

# 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

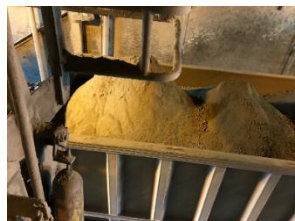
*Wayne State University*

S.K. Mohanty

*University of California-Los Angeles*

H. Boukhalfa, A. Migdisov

*Los Alamos National Laboratory*



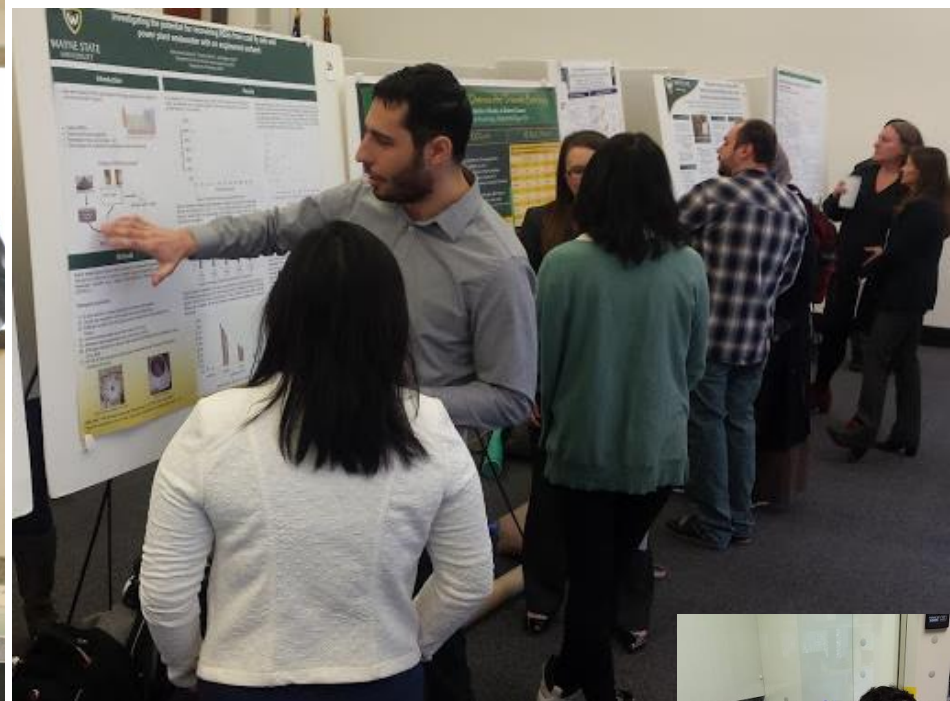
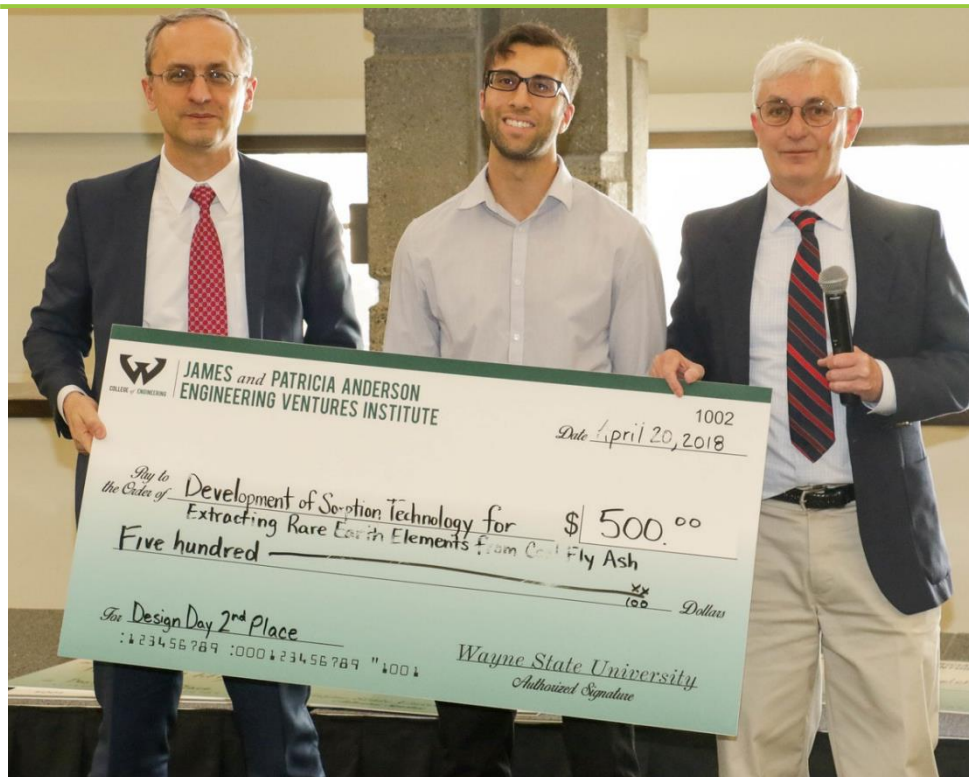
# Project Description and Objectives



## 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 (2<sup>nd</sup> 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

## Periodic Table of Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 <b>H</b> Hydrogen 1.00794	2 <b>He</b> Helium 4.002602																
3 <b>Li</b> Lithium 6.941	4 <b>Be</b> Beryllium 9.012182																
11 <b>Na</b> Sodium 22.98976928	12 <b>Mg</b> Magnesium 24.3050																
19 <b>K</b> Potassium 39.0983	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.955912	22 <b>Ti</b> Titanium 47.867	23 <b>V</b> Vanadium 50.9415	24 <b>Cr</b> Chromium 51.9961	25 <b>Mn</b> Manganese 54.938045	26 <b>Fe</b> Iron 55.845	27 <b>Co</b> Cobalt 58.933195	28 <b>Ni</b> Nickel 58.6934	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.723	32 <b>Ge</b> Germanium 72.64	33 <b>As</b> Arsenic 74.92160	34 <b>Se</b> Selenium 78.96	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 83.798
37 <b>Rb</b> Rubidium 85.4678	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.90585	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.90638	42 <b>Mo</b> Molybdenum 95.96	43 <b>Tc</b> Technetium (97.9072)	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.90550	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.8682	48 <b>Cd</b> Cadmium 112.411	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.710	51 <b>Sb</b> Antimony 121.760	52 <b>Te</b> Tellurium 127.60	53 <b>I</b> Iodine 126.90447	54 <b>Xe</b> Xenon 131.293
55 <b>Cs</b> Caesium 132.9054519	56 <b>Ba</b> Barium 137.327	57-71	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.94788	74 <b>W</b> Tungsten 183.84	75 <b>Re</b> Rhenium 186.207	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.217	78 <b>Pt</b> Platinum 195.084	79 <b>Au</b> Gold 196.966569	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.3833	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98040	84 <b>Po</b> Polonium (209)	85 <b>At</b> Astatine (209)	86 <b>Rn</b> Radon (222)
87 <b>Fr</b> Francium (223)	88 <b>Ra</b> Radium (226)	89-103	104 <b>Rf</b> Rutherfordium (261)	105 <b>Db</b> Dubnium (262)	106 <b>Sg</b> Seaborgium (266)	107 <b>Bh</b> Bohrium (264)	108 <b>Hs</b> Hassium (277)	109 <b>Mt</b> Meitnerium (268)	110 <b>Ds</b> Darmstadtium (271)	111 <b>Rg</b> Roentgenium (272)	112 <b>Uub</b> Ununbium (285)	113 <b>Uut</b> Ununtrium (284)	114 <b>Uuq</b> Ununquadium (289)	115 <b>Uup</b> Ununpentium (288)	116 <b>Uuh</b> Ununhexium (292)	117 <b>Uus</b> Ununseptium	118 <b>Uuo</b> Ununoctium (294)

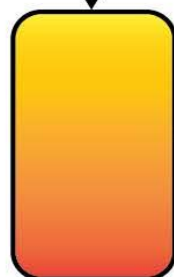
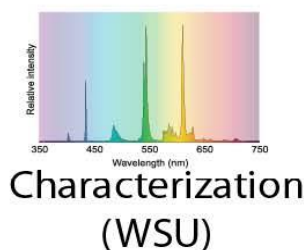
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

57 <b>La</b> Lanthanum 138.90547	58 <b>Ce</b> Cerium 140.116	59 <b>Pr</b> Praseodymium 140.90768	60 <b>Nd</b> Neodymium 144.242	61 <b>Pm</b> Promethium (145)	62 <b>Sm</b> Samarium 144.9127	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.92535	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.93032	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.93421	70 <b>Yb</b> Ytterbium 173.054	71 <b>Lu</b> Lutetium 174.967
89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.03806	91 <b>Pa</b> Protactinium 231.03688	92 <b>U</b> Uranium 238.02891	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (262)

# Project Flow-chart



Coal or fly ash  
with REEs



Hydro-thermal  
extraction  
(LANL)

Supernatant  
with REEs



Loading of REEs on  
Ligand-Osorb packed  
columns (WSU)

REE-free  
solution

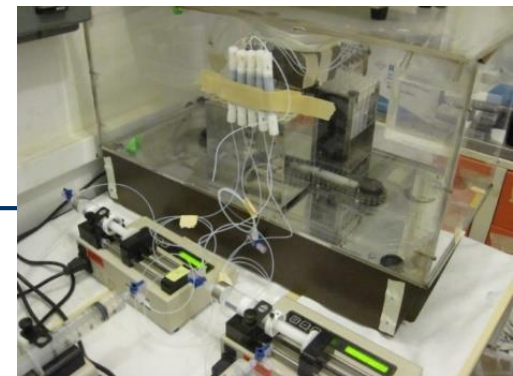
Strong  
Acid

**Concentrated  
REEs**



Leaching of  
REEs from Ligand-Osorb  
packed columns (WSU)

