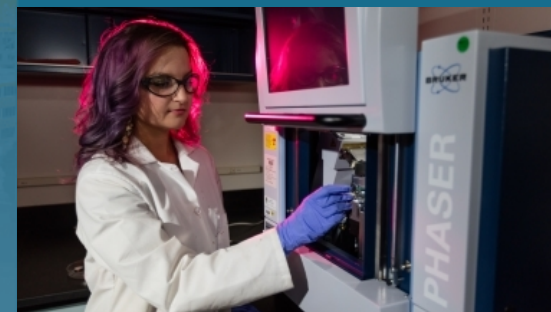




Synthesis and Evaluation of Novel Materials for Anionic Sorption



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Clay Minerals Society Annual Meeting

Austin, Texas

May 22, 2023

Summary

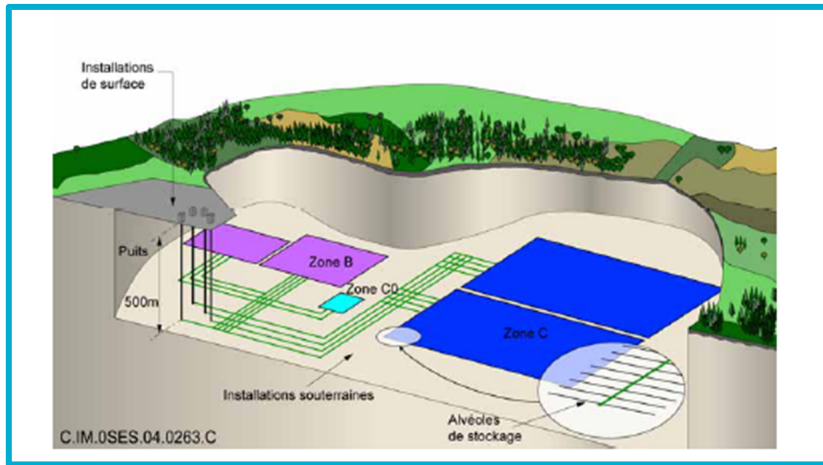


- Background and motivation
 - Iodide
 - Arsenate
- Material characterization
- Material modification
- Performance tests
- Discussion (mechanism)
- Summary and future work

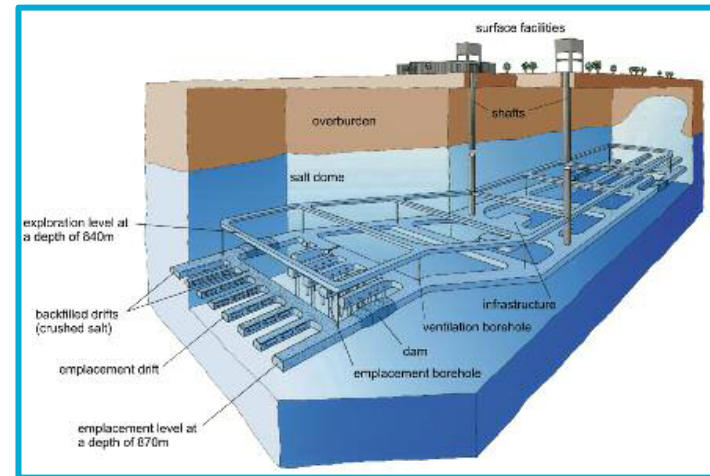
Background and Motivation



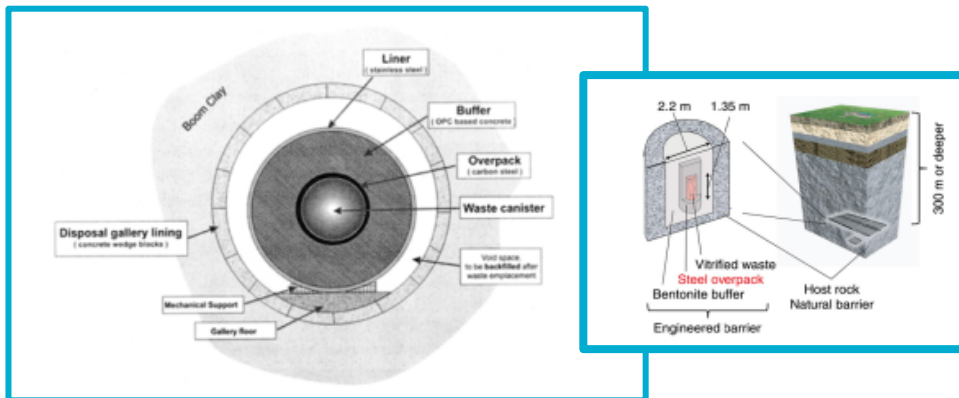
Disposal Concepts



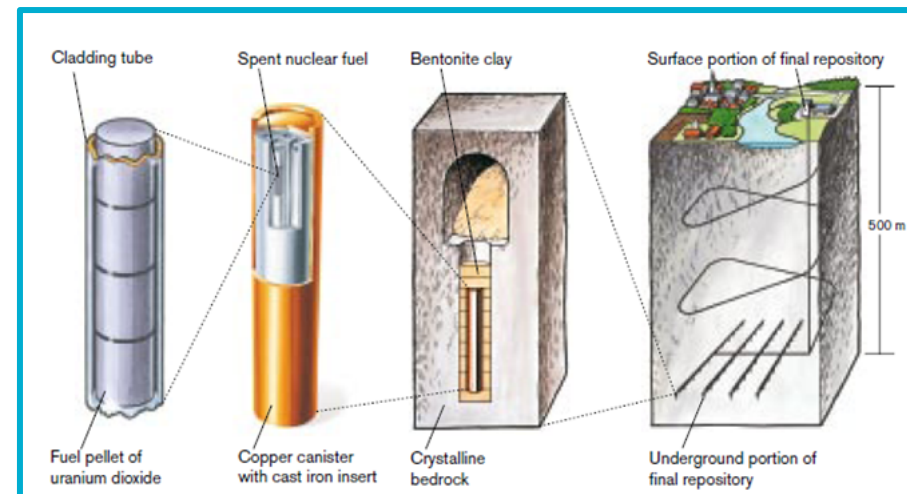
Mined repositories in clay/shale (ANDRA 2005)



