Rare earth recovery for clean technologies

Application of Biosorption for Rare Earth Recovery from Coal Byproducts

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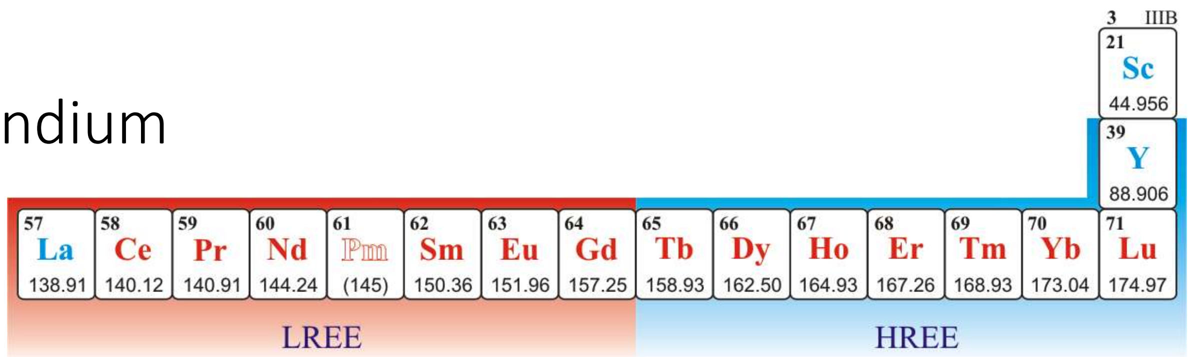
Rare Earth Elements are in high demand and there is an urgent need for domestic production

- Lanthanides + yttrium + scandium



- Critical materials for electronics, renewable energy, and defense industries




- Unstable global supply market for REEs

Project Goal

To develop a biosorption technology for rare earth recovery that is cost-effective and environmental friendly

Post-combustion ash

- 120 M tons /yr production in US
- 45% recycled (mostly cement)
- Remaining 55% landfilled
- Contaminate source (As, Hg, Se, Cr, Pb)
- Relatively high REE (300- 500 ppm)

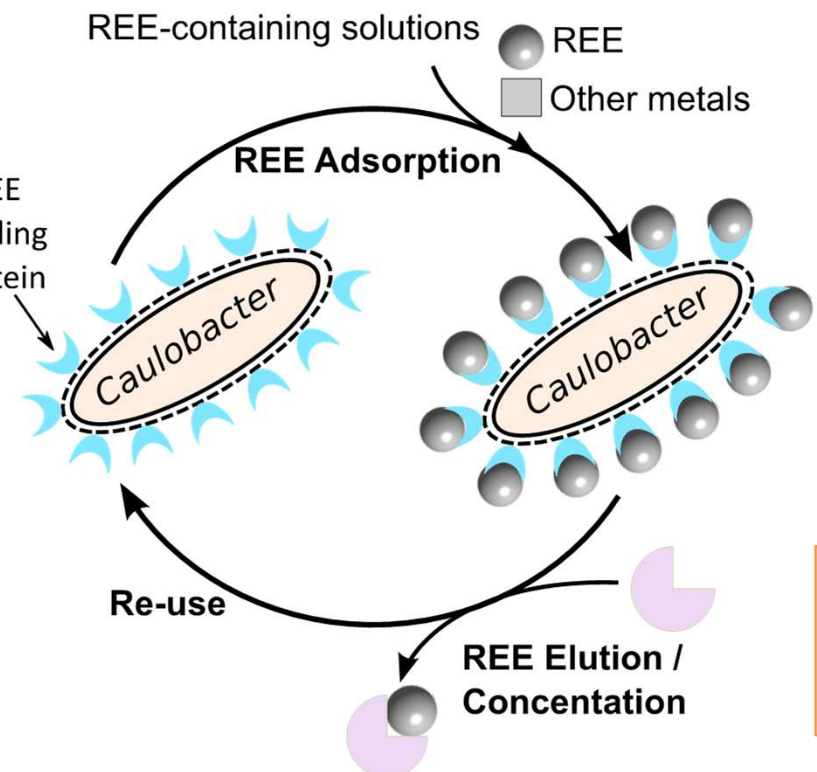
Pre-combustion coal byproducts

- Less well-characterized
- REE content varies greatly
- Ion-adsorption clays (easier to leach)

Provides a case study into the use of bioengineered microbes to extract useful elements from coal byproducts

