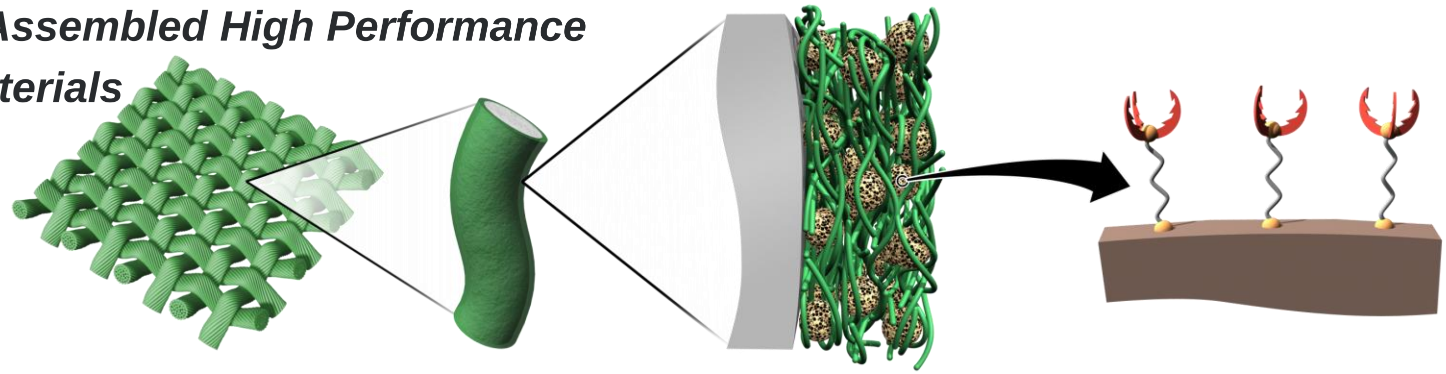
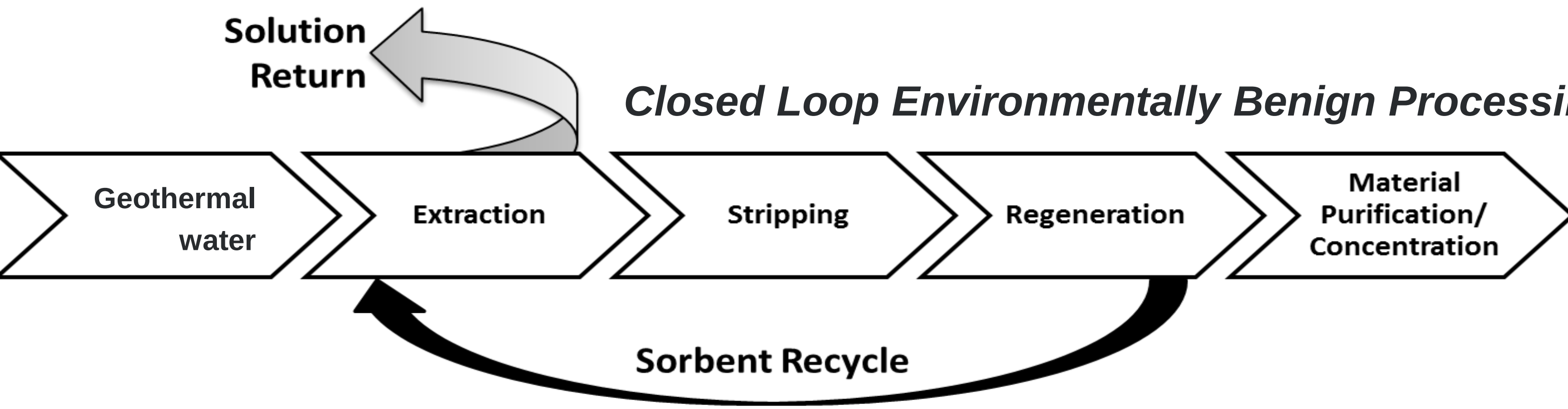
Geothermal Technologies Office 2015 Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Rationally Assembled High Performance Sorbent Materials





