COUPLED HYDROTHERMAL EXTRACTION AND LIGAND-ASSOCIATED SWELLABLE GLASS MEDIA RECOVERY OF RARE EARTH ELEMENTS FROM COAL FLY ASH

Timothy Dittrich[1], Matthew Allen[2], Sanjay Mohanty[3], Hakim Boukhalfa[4], Artaches Migdissov[4], and Shawn McElmurry[1]

[1]Civil and Environmental Engineering – Wayne State University, Detroit, MI; [2]Chemistry– Wayne State University, Detroit, MI; [3]Civil and Environmental Engineering – University of California-Los Angeles; [4]Earth System Observations – Los Alamos National Laboratory, Los Alamos, NM

PROJECT DESCRIPTION

This project will investigate the use of hydrothermal leaching under alkaline conditions to rapidly dissolve rare earth elements (REEs) from coal ash solids to an aqueous solution; transfer REEs from the solution to an Osorb platform (commercially available swellable organically modified silica) functionalized with the appropriate ligand system; and extract the REEs to an acidic aqueous system that will have high concentrations of the targeted REEs (2–10 percent by weight). The project will examine the potential to couple hydrothermal leaching of coal fly ash with a custom-engineered, ligand-associated media to provide an organic solvent-free method of extracting and recovering REEs. The fly ash feedstock will be collected from Detroit area coal-fired power plants, characterized for composition, and subjected to a bench-top batch hydrothermal leaching/dissolution process inside custom-built pressure reactors. Ligands known to be effective in lanthanide/actinide separation will be evaluated based on a series of criteria, such as selectivity and association to Osorb through hydrophobicity. Batch experiments will be conducted to establish the best conditions (e.g., pH, eluent, etc.) and best ligand systems for effectively extracting REEs from the alkaline feed solution obtained from the hydrothermal leaching process. Once the Osorb-ligand extraction system is optimized for REE concentration, a pH adjusted aqueous solution will be used to back-extract and concentrate the REEs into a heavily REE-laden solution.

OBJECTIVES

1) Hydrothermal extraction of REEs

2) Select lanthanide-specific ligands to associate with solid phase (organosilica)

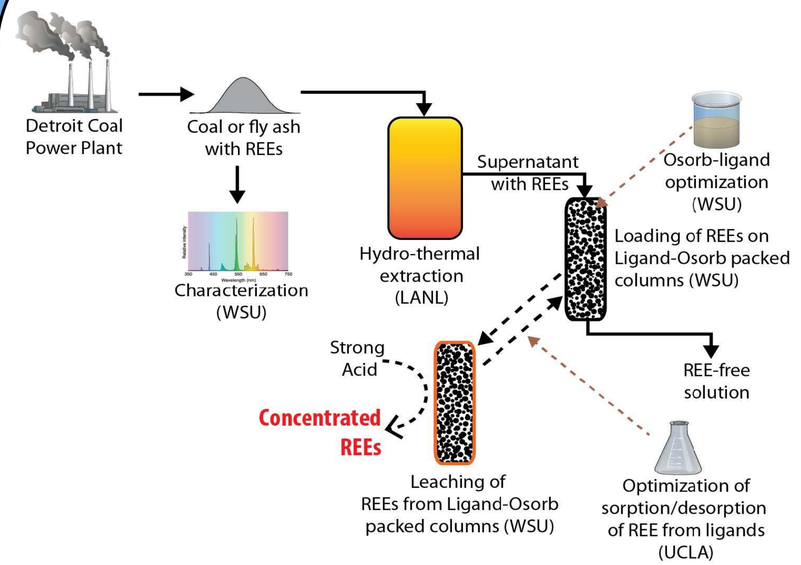
3) Optimize attachment of ligands to the solid phase to allow for flow-through separations

4) Test pH conditions for back-extraction

5) Evaluate resilience of material through cycling

Task	6 months	12 months	18 months
1			
2	Hydrothermal extraction		
3	Ligand selection		
4	Ligand attachment to OSORB		
5	Evaluate REE sorption		
6	Evaluate REE Recovery from solid phase		
7	Model ligand-OSORB-REE system components		

FLOW CHART AND TASKS

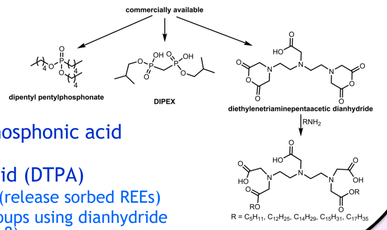


Tasks 1&2) Ash collection and hydrothermal Extraction

- Optimize variables
  - T (150-350°C)
    - Isothermal/variable
  - Ligand system
    - Cl, SO_4^{2-}, CO_3^{-2}
  - Leaching conditions
    - pH, time
  - Quenching conditions
    - Cooling cycle, pH adj.
- Compare to HF digestion
  - Trenton and NIST SRM 1633C

Task 3) Ligand Selection

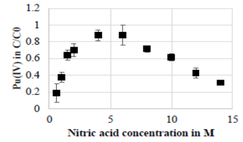
- Test 3 ligand types
  - dippentyl pentylphosphonate
  - P,P'-di(2-ethylhexyl)methanediphosphonic acid (DIPEX)
  - diethylenetriaminepentaacetic acid (DTPA)
    - dissociates under acidic conditions (release sorbed REEs)
    - functionalized with hydrophobic groups using dianhydride and alkylamines (denticities from 1-8)



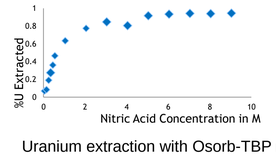
PRELIMINARY RESULTS

Tasks 4-6) Ligand attachment and metal ion sorption

- Osorb®
  - Swellable organically modified silica (SOMS)
  - Bridged silane
  - ~600 m^2/g surface area
  - Can accumulate >4x mass in nonpolar ligands (Edmiston and Underwood, 2009)
- Tri-butyl phosphate (TBP-associated Osorb)
- Similar behavior to liquid/liquid extraction



Extraction of Pu(IV) onto a polypropylene membrane with immobilized TBP



Uranium extraction with Osorb-TBP media
-94% recovery from 1000 ppm U
-Successful strip/cycle

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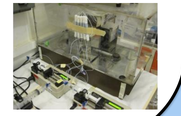

FUTURE MILESTONES

Milestone	Quantitative Measurement	Planned Completion Date	Investigator
Obj. 1. Establish feasibility of hydrothermal extraction	> 300 ppm T-REEs in hydrothermal extraction liquid	8/15/2018	Boukhalfa & Migdissov
Obj. 2. Select/characterize two commercial ligands	Two commercial ligands are >99% pure to identity	8/15/2018	Allen
Obj. 3. Load ligands to Osorb platform	Achieve surface coatings of ~50% by wt with first 2 ligands	12/1/2018	Dittrich
Obj. 4. Successful test of ligand-Osorb system with 2 commercial ligands	Achieve >95% sorption of REEs from extraction liquid (by mass)	4/1/2019	Mohanty
Obj. 5. Successful pH-optimized strip with 2 commercial ligands	Recover minimum of 2wt% T-REE concentrate	8/1/2019	Dittrich
Obj. 6. Successful modeling of the ligand-Osorb-REE system	List of modeled/calculated system parameters/coefficients	9/1/2019	McElmurry

ACKNOWLEDGEMENTS

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