CMI: a selective adsorption approach with bioengineered REE-adsorbing microbes

Step 1:
Bioengineer microbes

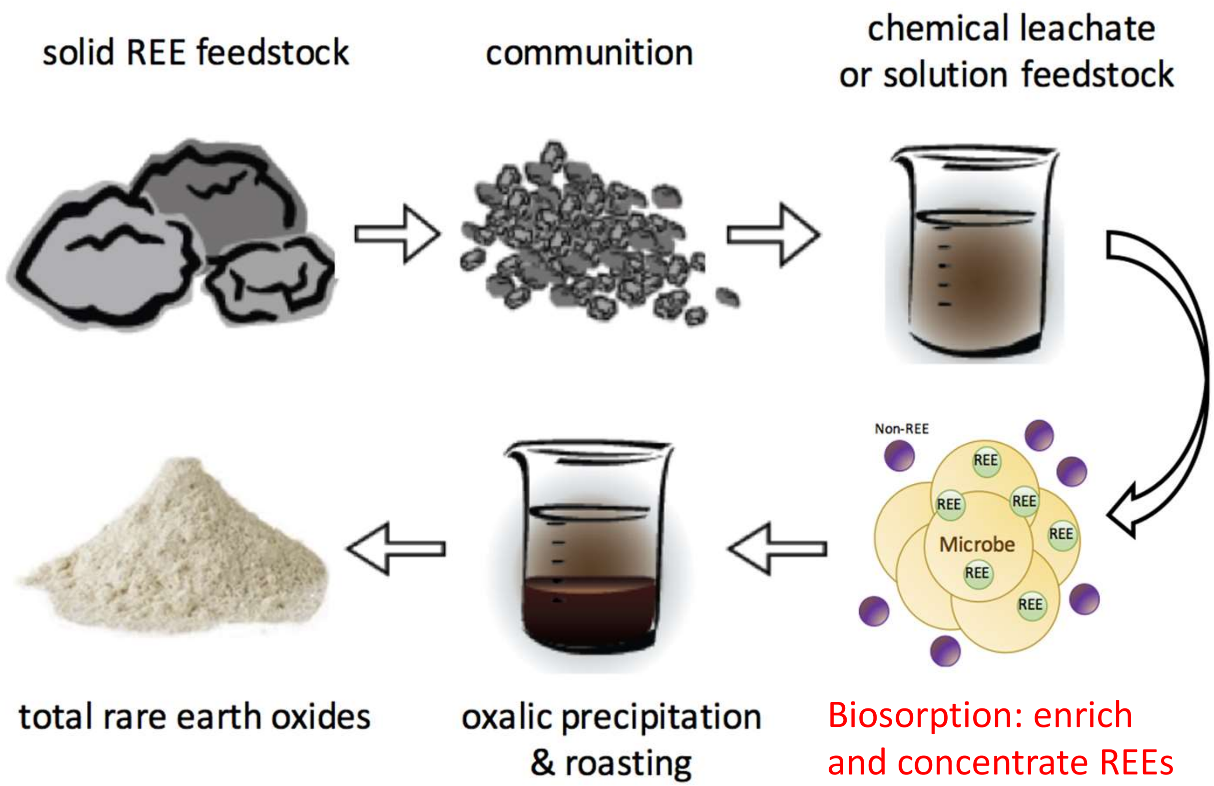


Step 2:
Rare earth biosorption

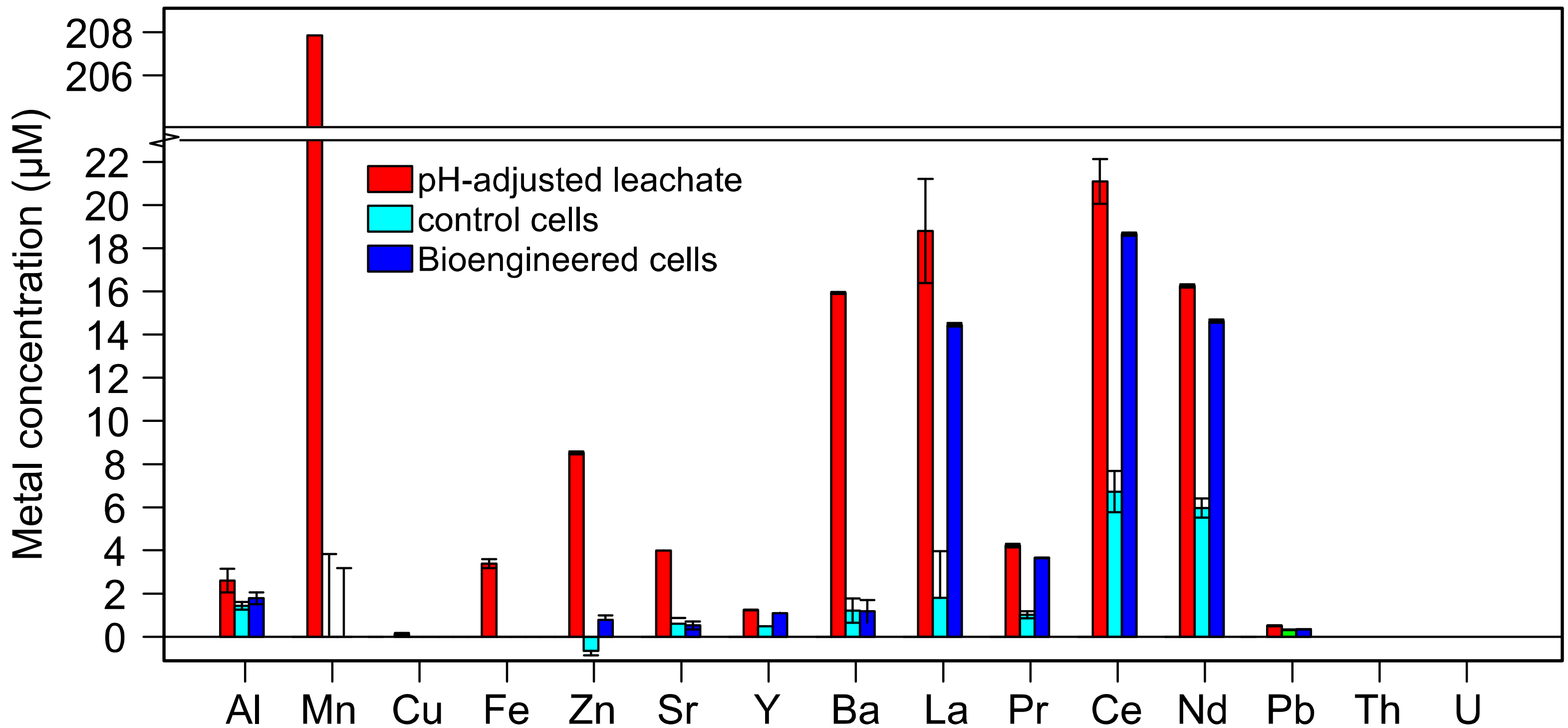
Step 3:
Rare earth recovery

Leverages previous work funded by Critical Materials Institute, Patent Pending

Enable usage of low-grade REE sources for downstream REE purification

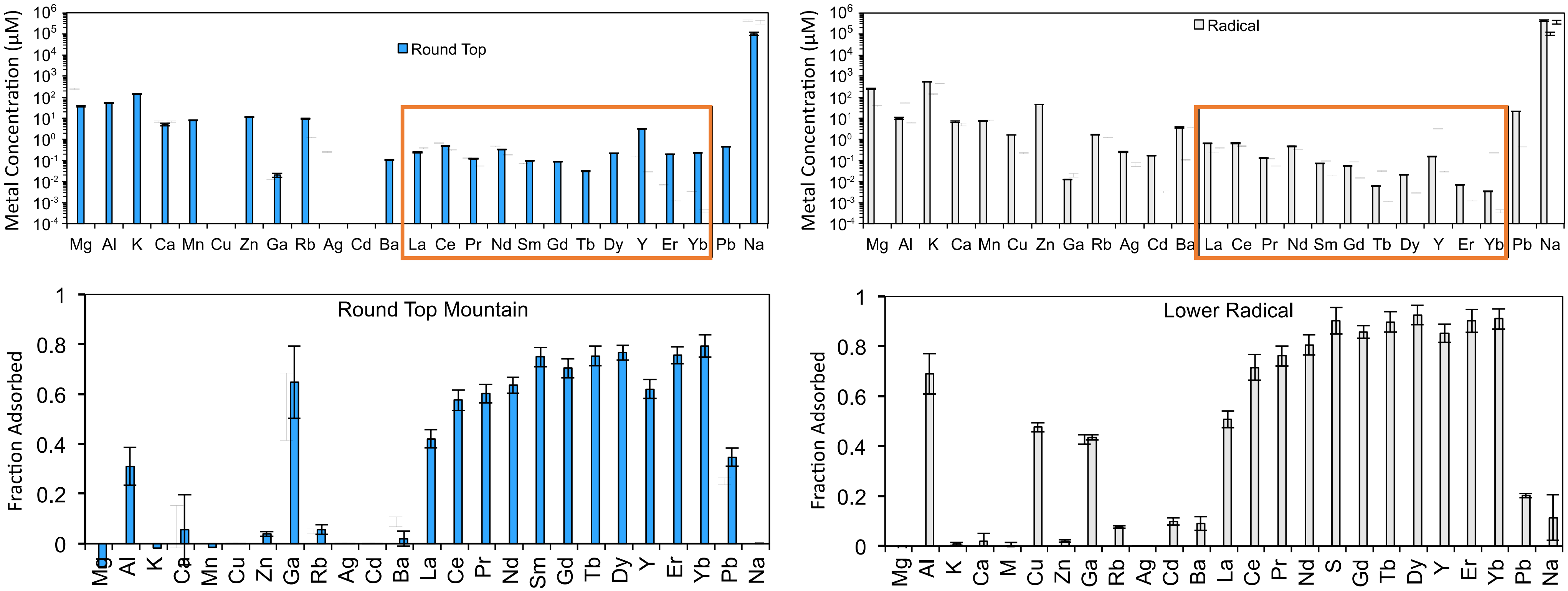


CMI: Bioengineered microbe outperforms control strain tested with sediment samples from Bull Hill



Park *et al*, *Environ Sci Technol,* 2016, *50* (5), 2735-42

CMI: Biosorption shows high selectivity for REEs with mine tailing leachates



Main objectives of TCF and FWP

