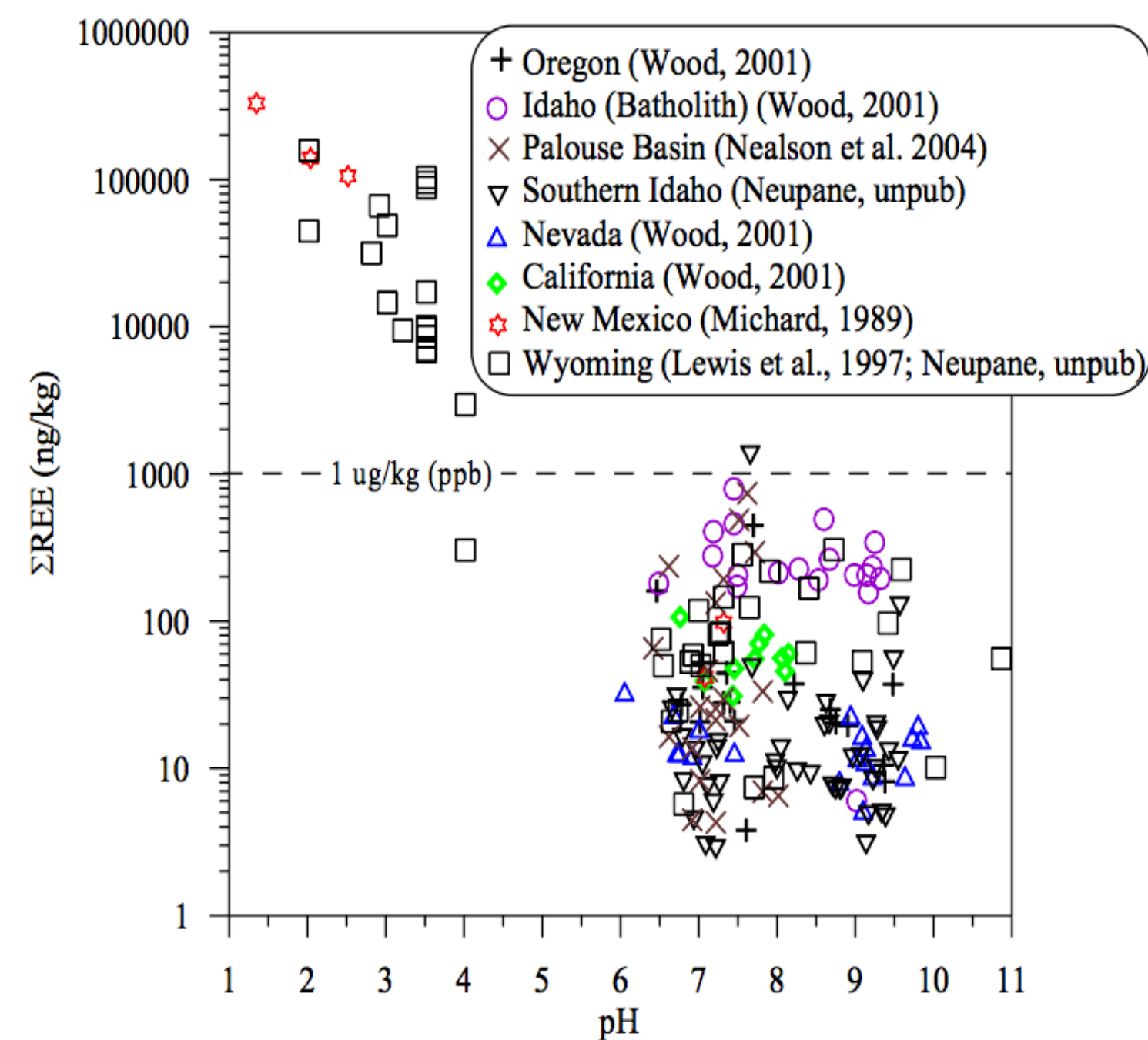


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Critical Materials in Geothermal Fluids

- Geothermal Brines contain energy significant metals within the supersaturated brine due to rock dissolution
- REE within geothermal brines represent a significant untapped resource

