Selective Recovery of Metals From Geothermal Brines

Project Officer: Holly Thomas
Total Project Funding: $500,000
May 12, 2015

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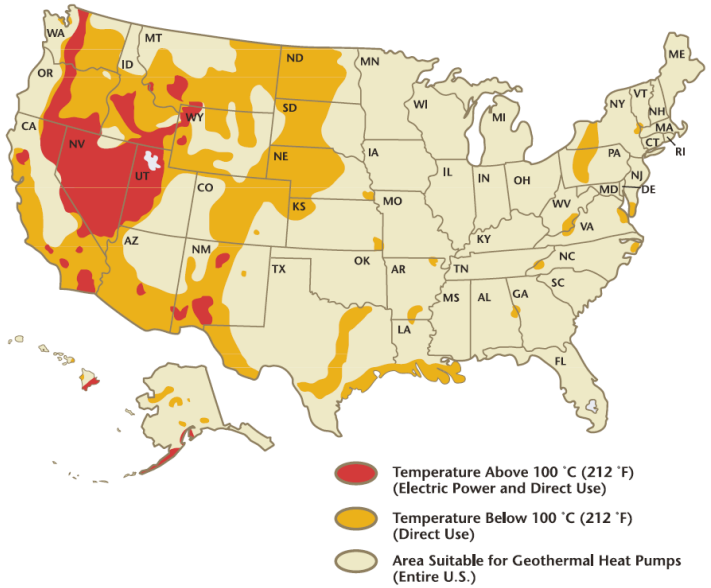
Track : Low Temperature; Metal Recovery

Relevance/Impact of Research

- Geothermal fluids have a complex chemical composition determined by the composition of rocks, and the temperature and pressure experienced by the fluid and rocks
- Alkaline and alkaline earth metals such as Na^+, K^+, Ca^{2+} and Mg^{2+} are usually present in very high concentrations posing a challenge to the separation of other metals, often requiring high volume of solvents and multiple steps
- ***Selective high capacity sorbents will separate metal more efficiently***

Brine Metal	mg/Kg
Li	200-400
Na	47,000-65,000
K	12,400-16,700
Ca	21,500 – 27,400
Mn	1280-1560
Zn	280-1160
Pb	70-240

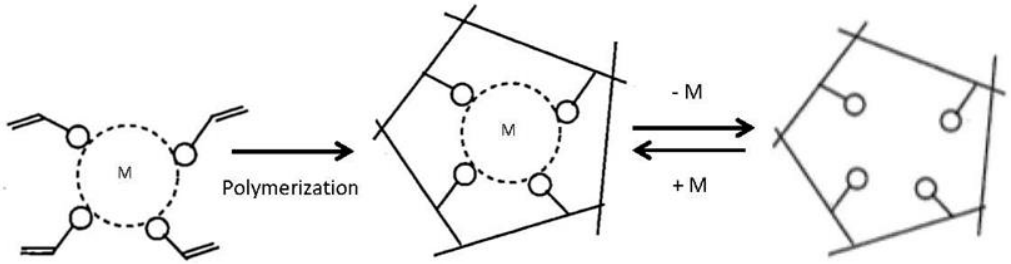
Geothermal fluid composition in Imperial , Salton Sea, and Brawley (D. Gallup , 1998)



Green and Nix, NREL/TP-840-40665 (2006)

Project Objective

- Develop high capacity reusable low-cost sorbents based on ***metal ion imprinted polymers*** for the selective solid phase extraction of lithium and manganese from medium-to-low temperature geothermal fluids



- Selective high capacity sorbents will extract metals more efficiently and lower the cost of production of lithium and manganese compounds from thermal fluids. This is expected promote geothermal power production - especially for low-to-medium temperature geothermal fluids - by creating an ***additional value stream*** from metal recovery

Scientific/Technical Approach

- Develop ion imprinted polymer sorbents with
  - High binding capacity
  - Selectivity
  - Fast binding kinetics
  - Ease of regeneration
  - Good chemical and temperature stability up to 100^{o}C