Improve scalability: develop cell immobilization strategies to enable flow through operations

Microbial systems engineering ⟷ Chemical process engineering

- *Caulobacter* biofilms (TCF)
- Designer *E. coli* Biofilm (FWP)

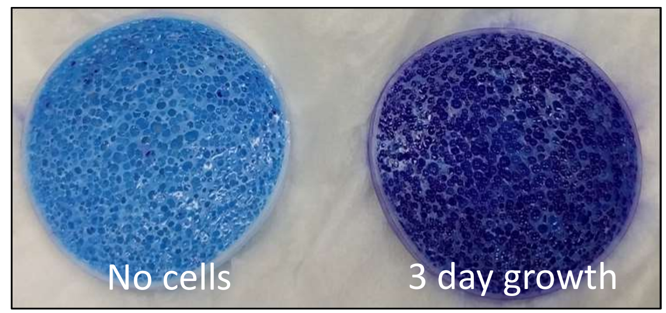
- Column chromatograph (TCF)
- Airlift bioreactor (FWP)

TCF tasks

- Test and compare surface attachment vs polymer embedding for cell immobilization;
- Conduct and compare basic economic predictions

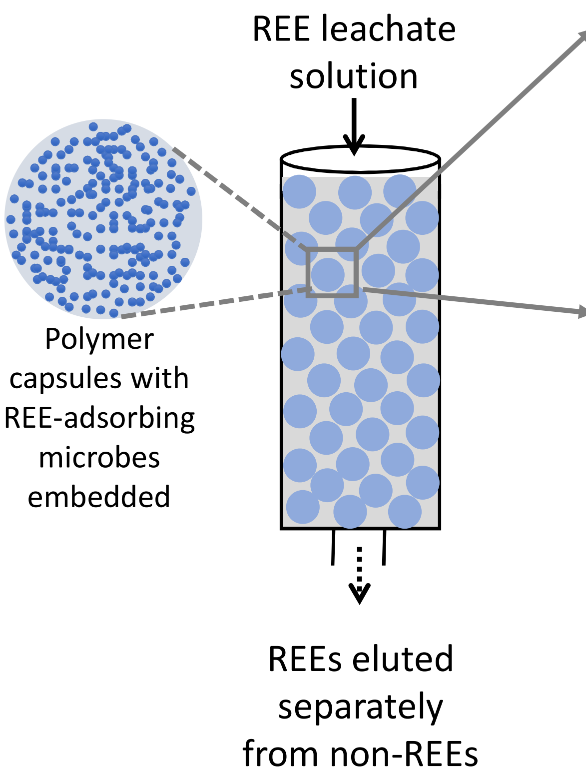
TCF: *Caulobacter* immobilization on biofilm carriers used by wastewater treatment plants

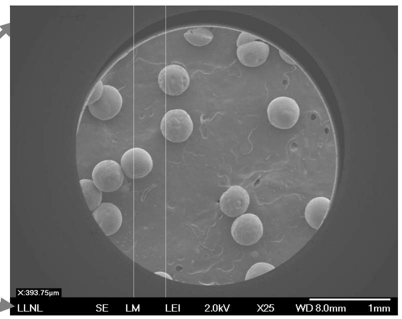
Mutag BioChip™
High surface area for biofilm growth
(> 4,000 m^2/m^3)



