

Coupled Hydrothermal Extraction and Ligand-Associated Swellable Glass Media Recovery of Rare Earth Elements from Coal Fly Ash

T.M Dittrich, M. Dardona, J. Hovey, and M.J. Allen

Wayne State University

S.K. Mohanty

University of California-Los Angeles

H. Boukhalfa, A. Migdissov

Los Alamos National Laboratory


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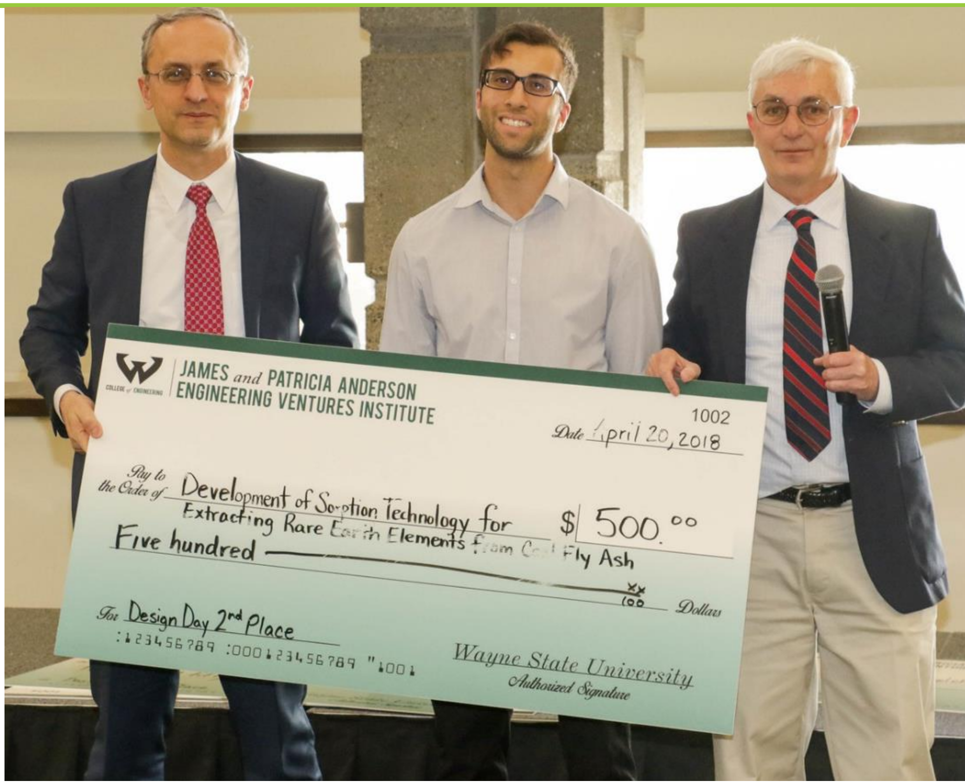
Project Description and Objectives

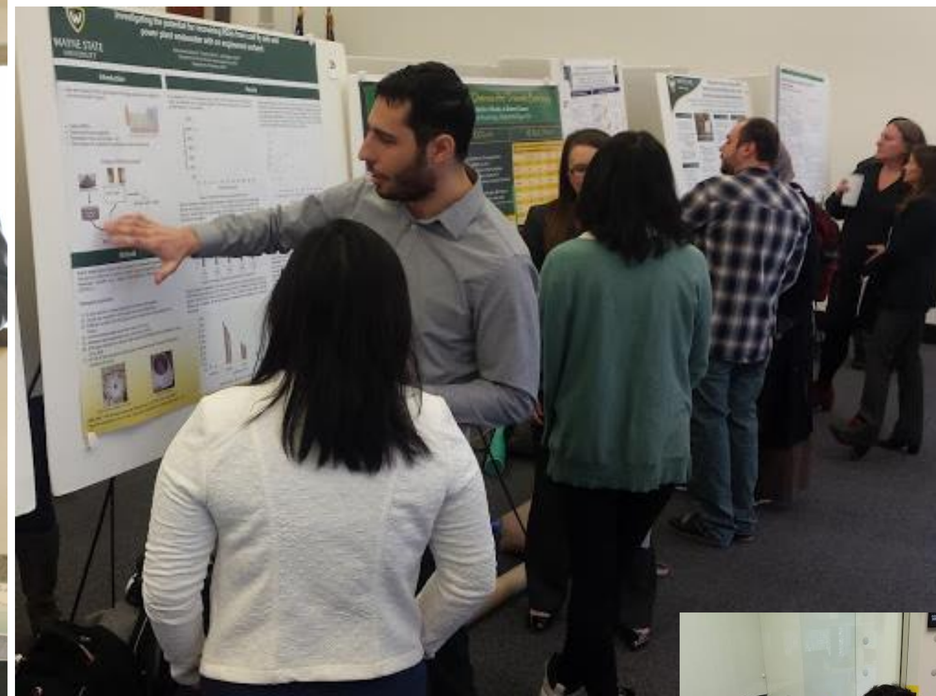
NATIONAL ENERGY TECHNOLOGY LABORATORY

Purpose of Project

- AOI 2: DE-FOA-0001718 Award DE-FE-0031565 (Maria Reidpath)
- **Couple a novel application of hydrothermal extraction with the advancement of a state-of-the-art organosilica platform by engineering ligand selectivity**
- **Supported liquid extraction (SLE) or extraction chromatography (EXC)**
- **GOAL: Economical REE separation that minimizes use of solvents and acids (>2 wt% recovery)**
- DRIVING QUESTION: Can we use hydrothermal extraction to reduce need for acid, while engineering ligands to extract REEs from the resulting solution?
- **Technology benchmarking** –nitric acid dissolution and liquid-liquid extraction (solvent extraction)
- Current Status of project
    - <13 months into project – exceeded most milestones so far
    - Project goals remain same as originally proposal – transition from new concept to bench scale (in prep for pilot-scale)
- **Industry/input or validation** – Just reaching stage to reach out for feedback with preliminary results

Accomplishments





- ACS Fall National Meeting (Boston, MA)
- SME National Conference (Denver, CO)
- ACS Spring National Meeting (Orlando, FL)
- Bilal Syed (2nd of 74) Design & Innovation Day
- Mohammed Dardona (Best poster award)

Outline

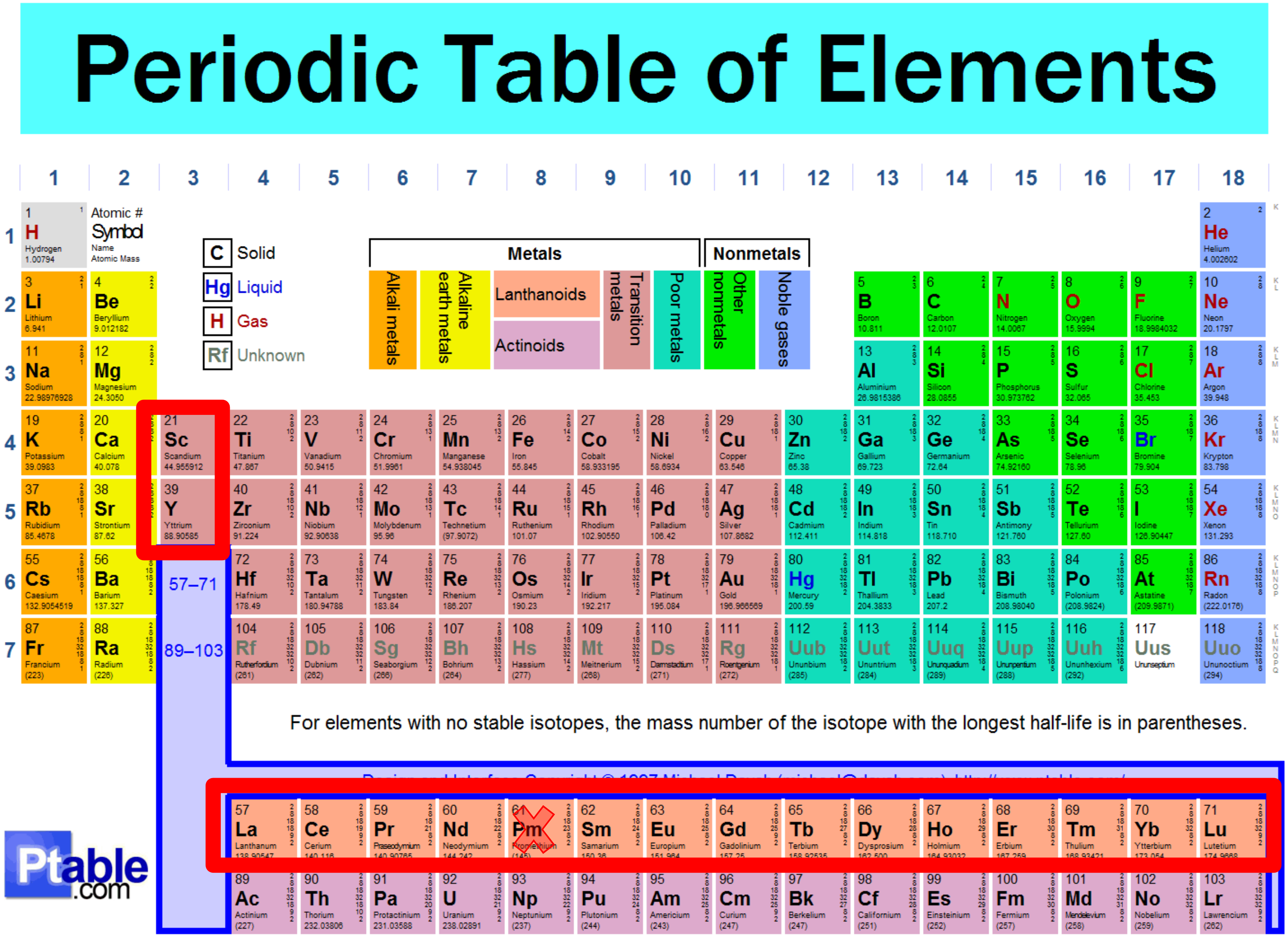
- Overall Objective
  - Economically feasible dissolution, concentration, and recovery (REEs)
  - Minimize use of solvents and acids, where possible
  - Fly ash (and FGD sludge)
- Project Team
- Sample Collection and Experimental Setup
  - (Obj. 1a) Trenton Channel and Monroe Power Plants near Detroit, MI
  - (Obj. 1b) Hydrothermal digestion process
  - (Obj. 2) Selection and synthesis of ligands
  - (Obj. 3) Ligand association to organosilica (media)
  - (Obj. 4) REE sorption to ligand-organosilica media (capacity, selectivity)
- Milestones
- Future Work

Project Objectives and Partners

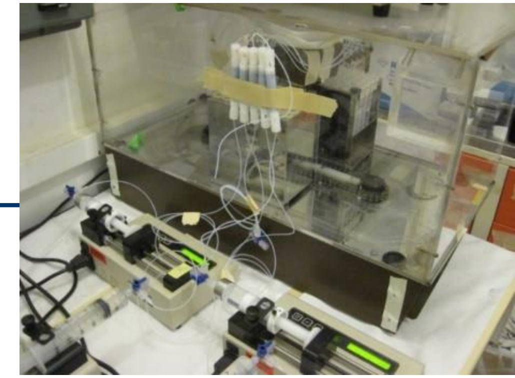
- INTERDISCIPLINARY TEAM
  - Wayne State U., UCLA, and LANL