- Preparation of Ion Imprinted Polymers
  - Nature of polymer and ligands
  - Degree of crosslinking
  - Methods of forming macroporous polymer beads

Scientific/Technical Approach

(1) Prepare polymerizable ligands with good affinity for lithium and manganese

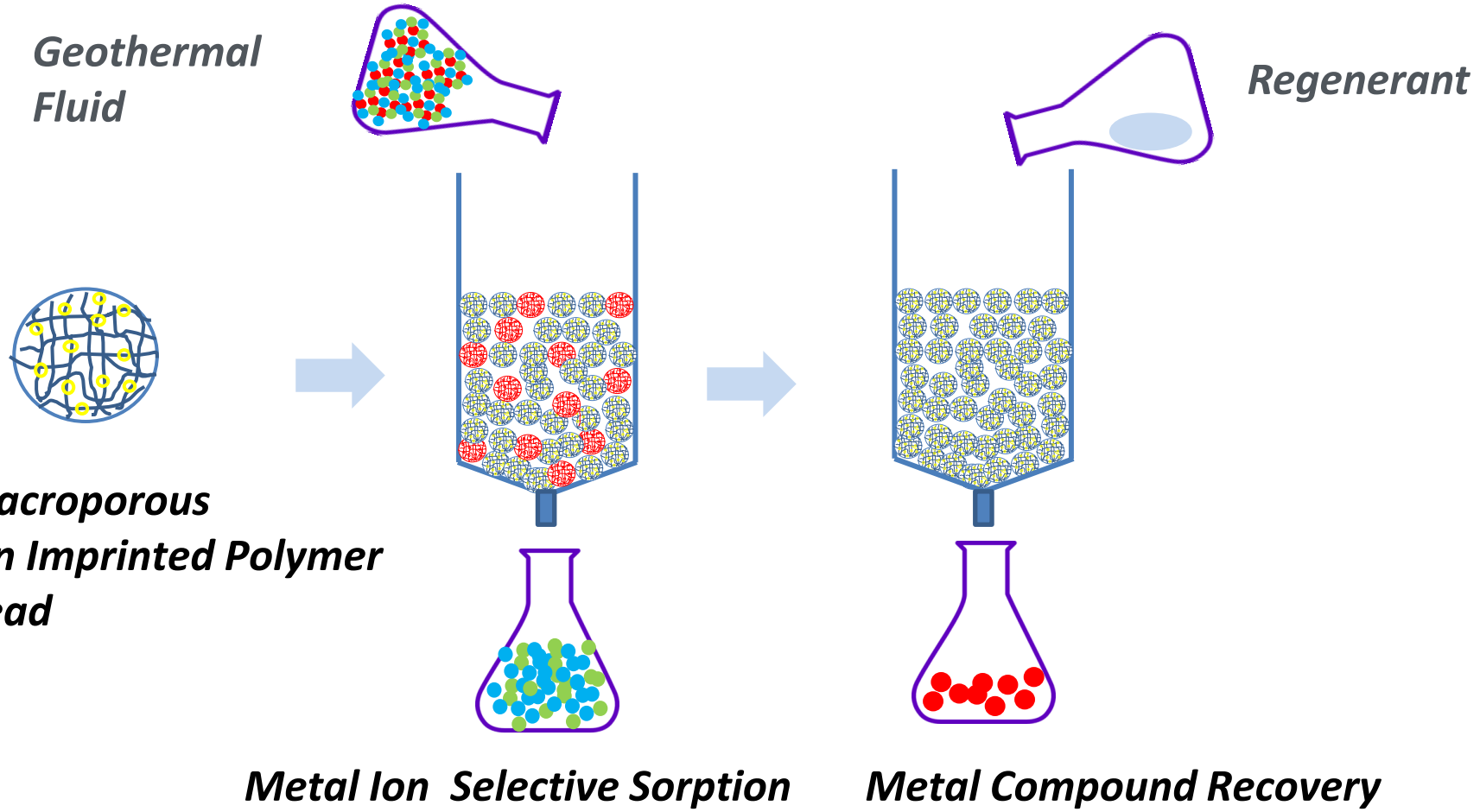
(2) Prepare macroporous imprinted polymer beads by crosslinking polymerization