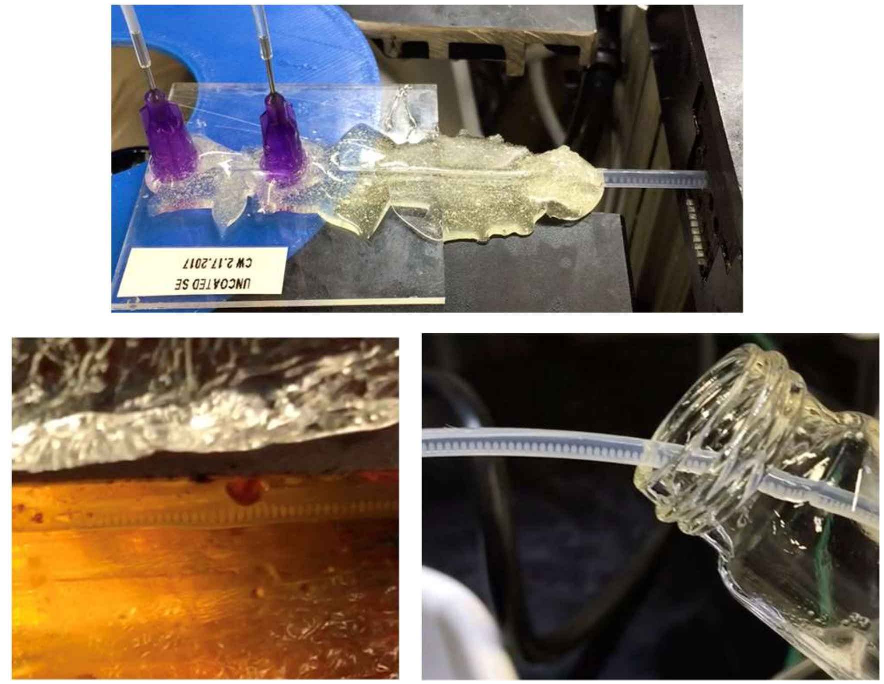
- Crystal violet staining revealed successful colonization of *Caulobacter*

TCF: Cell encapsulation and column chromatography



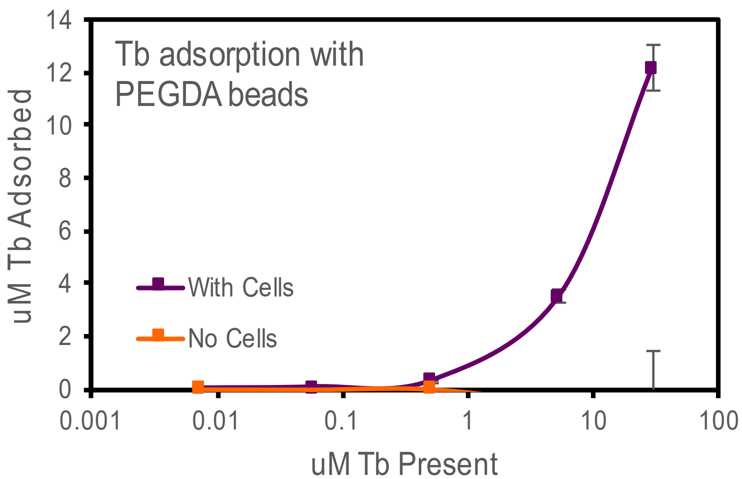


SEM of capsules
F. Qian (LLNL)



Capsule synthesis via a microfluidic device

TCF: Cell encapsulation and column chromatography - progress to date



- PEGDA shows clean metal adsorption background

✓Choice of polymer material (PEGDA)

✓Increase throughput of capsule synthesis

✓Increase cell loading per capsule

✓Optimize bead size and pore size

✓Tested adsorption capacity

✓Tested adsorption kinetics (< 5 min)

Major tasks for FWP (and TCF)

Duke U.

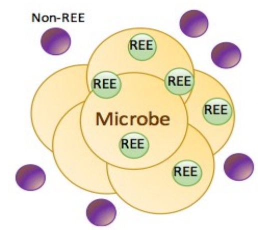
Characterize feedstocks

Compare different leaching methods

Leachate compatibility with biosorption

↔

LLNL



Bioengineering *E. coli* biofilms (FWP)

Caulobacter biofilms (TCF)

→ Bioreactor (FWP)

Cell encapsulation (TCF)

→ Column chromatography (TCF)

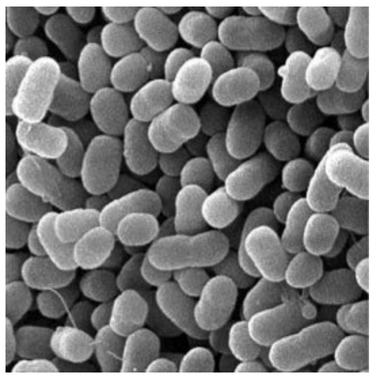
↔

Purdue U.

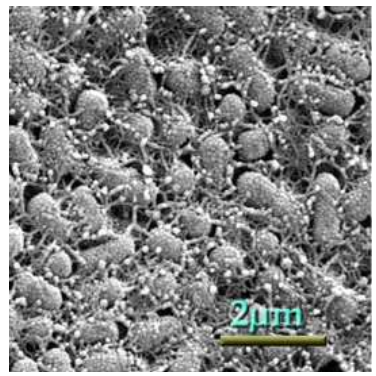
Economic & Environmental Analysis

FWP: Bioengineering curli for surface attachment and REE recovery

- Curli



+ Curli

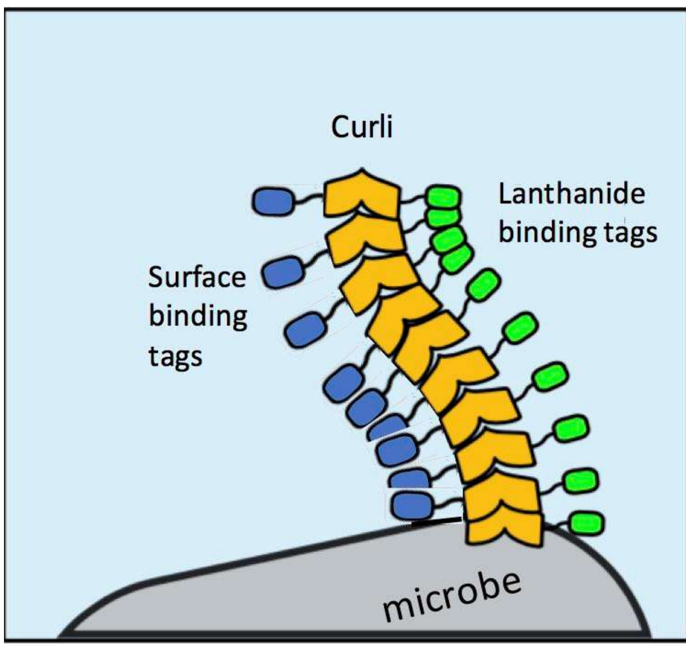


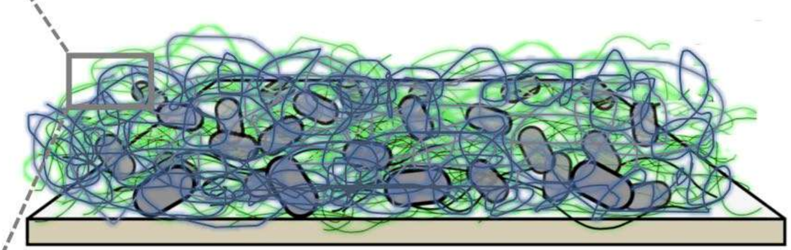
Electron microscopy images of bacterial curli

Ref: Lim et al. (2010). Journal of Microbiology and Biotechnology. 20 (1): 5–14.