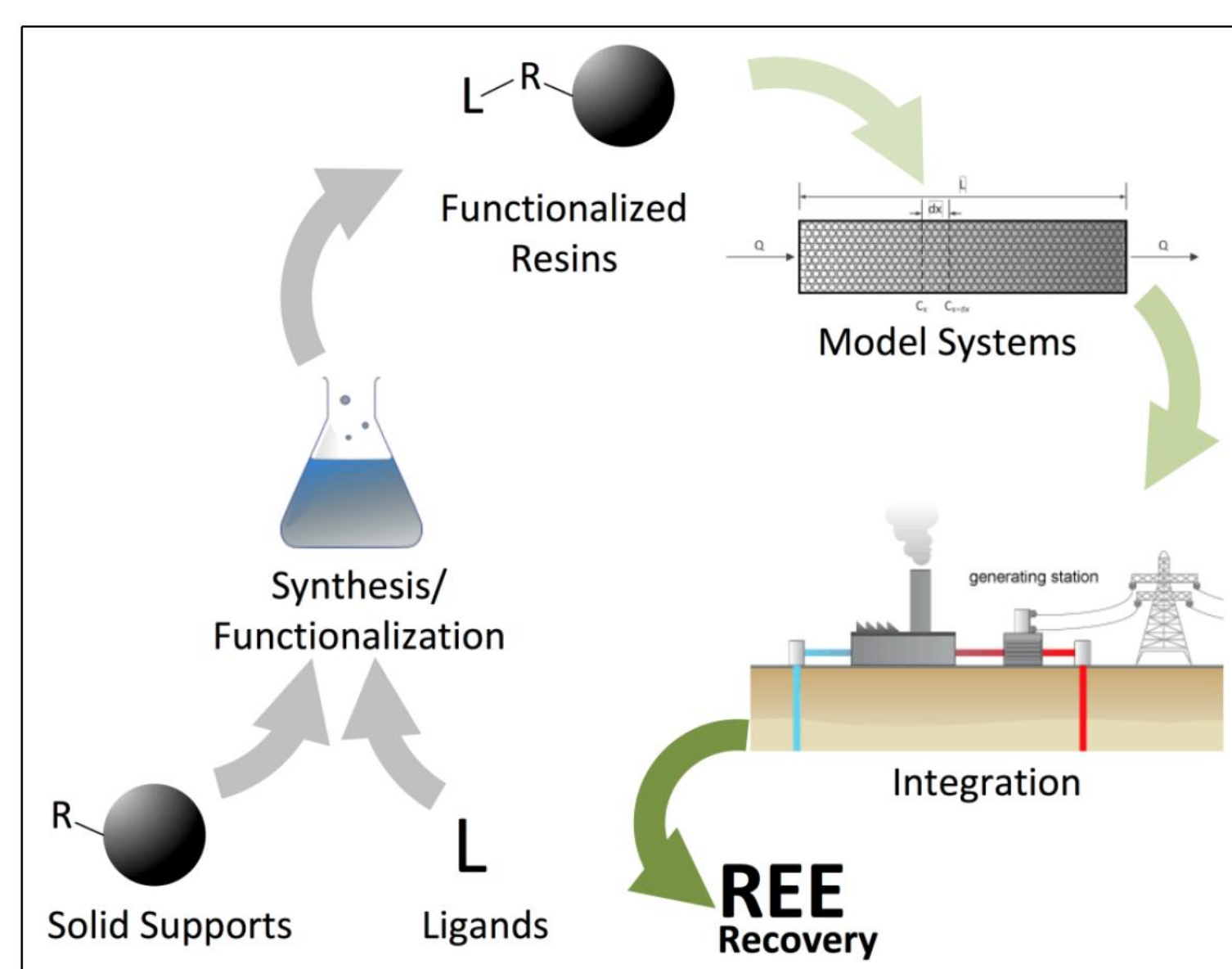


Neupane G.; Wendt, D. S. "Assessment of Mineral Resources in Geothermal Brines in the US." Proceedings, 42nd Workshop on Geothermal Reservoir Engineering, Stanford, California, SGP-TR-212, 2017.

- Selective extraction is a challenge for REE
 - Often co-extract other metals (U, Th, transition metals)
 - Imprinting offers method to selectively extract REE
- Crosslinked polymers imprinted with an REE selective ligand, diethylenetriamine-pentaacetic acid (DTPA), were synthesized to extract REE from geothermal brines
 - Need to balance crosslinking with ligand density
- Supported imprinted adsorbents is a preferred alternative for economical utilization