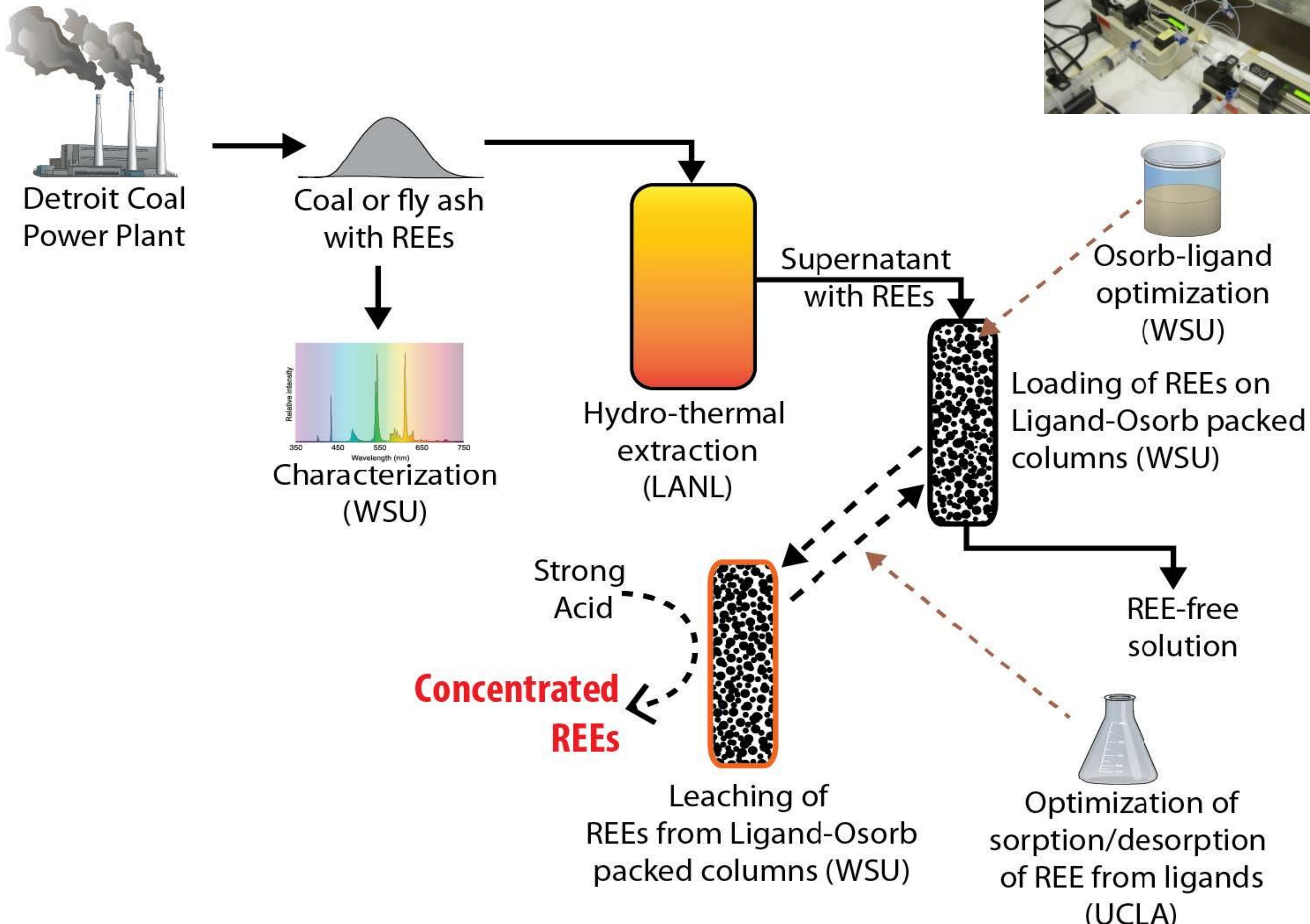
1) Hydrothermal extraction of REEs
   - Similar process for trinitite dissolution (LANL)
2) Select lanthanide-specific ligands to associate with solid support (organosilica)
   - Dr. Allen (WSU) – lanthanide coordination chemistry for MRI and catalysis applications (AAAS Fellow 2018-Chem)
3) Optimize attachment of ligands to the solid support to allow for flow-through separations (EXC)
   - Drs. Dittrich and Mohanty
4) Test pH conditions for back-extraction
5) Evaluate resilience of material through cycling

Leveraging similarities to actinides



Project Flow-chart





Ligand-associated Osorb (TBP)

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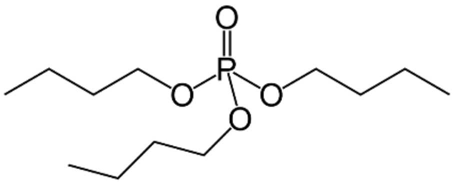
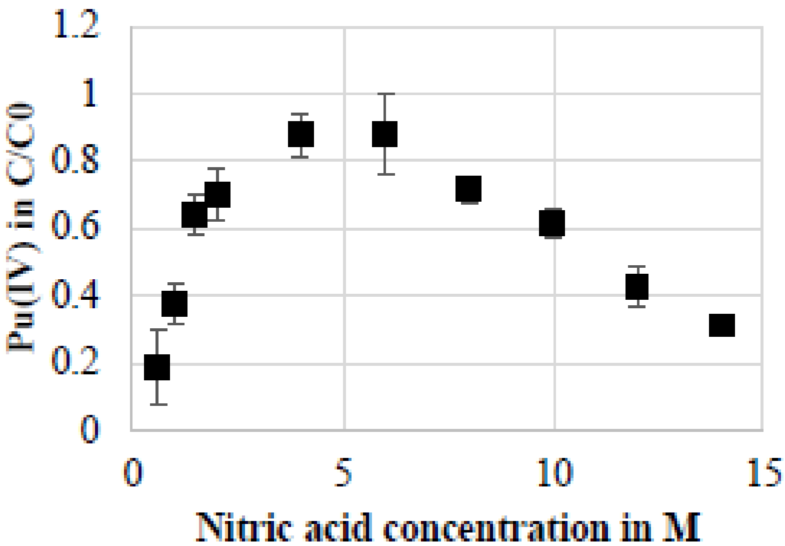
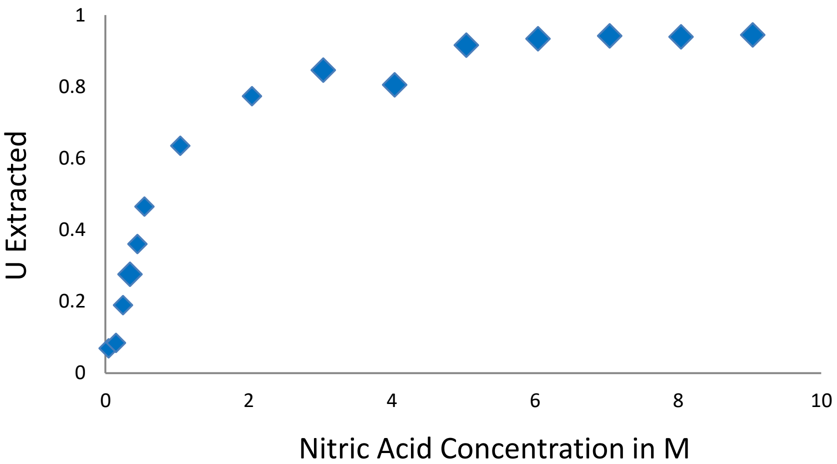
- Osorb® (ABS Materials, Wooster, OH)
  - Swellable organically modified silica (SOMS)
  - Bridged silane
  - ~600 m^2/g surface area
  - Can accumulate >4x mass in nonpolar ligands (Edmiston and Underwood, 2009)
- Tri-butyl phosphate (TBP-associated Osorb)
- Similar behavior to liquid/liquid extraction