- Curli are the major proteinaceous component of a complex extracellular matrix produced by many bacteria.
- Curli fibers are involved in adhesion to surfaces, cell aggregation, and biofilm formation.

FWP: Designer Biofilms: Bioengineering of curli with surface binding tags and lanthanide binding tags for surface attachment and REE recovery





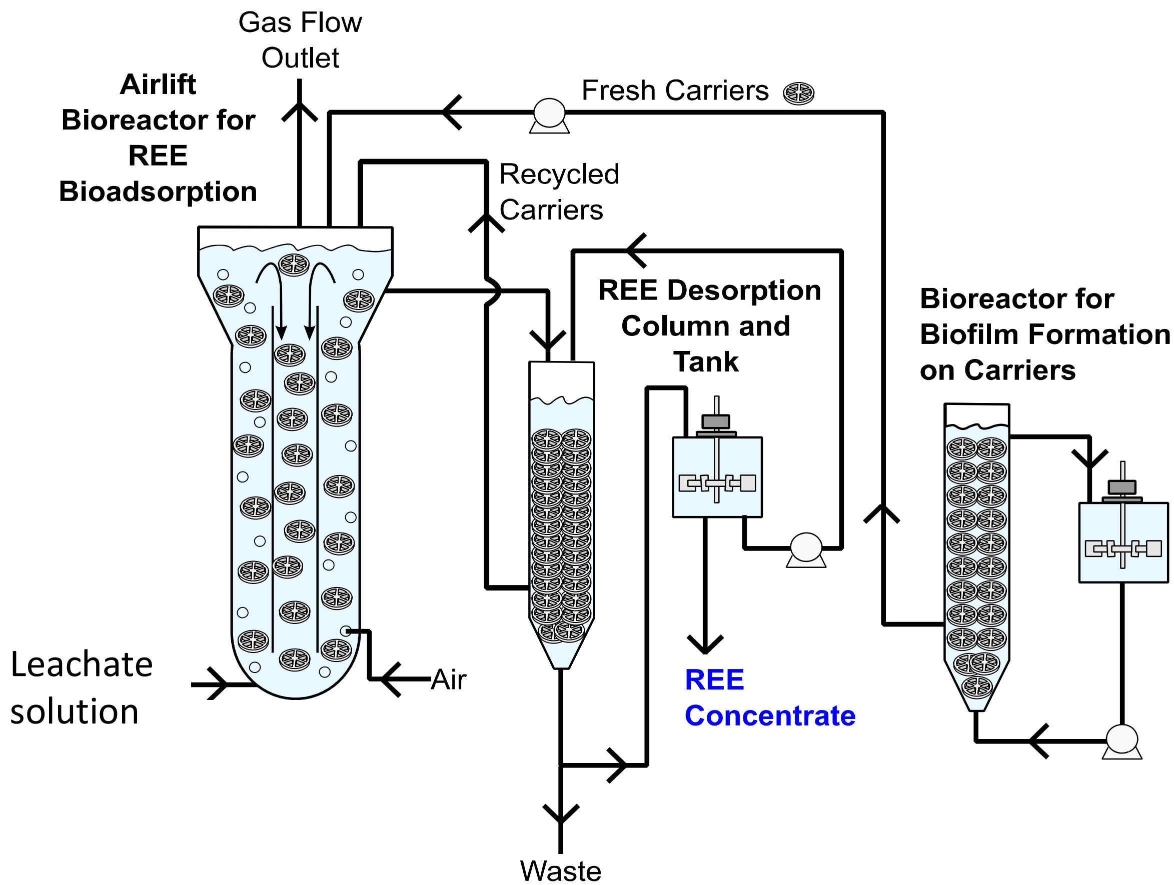
REE recovery in a flow through system using multi-functional biofilms

Ref: Nguyen et al *Nature Communications* 4945 (2014)