Recovery of Rare Earths, Precious Metals and other Critical Materials from Geothermal Waters with Advanced Sorbent Structures

Project Officer: Holly Thomas

Total Project Funding: $375k (DOE) + $275k cost share

May 11-14, 2015

Principal Investigator:

Dr. R. Shane Addleman

Pacific Northwest National Laboratory

Program Relevance/Impact/Objective

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Relevance:

- Develop value added technology to improve economic viability of geothermal power plants through recovery of valuable minerals contained within geothermal brines

Impact:

- Increase and utilization of geothermal power through cost reduction with a value added processes
- Provide “green” domestic supply of critical and valuable minerals

Objective:

- Develop and demonstrate flexible, scalable mineral extraction technology for geothermal brines based upon advanced solid phase sorbent materials.

Challenges and Barriers

- Solid phase extraction is a proven technology
  - *Unfortunately existing materials and methods fail for this applications.*
  - New technology required for economically viable mineral recovery process (from geothermal brines)
- Recovery of trace minerals has many challenges and barriers:
  - huge solution volumes/flow rates
  - even “low temp” geothermal conditions are hotter most other process solutions
  - variable AND *<u>very low</u>* concentrations of valuable materials
    - rare earths (REs), precious metals (PMs), and other critical/strategically valuable materials (CMs) such as Zn, Mn, Te, Sc, Se and U.
  - high ionic strength reduces collection process efficacy
  - high loading of low-value competing and confounding materials (e.g., Fe, Si)
  - “hard” inorganic (silicate and carbonate) and “soft” (biological) fouling
  - corrosive and widely divergent chemical conditions

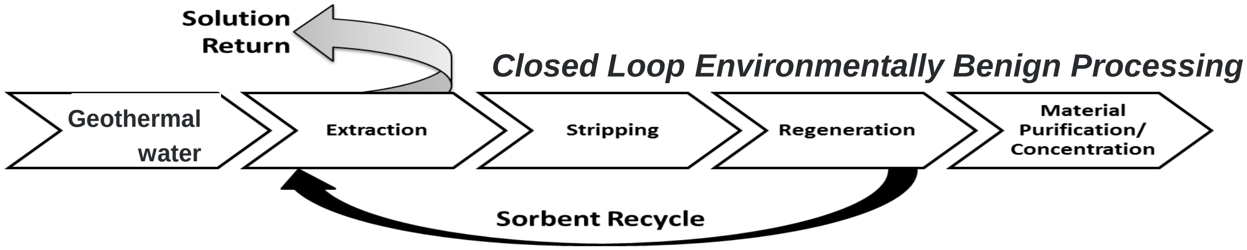
Program Innovation and Unique Value

1. A systematic study evaluating the feasibility of solid phase extraction technology (commercial off-the-shelf and novel advanced sorbent materials) for strategic mineral recovery from challenging solutions, such as geothermal brines, has not been undertaken.

2. This effort leverages recent advances in chemistry, material science and nanoscience to provide fast, flexible, scalable, efficient, environmental friendly recovery of trace levels of valuable minerals from challenging solutions.

3. The project will provide a compact, clean, scalable, flexible, efficient technology for the extraction of strategic minerals from geothermal brines and other process flows of relevance to DOE.

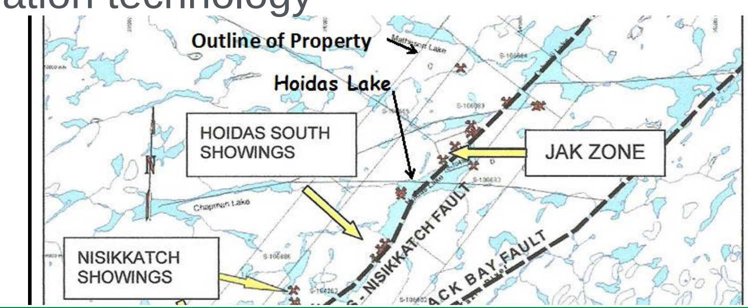
4. The techno-economic analysis (TEA) of solid-state sorbent technology will provide guidance for when and where this technology would be viable.