Optimization of  
sorption/desorption  
of REE from ligands  
(UCLA)



Osorb-ligand  
optimization  
(WSU)

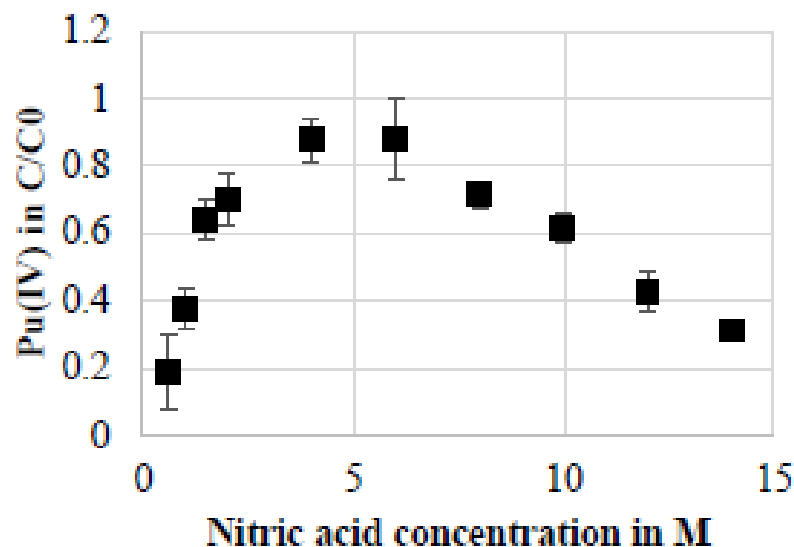
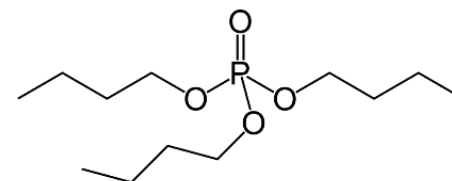


# Ligand-associated Osorb (TBP)

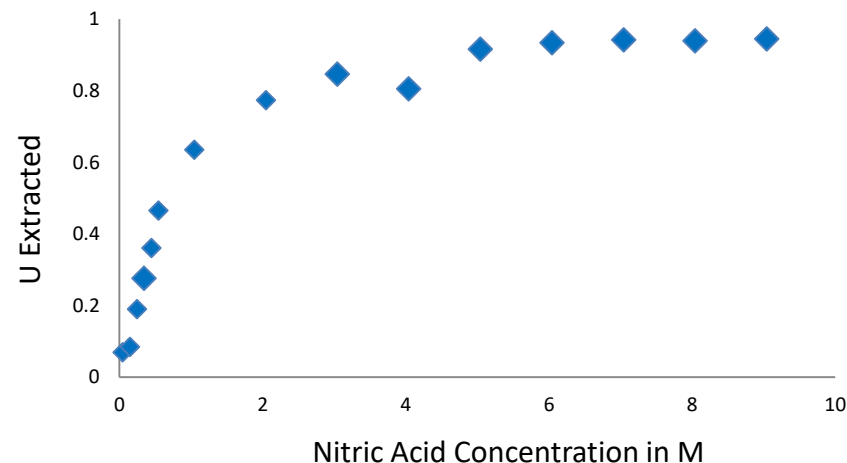


www.absmaterials.com

- Osorb® (ABS Materials, Wooster, OH)
  - Swellable organically modified silica (SOMS)
  - Bridged silane
  - ~600 m<sup>2</sup>/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



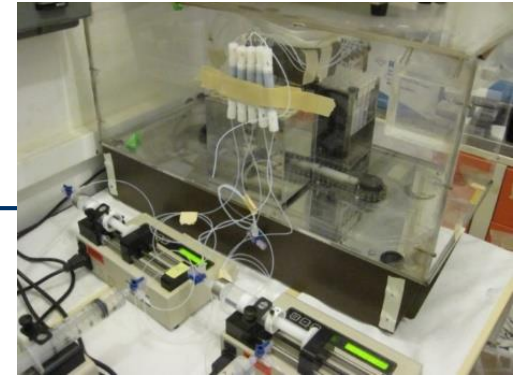
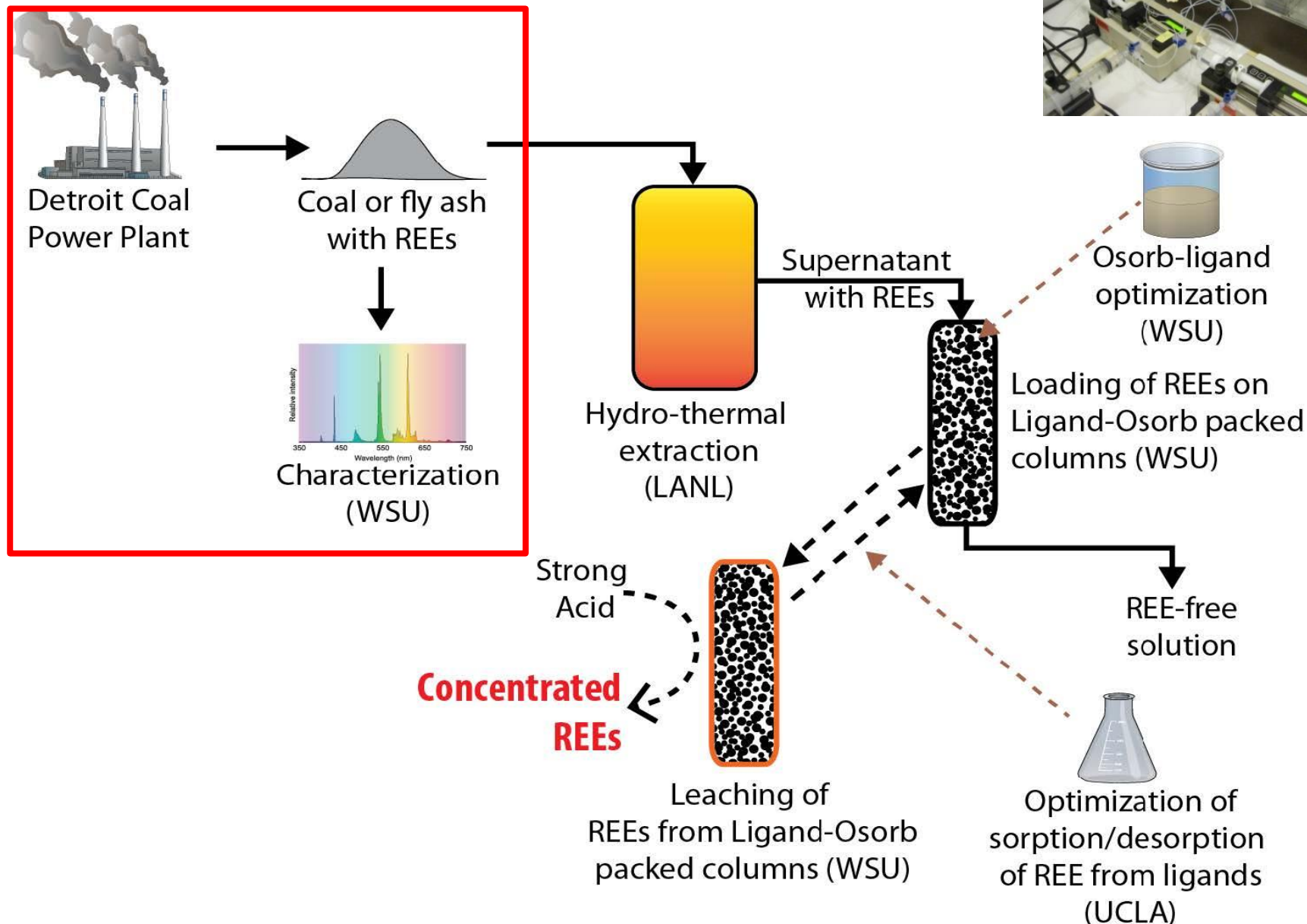
Extraction of Pu(IV) onto a polypropylene membrane with immobilized TBP



