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A LOW-COST, HIGH-PERFORMANCE ANIONIC GETTER MATERIAL WITH APPLICATIONS FOR ENGINEERED BARRIER SYSTEMS

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Our results show that a glycoboehmite precursor material can be chemically modified with divalent cationic species, for example, Nickel, to create an effective getter for anionic species. The viability of this novel class of materials is established by a variety of characterization methods, including surface area measurements, scanning electron microscopy, elemental analysis, and sorption capacity measurements. We will present the results of sorption capacity and surface area measurements that show the high sorption capacity of this novel class of getter materials. Our study shows that the divalent cation modification can increase the sorption capacity by as much as a factor of two.

I. INTRODUCTION

One of the main functions of bentonite buffer and/or backfill in the engineered barrier system (EBS) is to capture and isolate cationic radionuclides in the near-field environment. Because of this design feature, and the dose release in the safety case for a deep geologic repository is frequently driven by the release of anionic species, for example, Iodine-129. An EBS design that includes materials that provide some measure of sorption for anionic species would potentially enhance the safety case where anionic species dominate the radionuclide dose release to the far-field. This work presents a novel, low-cost anionic getter material that could potentially be incorporated into an EBS design.

I.A. **Methods**

I.A.1. Glycoboehmite Synthesis

A Parr Instruments stainless steel reaction vessel (600 mL capacity) was loaded with 10 g of Gibbsite ($Al(OH)_3$, Micral Corporation) and 0.46 g KOH with 300 mL of 1,4 butanediol. The vessel is sealed and vacuum applied to the exhaust port for 20 minutes to remove entrapped air. Next N_2 gas is bubbled through the chamber using the sampling tube for 20 minutes to create an inert atmosphere. The sealed vessel is heated under stirring using a 3 hour ramp to 250 °C, followed by a hold of 24 hr at 250 °C before cooling to ambient temperature. The white precipitate is recovered using four cycles of centrifugation at 4500 rpm for 5 minutes, with resuspension in isopropyl alcohol.

I.A.2. Characterization and Ni-modification

Surface area measurements were completed on the unaltered glycoboehmite using a Tristar 3000 BET surface area analyzer with degas conditions 30°C hold for 30 minutes with additional 140°C soak for 120 minutes. Glycoboehmite BET surface area was $82.76 m^2/g$. Initially there was a visible amount of condensation that was left on the tubes after the degas phase, indication water was still present. Using an oven, the glycoboehmite was heated to 90°C until there was no change in mass, which took about 12 days. The BET surface area was measured again and no condensation formed and the surface area was $156.55 m^2/g$.

The glycoboehmite was then modified by introducing nickel to the surface in order to increase sorption capacity for pollutants such as arsenic. 0.05g of the heated glycoboehmite was added to 30mL of 0.01M $NiCl_2$ solution, this was placed on a shaker table and left overnight. The glycoboehmite/$NiCl_2$ solution was centrifuged and the supernatant was decanted the remaining solids were allowed to dry in oven at 60°C for 48 hours, yielding the new "nickel modified glycoboehmite"; with a BET surface area of $186.0161 m^2/g$.

I.A.3. Arsenic Sorption Tests

Reactors were prepared with three different sample types: 1) the heated glycoboehmite, 2) the nickel modified glycoboehmite, and 3) a control. 0.1g of solid was added to 19.9mL of 18.2 Megaohm-cm deionized water and left on a shaker table for 24 hours. After overnight equilibration, the reactors were spiked with 0.1ml 0.01M sodium arsenate; total arsenic concentration was 3.75ppm. Reactors were then allowed to shake for 24 hours. Reactors were centrifuged and filtered using 0.2um syringe filters and acidified using optima grade concentrated nitric acid (for every 1mL of sample 10ul acid was added). Arsenic concentrations were analyzed using ICP-OES at the 193nm wavelength. The kD values were then calculated.

II. Results

The nickel modified glycoboehmite showed a 40-fold increase in arsenic removal compared to the unmodified glycoboehmite.

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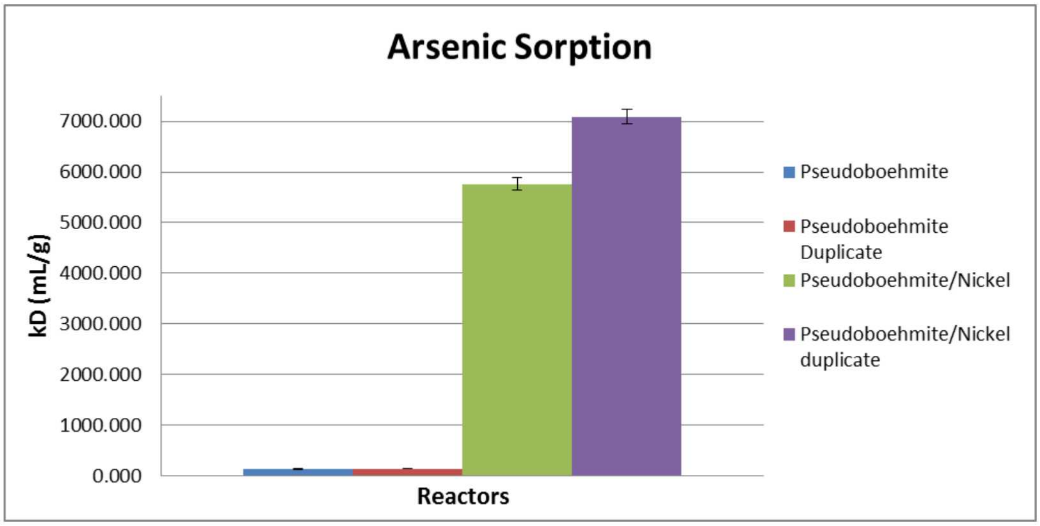

Fig. 1. This figure shows the kD values (in duplicate) for the unmodified and nickel modified material.

TABLE I. kD values for the values (in duplicate) for the unmodified and nickel modified material.

Sample	kD average	% As removal
Pseudoboehmite	132.755	40.299
Pseudoboehmite Duplicate	138.062	40.855
Pseudoboehmite/Ni	5760.956	96.640
Pseudoboehmtite/Ni Duplicate	7093.809	97.257

III. CONCLUSIONS

A simple set of proof of concept experiments were performed to explore the potential of using gycol-exfoliated boehmite (“glycoboehmite”) as a low-cost starting material for a class of anionic getter materials. Results show that the nickel-modified exhibits a 40-fold increase in sorption efficiency. Future work will include assessment of the long-term viability of this material in a repository setting, as well as reversibility and stability of the anion-loaded getter.

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