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# Selective Recovery of Critical Materials from Geothermal Fluid



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U. S. Department of Energy Small Business Voucher Program

**Selective Recovery of Critical Materials from Geothermal Fluid**

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## **Abstract**

This project, funded by the DOE Small Business Voucher program, assisted the partner with the development of ion-imprinted adsorbents for the selective extraction of rare earth elements (REE) from geothermal brines. This effort seeks to utilize a currently untapped resource thus diversifying the U. S. REE market. The initial stage of the program focused on the adsorbent developed by partner and optimization of the adsorbent. The adsorbent was based upon an ion imprinted ligand that was copolymerized with a crosslinker to generate the REE selectivity. During this task, the adsorbents were irradiated via electron beam at the NEO Beam Electron Beam Crosslinking Facility (Mercury Plastics, Middlefield, OH) to induce further crosslinking. The irradiation crosslinked adsorbents exhibited no difference in the Fourier transform infrared spectroscopic (FTIR) analysis suggesting inefficiency in the crosslinking. In the later stage of the effort, a new method was proposed and studied at ORNL involving a new partnership between the partner and a commercial polymer vender. This resulted in a new material being developed which allows the partner to utilize a commercial support and integrate the synthesis into a production-ready product stream. This will enhance the route to commercialization for the partner resulting in a quicker market penetration for the product. The new adsorbent exhibits selectivity for REE over transition metals commonly found within geothermal brines. Further optimization is required for enhanced selectivity, capacity, and intra-lanthanide separations.

## **Statement of Objectives**

The objective of this program is to assist the partner in the optimization of the adsorbent developed by the partner. This optimization will focus on geothermal applications for deployment. Goals include enhanced rare earth element (REE) selectivity, lower cost, simplified deployment.

## **Benefits to the Funding DOE Office's Mission**

This research program has multiple benefits to the DOE Geothermal Technologies Office mission as well as the DOE mission. First, the effort assists in the development of an adsorbent that is capable of extracting energy critical materials from geothermal brine solutions. Secondly, it increases the value of the geothermal well while providing an off-set for the well operational cost through the generation of a new revenue stream from the sale of the extracted REE. The value-added nature of the adsorbent, the development of an adsorbent from a small business, and the new REE product stream are all beneficial to the U. S. DOE.

## **Technical Discussion of Work Performed by All Parties**

Discussions with the partner resulted in the transferal of technological understanding and samples, including precursor monomers and final polymer adsorbents. This resulted in ORNL researchers duplicating the synthesis of the partner adsorbents. This was performed as outlined by procedures provided by partner. In this effort, the rare earth element (REE) selective ligand precursor was reacted with an amine to provide the polymerizable ligand. This was further crosslinked via free-radical polymerization with divinylbenzene to yield the adsorbent. The selectivity is generated by adding REE during the polymerization to coordinate the polymerizable ligand, thus "imprinting" the site. The imprinted site achieves selectivity through size exclusion once the REE is removed.

The resulting adsorbent synthesized at ORNL was plagued by the inability to completely remove the imprint metal. This hindered testing as it would artificially enhance the extraction percentage. This challenge was never overcome. In the process, several methods were attempted to remedy the situation while maintaining selectivity. The first of which was the utilization of electron-beam irradiation to cross-link the polymer. The pre-polymerized polymer, using lesser amounts of DVB was irradiated at the NEO Beam Electron Beam Crosslinking Facility (Mercury Plastics, Middlefield, OH). The powder was double-bagged in zipper-sealed bags and degassed under nitrogen in a nitrogen atmosphere glovebag three times prior to irradiation. The polymer was loaded onto dry ice pellets within a polystyrene container and covered with cardboard. The samples were irradiated at 24.2 kiloGray (kGy) per pass for 2 passes on a bed of dry ice pellets. Figure 1 is a picture of the adsorbent in the zipper-seal bags post-irradiation. The received dose was verified by alanine strips, measured by a Bruker EPR after irradiation (dose data collected and maintained by Dr. Roberto Uribe, Kent State University). The samples were analyzed by Fourier transform infrared (FTIR) spectroscopy after irradiation. Figure 2 & 3 are the pre- and post-irradiation FTIR spectra for the polymers. The spectra show no significant discernable differences between the pre- and post-irradiation samples. This is understood through an evaluation of the polymer. Since the generated polymer is predominately styrenic, which exhibits exceptional radiation stability, little cross-linking is expected. This is verified by the FTIR spectrum.



Figure 1: Sorbent irradiated at the NEO Beam Electron Beam Crosslinking Facility.