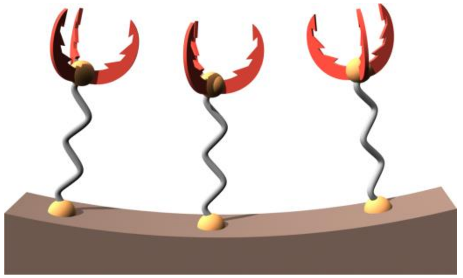
Program Innovation and Unique Value

Multidisciplinary Team

- Pacific Northwest National Laboratory (Washington)
  - Expertise in sorbent technology development and evaluation
- University of Oregon, Department of Chemistry
  - A partner for sorbent synthesis of advanced surface chemistry.
  - A cost share contributor
- Barr Engineering (Minnesota)
  - An engineering firm with experience in feasibility analysis and development of mineral resources
  - A cost share contributor
- Star Minerals Group Ltd (Montana)
  - A strategic and critical resource exploration and extraction company with interests in the development of new collection and separation technology
  - A significant cost share contributor



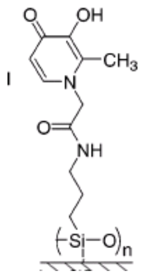
- Better Surface Chemistry
  - For Capture: high affinity and selectivity
  - For Release/Recovery: better uniformity and stability/durability
  - Balancing Demands (*i.e.,* high affinity chemistry vs. reversibility)



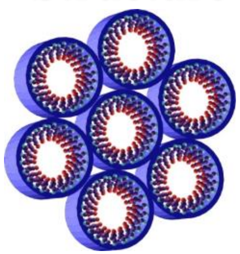
- Better Structures for Collection
  - Higher surface area to improve capacity
  - Balance performance with durability/lifetime
  - Application relevant form factor (*i.e.,* resistant to fouling, minimal pressure drop)
- Integrate Best Chemistries with Best Structures
  - Evaluate *relevant* and useful configurations
  - COTS materials, novel materials, hybrid combinations
  - Collection, release, operational lifetime

Techno-economic analysis will be done with *real* data from preferred systems

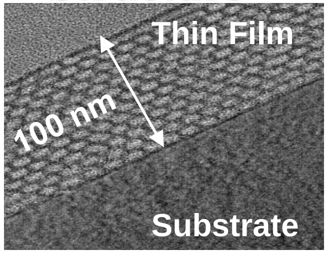
Surface Chemistry ⇨ **Micro/Nano Structure** ⇨ **Macroscopic Structure**



Selectivity
High affinity



High surface area/capacity
Rapid kinetics



Thin films | Membranes
Particles | Filters
Monoliths | 3D structures

Scientific/Technical Approach Project Flow

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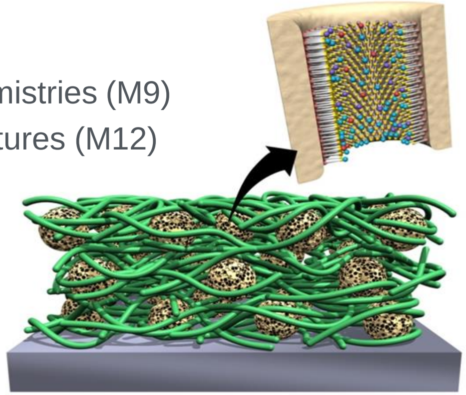
- **Year 1**
  - Task 1. Program Initiation and Analysis of Geothermal Fluids
    - Milestone 1.1 Assemble Core List of Critical Challenges for Solid State Sorbent Technology for Geothermal Mineral Extraction (M3)
    - Milestone 1.2 Complete Analysis of Geothermal Fluids (M6).
  - Task 2. Evaluation of Solid-State Sorbent Technology (M1-M12)
    - Milestone 2.1: Complete the Down-Select to the Most Effective Sorbent Chemistries (M9)
    - Milestone 2.2: Complete the Down-Select to the Most Effective Sorbent Structures (M12)