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

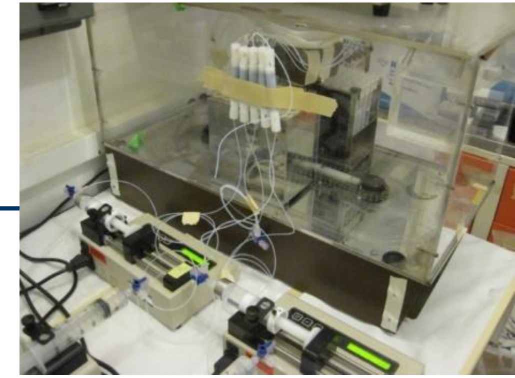


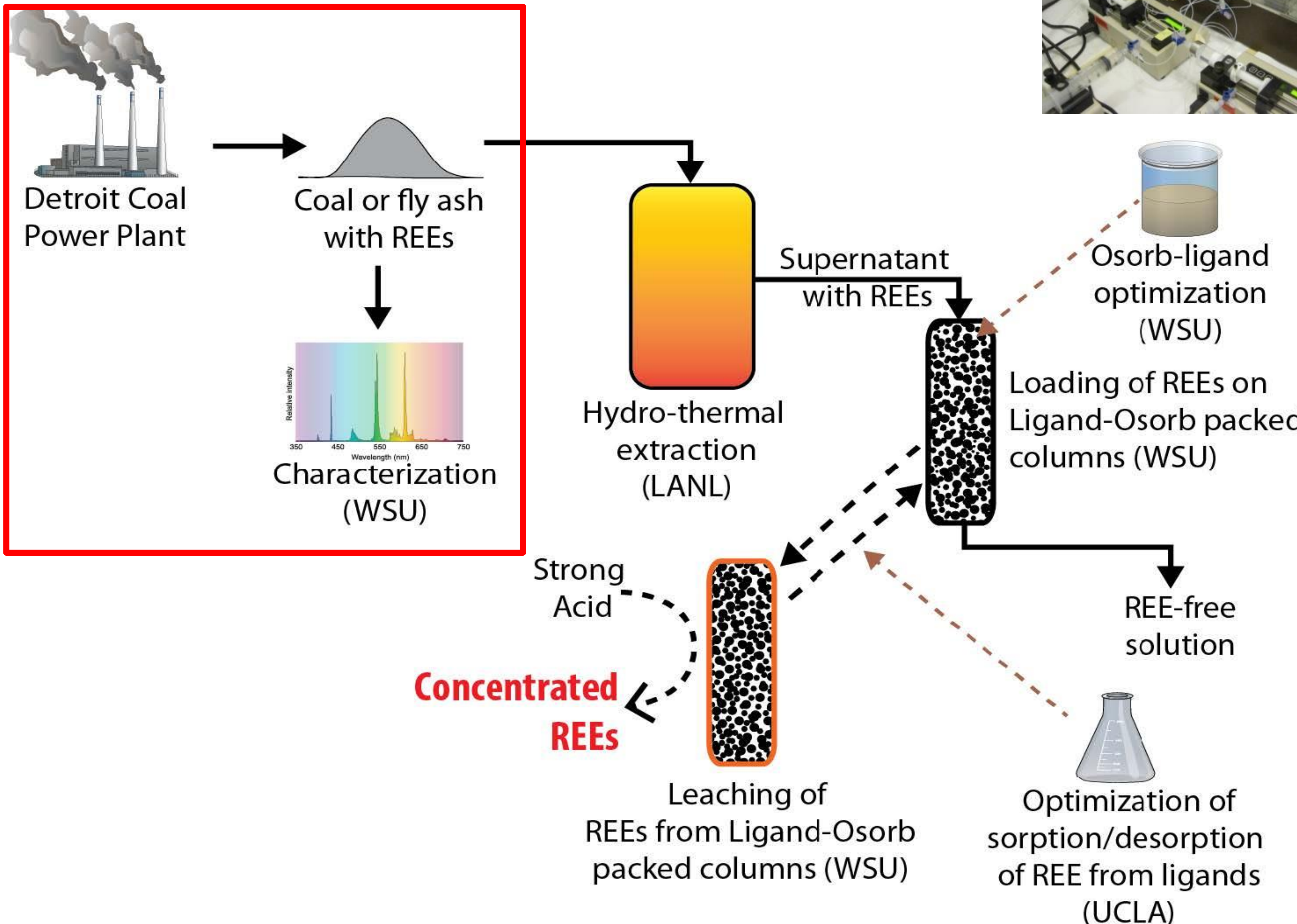
Uranium extraction with Osorb-TBP media

-94% recovery from 1000 ppm U

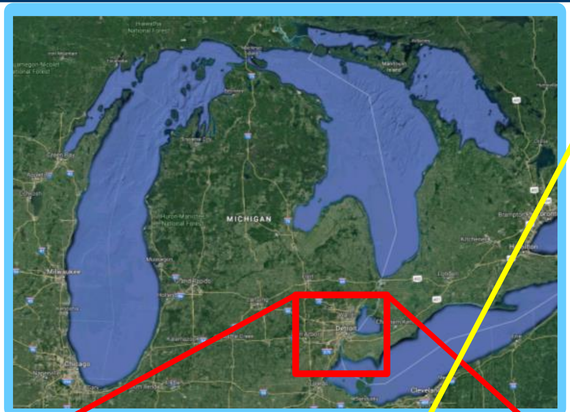
-Successful strip/cycle

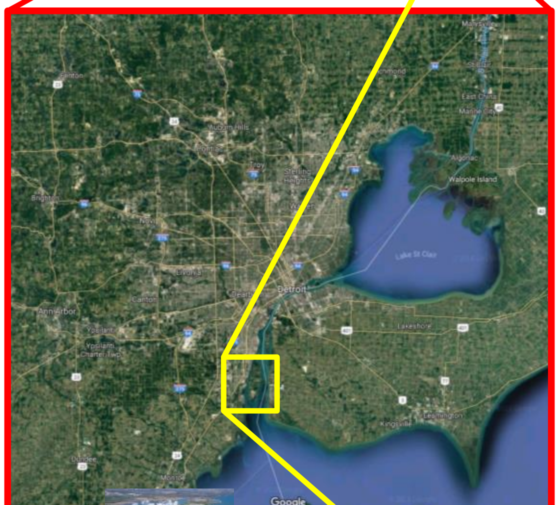
Project Flow-chart

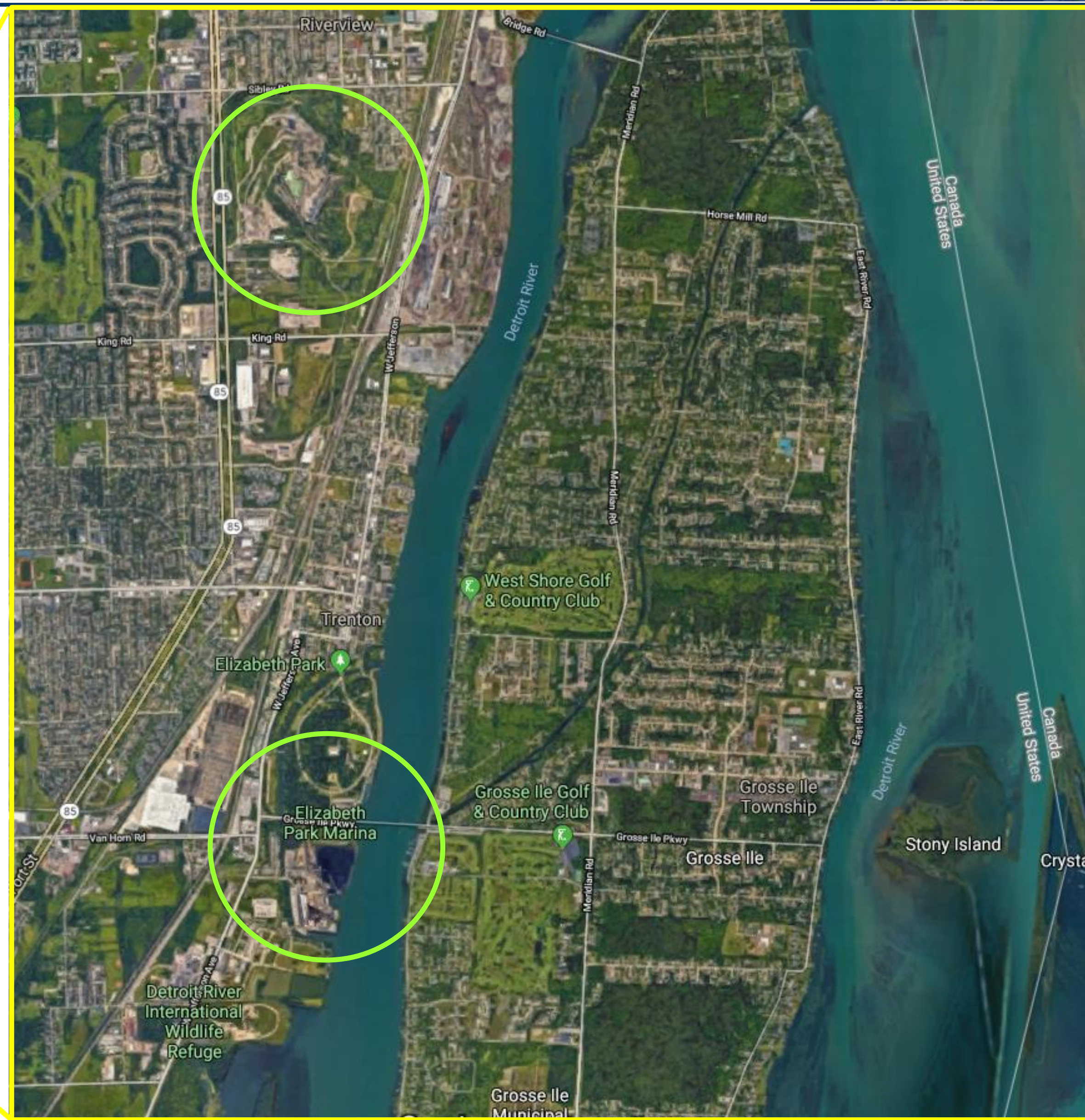




Detroit, MI


MICHIGAN


Detroit
Ann Arbor
Google

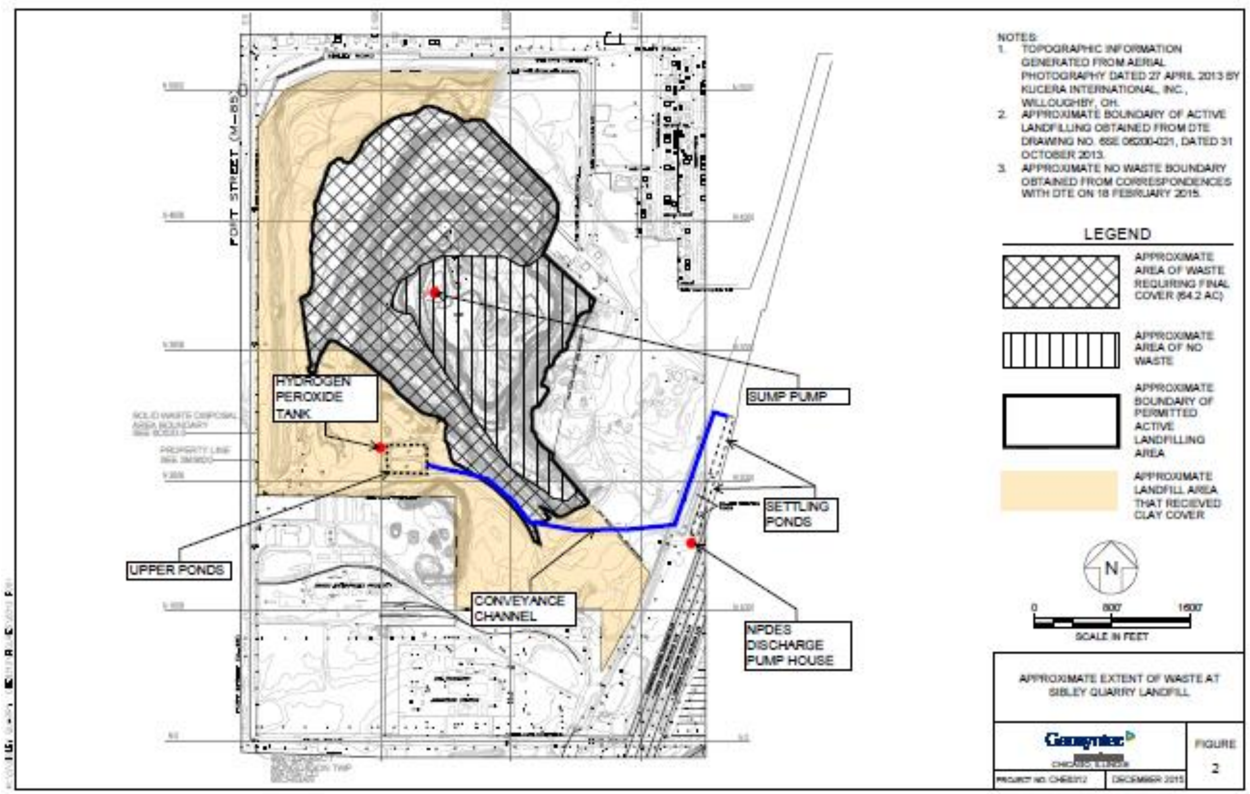

Riverview
Bridge Rd
Sibley Rd
Meridian Rd
Horse Mill Rd
King Rd
King Rd
W Jefferson
Detroit River
East River Rd
Canada
United States
West Shore Golf
& Country Club
Trenton
Elizabeth Park
Grosse Ile Golf
& Country Club
Elizabeth
Park Marina
Grosse Ile Pkwy
Van Horn Rd
Grosse Ile
Township
Grosse Ile
Stony Island
Crystal
Detroit River
Canada
United States
Detroit River
International
Wildlife
Refuge
Grosse Ile
Municipal

Trenton Channel and Monroe Power Plants

- Trenton Channel
  - 536 MW plant (Unit 9)
  - Mostly low sulfur western coal
- Monroe Power Plant
  - 3,066 MW plant
  - FGD process
  - Low sulfur/high sulfur blends
  - Up to 15% petcoke
- ALL ash and wastewater sludge disposed in Sibley Quarry

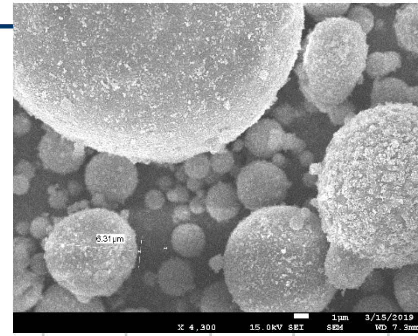
Sibley Quarry Landfill (Trenton, MI)

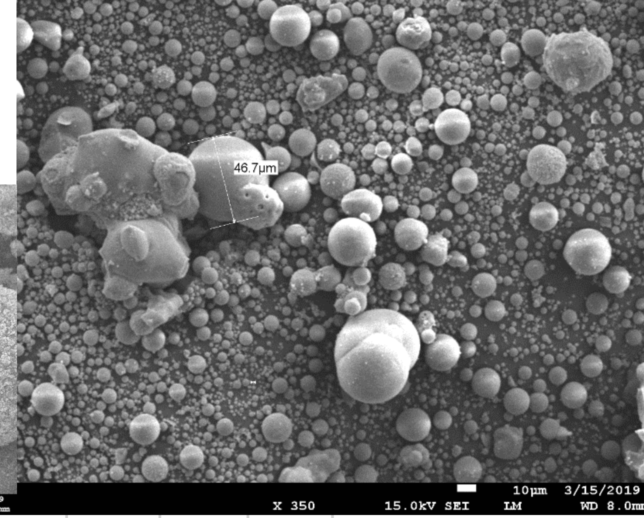
- 300’ deep limestone quarry (mid 1800’s)
- 1951 – DTE acquired (Type III Industrial Waste Landfill)
- 10,000-15,000 yd^3/mo of CCR
- 1.5 MGD pumping rate to isolate CCR from groundwater