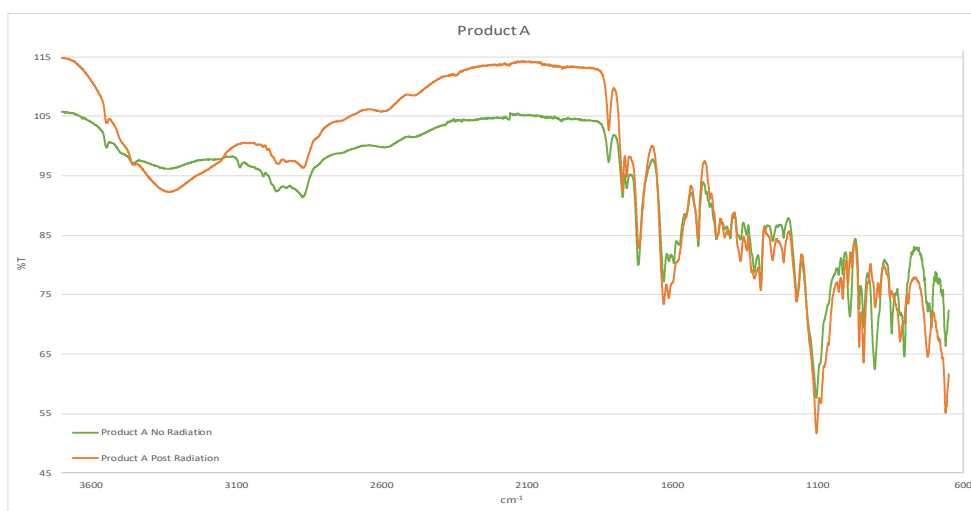


Figure 2: The FTIR spectrum of the irradiated polymer (Sample A).

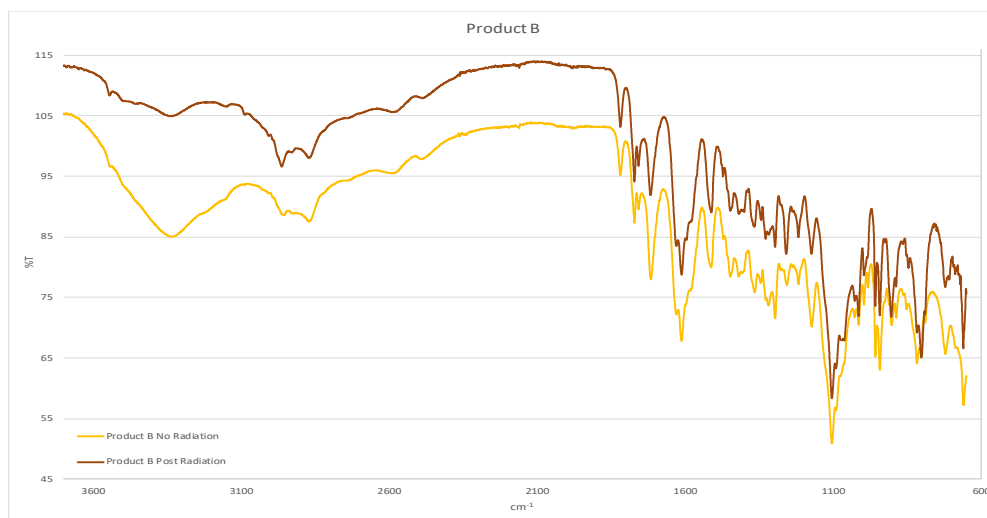


Figure 3: FTIR spectrum of sample B post-irradiation.

Secondly, the synthesis was modified to include a sacrificial chelation ligand that would assist in the removal of the REE. This method was chosen due to the difficulty in removing the REE metal post-polymerization. Through the coordination of the REE metal through both the polymerizable ligand and the sacrificial ligand, it was believed that the site would be more accessible while maintaining a favorable size of the coordination “pocket” for extraction. This method was plagued by similar challenges as the initial method. This included the inability to effectively remove the REE template and ambiguity in the removal of the sacrificial ligand. While the removal of the sacrificial ligand may not be a challenge, if the ligand is not stable within the pocket, the ligand could facilitate leaching of the metal thus lowering the extraction efficiency. Given this, the sacrificial ligand method was abandoned.

Finally, significant effort was directed at assisting the partner in the translation of their imprinted ligand onto a commercial support. This method simplifies the deployment for the partner through a secondary partnership with the commercial vender. The project involved several steps: (1) matching the surface chemistry of the commercial particle with the ligand, (2) determining the effective distance from the surface (anchor length), and (3) ensuring the site maintains size selectivity (imprinting). The surface amines of the particle ensured ease of anchoring secondary ligands onto the surface. The linker itself was studied to determine the most effective linker for the ligand and to imprint the site. Once the linker was matched with the surface, it was matched to the ligand via complimentary chemistry for anchoring the linker onto the surface, *i.e.* 1,4-diaminobenzene was utilized to anchor the ligand to the linker. This facilitated a site that the REE could coordinate while achieving high capacities. The capacity is a concern given the number of active sites on the particle. If the particle is covered with a monolayer of sites, the capacity will not be diminished. However, if the surface chemistry inhibits the monolayer coverage, the capacity will be negatively impacted. This is the reason for the linker utilization over simply reacting the ligand precursor to the surface. Spatial organization on the surface, coupled with steric hinderance of the surrounding ligands, could enforce a minimal number of active amines on the surface being utilized.