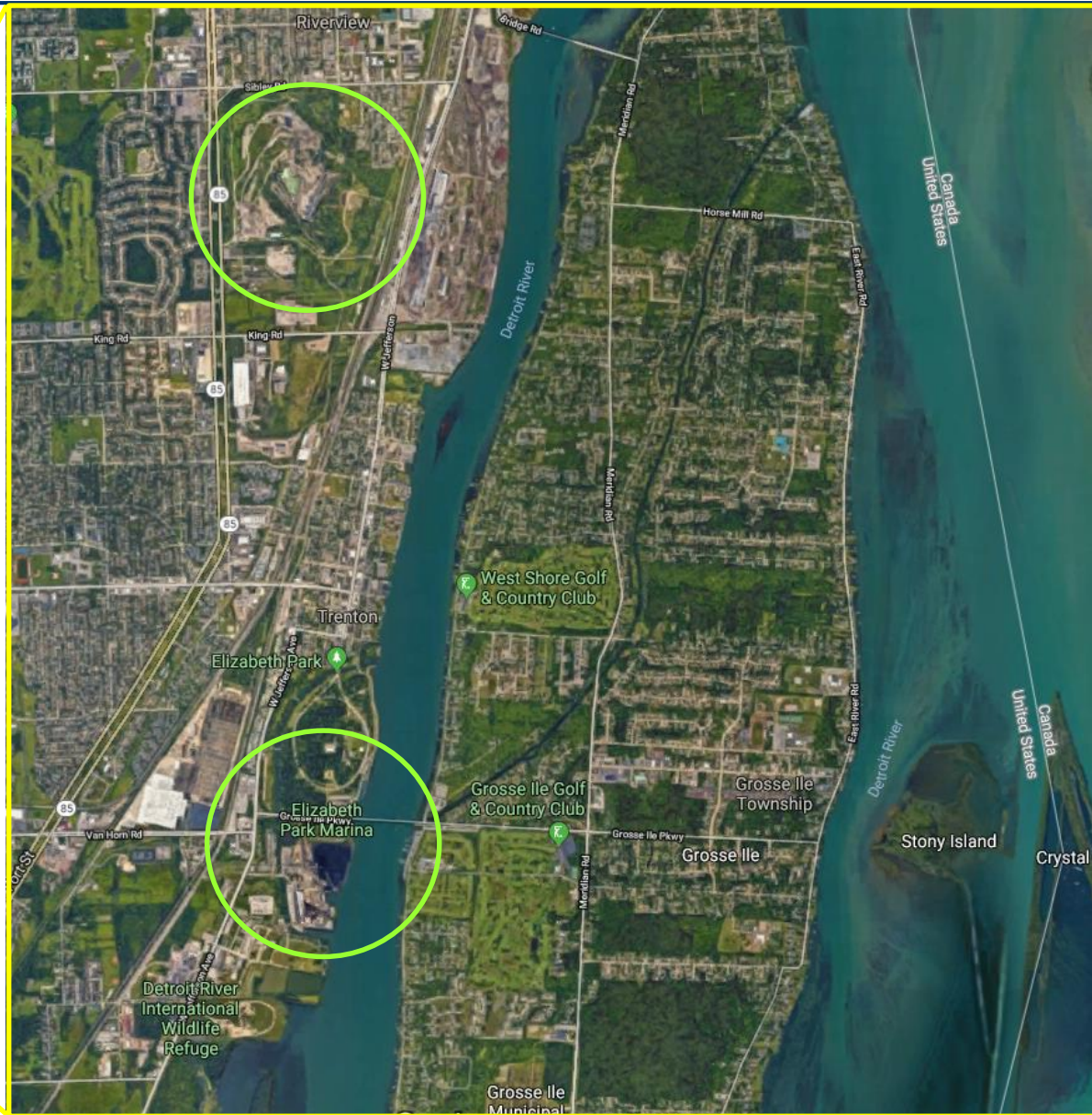
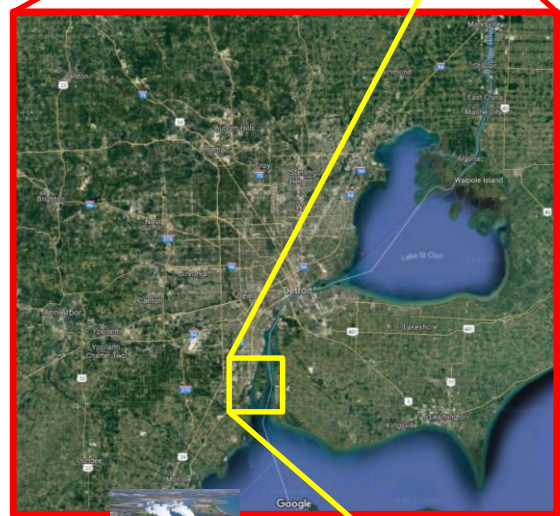
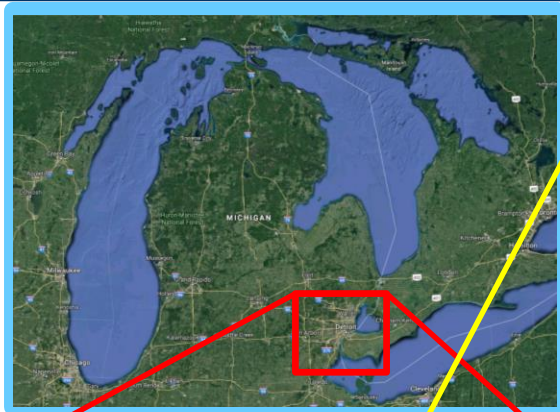
Uranium extraction with Osorb-TBP media  
-94% recovery from 1000 ppm U  
-Successful strip/cycle



# Project Flow-chart



# Detroit, MI



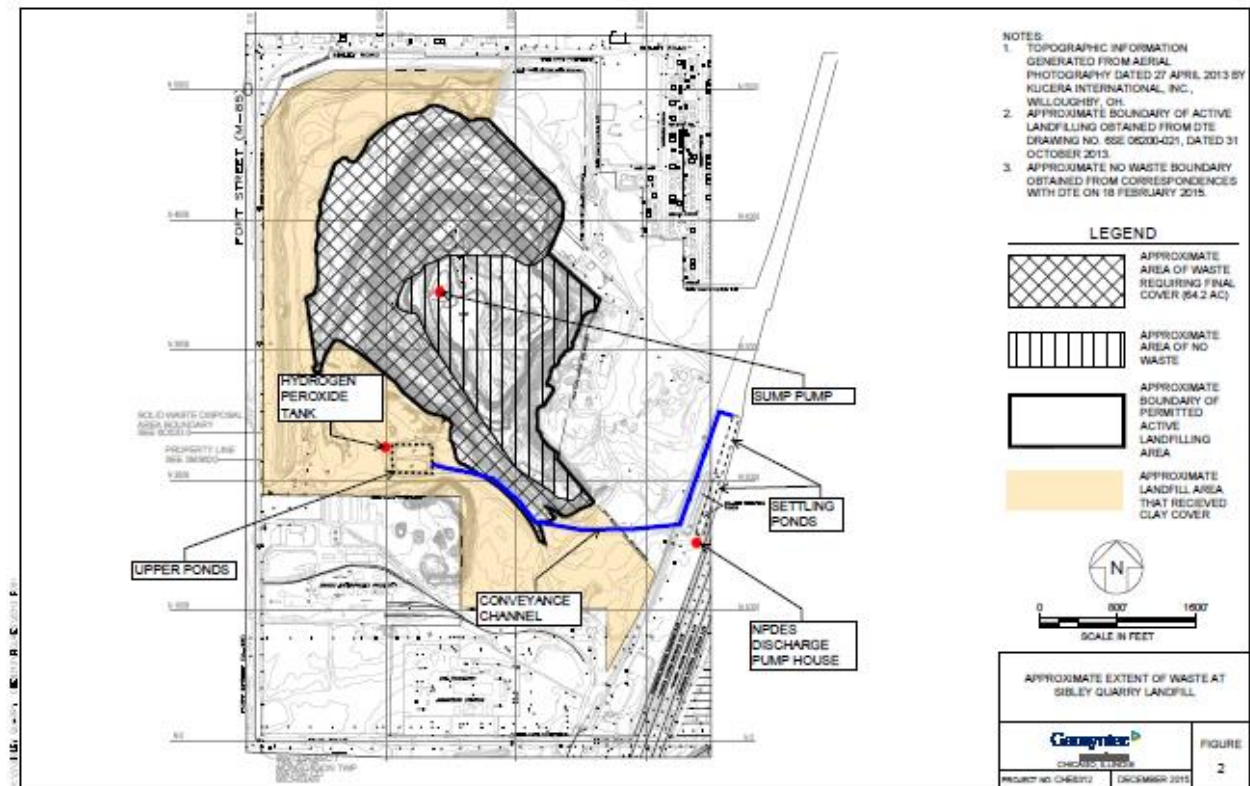
# Trenton Channel and Monroe Power Plants

- 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)

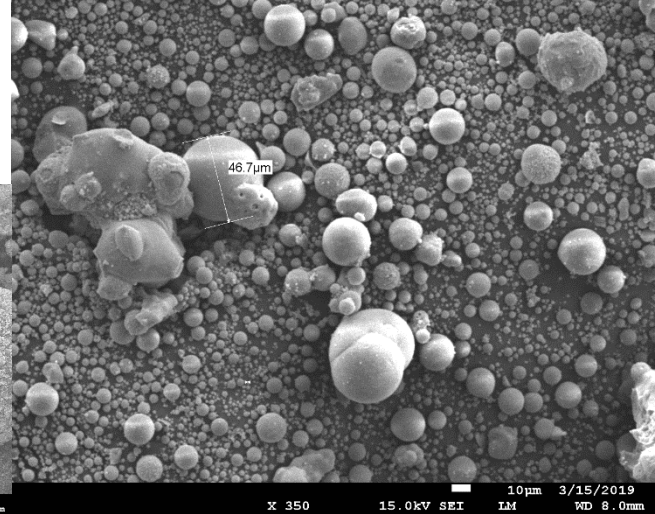
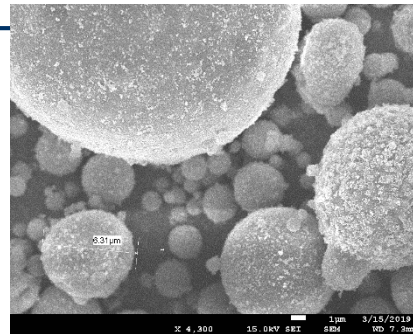
- ❑ 300' deep limestone quarry (mid 1800's)
- ❑ 1951 - DTE acquired (Type III Industrial Waste Landfill)
- ❑ 10,000-15,000 yd<sup>3</sup>/mo of CCR
- ❑ 1.5 MGD pumping rate to isolate CCR from groundwater