Mined repositories in salt (BMW 2008)



Engineered Barrier System Components



Mined repositories in crystalline rock (SKB 2011)

Background and Motivation

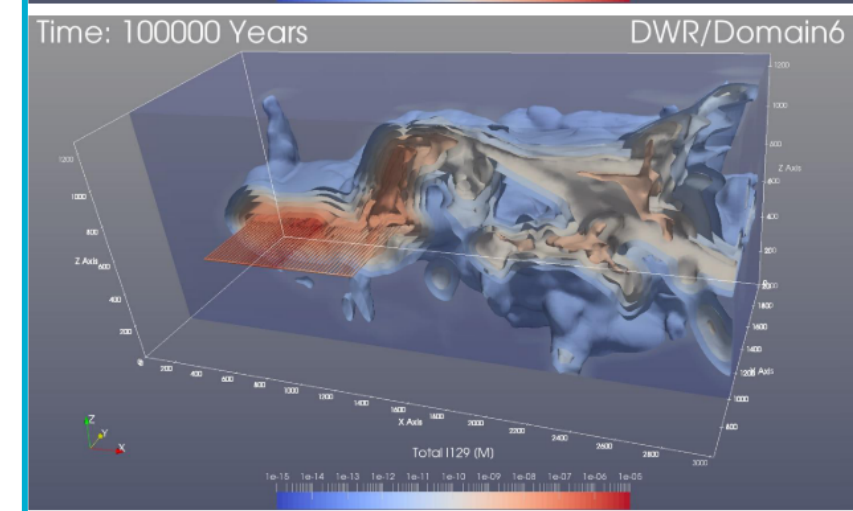
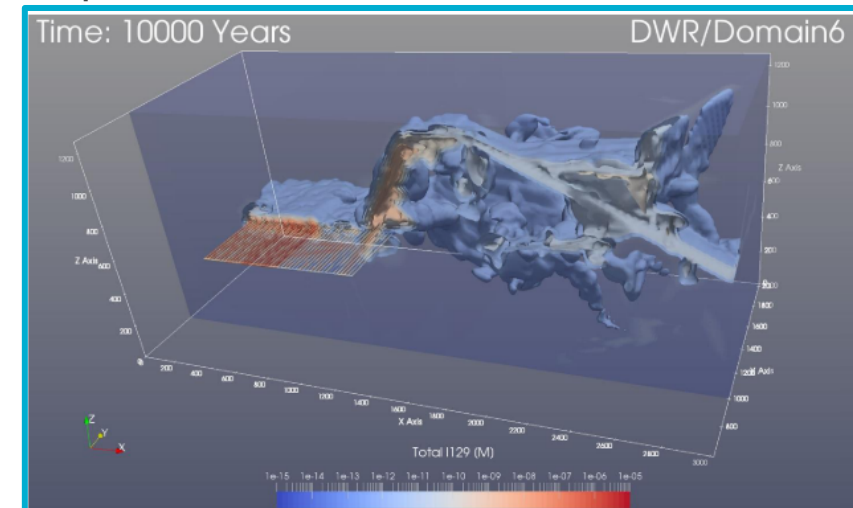
Iodide (I⁻)

- 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.
- 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- ¹²⁹I due to long half life of 15.7 million years
- The DOE Hanford Site is another example of remediation issues particularly ¹²⁹I contamination in the subsurface from former plutonium production.

Moore et al. 2020

Performance Assessment (PA Models)

- Thermal-hydrological-chemical processes simulated via PFLOTRAN

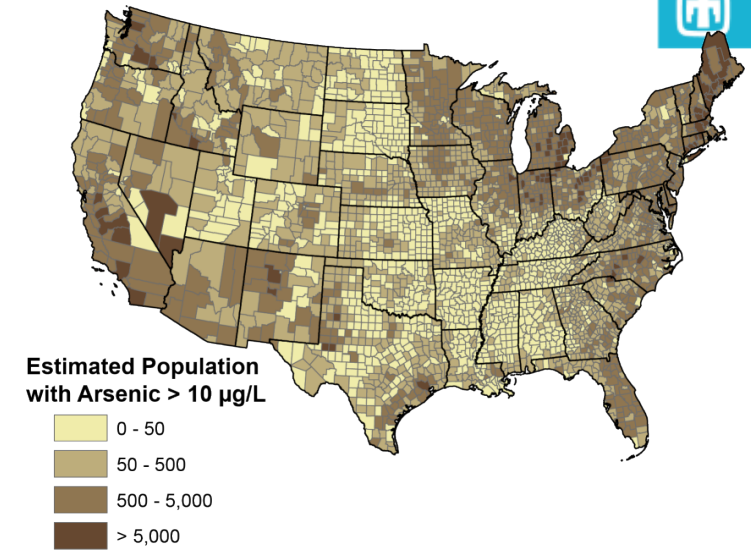


Background and Motivation

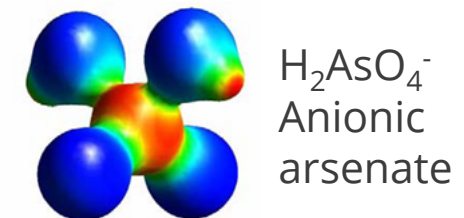
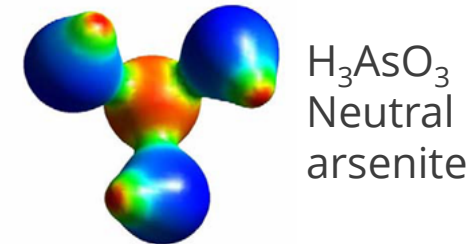
Arsenic

- On January 22, 2001; the EPA adopted a new standard for arsenic in drinking water to 10 ppb, replacing the old standard for 50 ppb.
 - Based on an NRC 1999 arsenic drinking water report
 - Epidemiological studies in Taiwan, Chile, and Argentina found that “ingestion of arsenic in drinking water poses a hazard of cancer of the lung and bladder, in addition to cancer of the skin”
 - Even at low concentrations, exposure to As increases the risk of cardiovascular disease and stroke.