The metal coordination studies involved gadolinium as the REE metal of interest and metals that are common for geothermal brines, namely copper, zinc, and nickel. The selectivity of gadolinium over the transition metals was confirmed in the mass-based capacity extraction studies. The mass-based capacity is chosen for the representation due to the economic assessment. This is due to the mass of the adsorbent and extracted metals dominating several factors including sizing of equipment (e.g. cranes, trucks, etc.) and required man-power. While this may not provide an accurate representation of the adsorption as a dry weight distribution may, the trends will still hold. To examine selectivity, three separate solutions were made containing gadolinium and one of three transition metals. The transition metals used to study selectivity were copper (added as copper(II) perchlorate hexahydrate), nickel (added as nickel(II) chloride), and zinc (added as zinc(II) chloride). The concentration of gadolinium and each respective transition metal were all 50 mmol in the reuptake solutions. The mass of resin added to the Gd/Cu solution, Gd/Ni solution, and Gd/Zn solution was 0.6119 grams, 0.6121 grams, and 0.7294 grams, respectively.

The mass of resin measured for each metal reuptake solution was then added to a sealed Erlenmeyer flask containing 250 mL of the gadolinium/transition metal solution and placed on a shaker plate at 200 rpm. The solution was stopped, and 5 mL aliquots were taken for analysis after 5 minutes, 15 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, and 72 hours. The aliquots were diluted in a 2%  $\text{HNO}_3$  matrix and the concentrations of each were measured using ICP-OES in the range of 1 ppm to 100 ppm.

Figure 4 displays the extraction of the metals as a function of time. This adsorbent requires further optimization; however, we can glean some information to guide the optimization. First, the kinetics

appear to be quite rapid for lanthanide extractions followed by an increase in the relative capacity of the transition metal. Secondly, the imprint site is too flexible, most likely due to the choice of surface linker. This results in the exchange of the lanthanide with the transition metal over time. Apart from the gadolinium in the presence of zinc, the capacities appear to equilibrate with time. The capacities will be dependent upon the concentration of the metals being extracted; however, the observed capacities exhibit promise. Enhanced selectivity is achievable as well with a tailored approach for the surface grafting linker on the polymer trunk bead.

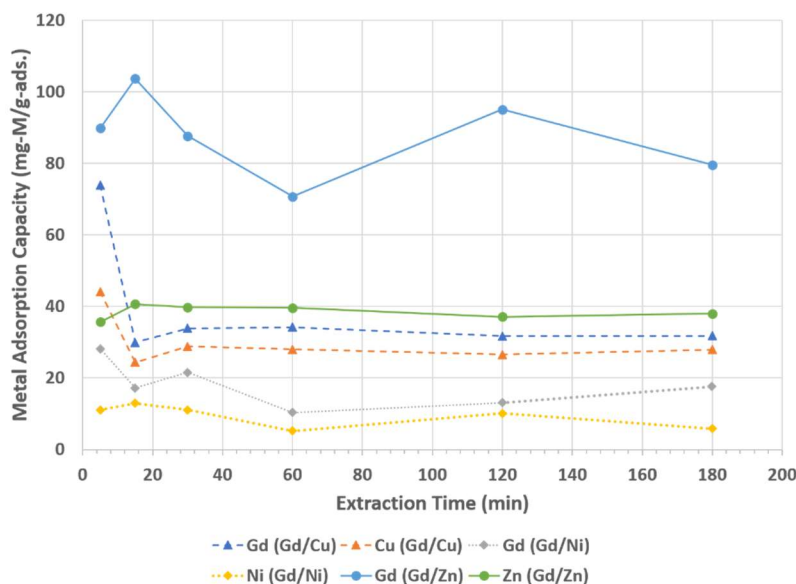


Figure 4: Adsorption capacity as a function of time for the imprinted resin beads.

### Subject Inventions (As defined in the CRADA)

The development of the adsorbent bead, in collaboration with the partner, may be subject to patent protection. This work is focused on expediting the development of the adsorbent through the use of a commercial support trunk.

### Commercialization Possibilities

The adsorbent developed in collaboration with the partner is poised for commercialization after optimization. This will facilitate the translation of the synthesis to the partners commercial vender for mass production. The adsorbent will be multi-functional in deployment, while enabling the direct replacement of existing adsorbents through the partner's vender.

### Plans for Future Collaboration

The partner and ORNL have partnered on a Critical Materials Institute proposal to extract REE from various sources, including phosphate mine product/waste streams. Future collaborations can include other potential product streams that will enhance the partner's product line.

### Conclusions

The partnership has resulted in a rapidly deployable adsorbent, utilizing a commercial support as a trunk material. The adsorbent exhibits selectivity toward gadolinium over transition metals relevant to the



geothermal brines for which the adsorbent was developed, specifically nickel, copper, and zinc. The adsorbent demonstrates promise for high selectivity and thereby higher capacities through optimization of the surface linker group. The development of the adsorbent based upon the commercial trunk will further enable market penetration via the direct replacement of current adsorbents with the more selective adsorbent developed herein thereby enabling the partner to realize the adsorbent potential.

Final Report Certification  
for  
CRADA Number CRADA/NFE-16-06377

Between

UT-Battelle, LLC

and

Anaclisis, LLC  
(Participant)

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For the Participant:

  
Athanasios Karamalidis

(Name)

CEO

(Title)

02/27/2018

(Date)