Fly ash and sludge collection– Detroit, MI

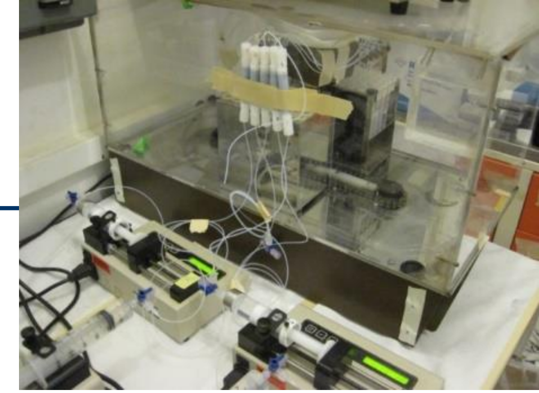
REE content of coal blends

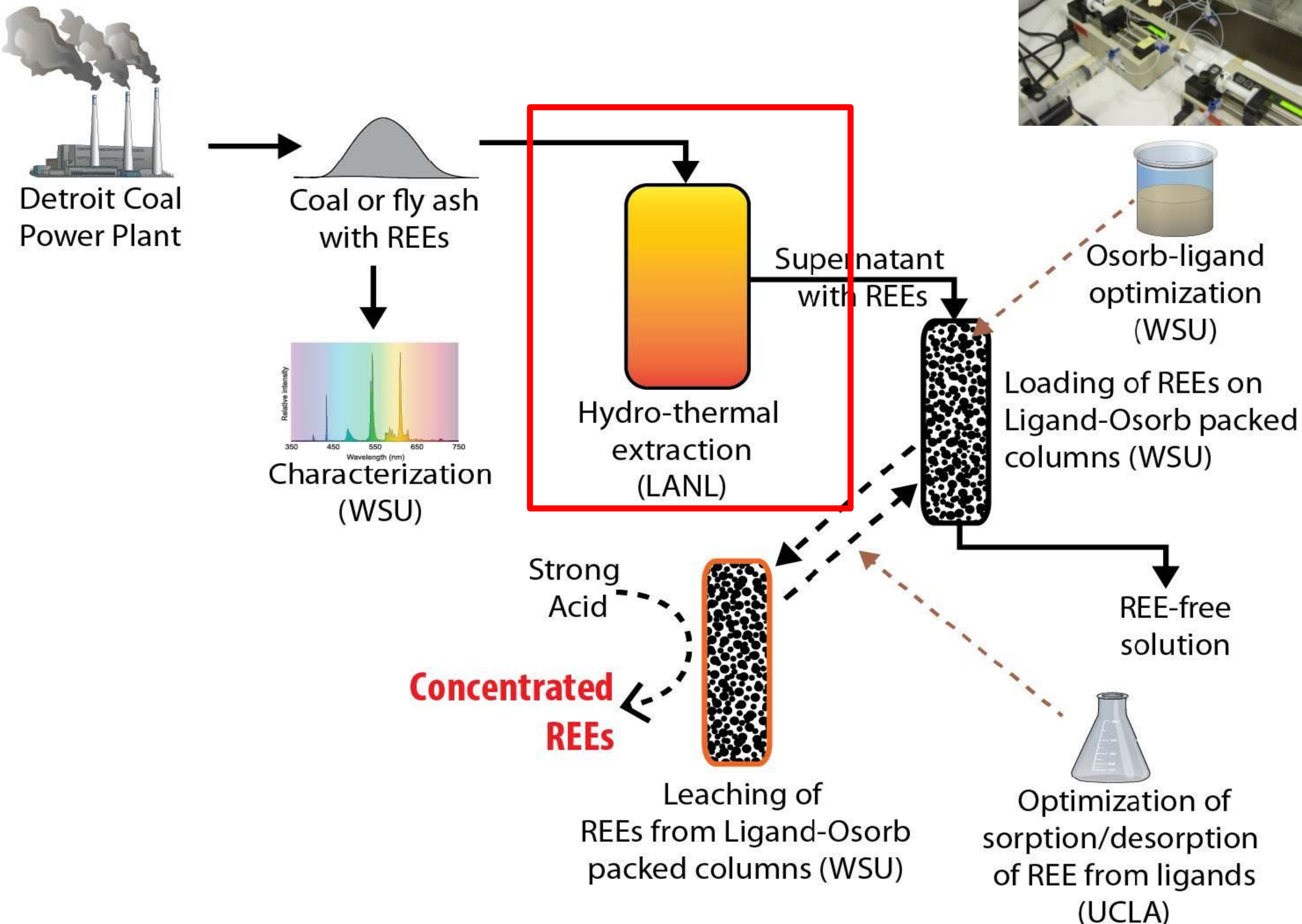




Sample ID	Sc 45 (ppm)	Ce 140 (ppm)	Dy 164 (ppm)	Er 166 (ppm)	Eu 153 (ppm)	Ho 165 (ppm)	La 139 (ppm)	Lu 175 (ppm)	Nd 142 (ppm)	Pr 141 (ppm)	Sm 152 (ppm)	Gd 158 (ppm)	Tb 159 (ppm)	Tm 169 (ppm)	Yb 174 (ppm)	Total REE minus Y (ppm)	Th 232 (ppm)
Trenton Channel, Detroit	NA	100.21	7.16	4.50	2.49	1.48	51.04	0.59	46.09	11.90	10.08	9.18	1.26	0.61	3.77	250.36	NA
DI water blank	0.022	0.0008	0.0006	0.0004	7E-04	0.0006	0.0004	0.00068	0.0005	0.00128	0.0006	0.00084	0.0008	0.0006	0.0006	0.03	0.00069
WSU-1A (Monroe 75/25)	61.65	121.40	9.40	5.49	2.67	1.94	57.13	0.77	55.42	12.76	11.16	11.35	1.66	0.78	4.97	358.56	22.01
WSU-2A (Monroe 75/25)	61.10	124.26	9.65	5.64	2.66	1.89	57.60	0.71	56.03	13.01	11.11	11.71	1.64	0.81	4.84	362.67	21.54
WSU-3A (Monroe 75/25)	57.91	117.81	9.51	5.16	2.57	1.81	55.39	0.71	54.01	12.33	10.76	11.19	1.55	0.75	4.86	346.31	21.63
WSU-4A (Monroe 75/25)	57.33	123.12	9.59	5.79	2.68	1.86	57.93	0.74	58.53	13.04	11.02	11.84	1.58	0.77	4.96	360.79	21.30
WSU-1B (Monroe 70/15/15)	52.15	94.01	7.42	4.19	2.00	1.45	44.83	0.59	43.83	9.91	8.28	8.40	1.16	0.58	3.69	282.49	18.91
WSU-2B (Monroe 70/15/15)	49.18	94.01	7.07	4.03	2.16	1.41	44.81	0.55	43.58	9.83	8.34	8.58	1.23	0.58	3.63	279.00	18.31
WSU-3B (Monroe 70/15/15)	50.58	93.72	6.68	4.04	2.14	1.36	45.17	0.55	41.86	9.72	8.14	8.58	1.15	0.55	3.69	277.92	19.46
WSU-4B (Monroe 70/15/15)	50.53	98.79	7.45	4.25	2.16	1.48	47.79	0.59	46.04	10.41	8.89	8.91	1.22	0.62	3.90	293.03	20.16