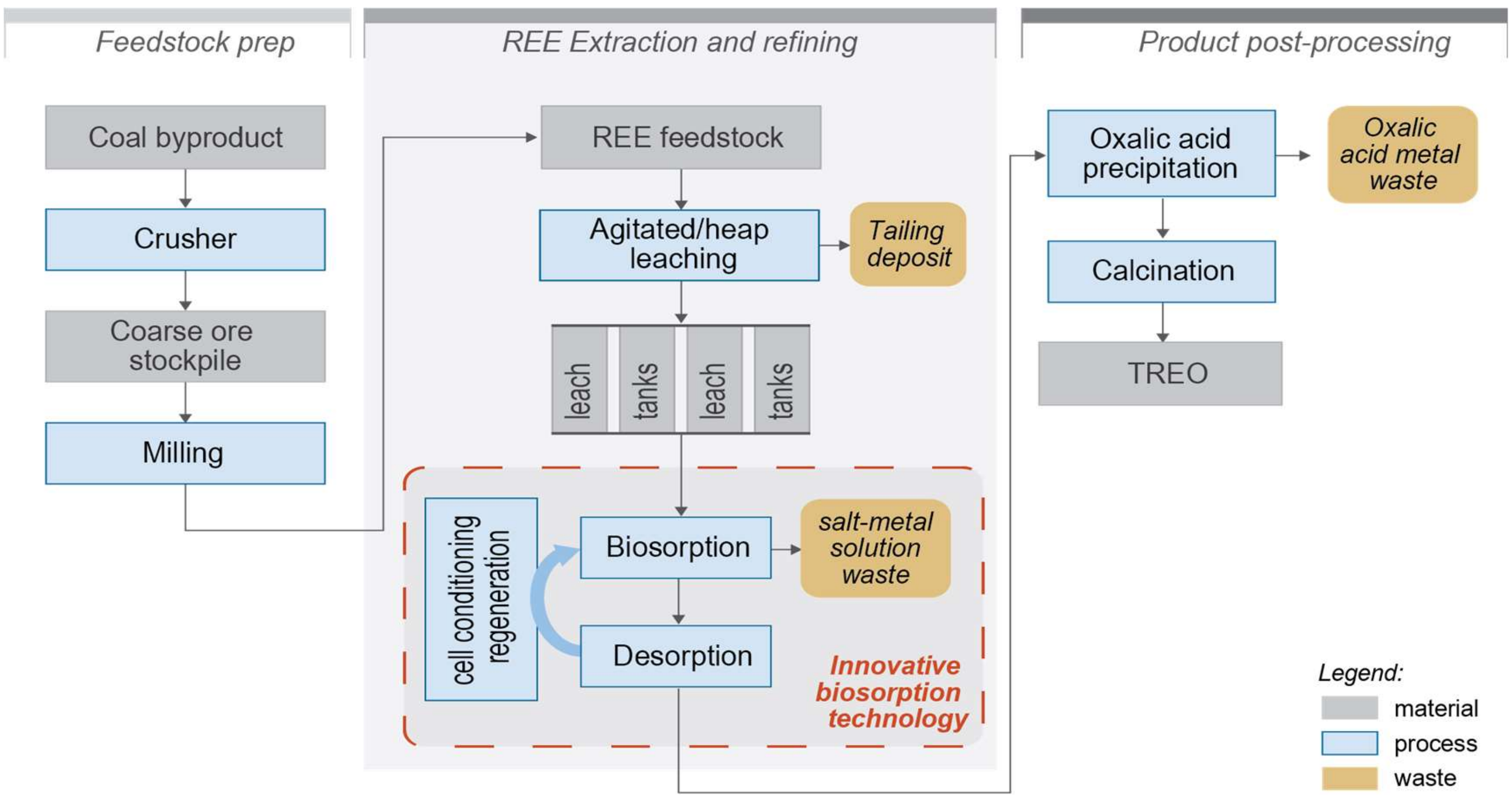
FWP: Test of an airlift bioreactor for REE recovery

10 mm

Biofilm carriers



Process flow for converting coal byproducts to Total Rare Earth Oxides



Preliminary techno-economic analysis

Feedstock: 50,000 tons/yr

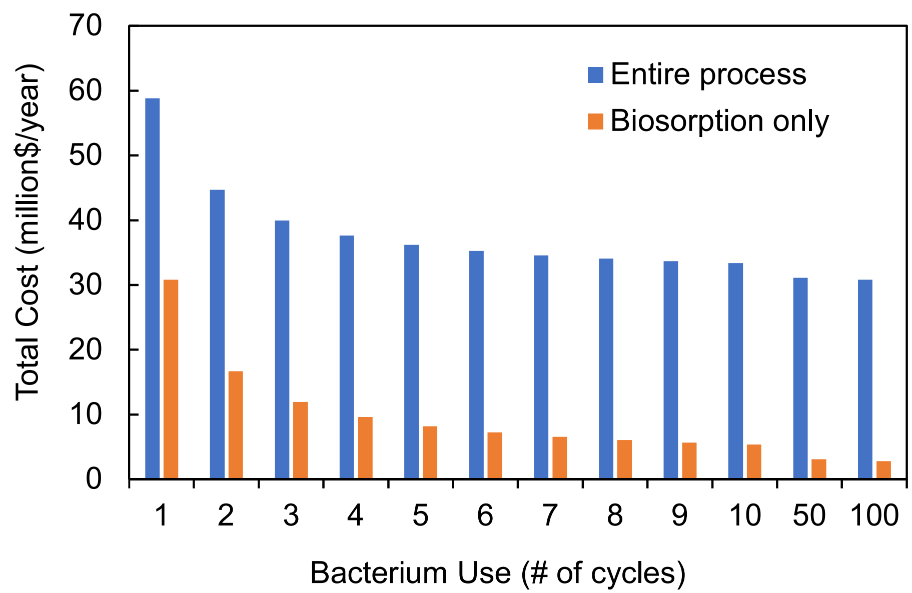
REE content: 337-603 ppm

Unit production cost ($/kg TREO)	136-227
Production cost (M$/yr)	33
Current TREO basket price ($/kg TREO)	306-368
Total revenue (M$/yr)	69

Processing Steps	**Cost %**
Pre-processing	81 %
Biosorption	16 %
Oxalic precipitation & Roasting	3 %
Total	100%

Sensitivity analysis

Cost savings from bacteria recycle and reuse



Ref: Jin et al. ACS Sustainable Chem. Eng. 2017, 5, 10148−10155

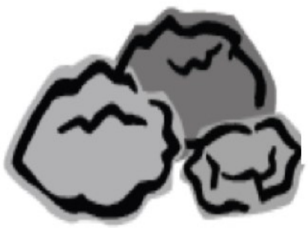
Samples/feedstock to consider

Feedstock type	Location	REE content (ppm)	Power plant information	Other notes
Fly ash from ESP hopper, and holding pond	Central Appalachian coal basin	500-700	Kentucky, South Carolina power plants	Taggart et al (DOI: 10.1021/acs.est.6b00085)
Fly ash from ESP hopper	Power River Coal Basin	300-400	Texas, South Carolina power plant	Taggart et al
Fly ash from ESP hopper	Illinois Basin	400-500	Kentucky power plant	Taggart et al
Pre-combustion coal byproducts; Lignite	Navajo Indian Reservation in northern Arizona	100-300	N/A	Personal communication with Navajo Transitional Energy Company. Dan Laudal, personal communication
Ion adsorption clay	A surface mine, PA	300-500	N/A	Peter Rozelle et al DOI: 10.1007/s40553-015-0064-7
Acid Mine Drainage	Appalachian streams	Solution phase and sludge (100-300)	N/A	Paul Ziemkiewicz, West Virginia University

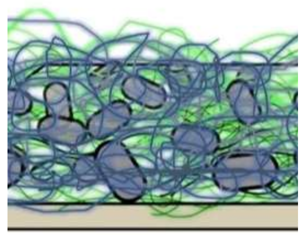
Industry engagement

- Navajo Transitional Energy Company
- North American Coal Corporation
- Native American Mining Solutions LLC
- Innovation Metals Corporation
- Thor ORE