- Inorganic arsenic in groundwater usually exists as a combination of neutral As^{III} (arsenite) and anionic As^{V} (arsenate)
 - Arsenite has the oxidation state +III
 - Arsenate has the oxidation state of +V
 - Removing $\text{As}(\text{V})$ is easier than removing $\text{As}(\text{III})$ because $\text{As}(\text{III})$ has to be oxidized first to $\text{As}(\text{V})$ before removal process



<https://www.usgs.gov/mission-areas/water-resources/science/arsenic-and-drinking-water>



Boehmite

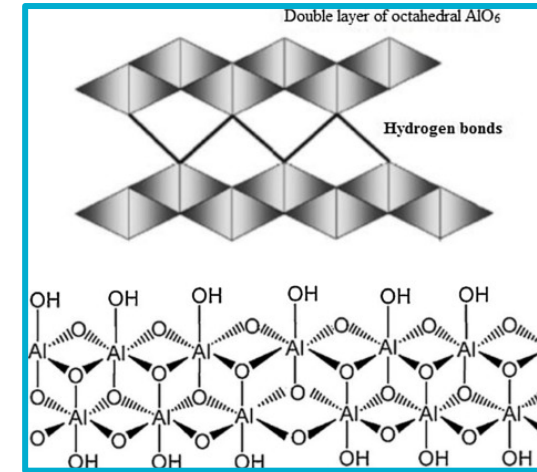
- Aluminum oxyhydroxide (γ -AlO(OH)): commercially used because of its high surface area as a catalyst support material or adsorbent.

Glycoboehmite

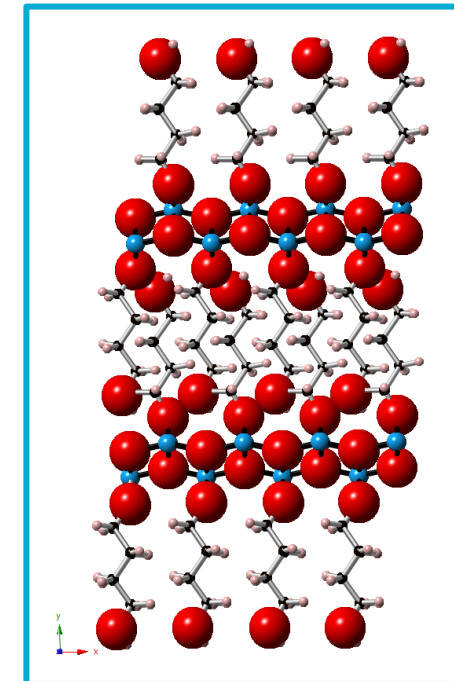
- Aluminum oxyhydroxide boehmite synthesis using a glycothermal reaction in 1,4-butanediol
 - Under synthesis conditions the atomic structure of the boehmite phase is altered by chemisorption of the glycol solvent in place of interlayer hydroxyl groups

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

M. Inoue, (2004)



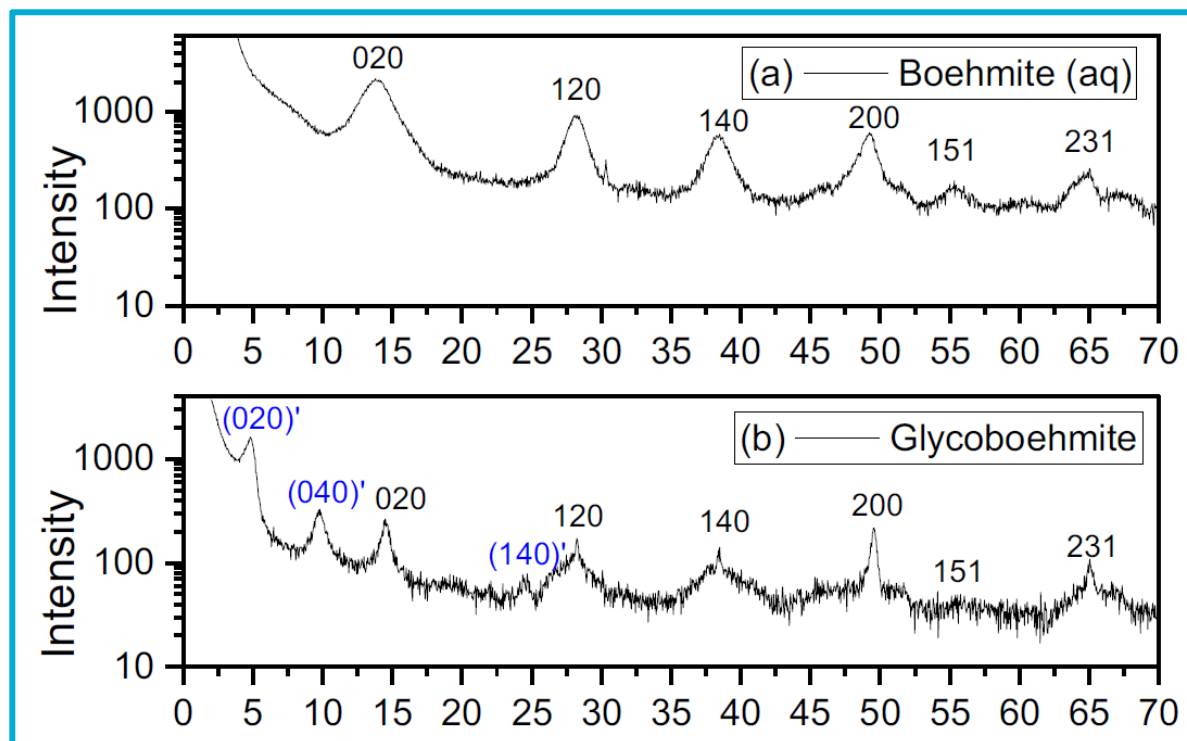
M.Mohammadi, et.al. (2021)



Bell, N. et. al. (2021)

XRD

- Glycoboehmite exhibits several peaks in common with boehmite
- New peaks at 4.8, 9.8, and 24.5 degrees 2θ resulting from intercalated organic glycol
- (020) peak shift indicates the interlayer structure is expanded by the glycol substitution for the interlayer hydroxyl groups



Position of (020)' values, and estimated interlayer spacing.