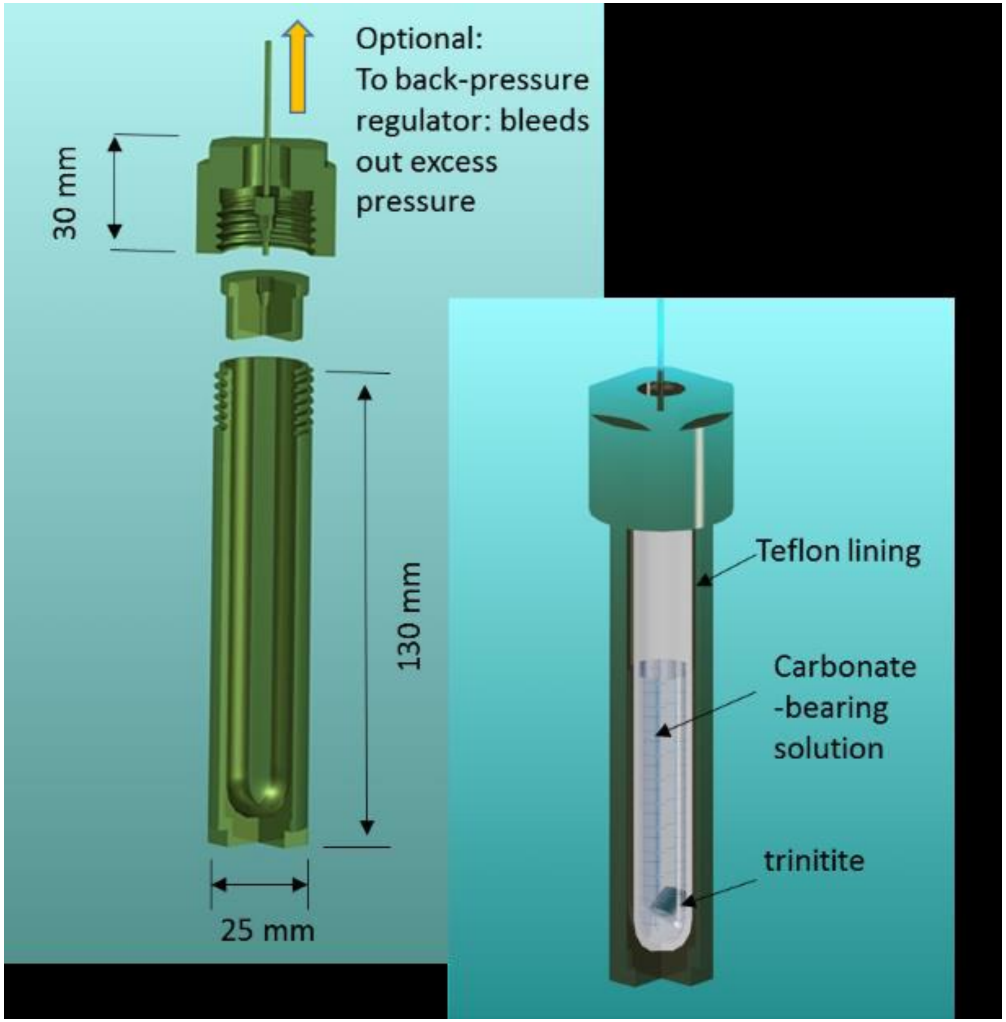
Project Flow-chart

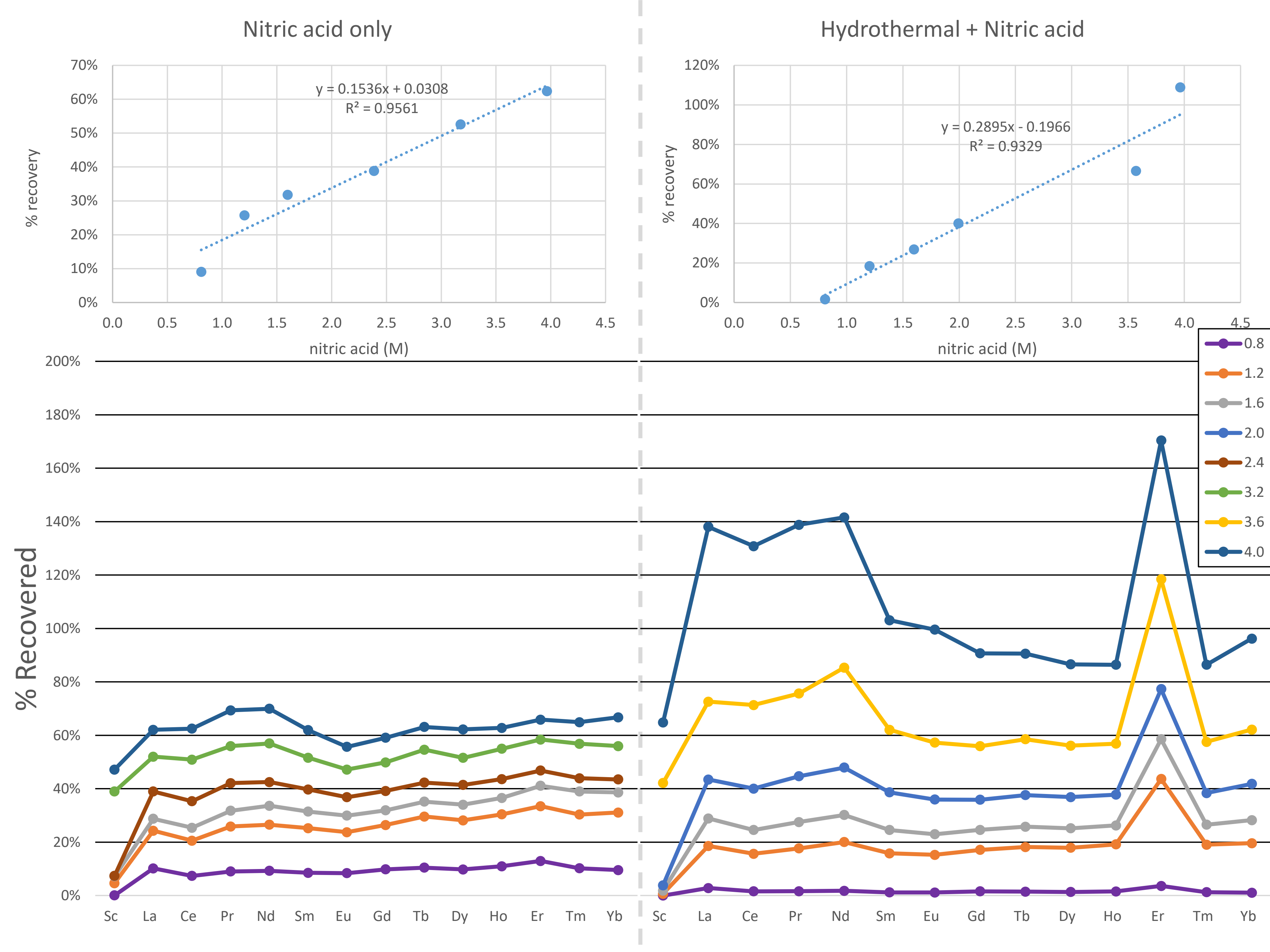




Hydrothermal Extraction

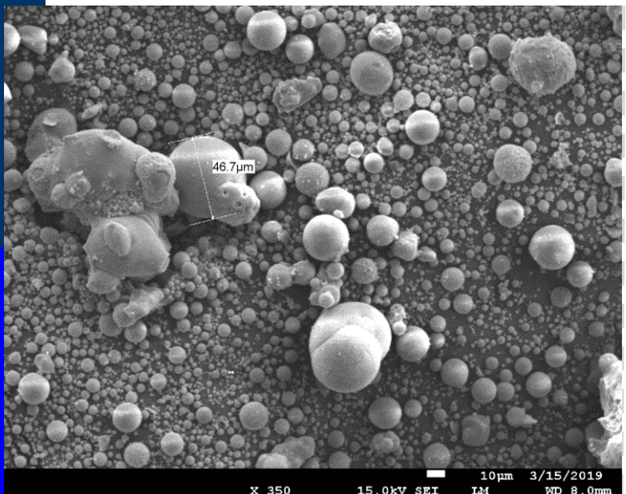
- Artas Migdissov and Hakim Boukhalfa (LANL)
- Optimize variables
  - T (150-350°C)
    - Isothermal/variable
  - Ligand system
    - Cl, SO_4^{2-}, CO_{3-}^{2}
  - Leaching conditions
    - pH, time
  - Quenching conditions
    - Cooling cycle, pH adj.
- Compare to HF digestion
  - DTE ash and NIST SRM 1633C

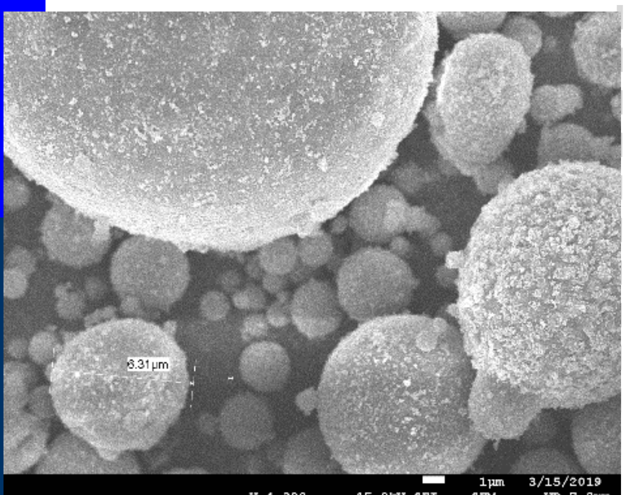




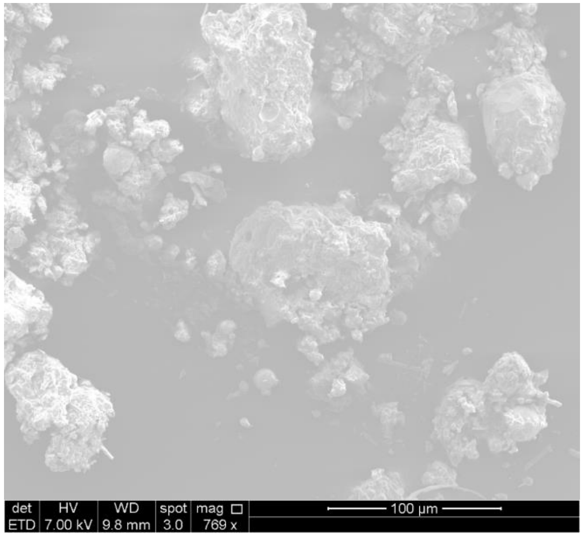
Nitric acid only
Hydrothermal + Nitric acid
y = 0.1536x + 0.0308
R² = 0.9561
y = 0.2895x - 0.1966
R² = 0.9329
% recovery
nitric acid (M)
% Recovered
0.8
1.2
1.6
2.0
2.4
3.2
3.6
4.0
Sc
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb

SEM verification of alteration

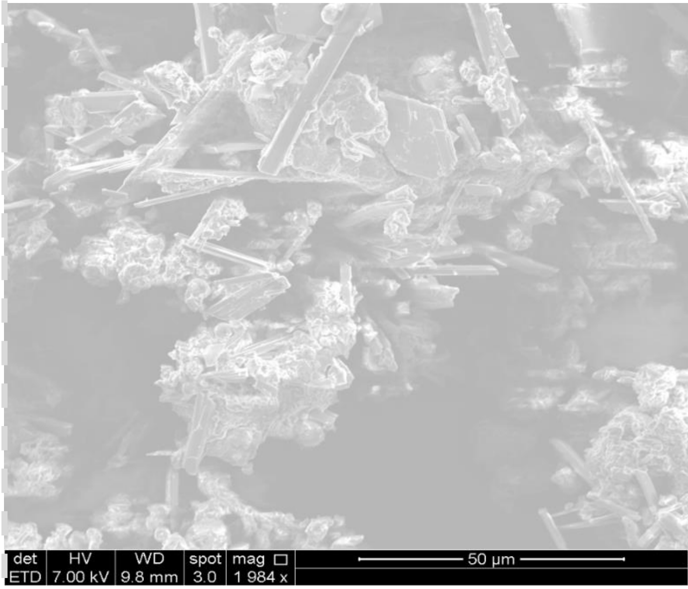




Unaltered Ash

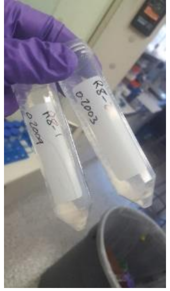


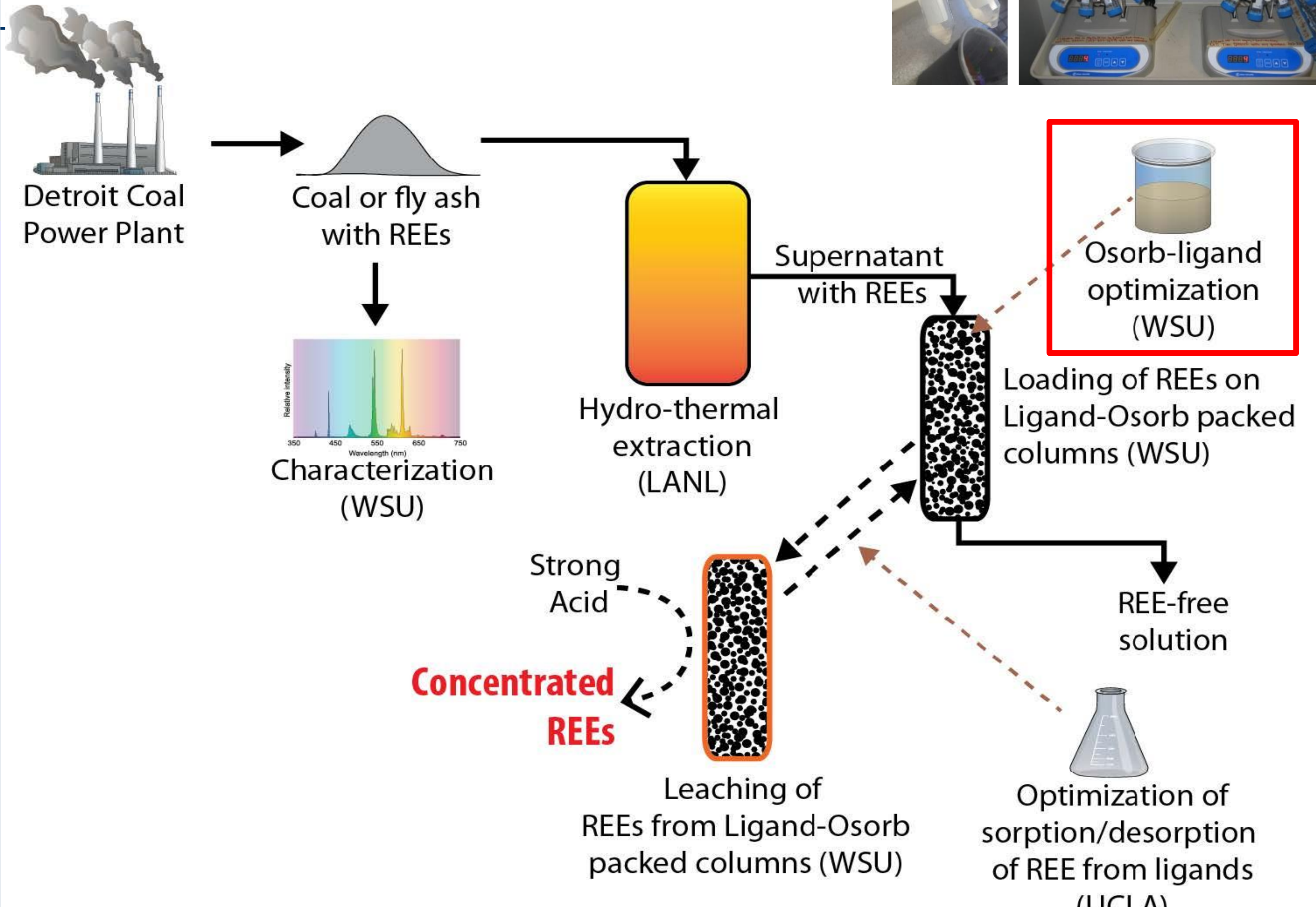
Hydrothermally Altered Ash



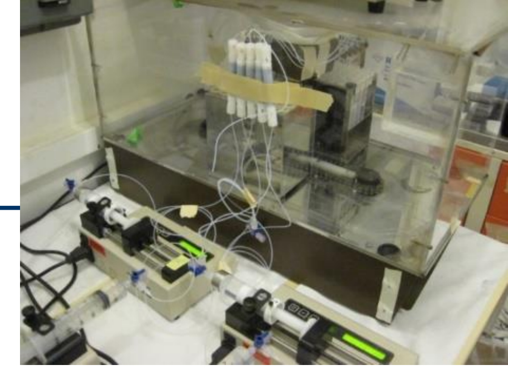
Hydrothermally Altered Ash after acid leached