Methods

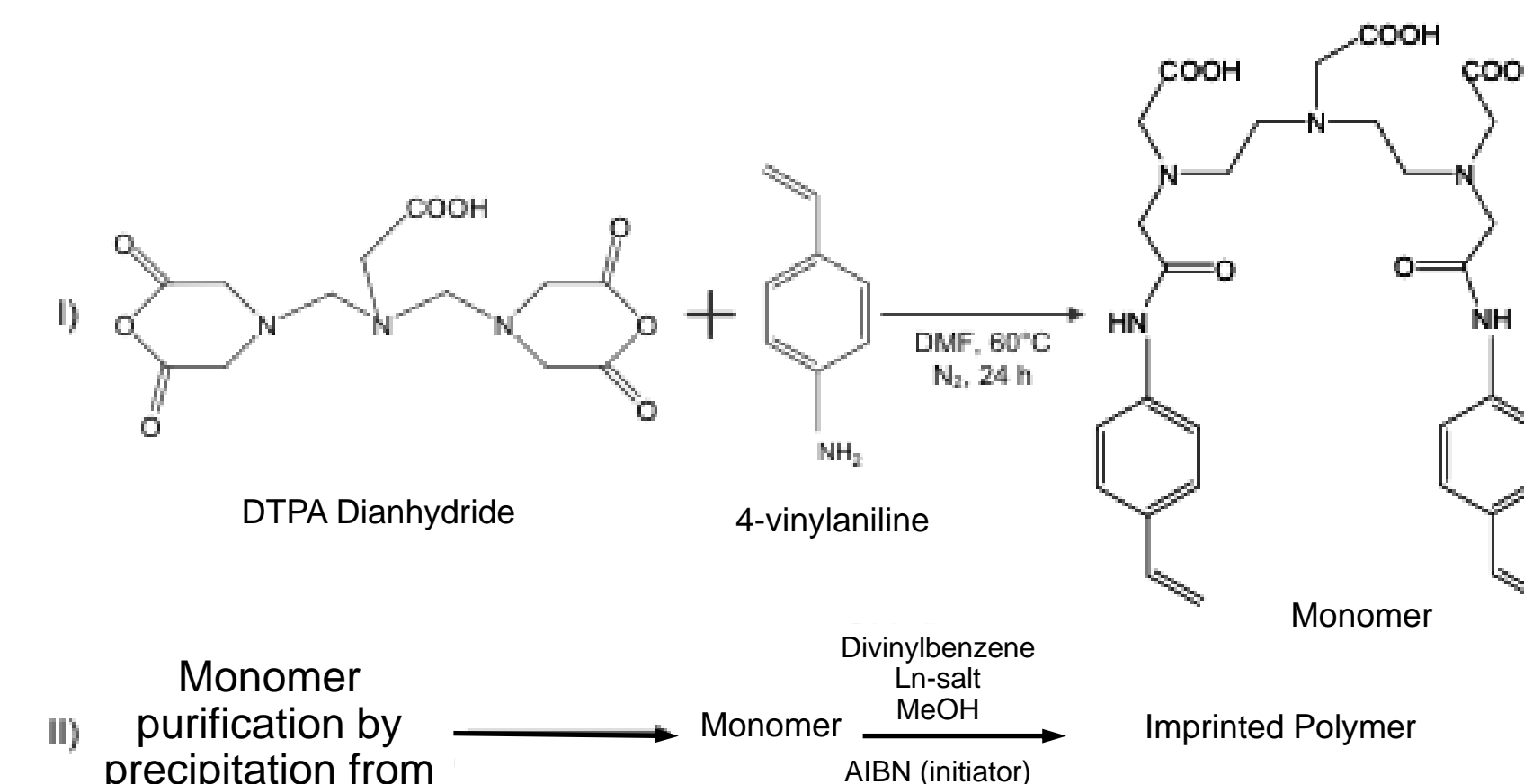
- Synthesis of imprinted polymer
 - Crosslink imprinted ligand within divinylbenzene matrix
 - Remove template metal
 - Extract REE selectively from geothermal brines
- Supported imprinted polymer
 - React imprinted ligand with commercially available macroporous resin
 - Remove template metal
 - Advantages include partnership with commercial resin supplier (market opportunity)
 - Uniformity of support resin for hydrodynamic considerations
 - Higher ligand density



Deployment method for REE extraction from geothermal brines; from Thomas, H.; Reinhardt, T. P.; Segner, B. "Low Temperature Geothermal Brine Recovery Program." Proceedings, Fortieth Workshop on Geothermal Reservoir Engineering, Stanford, California, SGP-TR-204, 2015.

- Testing of the adsorbents utilize a simulated brine based upon a characterized geothermal fluid
- Anactisis is identifying geothermal companies for potential partnerships in resource recovery