- **Go/No Go Decision M12**

- **Year 2**
  - Task 3. Optimization and Demonstration of Solid-State Sorbent Technology *(M13-21)*
    - Milestone 3.1 Complete Optimization of Preferred Sorbent Materials (M18)
    - Milestone 3.2: Demonstration of Preferred Sorbent Materials (M21)
  - Task 4 Techno-economic Analysis of Solid State Sorbent Technology for Cost-Effective Geothermal Mineral Extraction (M13 –M24)
    - Milestone 4.1: Complete Basic Conceptual TEA Model for use of Solid State Sorbent Technology in Brines (M15)
    - Milestone 4.2: Complete TEA for Solid State Sorbent Technology for Cost Effective Geothermal Mineral Extraction (M23)

A systematic study demonstrating the feasibility of advanced solid phase extraction technology for strategic mineral recovery from challenging solutions such as geothermal brines has not been undertaken.

Accomplishments, Results and Progress FY2015

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Accomplishments/Progress to date (3/31, only 6 months into project)

Task 1. Program Initiation and Analysis of Geothermal Fluids

- Milestone 1.1. Reviewed and refined critical challenges for success
  - at program kickoff meeting with whole team and subsequently with technical monitoring committee.
- Milestone 1.2.
  - Investigated literature and industrial sources on composition of geothermal fluids.
    - Conclusions: chemistry and mineral loading in geothermal brines *highly* variable.
    - Publish review in collaboration with other GTO programs?
  - Explored areas with valuable mineralization that coincide with geothermal resources
    - Fortuitous sampling at promising site in Idaho. Exploring other areas of interest.
    - Sampling and analysis protocol key for reliable data!

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Milestone 1.1 Assemble Core List of Critical Challenges for Solid State Sorbent Technology for Geothermal Mineral Extraction .	Same	On time End of Q1
Milestone 1.2 Complete Analysis of Geothermal Fluids	Same	On time End of Q2

Milestone 1.1 Assemble Core List of Critical Challenges…

The key critical parameters for the economically viable utilization of solid state sorbent technology for effective mineral extraction from geothermal fluids are:

- Sorbent affinity and capacity
  - Must be improved significantly over existing materials
  - Must be balanced with regeneration/recovery capability, cost and kinetics
- Sorbent kinetics
  - Faster kinetics enable higher process rates, smaller equipment foot print and better economics
  - Must balance kinetics vs efficiency (in particular for collection)
  - Strongly dependent on form factor of separation media
- Sorbent lifetime
  - Thermally and chemically stable
  - Fouling-biological and chemical (iron, silica, carbonate, etc).
  - Physical/mechanical stability
- Sorbent form factor
  - Low pressure drop and easily integrated into process
  - Function with suspended solids and surface fouling
- Mineral recovery from sorbents and sorbent regeneration
  - Chemically and physically regeneration of sorbents
  - Acid stripping SOP but not ideal
  - Carbonate and peroxides
  - Organic solvents and ligands
- Cost effectiveness
  - materials, recovery process, space, installation and operation

We are attempting "molecular mining"