Sample	2-Theta Value of (020) or (020)'	d(020) or d(020)'(Å)	Interlayer Distance (Å)
Boehmite (aqB)	13.9	6.38	4.38
Glycoboehmite (GB)	4.80	18.38	16.38

Low angle peak- suggests a larger expansion of the layers

Material Characterization

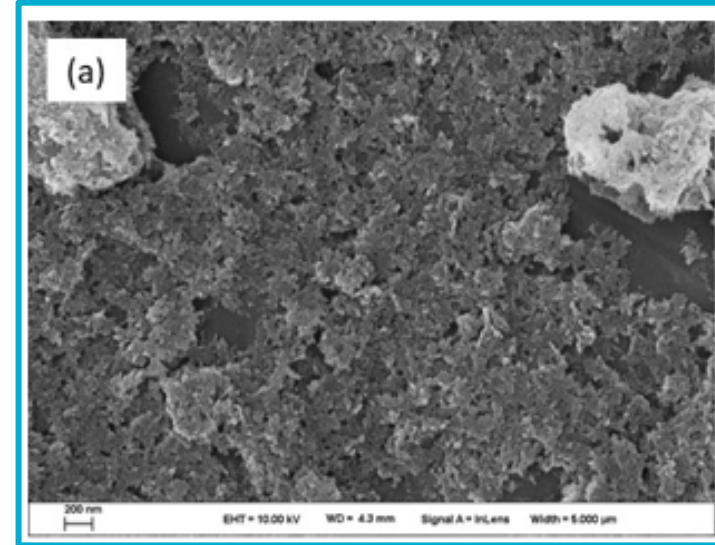
SEM

Boehmite (a)

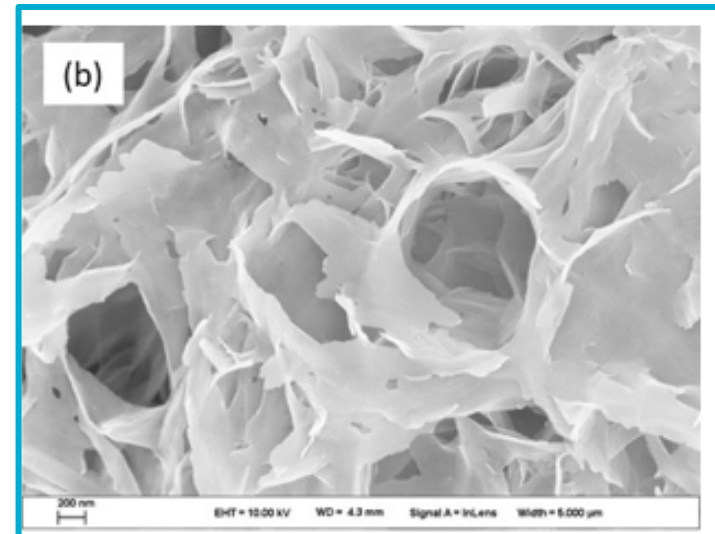
- ❑ Crystalline size is very small and aggregated
- ❑ Crystals are very small nano-platelets

Glycoboehmite (b)

- ❑ Larger, flaky particles “honeycomb” morphology-platelet material with irregular edges, and smooth face
- ❑ 24 hour reaction process creates very large sheet morphology



200nm scale bar



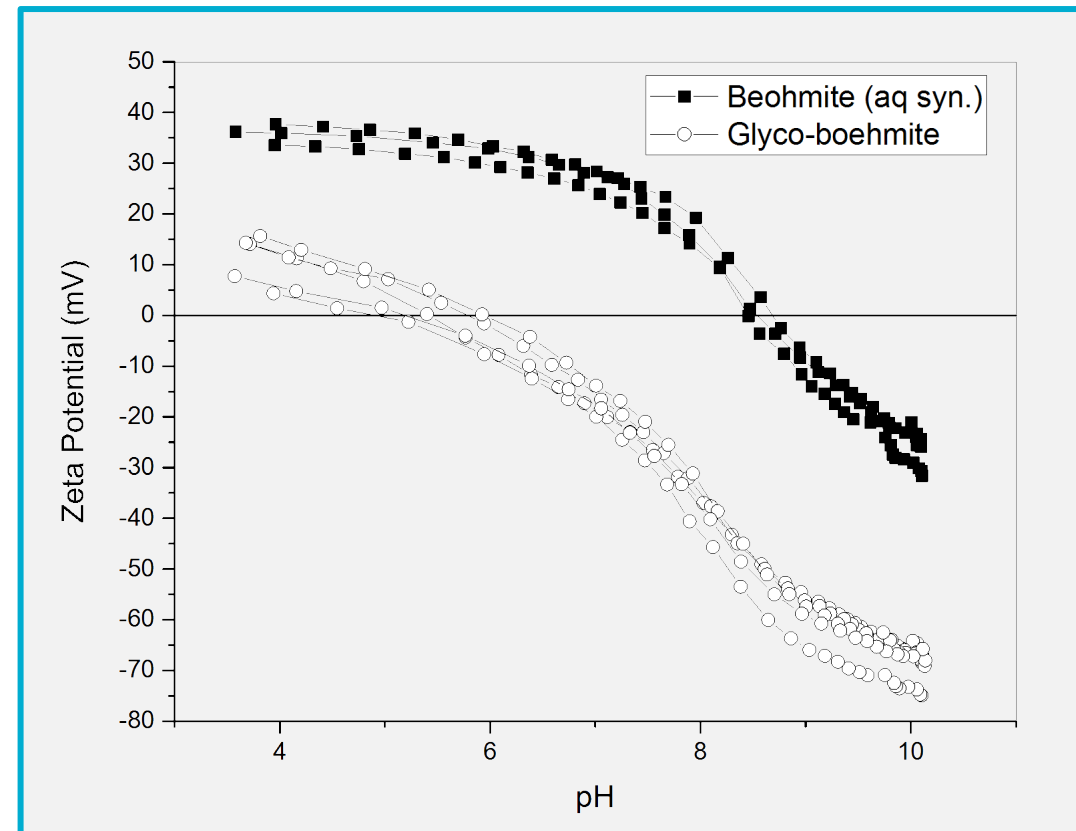
Zeta Potential (surface chemistry)