# Fly ash and sludge collection- Detroit, MI

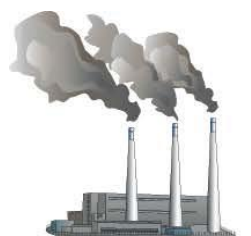


# REE content of coal blends

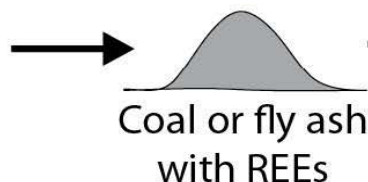


Sample ID	Sc 45 (ppm)	Ce 140 (ppm)	Dy 164 (ppm)	Er 166 (ppm)	Eu 153 (ppm)	Ho 165 (ppm)	La 139 (ppm)	Lu 175 (ppm)	Nd 142 (ppm)	Pr 141 (ppm)	Sm 152 (ppm)	Gd 158 (ppm)	Tb 159 (ppm)	Tm 169 (ppm)	Yb 174 (ppm)	Total minus Y (ppm)	REE (ppm)	Th 232 (ppm)
<u>Trenton Channel, Detroit</u>	NA	100.21	7.16	4.50	2.49	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
<u>WSU-1A (Monroe 75/25)</u>	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
<u>WSU-1B (Monroe 70/15/15)</u>	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

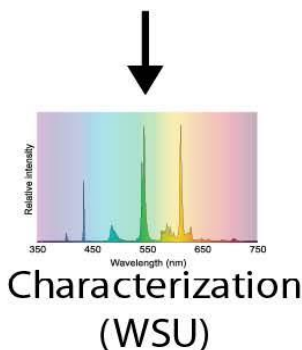
# Project Flow-chart



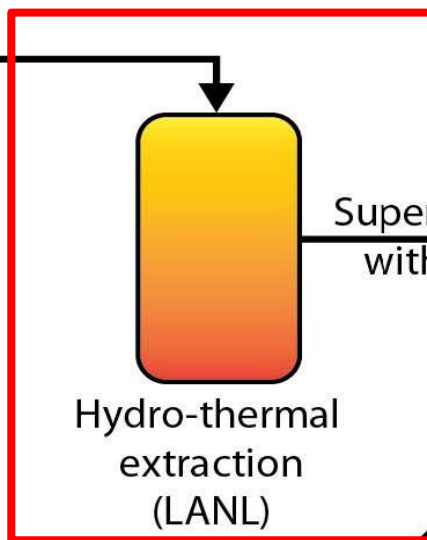
Detroit Coal Power Plant



Coal or fly ash with REEs

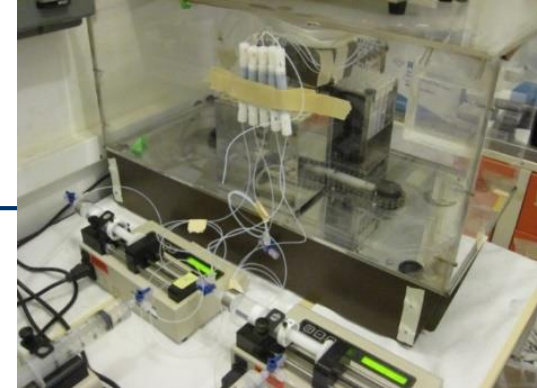


Characterization (WSU)



Hydro-thermal extraction (LANL)

Supernatant with REEs



Osorb-ligand optimization (WSU)



Loading of REEs on Ligand-Osorb packed columns (WSU)

REE-free solution

Strong Acid

**Concentrated REEs**



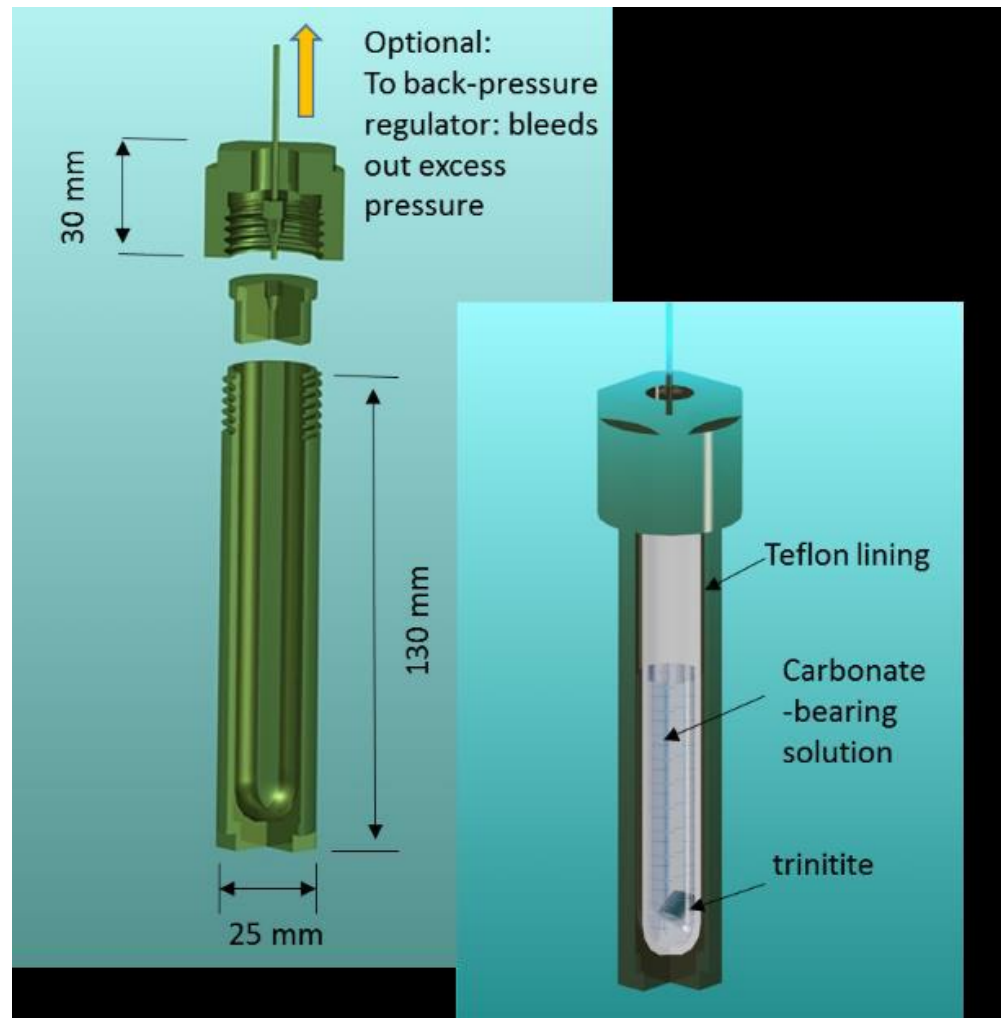
Leaching of REEs from Ligand-Osorb packed columns (WSU)



Optimization of sorption/desorption of REE from ligands (UCLA)

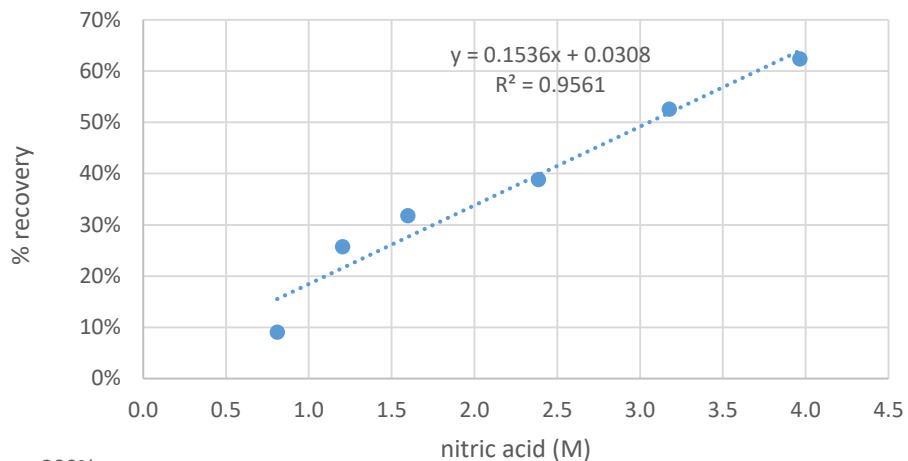
# Hydrothermal Extraction

- Artas Migdisov and Hakim Boukhalfa (LANL)
- Optimize variables
  - T (150-350 °C)
    - Isothermal/variable
  - Ligand system
    - Cl, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>
  - Leaching conditions
    - pH, time
  - Quenching conditions
    - Cooling cycle, pH adj.
- Compare to HF digestion
  - DTE ash and NIST SRM 1633C