The simple days of density separation are fading

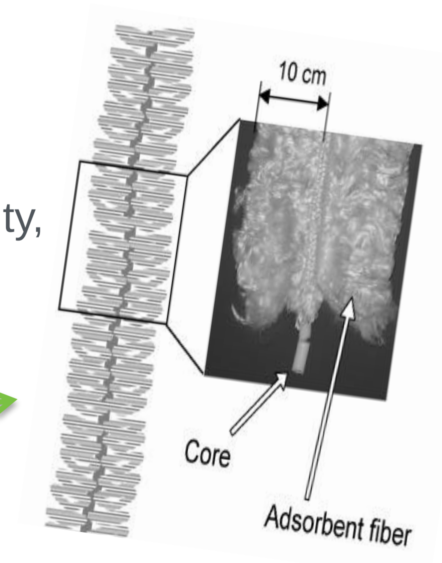
Accomplishments, Results and Progress FY2015

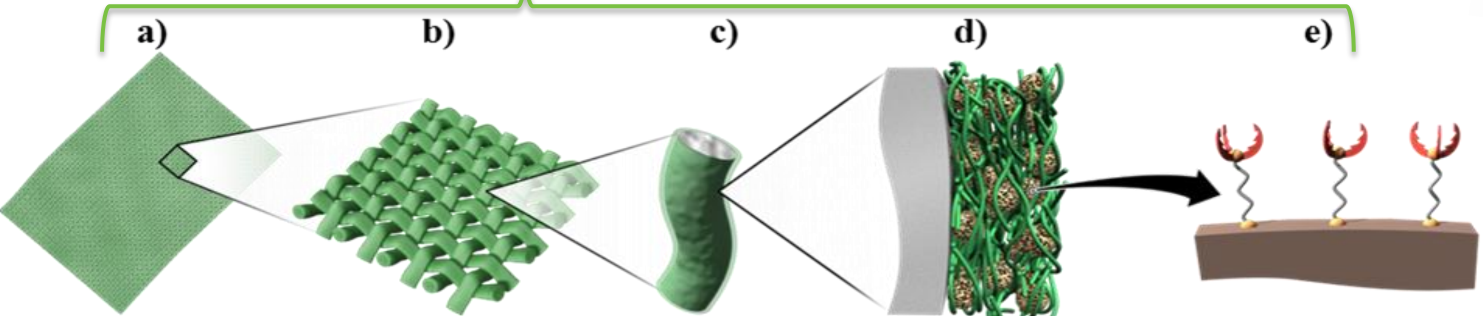
Accomplishments/Progress to date (3/31, only 6 months into project)

Task 2. Evaluation of Solid-State Sorbent Technology

- Began evaluation of sorbent chemistries (Task 2)
  - Reviewed and refine promising surface chemistries to pursue and evaluate
  - Assembled high performance COTS sorbent materials
  - Synthesis of novel high performance sorbent materials

- Began evaluating relevant sorbent structures (Task 2)
  - Parameters to consider: pressure drop, contact efficiency, durability, resistance to fouling, regeneration, manufacturability, cost
  - Structures: traditional packed bed, fluidized beds, mesh screens, modified membrane systems, novel composites, supported thin films, woven polymer fibers





Accomplishments, Results and Progress

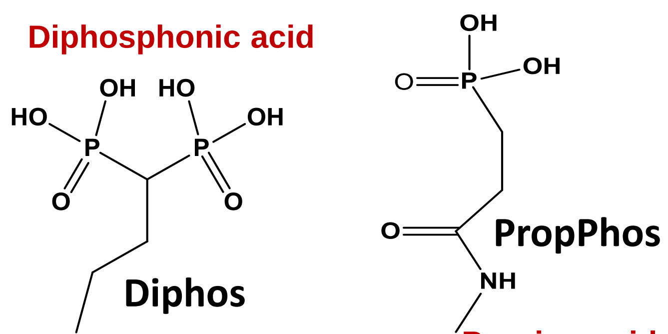
Subtask 2.1 Evaluate and Select Effective Surface Chemistry

- Complete evaluation of existing data sets
  - Organic and inorganic high surface area materials

- Selection, synthesis and assembly of sorbent materials underway.