Boehmite

- Isoelectric point 8.9
- Charge:
 - pH 4-6 is +35mV (plateau)
 - pH 10 is -35mV

Glycoboehmite

- Isoelectric point 5.2-6
- Charge:
 - Acidic conditions show a weaker strength in charge pH 4-6 0-+15mV
 - Basic conditions show a much higher value pH 10 is -70mV



Nickel modification

- Introduce divalent metal onto surface of glycol-boehmite
 - Glycoboehmite was soaked in 0.01M NiCl₂ or MgCl₂ solution overnight
 - Centrifugation- removing excess supernatant
 - Ni-modified glycol-boehmite was dried in 60°C oven

BET Surface Area/pH

Sample	BET Surface Area (m ² /g)	pH in solution (DI water)
Boehmite	181	7.5
Glycoboehmite	136	10.3
Glycoboehmite-nickel modified	163	5.1
Glycoboehmite-magnesium modified	165	Not measured

Performance Tests



Iodide

- ❑ Sorption Reactors
 - 0.1g of material
 - 7.425 mL deionized water
 - 0.075 mL 1000ppm I⁻ standard (final I⁻ concentration 10ppm)

- ❑ 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 kD value

Solid: liquid partitioning coefficient (mL/g)

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

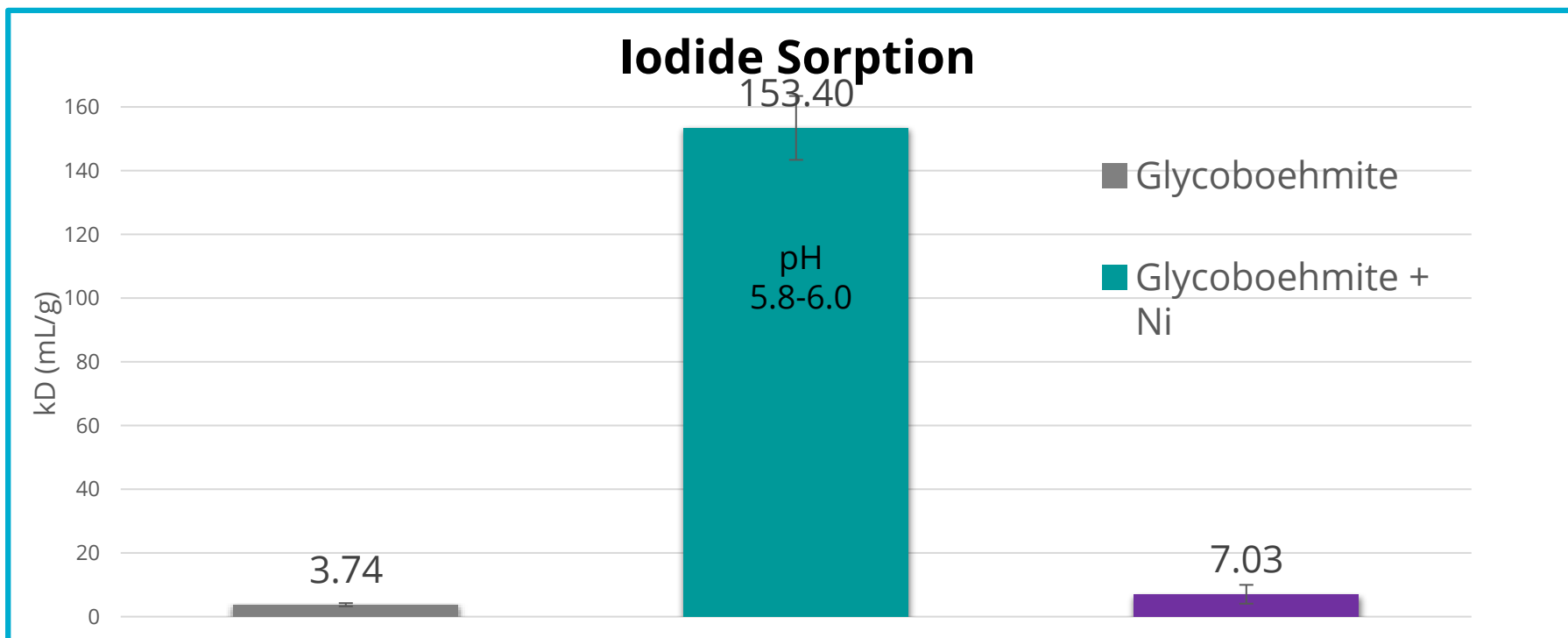
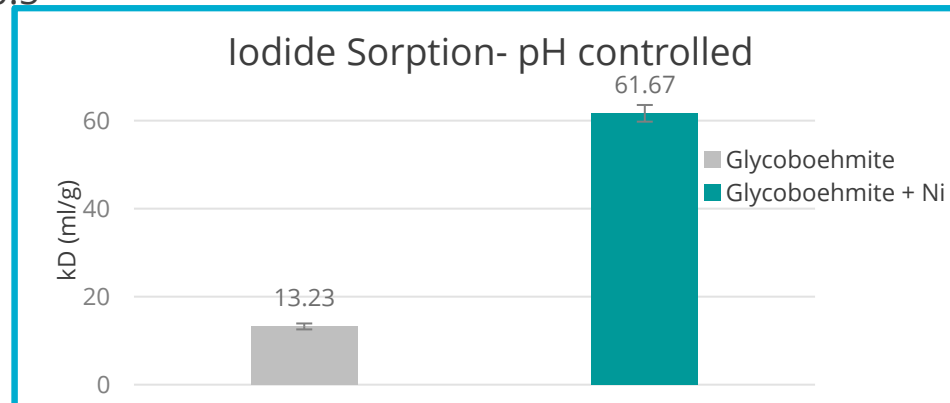
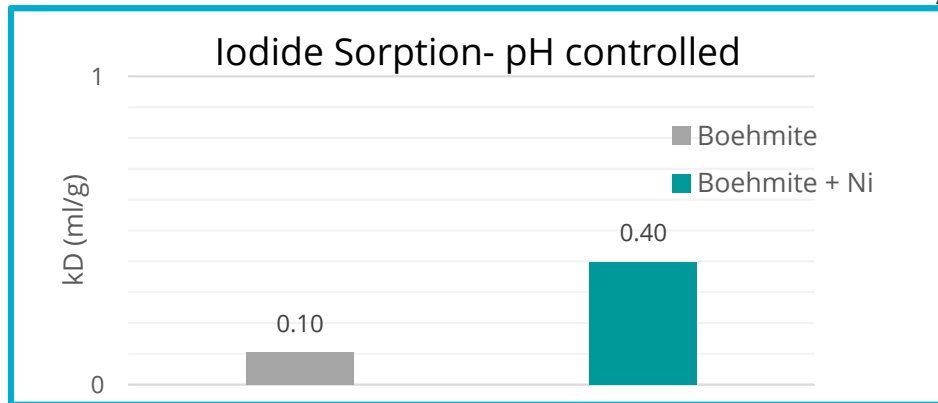
C₁ = initial aqueous anion concentration (mg/L)