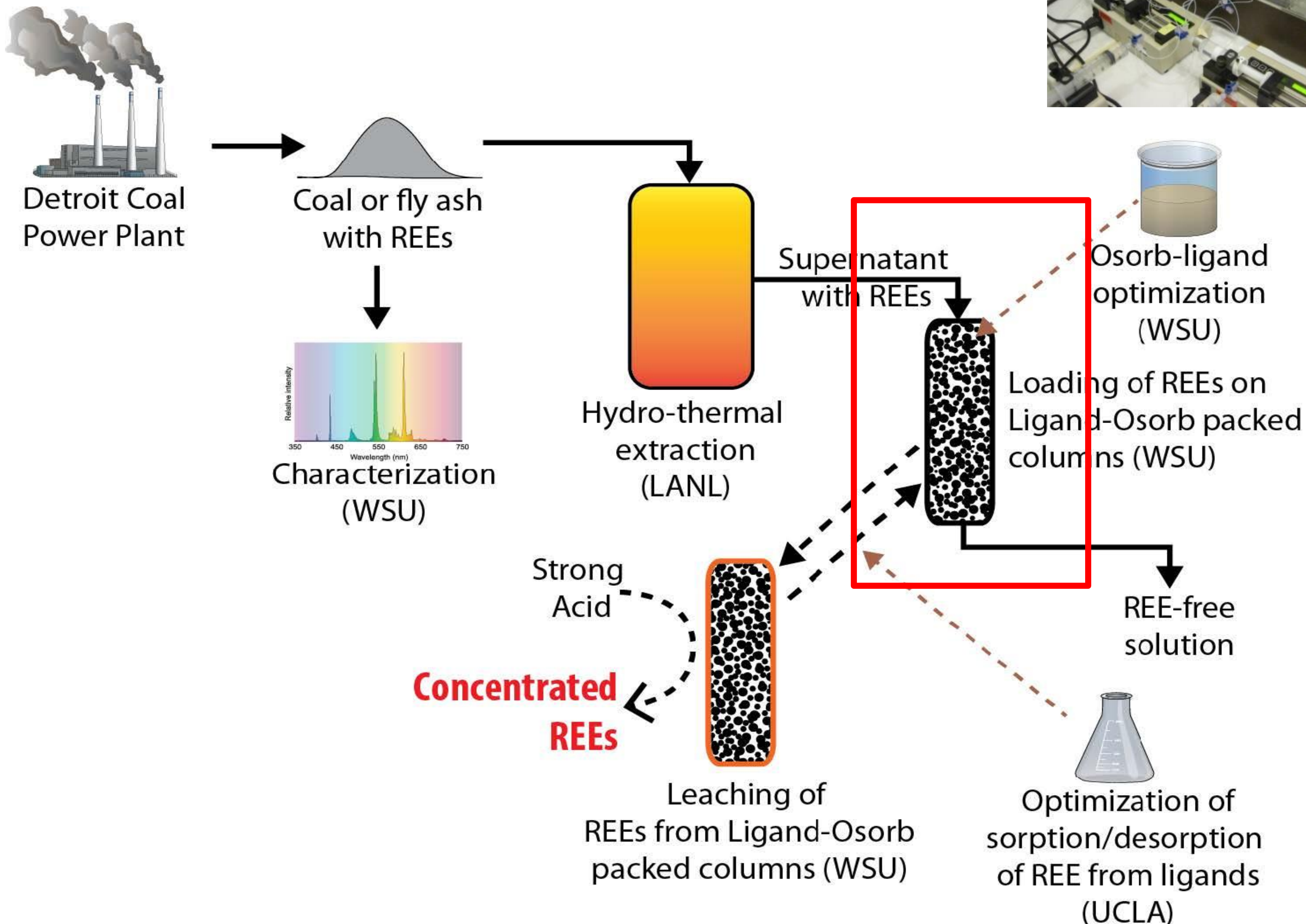
Project Flow-chart





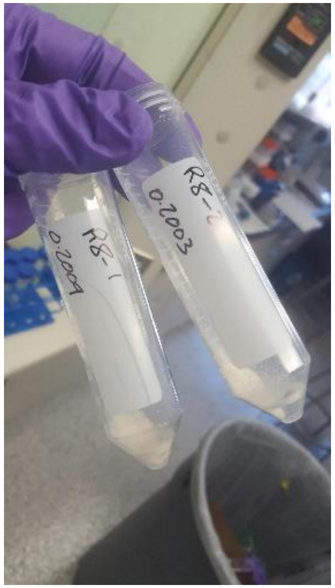
Project Flow-chart

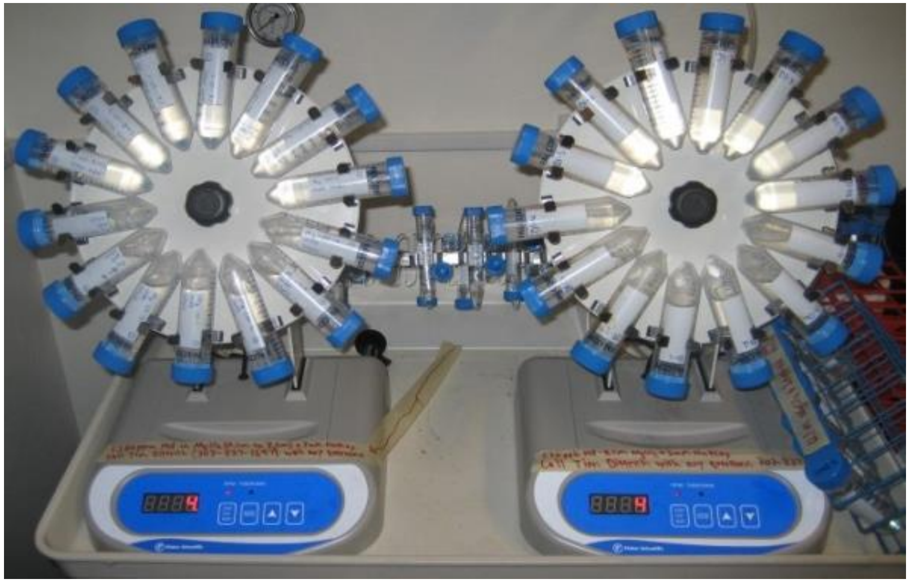




Neodymium sorption

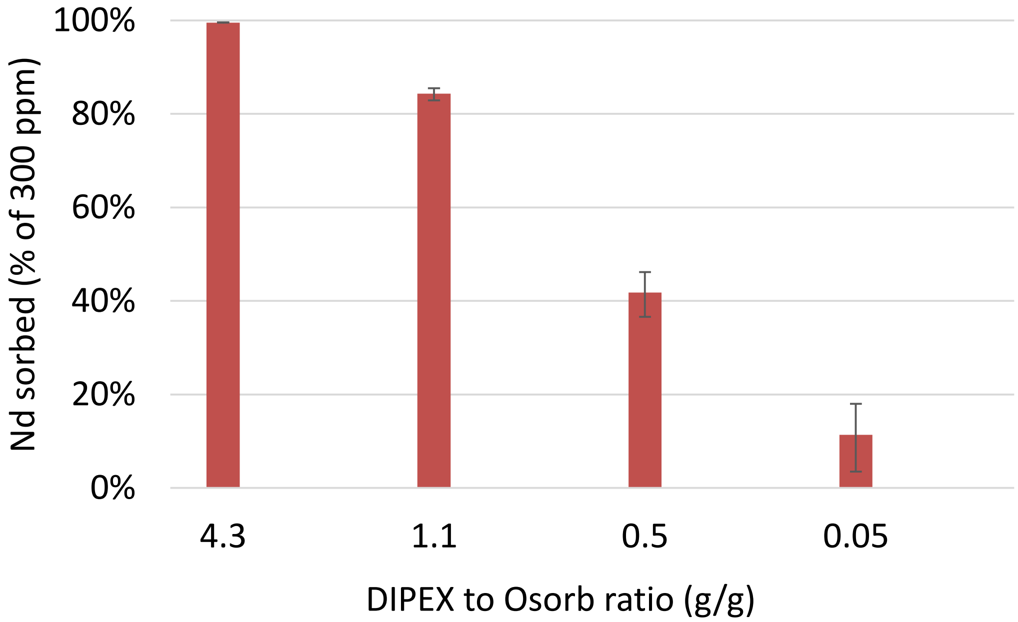
- 40 mL 300 ppm Nd (pH ~2)
- Rotate 24 h (0.2 g media)
- Measure Nd concentration via ICP-MS
  - Agilent 7700 (He and H_2 collision gas)



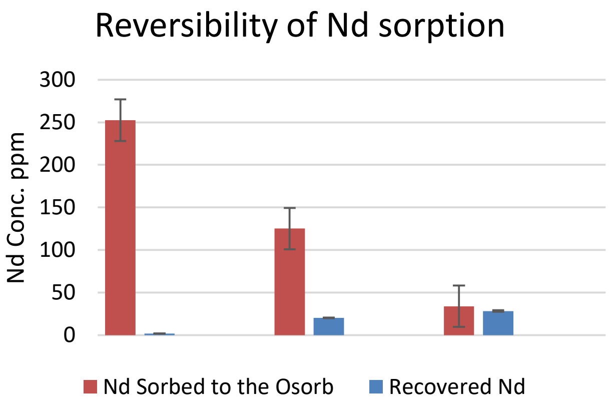


Nd sorption to DIPEX-Osorb

- 300 ppm Nd in pH 2 HNO_3
- 40 mL per 0.2 g media
- No competing ions (e.g., Fe^{3+}, Al^{3+})