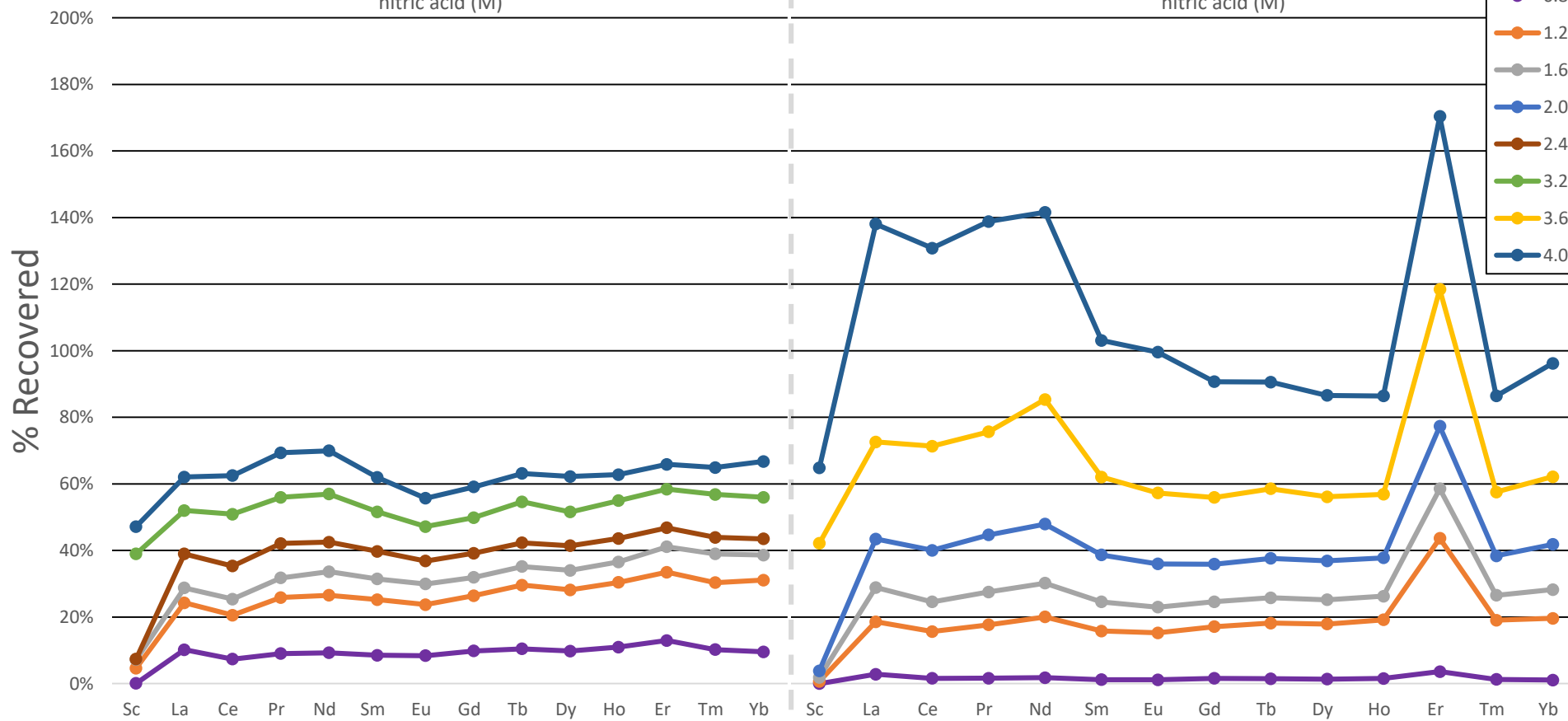
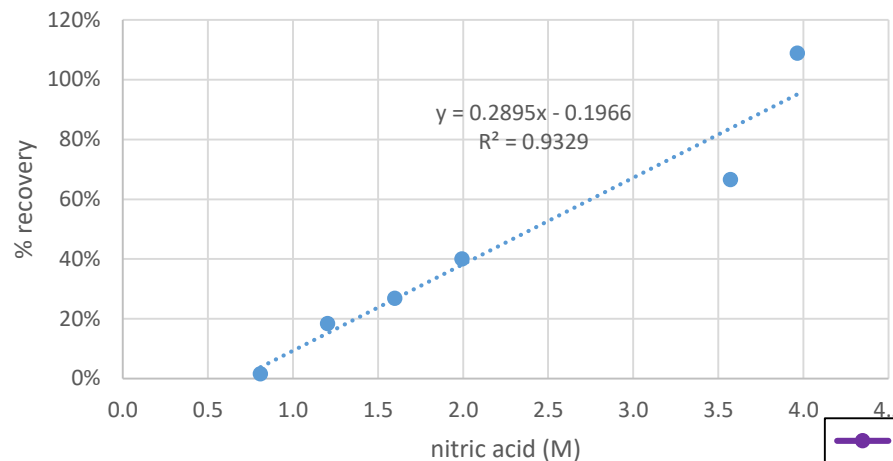




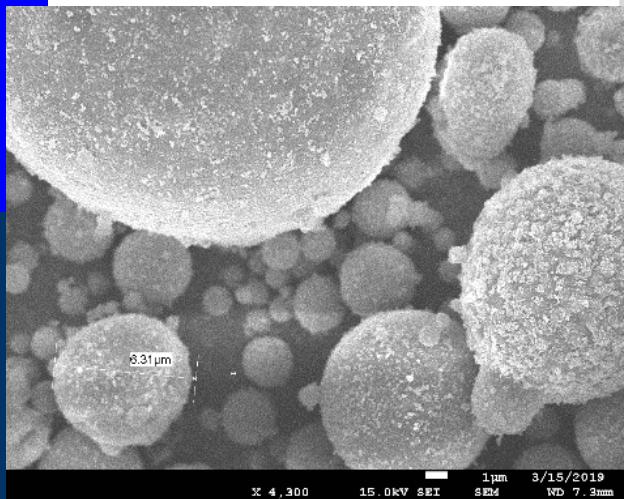
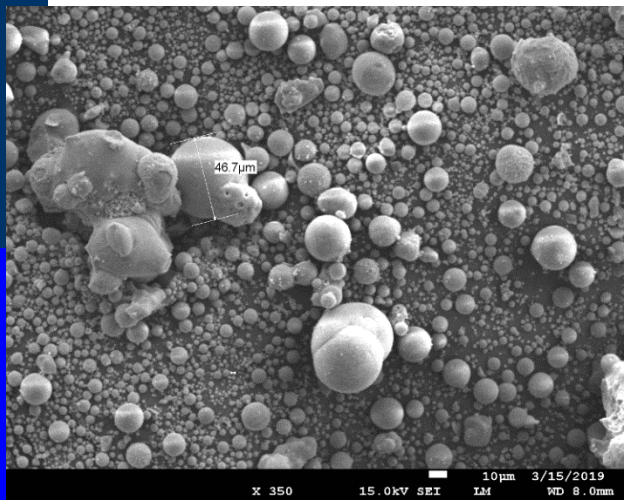
### Nitric acid only



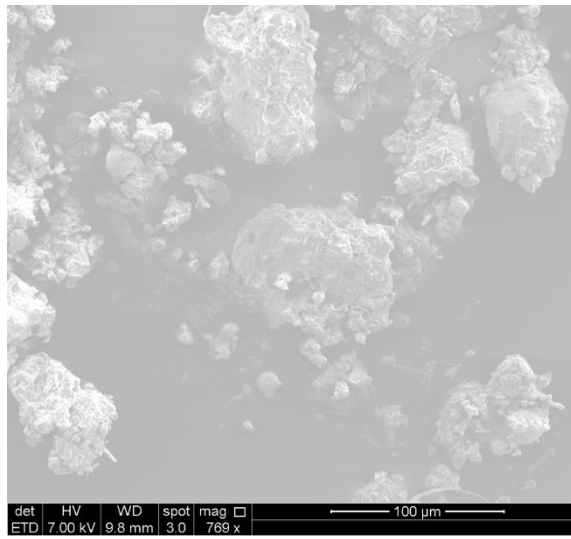
### Hydrothermal + Nitric acid



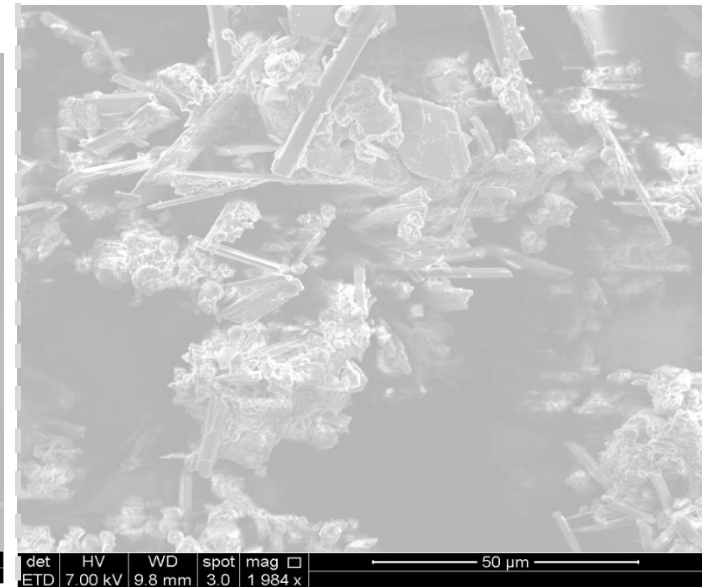
# SEM verification of alteration



**Unaltered Ash**



**Hydrothermally Altered Ash**

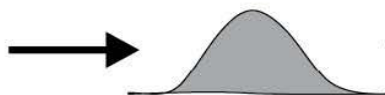


**Hydrothermally Altered Ash after acid leached**

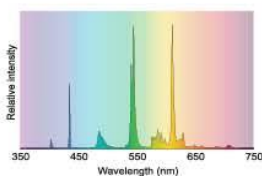
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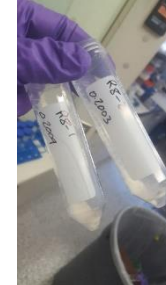
**Concentrated REEs**