C_f = final aqueous anion concentration (mg/L)

S = solid: solution ratio (g/mL)

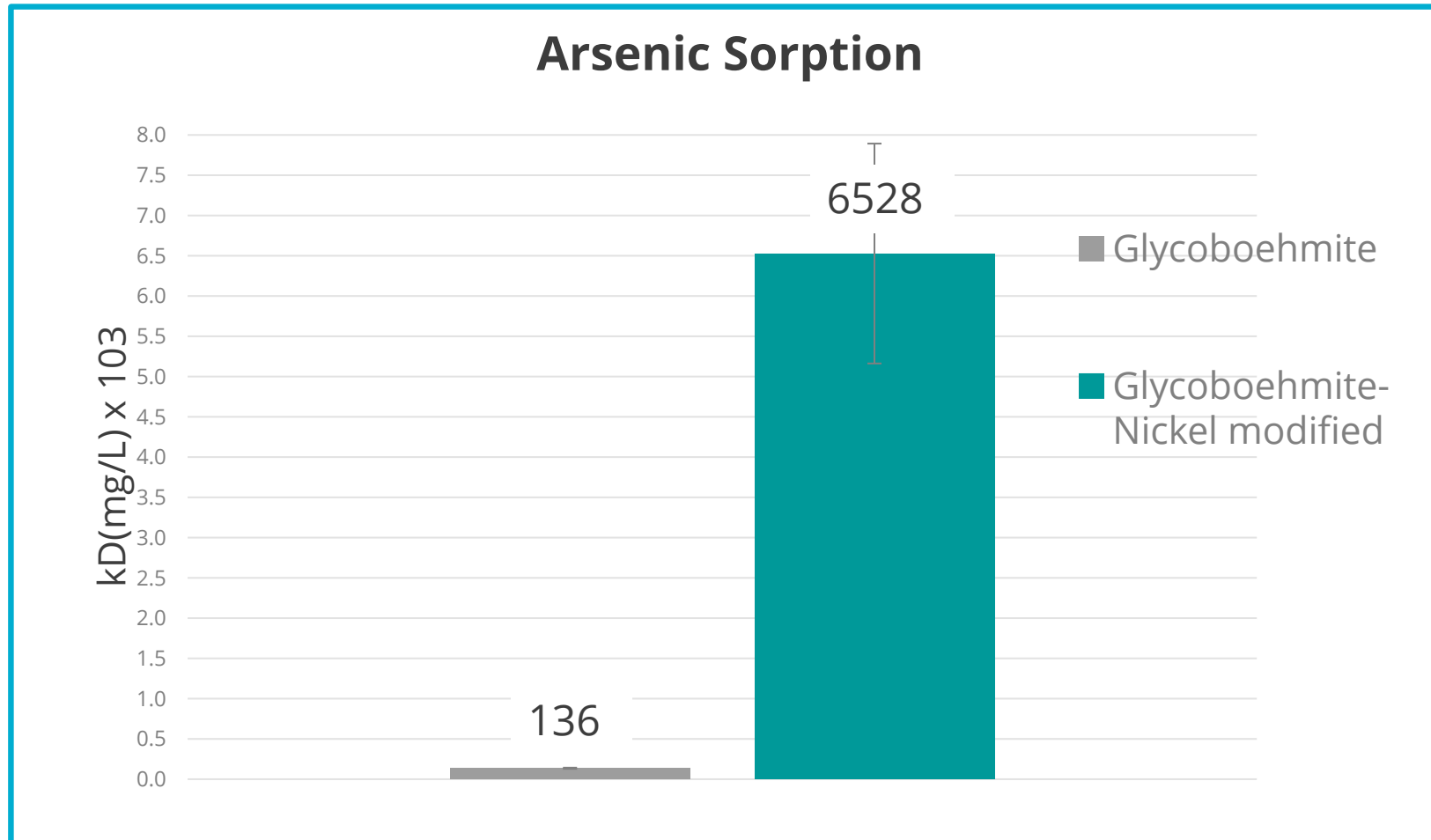


Iodide

pH
7.0 +/-0.5



Arsenic



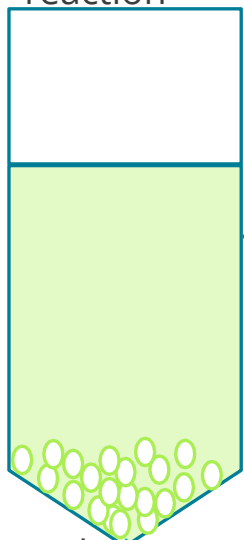
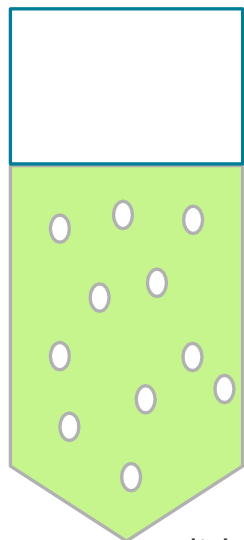
Patent number US11207658, Sorption agent. Method of making a sorption agent and barrier system.