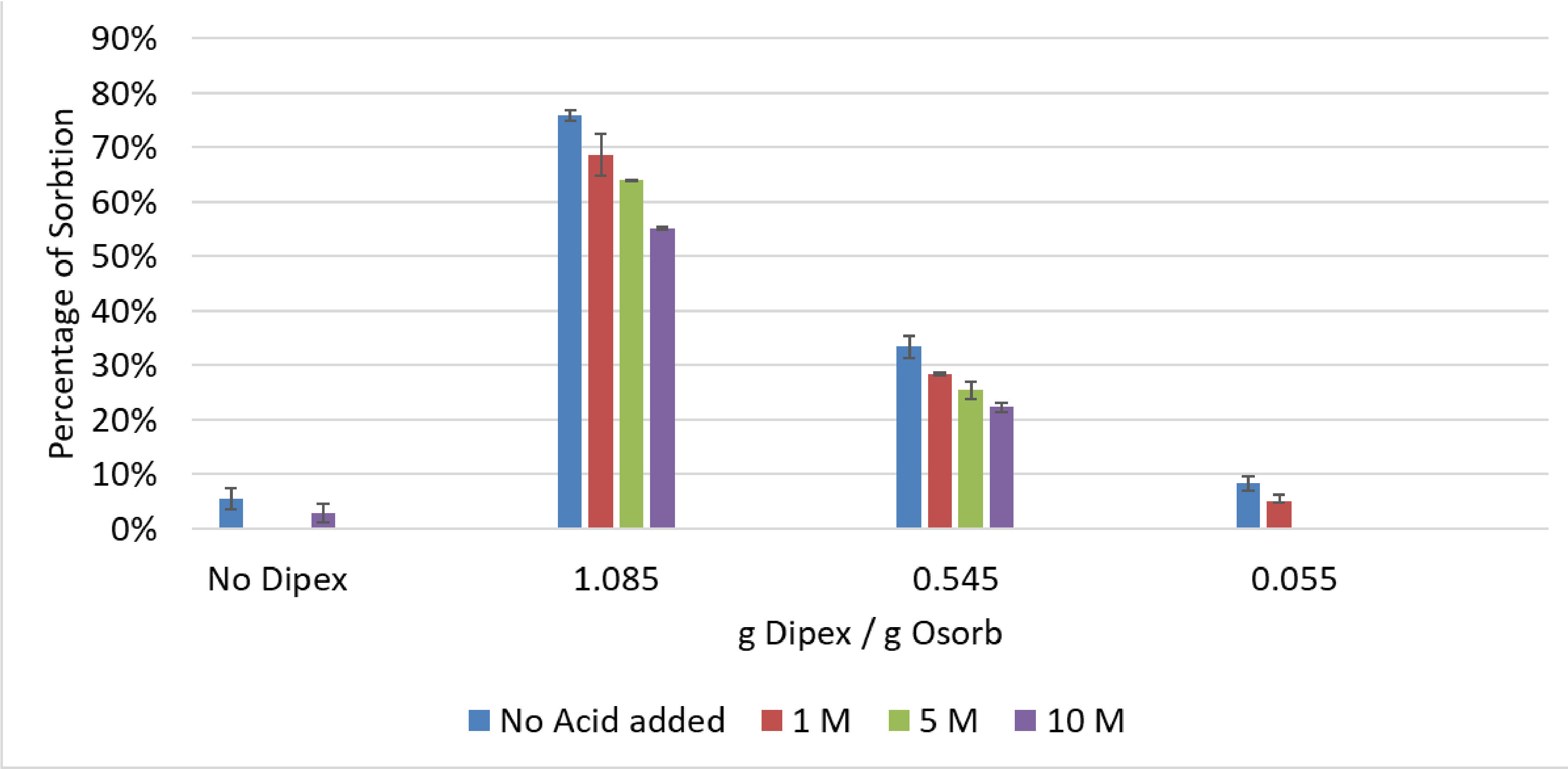


DIPEX/Osorb	mg Nd/g dry media
4.3	59.712
1.1	50.58
0.5	25.056
0.05	6.798

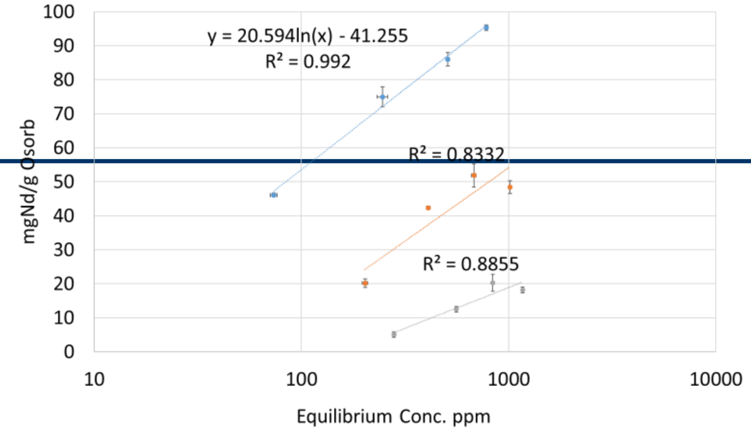


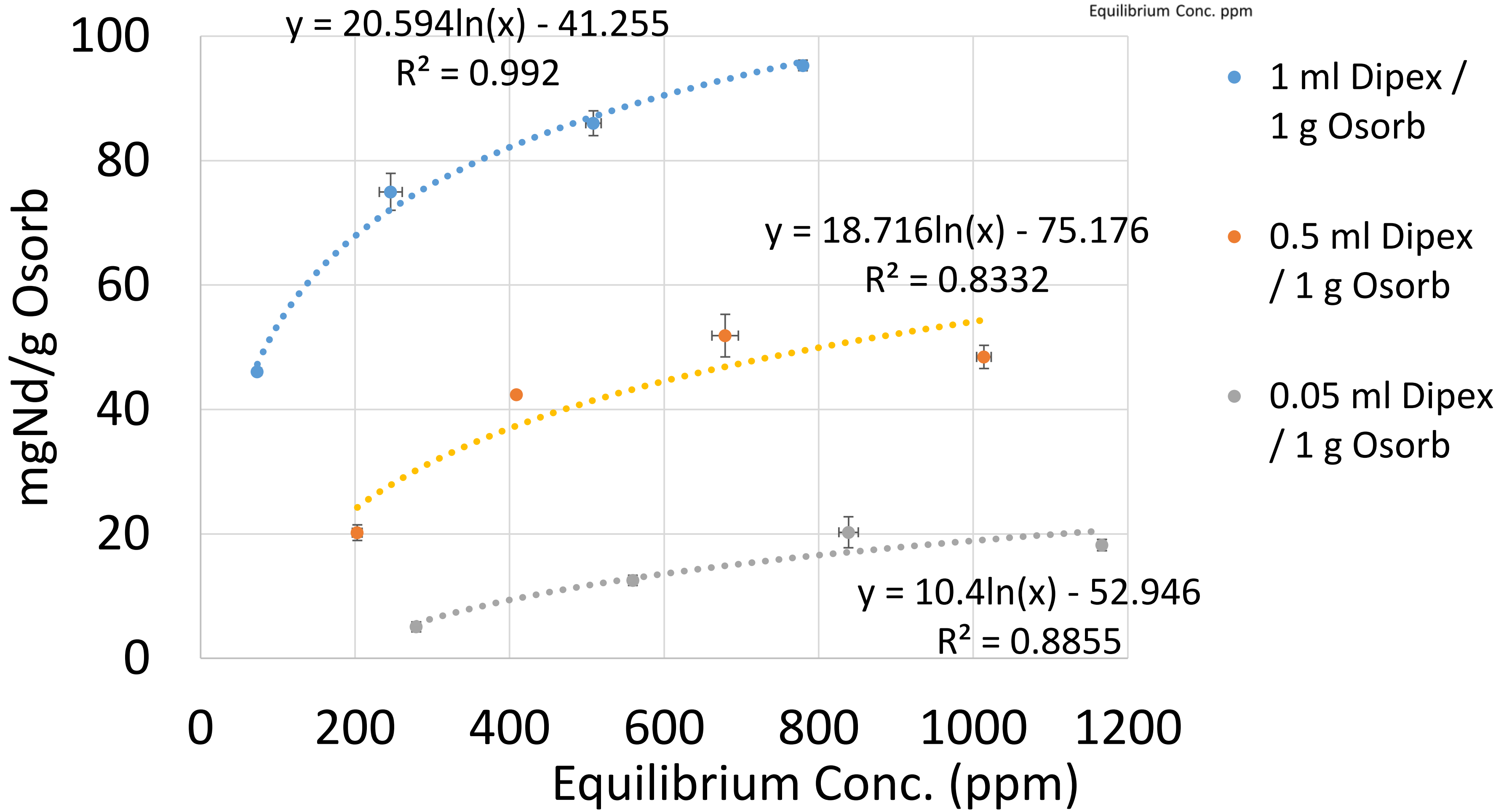
Nd sorption as function of HNO_3 conc (M)

- 300 ppm Nd (40 mL for 0.2 g media)