(3) Test sorbents for their metal binding capacity and selectivity in *batch process* at 45-100^{o}C

(4) Test lithium and manganese separation efficiency in synthetic and real brines

(5) Evaluate sorbents in *flow-through system*

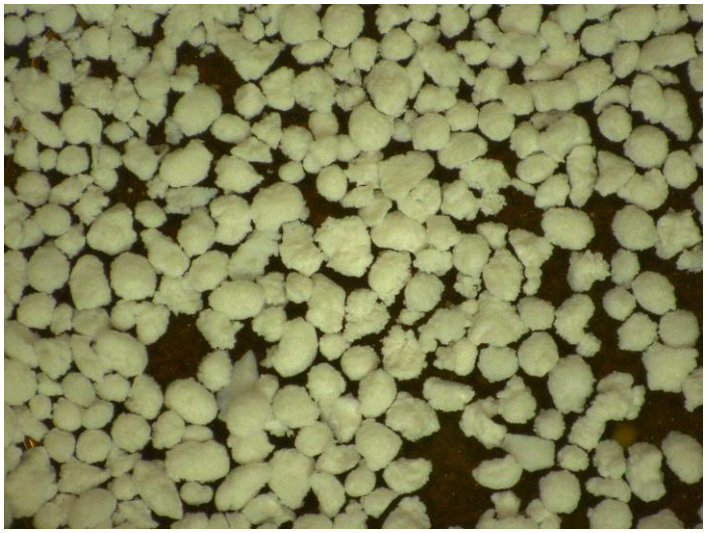
Solid Phase Extraction



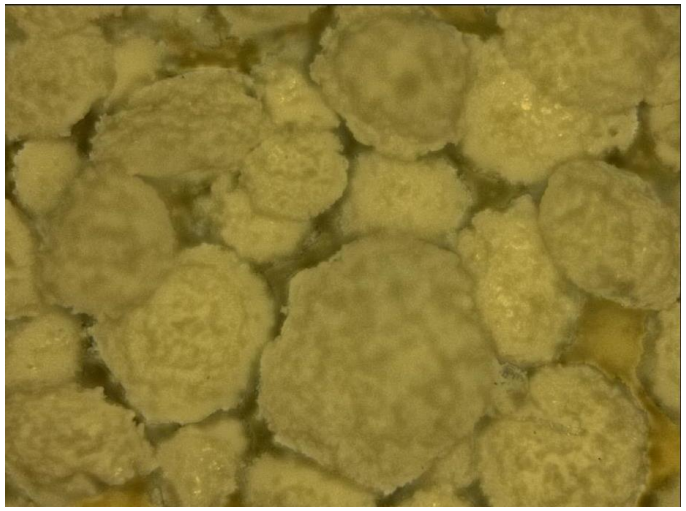
Ion Imprinted Polymer Beads

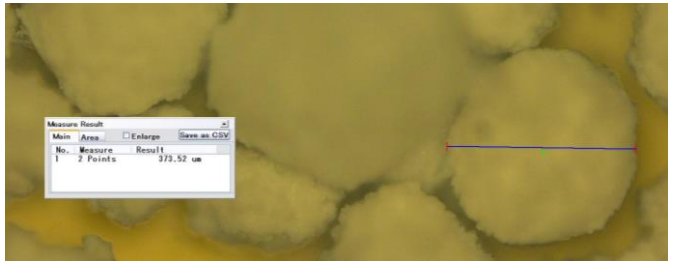
- Suspension polymerization is being used for the preparation of ion imprinted porous polymer beads
- The polymer beads are treated with mild acidic solution to leach out the template metal (lithium or manganese)
- The amount of metal in the leachate is determined by ICP-OES
- By determining the amount of metal leached out from the polymer, metal binding capacities up to 0.5 meq/g were observed