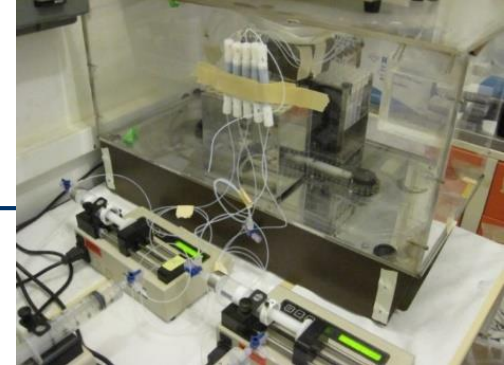
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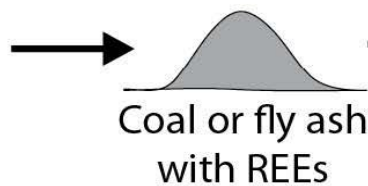
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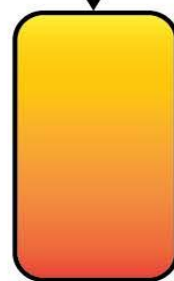
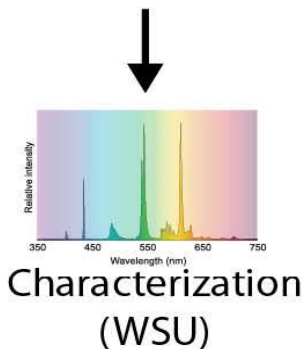
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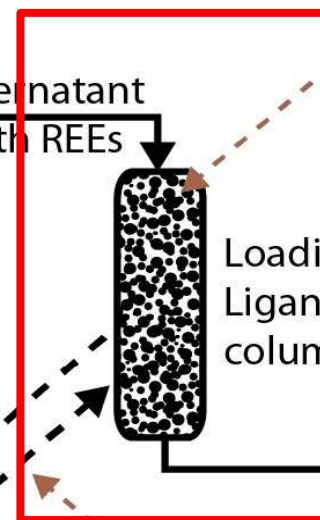


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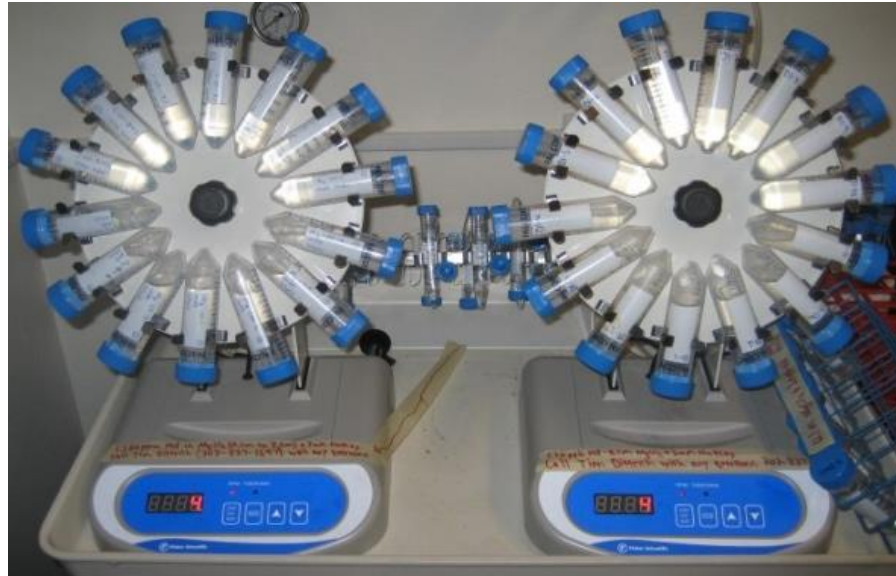
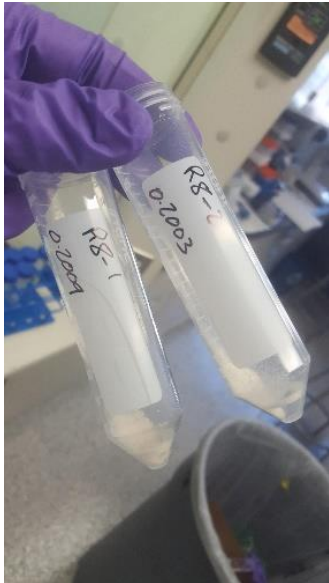
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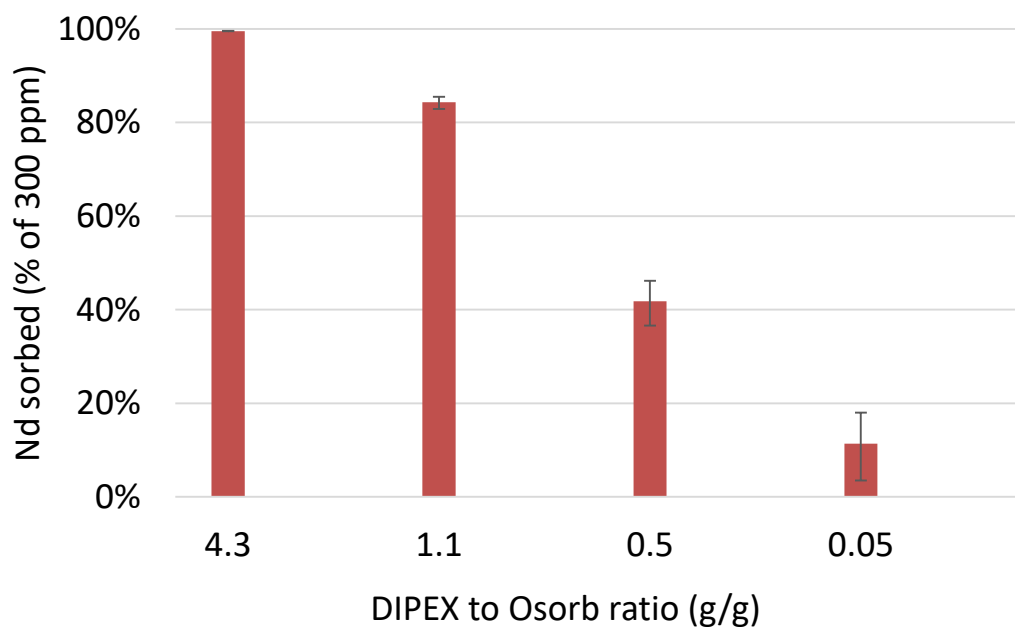
# Neodymium sorption

- 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<sub>2</sub> collision gas)

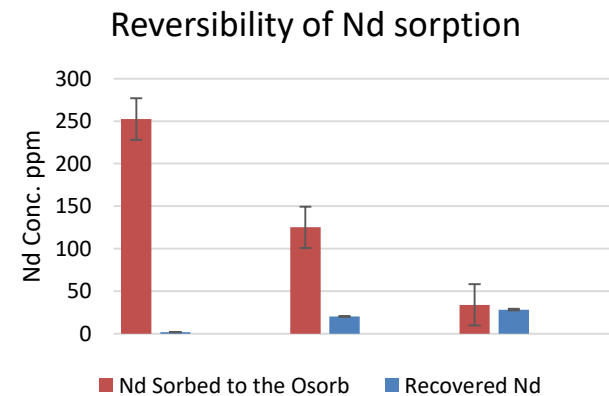


# Nd sorption to DIPEX-Osorb

- 300 ppm Nd in pH 2 HNO<sub>3</sub>
- 40 mL per 0.2 g media
- No competing ions (e.g., Fe<sup>3+</sup>, Al<sup>3+</sup>)