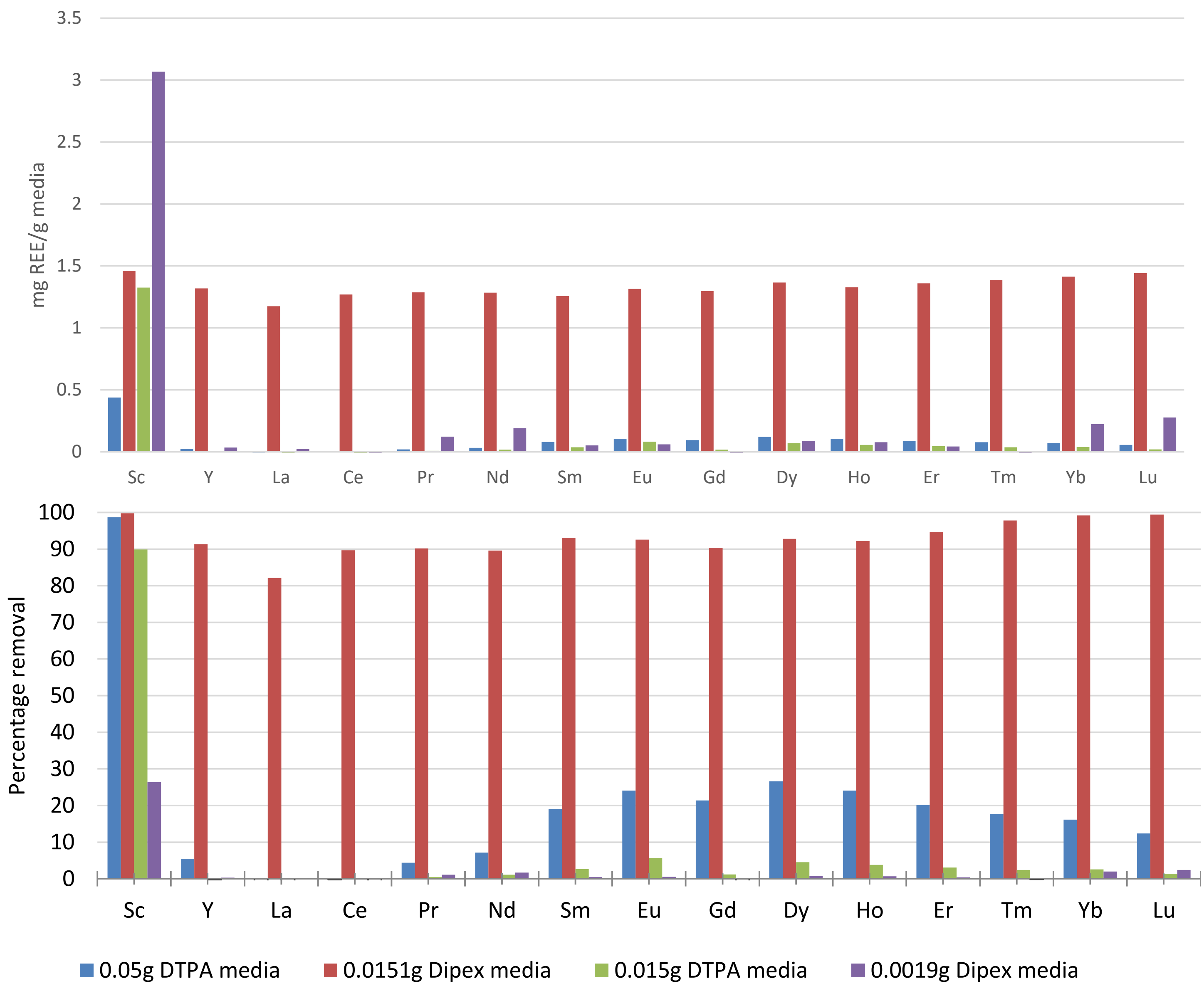


Sorption isotherms



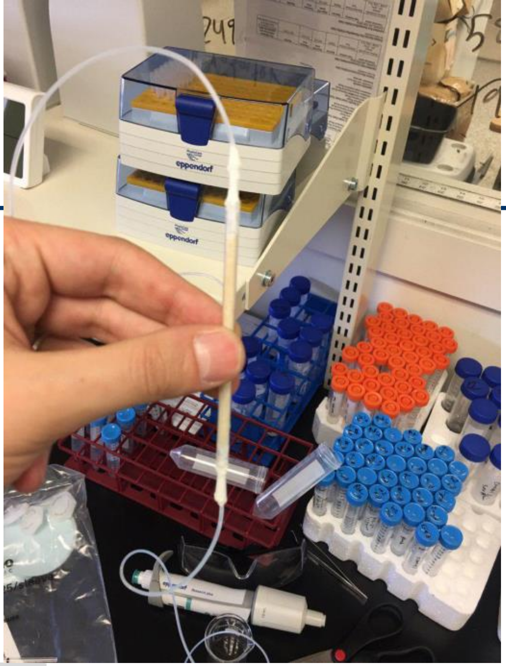


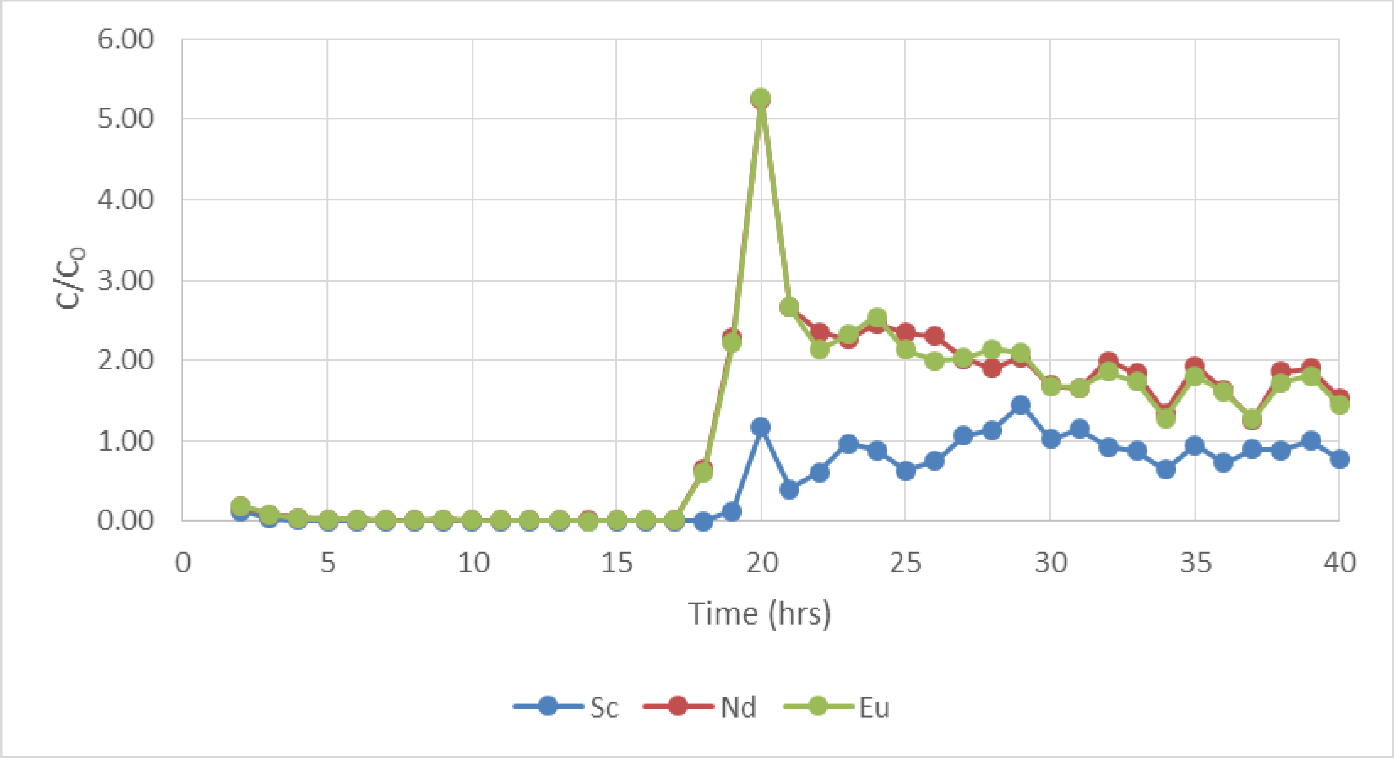
16 REEs; 2.5 ppm each (pH 2 HNO_3)



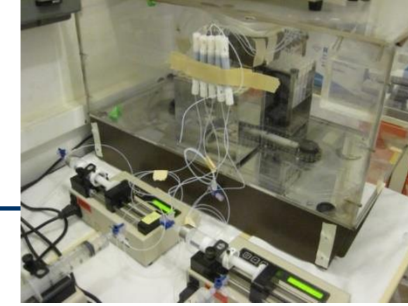
Breakthrough column

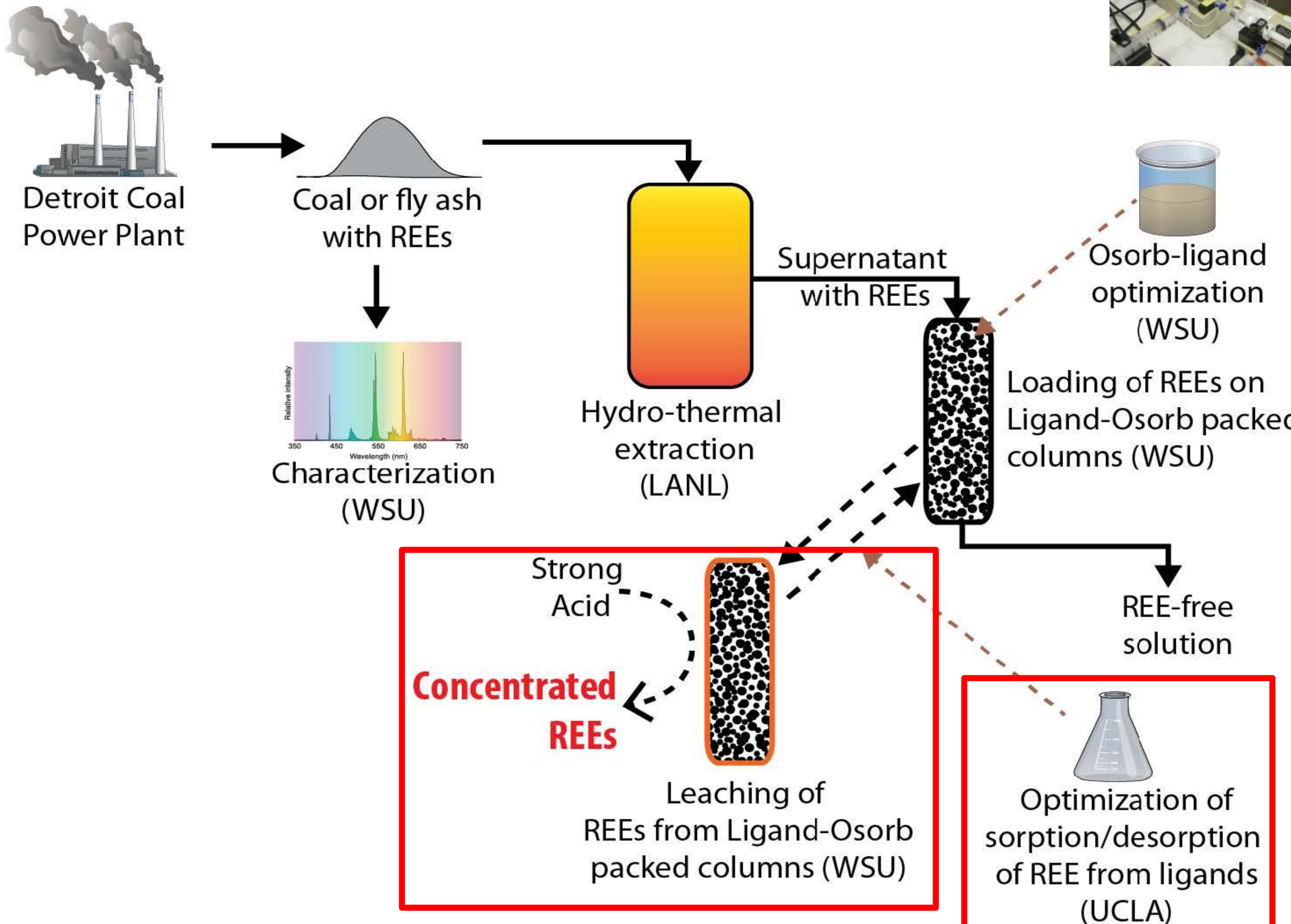
- 0.2 ml/h
- 0.075 g media
- Nd, Eu, and Sc (100 ppm each)





Project Flow-chart





Project Timeline

<table>
<tr><th>Task</th><th colspan="2">6 months</th><th colspan="2">12 months</th><th colspan="2">18 months</th></tr>
<tr><td>1</td><td colspan="4"></td><td></td><td></td></tr>
<tr><td>2</td><td colspan="4">Hydrothermal extraction</td><td></td><td></td></tr>
<tr><td>3</td><td colspan="4">Ligand selection</td><td></td><td></td></tr>
<tr><td>4</td><td></td><td colspan="3">Ligand attachment to OSORB</td><td></td><td></td></tr>
<tr><td>5</td><td></td><td colspan="5">Evaluate REE sorption</td></tr>
<tr><td>6</td><td></td><td colspan="5">Evaluate REE Recovery from solid phase</td></tr>
<tr><td>7</td><td></td><td></td><td colspan="4">Model ligand-OSORB-REE system components</td></tr>
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Milestone logs and measurements

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

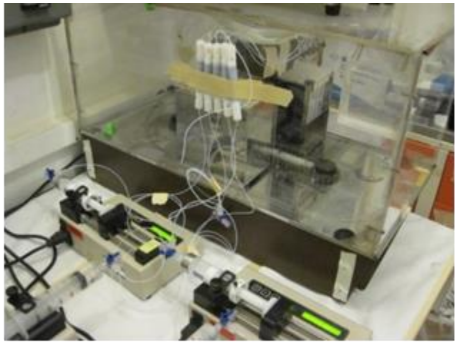
Future Work - Associate ligands to Osorb

1) Need to verify REE extraction efficiency from hydrothermal solutions

2) Test REE recovery from hydrothermal solutions

3) Column experiments for ligand-SOMS media prep

4) Stripping and precipitation to metal oxides



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Conclusions

- Successfully loaded ligands on organosilica by >400% (wt)
- Novel ligand derivatives have been synthesized, successfully loaded to Osorb, and have recovered Nd at pH 6 and 2
- More complex solution chemistry (and Fe competition) must be tested

Acknowledgement and Questions

- DOE/NETL grant #FE-0031565 (Maria Reidpath)
- Support from Oak Ridge National Lab
  - Ralph E. Powe Junior Faculty Enhancement Award
- LANL graduate staff (EES-14)
  - A. Strzelecki
- DTE and DTE Staff
  - Amanda Kosch, Kayla Maas, and Lisa Lockwood