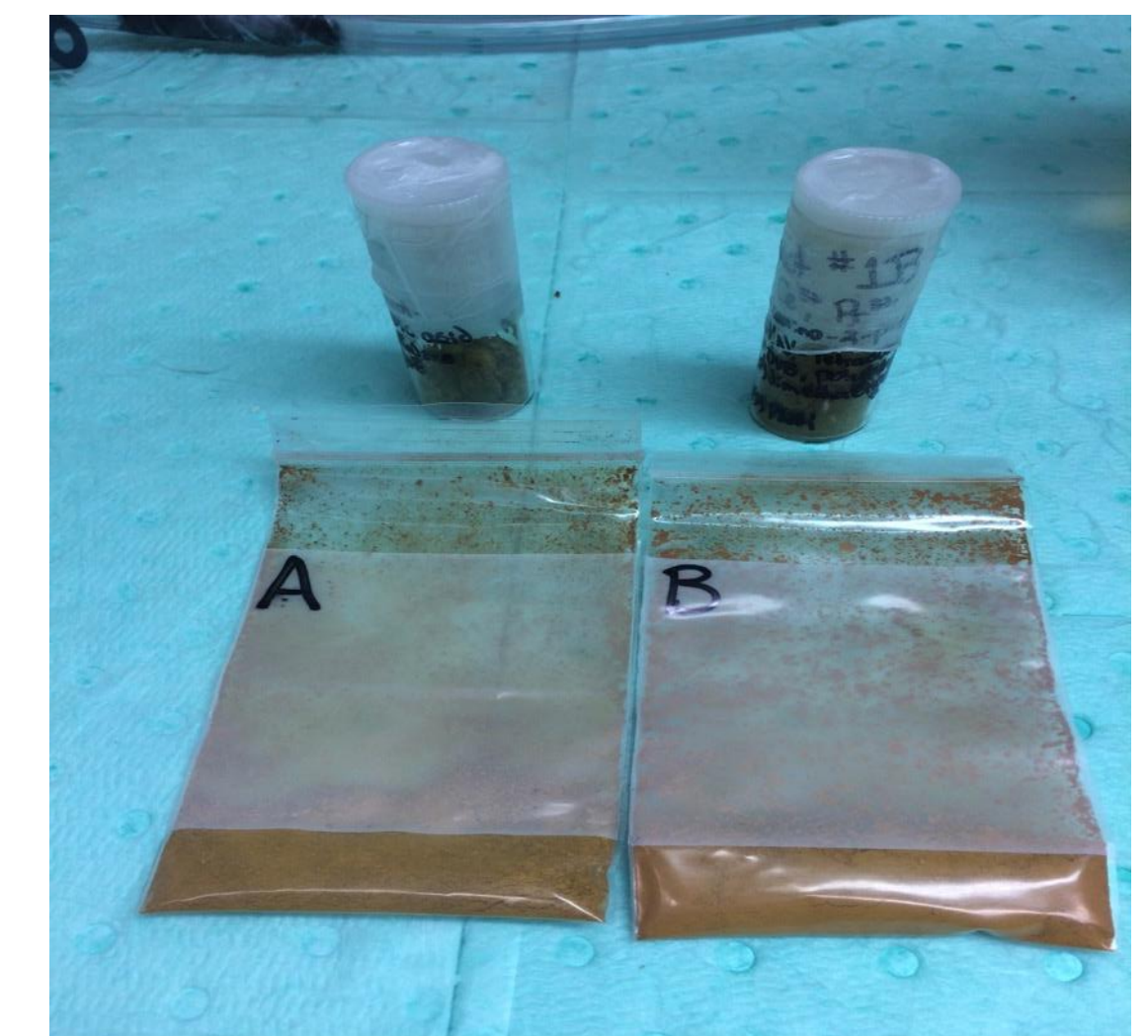
Adsorbent Synthesis



- Crosslinking with AIBN locks the imprinted monomer in place – removal of template can be challenging due to irregular porosity
- Irradiation crosslinking can provide enhanced selectivity
 - Imprinted adsorbents were crosslinked at the NEO Beam Electron Beam Crosslinking Facility (Mercury Plastics, Middlefield, Ohio); dose: 48 kGy, irradiated on dry ice
 - No visual change in the adsorbent
 - Samples are currently in screening



FTIR of irradiated adsorbent illustrating minimal change in the spectra suggesting no change in the adsorbent



Pictures of imprinted adsorbent (vials) and electron beam-irradiated adsorbent (bags)

- Working with Purolite, immobilization of the imprinted ligand onto commercial resins is being investigated to assist in commercialization
 - Primary amine resins are used as the support
 - Two approaches:
 - Open the dianhydride on the resin support in presence of lanthanide templating metal
 - Tether the dianhydride on the support via a diamine spacer, e.g. phenylenediamine, in the presence of the lanthanide to study the influence of the resin on the extraction
 - Synthesis is on-going
- Testing in the simulated geothermal brines is on-going

Conclusions and Future Work

- Template method provides route to sequester REE selectively while differentiating from the light, mid, and heavy REE
- Electron beam irradiation crosslinking does not appear to have improved the resin
- The development of a resin based upon a Purolite support can ease the transition to a commercial product
 - Establish the protocol to anchor the imprinted ligand on the Purolite resin
 - Determine the total REE capacity and selectivity
 - Establish the size selectivity within the REE group (light, mid, heavy) for the supported imprinted ligands

Acknowledgement

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