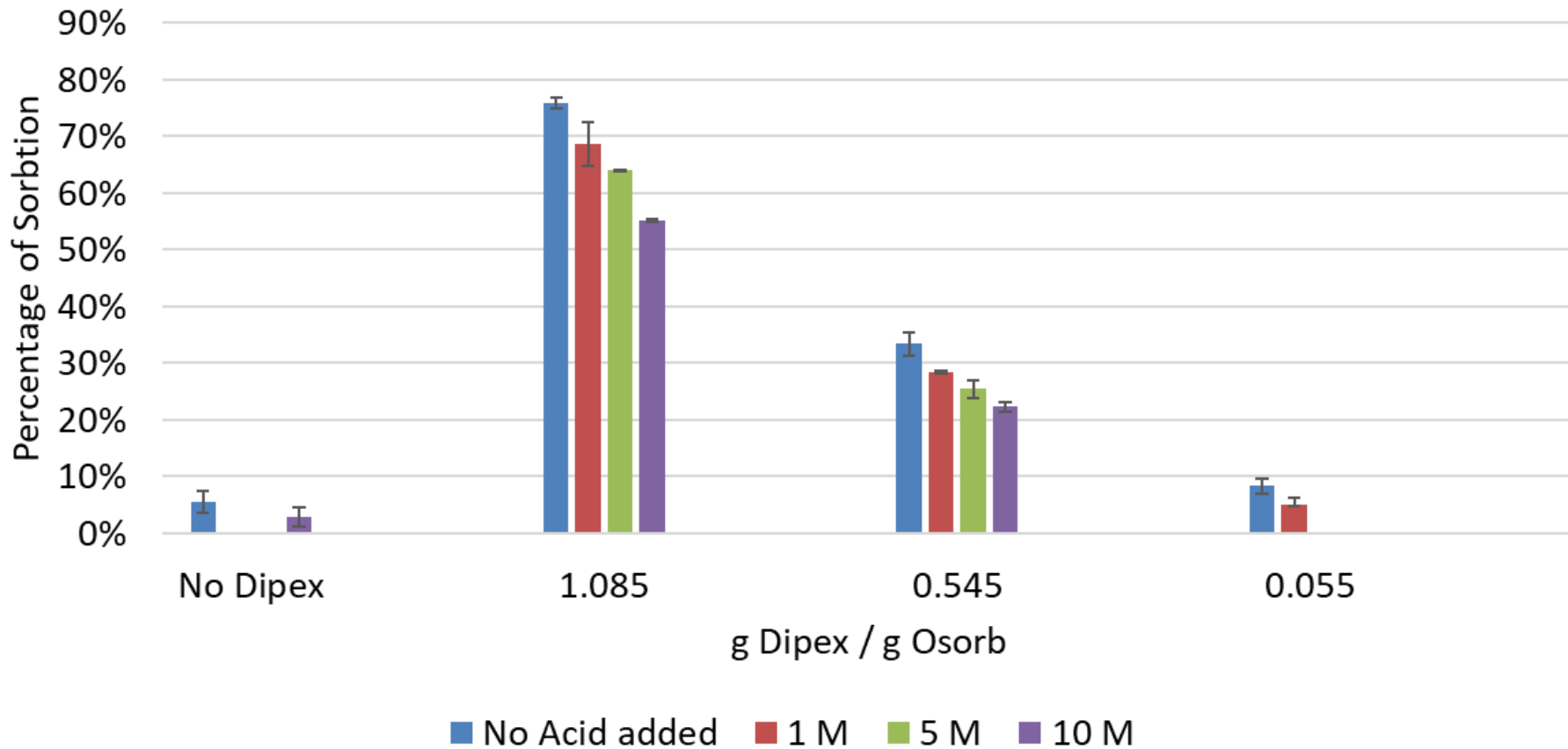


DIPEX/Osorb	mg Nd/g dry media
4.3	59.712
1.1	50.58
0.5	25.056
0.05	6.798

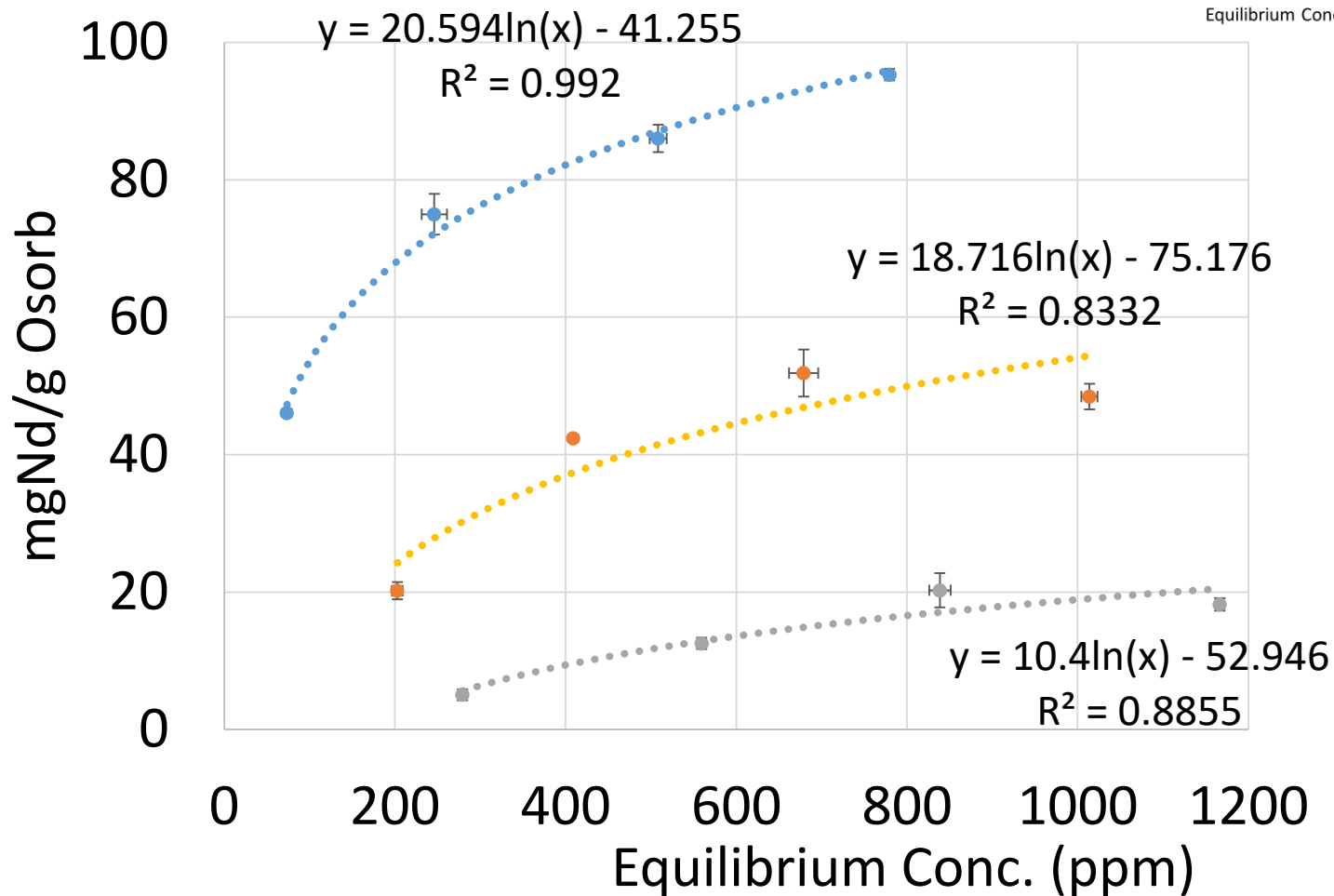
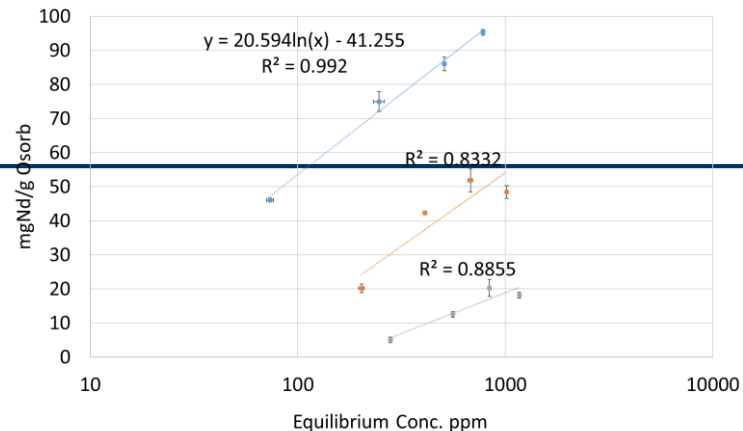


# Nd sorption as function of HNO<sub>3</sub> conc (M)

□ 300 ppm Nd (40 mL for 0.2 g media)