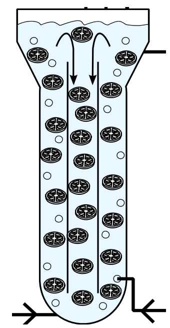
FWP: Progress to date



Leaching



E. coli biofilm



Bioreactor

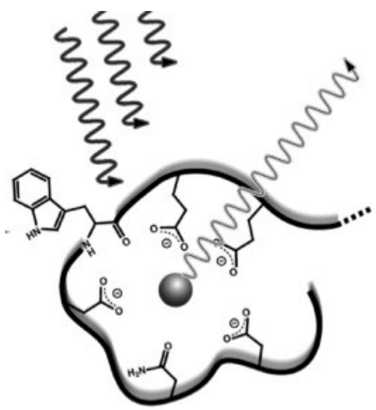
TEA and LCA

Progress to date:

- ✓ A postdoc candidate was identified with onsite interview scheduled in late April.
- ✓ In process of completing the paper work for subcontracts to Duke U. and Purdue U.
- ✓ Bioreactor purchase to be made in April.
- ✓ A service proposal entitled “Microbe-Mineral Interactions for Rare Earth Recovery” was submitted to Environmental Molecular Sciences Laboratory (EMSL, a DOE-funded user facility).

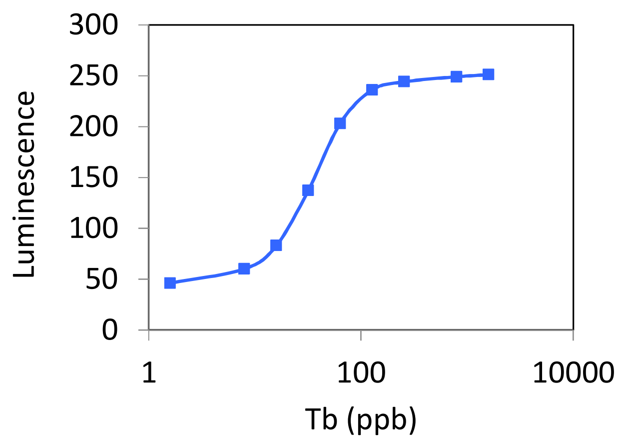
INL led FWP: New sensing mechanisms for rare earth detection in coal and coal byproducts