Cation Exchange



Glycoboehmite **before** in NiCl₂

Glycoboehmite **after** NiCl₂ reaction



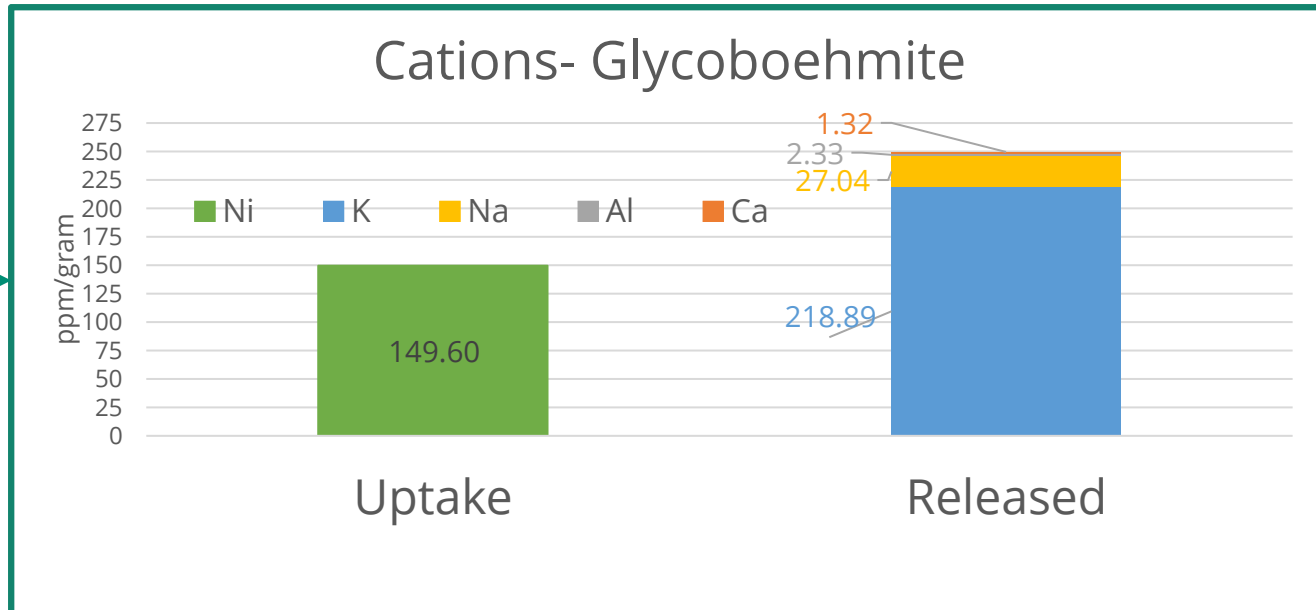
Supernatant elemental concentration analysis via ICP-OES

Solids recovered



Acid digestion

Elemental concentration analysis via ICP-OES/MS



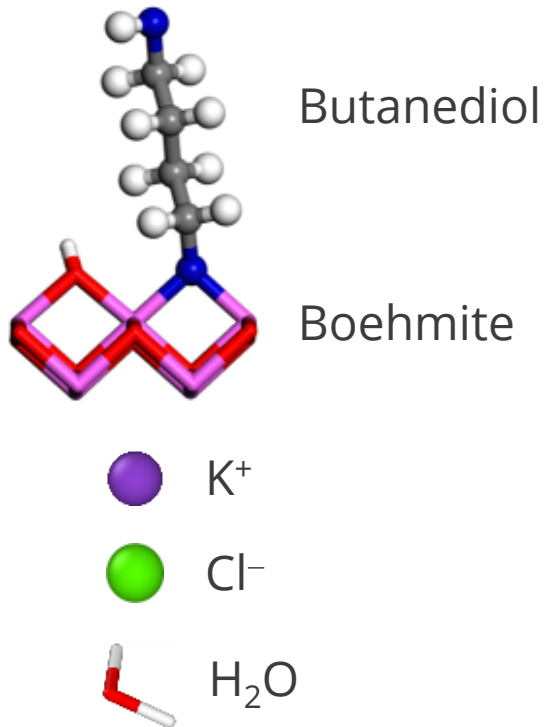
Sample	Al Wt%	C Wt%	Na (ppm)	Ca (ppm)	K (ppm)	Ni (ppm)
Glycoboehmite	36.8	8.08	1103	95.99	11732	N/D
Std dev	.85	.24	84	4.58	597	
Glycoboehmite + Ni modified	22.18	4.24	502.6	47.01	1302	6858
Std dev	.17	0.02	14.2	5.87	31.1	136

Towards understanding the mechanism



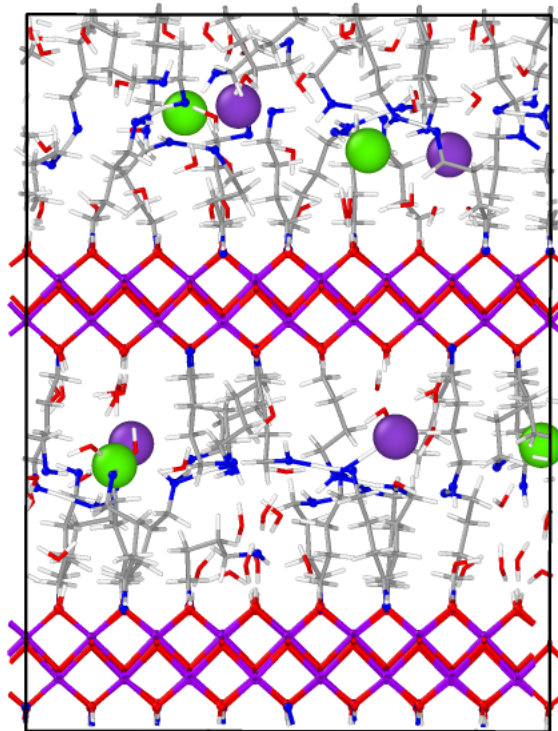
GB4 with KCl and Water

- Ions and alcohol groups remain far from boehmite surfaces.
- Water favors sites that enable H-bonding or ion hydration.