  Presently preferred/identified surface chemistries include:
  - Diphos
  - PropPhos
  - Amidoxime
  - Hydroxypyridinone
  - Silica, aluminia
  - Mn oxides
  - Best in class COTS materials
  - Materials from DOE-funded Critical Materials Hub?

Diphosphonic acid



Propionamide Phosphonic acid

- No sorbent material will be advanced unless it is;
  - effective, stable, reversible and economically scalable.

- Stripping chemistries to be evaluated in Yr2

  or preferred collection materials

Preliminary Data

Chemical Affinity (K_d) for RE Collection from (Simulated) Geothermal Fluids

Sorbent Material	K_d Nd
Custom Sorbents	
Diphos-nSilica	2 600
MnO_2-nSilica	315
PropPhos-nSilica	240
AcPhos-nSilica	67
3,4 HOPO-nSilica	10
Commercial Sorbents	
Ln Resin	140
SAX Resin	34
Diphonix Resin	29
RE Resin	16
Chelex 100 Resin	1
SCX Resin	1
Activated Carbon	0

K_d given in L/g sorbent
pH of 6.2 in seawater, Nd =50 ppb initially
50,000 mL/g solution to sorbent ratio
nSilica is nanostructured silica, 300 m^2/g
SAX is strong anion exchange resin
SCX is strong cation exchange

Future Directions

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- FY2015 Activities (last half)
  - Complete evaluation of surface chemistries for mineral capture from geothermal fluids (real materials and real comparative data—fundamentally new data set)
  - Complete evaluation of sorbent structures for operation in geothermal plants
  - Down select to preferred configuration(s)

Program risk is mitigated by competitive evaluation of multiple high performance materials. No single point failure.

- FY2016 Activities
  - Integrate preferred surface chemistries with preferred sorbents.
  - Test the performance and optimize preferred systems.
  - Perform a techno-economic Analysis (TEA) for solid state sorbent technology for cost effective geothermal mineral extraction (with real data).
  - Program Go/No Decision.
- Next Phase
  - Proceed with scale up development and evaluation of preferred materials and methods
  - Coordinate with specific geothermal plants/sites
  - Work with industrial collaborators for tech transfer/maturation

Future Directions

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Milestone or Go/No-Go	Status & Expected Completion Date
Task 2. Evaluation of Solid-State Sorbent Technology	In progress (M1-M12)
Milestone 2.1: Complete the Down-Select to the Most Effective Sorbent Chemistries	On schedule for end of Q3/M9
Milestone 2.2: Complete the Down-Select to the Most Effective Sorbent Structures	On schedule for end of Q4/M12
Go/No Go Decision	pending end of year 1
Task 3. Optimization and Demonstration of Solid-State Sorbent Technology	FY16 work (M13-21)
Milestone 3.1 Complete Optimization of Preferred Sorbent Materials	end of Q6/M18
Milestone 3.2 Demonstration of Preferred Sorbent Materials	end of Q7/M21
Task 4 Techno-economic Analysis of Solid State Sorbent Technology	FY16 work (M12-24)
Milestone 4.1: Complete Basic Conceptual TEA Model for use of Solid State Sorbent Technology in Brines	end of Q6/M15
Milestone 4.2: Complete TEA for Solid State Sorbent Technology	end of Q8/M23
Go/No Go Decision	pending end of year 2

Summary

- Existing separation/collection technology will fail in geothermal brines
  - New technology needed for economically beneficial/viable mineral recovery.

- Solid phase sorbent technology is proven, clean, scalable, flexible, efficient extraction method
  - Systems can be tailored to site specific needs (size/flow, mineral composition, etc.)
  - Primary focus of program is rare earth recovery. Other valuable minerals are not being ignored.
  - Advanced COTs and novel materials being competitively evaluated
  - Structure and chemistry are being independently assessed.