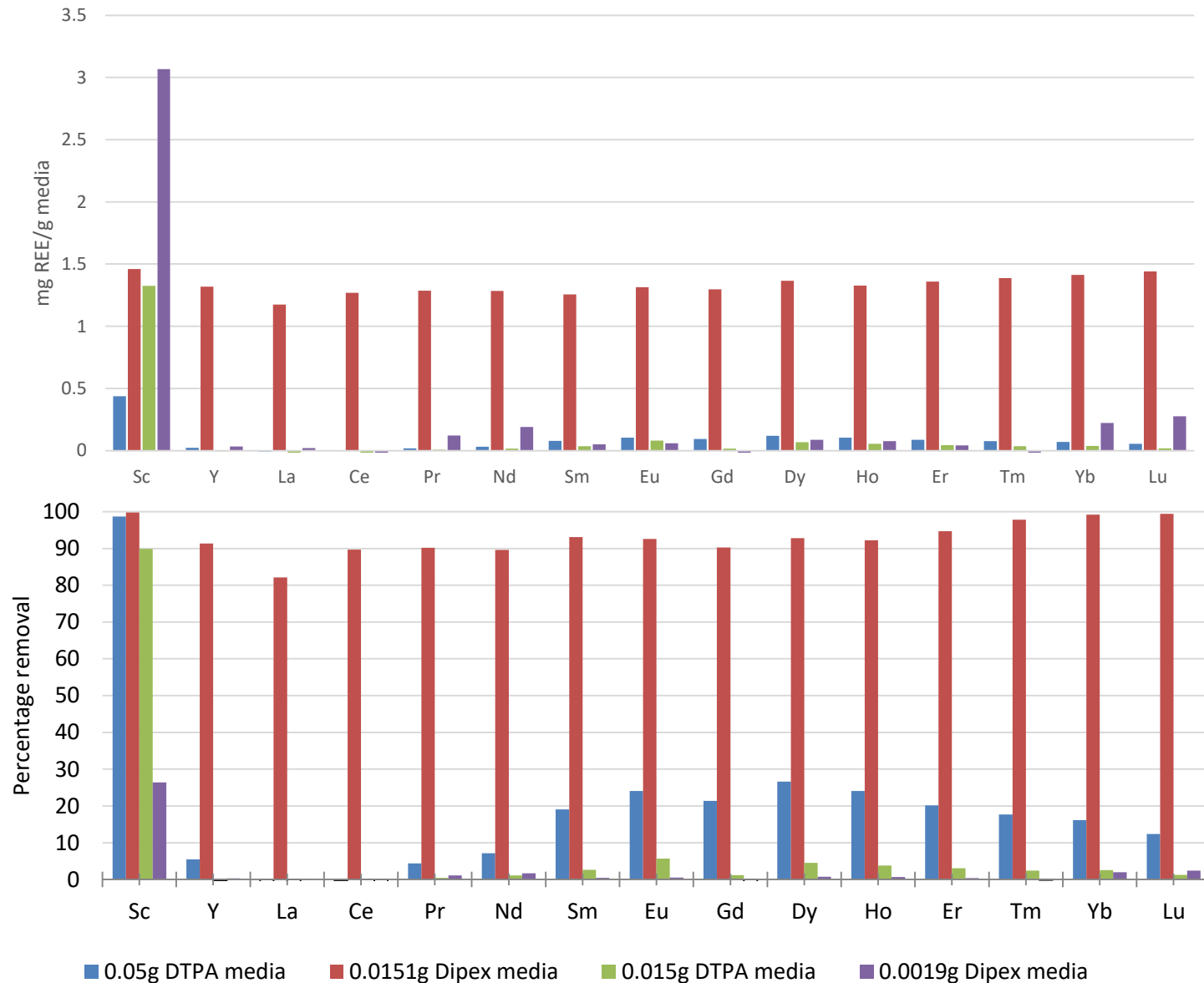
# Sorption isotherms



- 1 ml Dipex / 1 g Osorb
- 0.5 ml Dipex / 1 g Osorb
- 0.05 ml Dipex / 1 g Osorb

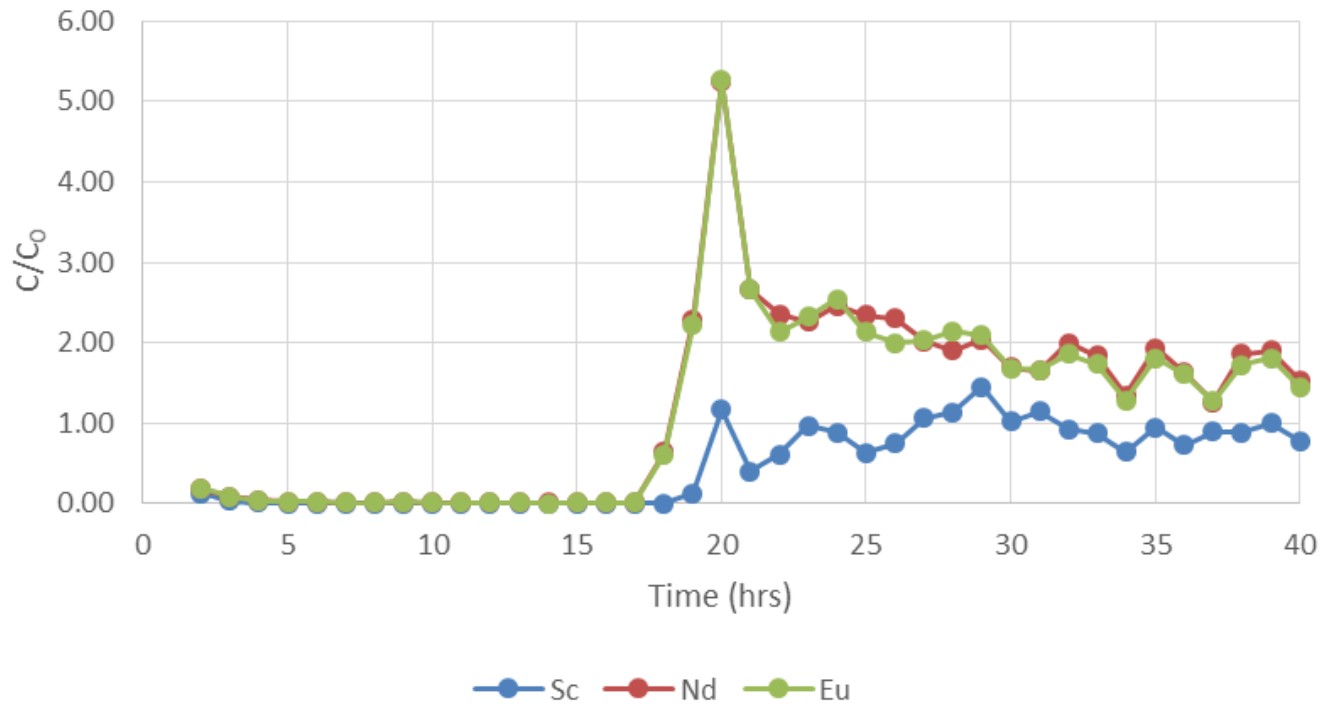


# 16 REEs; 2.5 ppm each (pH 2 HNO<sub>3</sub>)

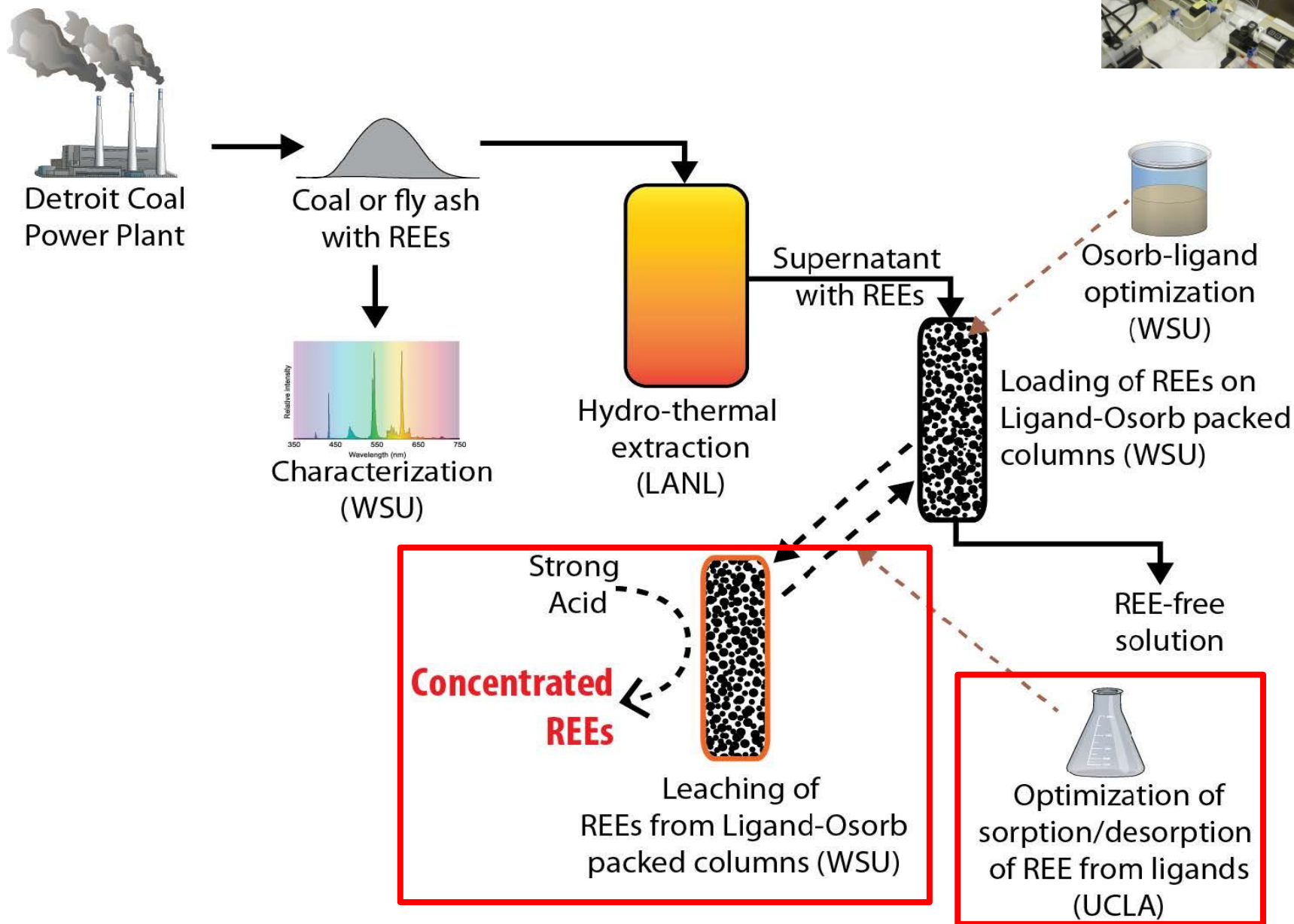


# Breakthrough column

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



# Project Flow-chart



# Project Timeline

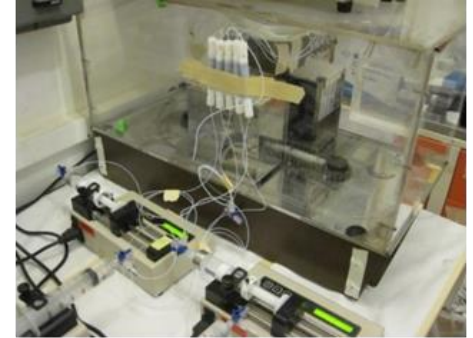
Task	0-6 months	6-12 months	12-18 months	18-24 months
1	Hydrothermal extraction			
2	Ligand selection			
3		Ligand attachment to OSORB		
4		Evaluate REE sorption		
5		Evaluate REE Recovery from solid phase		
6		Model ligand-OSORB-REE system components		
7				

# 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	Boukhalifa & Migdisov
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



# Conclusions

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- 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)
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- DTE and DTE Staff
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