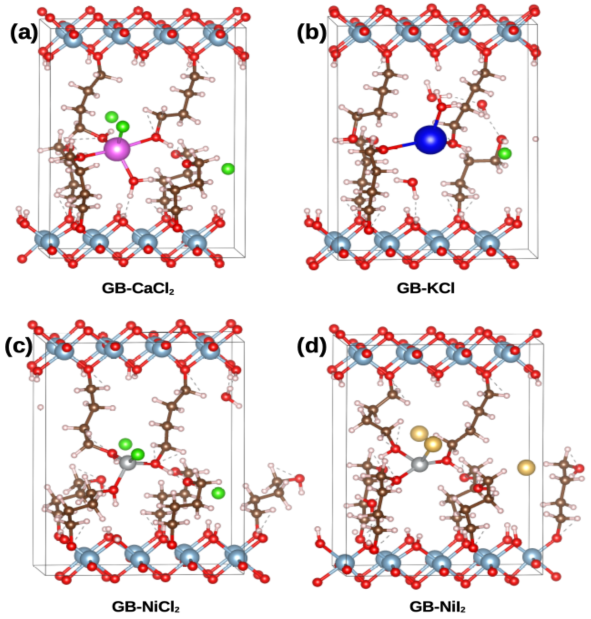
- GB has a much lower isoelectric point than boehmite (~9)
  - GB has partial substitution of surface hydroxyls with mono terminated glycol modifications
- Isoelectric point shift from 5.5 to 6.5 and a change in pH sweep profile when Ni^{2+} is adsorbed to the material
  - Additional positive surface charge from Ni^{2+} adsorbed into the hydrophilic interlayers through coordination with neighboring oxygen atoms from butanediols and surface hydroxyls
- As pH rises Ni^{2+} becomes hydrolyzed to NiOH at pH 8 and further to $Ni(OH)_2$ (strong downward trend)
  - The cancelation of the positive surface charge as the Ni hydrolyzes and adsorbs OH^- species shows additional negative charges are present from the solution



Molecular Modeling

Ab initio molecular dynamics (AIMD) simulations

- Metal ions initially immobilized in the interlayer
  - Form covalent bonds with oxygen atom from butanediols and water molecules
- Cl^- and I^- anion appear to form covalent bonds with Ca and Ni in the GB-$CaCl_2$, GB-$NiCl_2$, and GB-NiI_2 for charge compensation

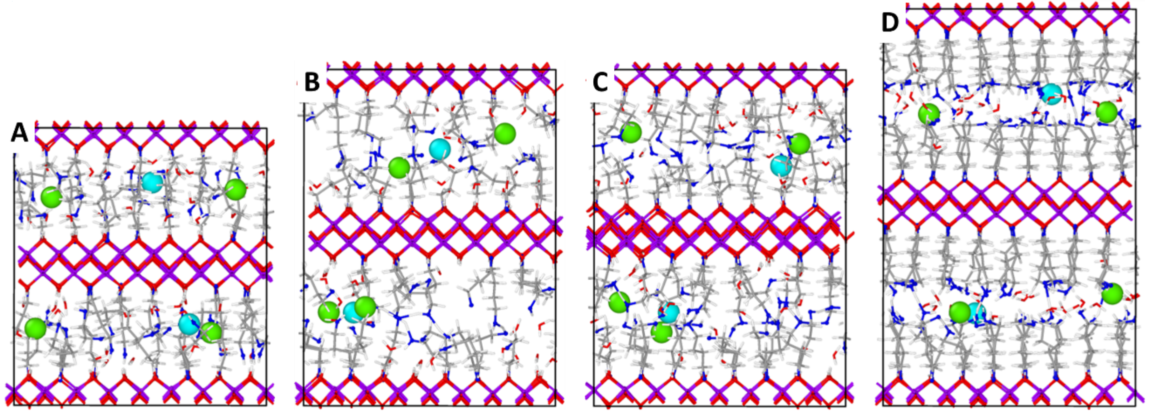


Al-Cyan, C-Brown, Ca-Magenta, Cl-Green, H-White
I-Yellow, K-Blue, Ni-Grey, O-red

CMD simulations

- XPS results- approximate loading 0.66 diol/u.c with a d-spacing of 11.7Å (XRD results)
- Here 0.5 diols/u.c show higher d-spacing (12.6Å for K^+ and 12.7Å for Ni^{2+})
- Experimental samples don't contain water in the interlayer

Ions	0.5	1.0	1.25	2.0
no ions, dry	**11.0**	12.2	15.1	16.7
K^+	**12.7**	14.3	15.7	18.3
Ni^{2+}	**12.6**	15.3	15.4	18.0
Ni^{2+}, dry	**12.2**	15.5	15.5	17.2



Snapshots from CMD simulations of GB with hydrated $NiCl_2$ interlayers at diol loadings of A) 0.5, B) 1.0, C) 1.25, and D) 2.0 diols/u.c. Color legend: Al, purple; O, red; H, white; C, gray, Ni, cyan, Cl, green. Periodic boundaries are shown as black lines.

Summary and Future Work

We have demonstrated a new high surface area sorbent material for anionic contaminant removal

- GB when reacted with divalent metals (Ca^{2+}, Mg^{2+}, and Ni^{2+}) a higher uptake of Ni^{2+} is observed while K^+ removal from the material is similar in all reactions
- GB has a 12 times higher sorption affinity for Ni^{2+} than boehmite when normalized by surface area
- When GB is functionalized with Ni^{2+} it has a 50 fold increase in kD for I^- and ASO_4^{3-} than GB-unreacted

Future work:

- Testing for stability/function at high temperature.
- pH dependence of I^- sorption
- Bentonite/material interaction
- Molecular modeling (particle edges)

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