- The program has novel technology and a multidisciplinary team engaged
  - PNNL, mineral industry, engineering assessment, university researchers

- The program will provide fundamental information on a critical material recovery technology that has broad application to geothermal brines as well as other DOE challenges (industrial recycling, environmental clean-up, FE process solutions)
  - Collection and recovery/regeneration chemistry
  - Evaluation of effective separation structures
  - Techno-economical analysis of trace mineral recovery with advanced sorbent materials

Additional Information
Program Work Plan

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WBS Detailed Schedule

2015: Oct | Nov | Dec | Jan | Feb | Mar | April | May | June | July | Aug | Sept

2016: Oct | Nov | Dec | Jan | Feb | Mar | April | May | June | July | Aug | Sept

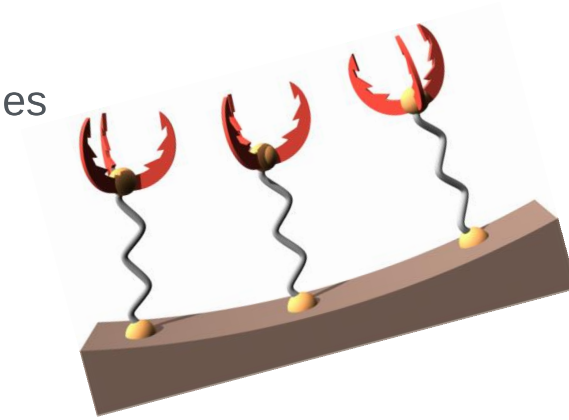
#	Task Name	Start	Finish
	Task 1		
1.0	**Program Initiation and Analysis of Geothermal Fluids (M1-M6)**	**10/1/2014**	**3/31/2015**
	Task 2		
2.0	**Evaluation of Solid-State Sorbent Technology (M1-M12**	**10/1/2014**	**9/30/2015**
2.1	Evaluate and Select Effective Surface Chemistry (M1-M12)	10/1/2014	9/30/2015
2.2	Evaluate and Select Effective Sorbent Structures (M3 – M12)	12/31/2014	9/30/2015
	Task 3		
3.0	**Optimization and Demonstration of Solid-State Sorbent Technology (M13-21)**	**10/1/2015**	**6/30/2016**
	Task 4		
4.0	**Techno-economic Analysis of Solid State Sorbent Technology for Cost-Effective Geothermal Mineral Extraction (M13 –M24)**	**10/1/2015**	**9/30/2016**
4.1	Conceptual Process Design and Material and Energy Balances: (M13-M24)	10/1/2015	9/30/2016
4.2	Identification of Major Equipment: (M13-M24)	10/1/2015	9/30/2016
4.3	Estimation of Capital and Operating Expenditures: (M13-M24)	10/1/2015	9/30/2016

#	Milestone Description	Milestone Date
1	1.1 Assemble Core List of Critical Challenges for Solid State Sorbent Technology for Geothermal Mineral Extraction (M3).	end of M3
2	1.2 Complete Analysis of Geothermal Fluids (M6).	end of M6
3	2.1 Complete the Down-Select to the Most Effective Sorbent Chemistries (M9)	end of M9
4	2.2 Complete the Down-Select to the Most Effective Sorbent Structures (M12)	end of M12
5	4.1: Complete Basic Conceptual TEA Model for use of Solid State Sorbent Technology in Brines (M15)	end of M15
6	3.1 Complete Optimization of Preferred Sorbent Materials (M18)	end of M18
7	3.2: Demonstration of Preferred Sorbent Materials (M21).	end of M21
8	4.2: Complete TEA for Solid State Sorbent Technology for Cost Effective Geothermal Mineral Extraction (M23)	end of M24
	Go/No-Go Decision Points and Risk Mitigation	
1	Program Decision Point 1: Demonstration of Effective Solid Phase Sorbents for Collection of Valuable Minerals from Geothermal Solutions (M12)	end of M12