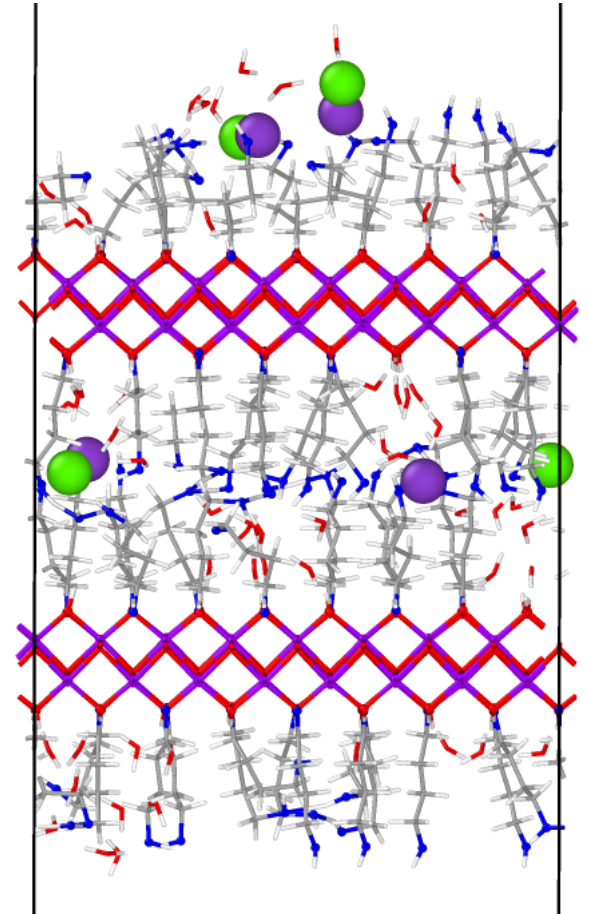


Greathouse, J.

Low diol content
1.0 diols/u.c.
Stable interlayers



Higher diol content
1.25 diols/u.c.
Internal and external surfaces
coated with diols



Summary and Future Work



- This work presents a novel, low-cost anionic getter material that could potentially be incorporated into an EBS design.
 - Glycoboehmite that was nickel modified showed a 30-fold increase in sorption for iodide compared to glycoboehmite
- Groundwater remediation can also be an application for the nickel modified glycoboehmite
 - Glycoboehmite that was nickel modified showed a 40-fold increase in sorption for arsenic (Patent US11207658) compared to glycoboehmite
- Continue to investigate and understand this material:
 - Modeling and simulations will investigate adsorption mechanisms of iodine, arsenic, and other toxic metals on nickel-modified GB; with systematic comparison with adsorption on pristine GB.

Funding

U.S. Department of Energy Office of Nuclear Energy, Office of Spent Fuel and Waste Science and Technology Research and Development Campaign



ANDRA 2005. *Dossier 2005: Argile. Synthesis: Evaluation of the Feasibility of a Geological Repository in an Argillaceous Formation*. Châtenay-Malabry, France: ANDRA.

BMWi (Federal Ministry of Economics and Technology, Germany) 2008. *Final Disposal of High-Level Radioactive Waste in Germany—The Gorleben Repository Project*. Berlin, Germany: Federal Ministry of Economics and Technology (BMWi). Available at <http://bmwi.de/EN/Service/search.html>.

SKB (Svensk Kärnbränslehantering AB [Swedish Nuclear Fuel and Waste Management Company]) 2011. *Long-Term Safety for the Final Repository for Spent Nuclear Fuel at Forsmark*, Technical Report TR-11-01. Three volumes. Stockholm, Sweden: Svensk Kärnbränslehantering

<https://www.usgs.gov/mission-areas/water-resources/science/arsenic-and-drinking-water>

M. Inoue, Y. Kondo, T. Inui. *Inorganic Chemistry*. 1988 Vol 27 Pages 215-221

M. Inoue. *Journal of Physics: Condensed Matter*. 2004. Vol 16 S1291-A1303

M. Siegel, P. McConnell, A. Ilges, H. Chen, A. Ghassemi, R. Thompson. *Arsenic water technology partnership*. DE-AC04-94AL85000

S. Sevougian, E. Stein, M. Gross, G. Hammond, J. Frederick and P. Mariner. Institution: Office of Scientific and Technical Information (OSTI) 2016

M. Mohammadi, M. Khodamorady, B. Tahmasbi, K. Bahrami, A. Ghorbani-Choghamarani. *Journal of Industrial and Engineering Chemistry*, Volume 97,2021,Pages 1-78.

N. S. Bell, M. A. Rodriguez, P. Kotula, J. N. Kruichak, B. A. Hernandez-Sanchez, M. R. Casillas, et al. *Applied Clay Science* 2021 Vol. 214 Issue 15

R. C. Moore, C. I. Pearce, J. Morad, S. Chatterjee, T. G. Levitskaia, R. M. Asmussen, *Science of the Total Environment* 2020 Vol. 716

A. Miller, J. Kruichak, M. Mills, Wang, Y. *Journal of Environmental Radioactivity* 2015 Vol. 147 Pages. 108-114

E. Matteo, C. Payne, A. Sanchez, N. Bell, Y. Wang, J. Kruichak, M. Mills. Patent number 11207658, sorption agent. Method of making a sorption agent and barrier system. Filing date 12/9/2021. Pub date 3/31/2022