Ion Imprinted Polymer Beads with Variable Size and Porosity

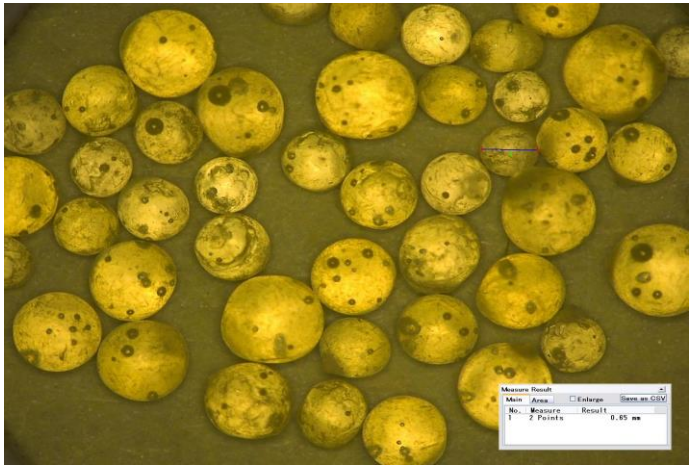


Li Imprinted Polymer Beads





Li Imprinted Polymer Beads - magnification



Mn Imprinted Polymer Beads

Polymer beads – size and porosity

- Particle size varies depending on the nature of monomers and polymerization conditions
  - 600-1000 micron
  - 200-400 micron
- Imprinted polymer beads with high surface area were prepared
  - Surface areas of more than 400 m^2/g were determined by BET analysis using nitrogen

Accomplishments, Results and Progress

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Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Prepare initial batch of Li imprinted polymer	Polymer isolated and characterized by FT-IR analysis and lithium content	12/31/14
Demonstrate Li imprinted polymer beads with ~ diameter of 250-500 micron and surface area of 100 m^2/g or more	Polymer beads were prepared and shown to have 200-400 μm diameter with optical microscope. Surface area of 430 m^2/g was determined by BET analysis	3/30/15
Demonstrate Mn imprinted polymer beads with diameter of about 250-500 micron and surface area of 100 m^2/g or more	Polymer beads were prepared and characterized with optical microscope. The beads diameter is~600-1000 μm.	In progress

Future Directions

- Evaluate the sorbents metal uptake for different concentrations of lithium and manganese under batch equilibrium conditions
  - at variable temperature (up to 100^{o}C) and pH
- Evaluate metal binding selectivities in binary mixtures and synthetic/real brines under batch equilibrium conditions
- Evaluate metal uptake in flow-through system
- Evaluate sorbent regeneration and perform durability test

Future Directions

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Milestone or Go/No-Go	Status & Expected Completion Date
Sorbent binding capacity of 0.4meq/g for Li and Mn at 45°C (batch test)	In progress. 6/30/2015
Li and Mn imprinted polymers with separation efficiency of 90% using brine at 40°C	No/no-go decision point 9/30/2015
Scale-up preparation of Li and Mn imprinted polymers	12/31/2015
Li and Mn imprinted polymer with capacity of 0.5 eq/L at 75-100°C (flow-through tests)	12/31/2015
Li imprinted polymer with capacity of 4g/L and separation efficiency of 95%; Mn-imprinted polymer with capacity of 0.5 meq/L and separation efficiency of 90%. Operation temperature of 45-100C.	3/30/16

Mandatory Summary Slide

- We have prepared polymerizable ligands for binding lithium and manganese ions, and imprinted polymers by polymerization crosslinking
- We have demonstrated the feasibility of preparing lithium and manganese imprinted polymers in the form of porous high surface area beads with diameter $\geq$ 200 micron for use in column separation
- Imprinted polymers with available metal binding capacities up to 0.5 meq/g were prepared
- The polymer metal uptake and selectivities as a function of pH and temperature are currently being evaluated