Additional Information

Subtask 2.1 Evaluate and Select Effective Surface Chemistry

- Evaluation of high-performance sorbents (COTS and novel materials) to recover value added minerals from geothermal (and other selected) solutions.
- Parameters for surface chemistry evaluation:
  - High affinity
  - Selective for valuable minerals
  - Synthetically scalable and amendable to high surface densities
  - Stable thermally and chemically
  - Easily reversible and durable
    - Enables mineral recovery and reuse



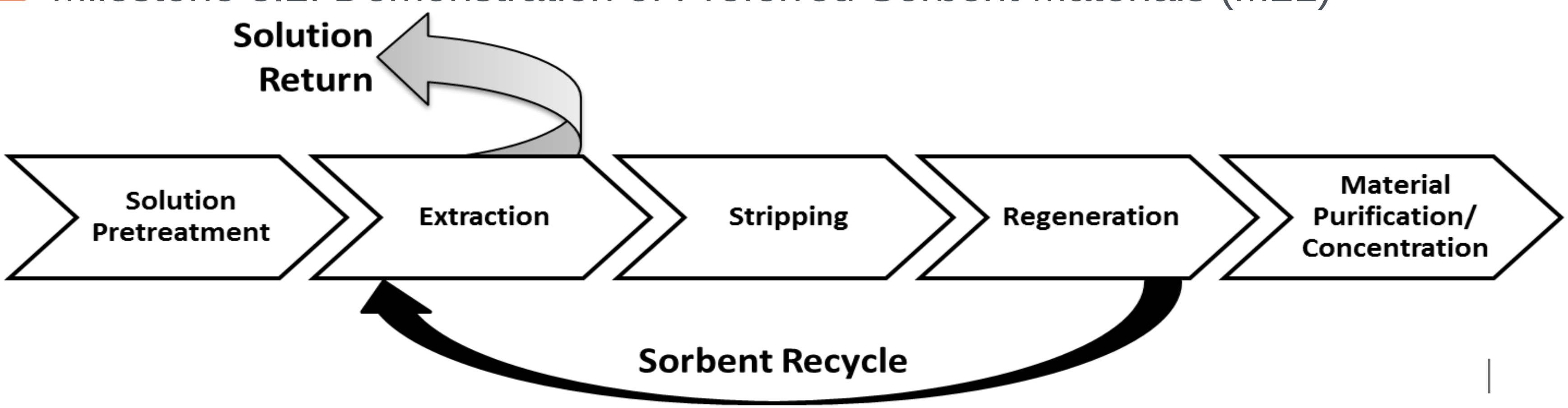
<u>Organic surface chemistry</u>
-better selectivity
-higher affinity
-lower temp stability

<u>Inorganic surface chemistry</u>
-high temp stability
-cheaper
-less selectivity

Additional Information

Task 3. Optimization and Demonstration of Solid-State Sorbent Technology (Year 2)

- Integrate Best Chemistries with Best Structures.
  - Test Performance
    - Uptake efficiency and capacity
    - Lifetime/resistance to fouling
    - Compare to existing COTS materials
    - Viable stripping and regeneration methods
  - Several iterations and down selection cycles
  - Feed data into Techno-economic analysis
  - Milestone 3.1 Complete Optimization of Preferred Sorbent Materials (M18)
  - Milestone 3.2: Demonstration of Preferred Sorbent Materials (M21)



Additional Information

Task 3. Optimization and Demonstration of Solid-State Sorbent Technology (Year 2)

- Stripping and regeneration methods
  - Acidic
  - Carbonate
  - Acidified ligands (i.e. thiourea, EDTA, TBP)
  - Compressed fluids
  - ?
- Opportunity to separate, concentrate, (semi) purify of minerals collected by sorbent materials
  - U and Th
  - RE's
  - Heavy metals
    - Hard
    - Soft
- Refresh and regenerate sorbents