Ex/Em 280/544 nm



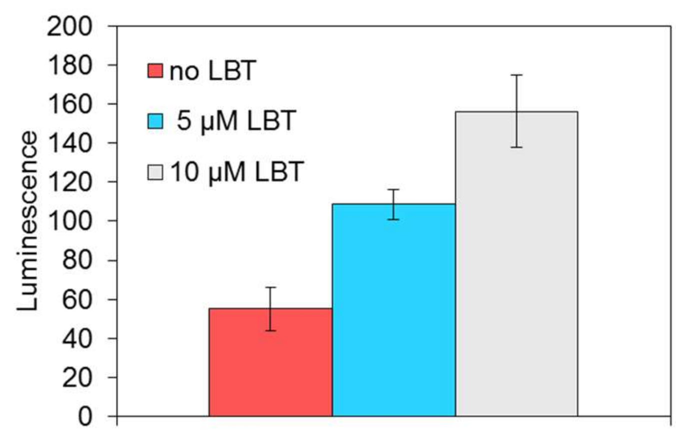
Ref: Liang, et al. (2013). JACS

Synthetic Tb solution



Peptide standard curve – 500 nM

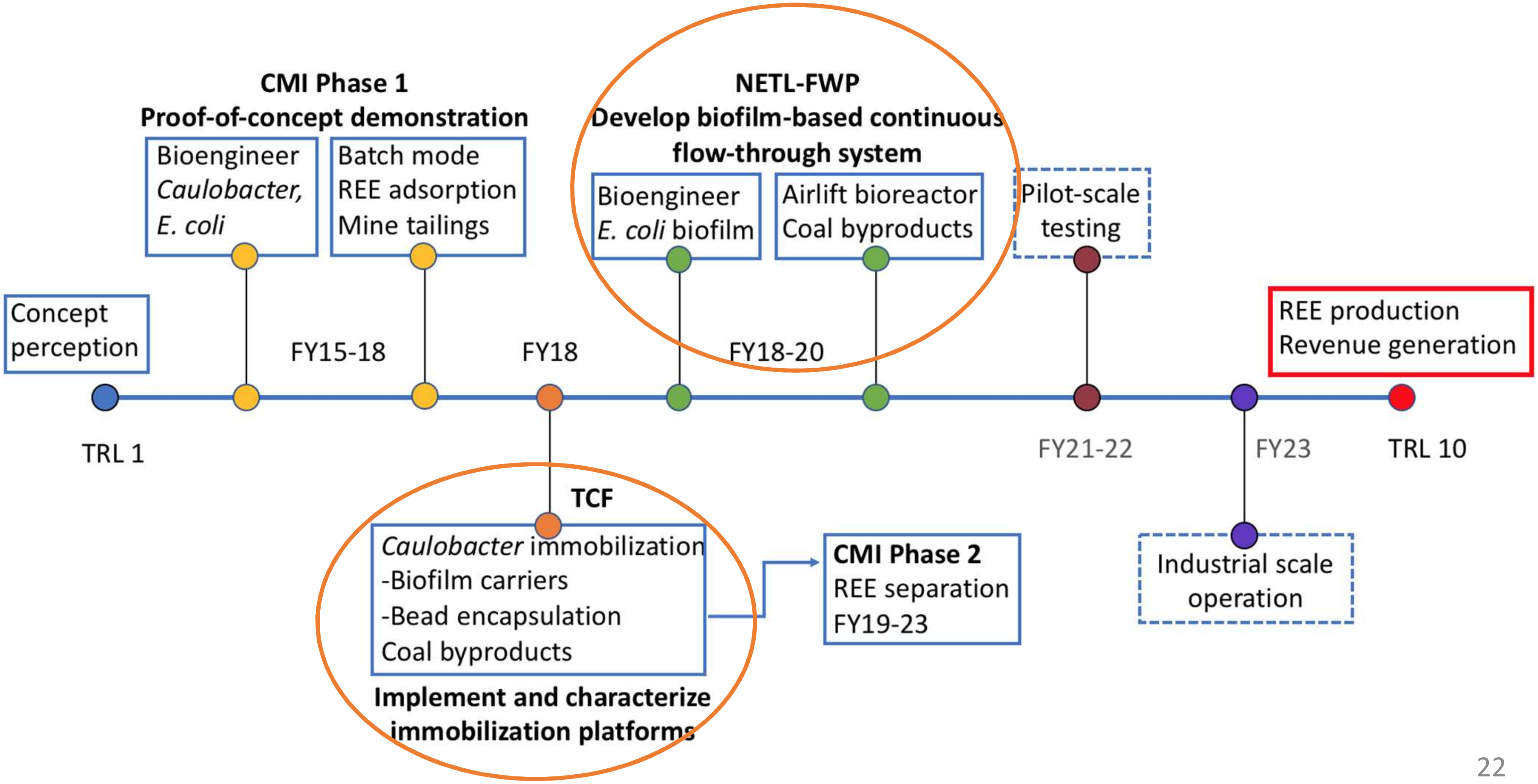
Fly ash leachate



< 10 ppb Tb

- A collaborative project with INL (lead), Rutgers U., LLNL, UCD, and OLI Systems
- High throughput rapid screening of REEs in various solutions

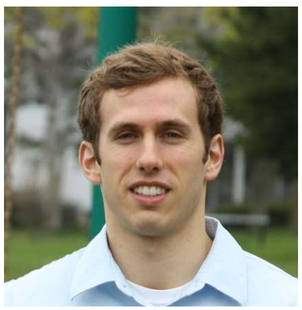
Overview and outlook of LLNL-led biosorption technology development and commercialization plan



Acknowledgements

Research Team at LLNL

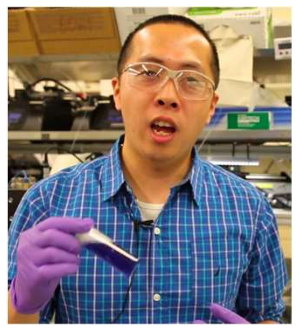
Dan Park



Co-PI

Aaron Brewer

Congwang Ye



Collaborators:

- Heileen Hsu-Kim (Duke U.)
- John Sutherland (Purdue U.)
- Yat Li (UC Santa Cruz)

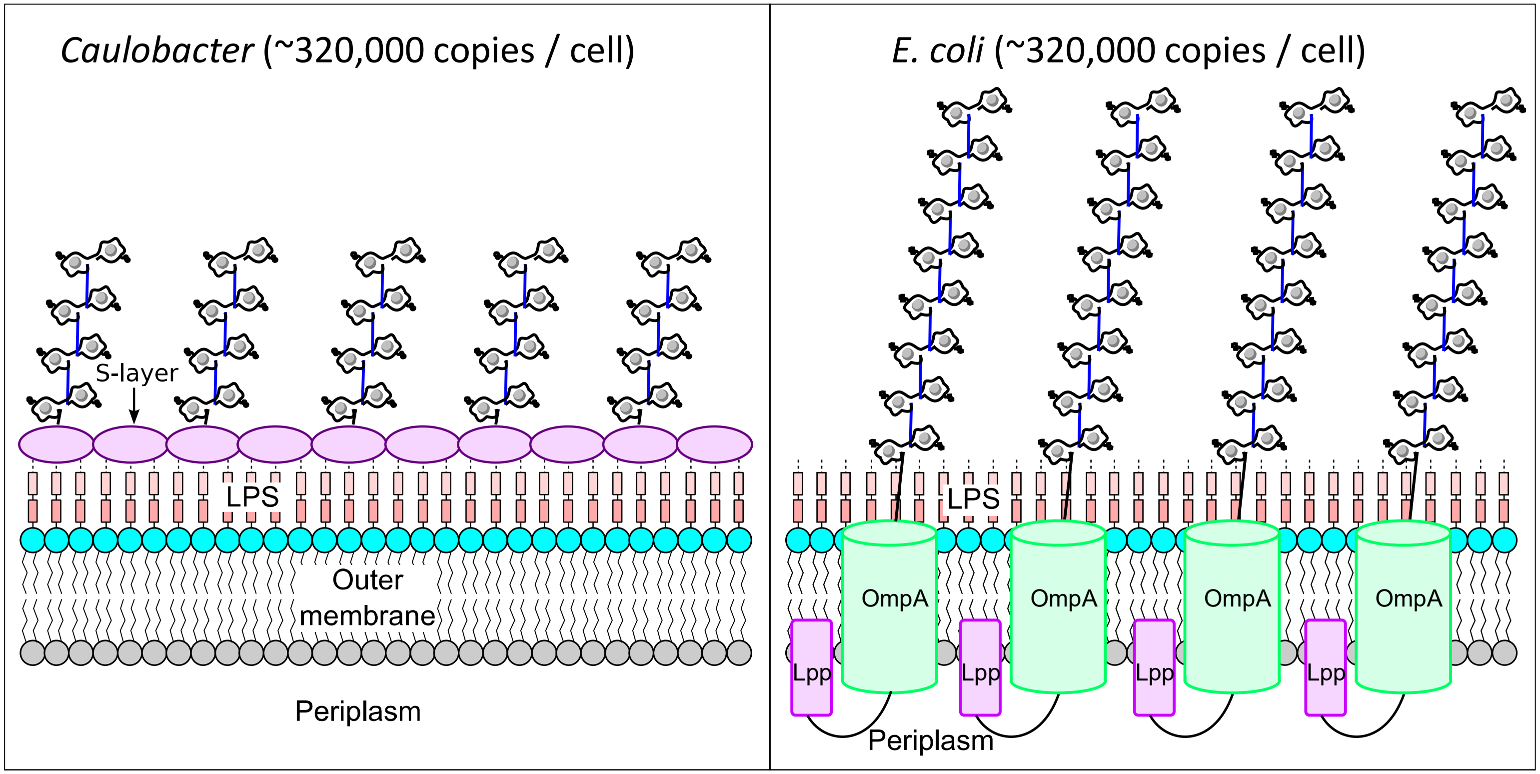
Environmental Molecular Sciences Laboratory (EMSL)

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY | CMI Critical Materials Institute

Lawrence Livermore National Laboratory

Bioengineer bacteria to display lanthanide binding tags on cell surface

Anchor LBT on the cell surface using two different methodologies



Park et al *ES&T, 2016*

Park et al *ES&T, 2017*

Bioengineered microbes exhibit high selectivity for REEs of high criticality

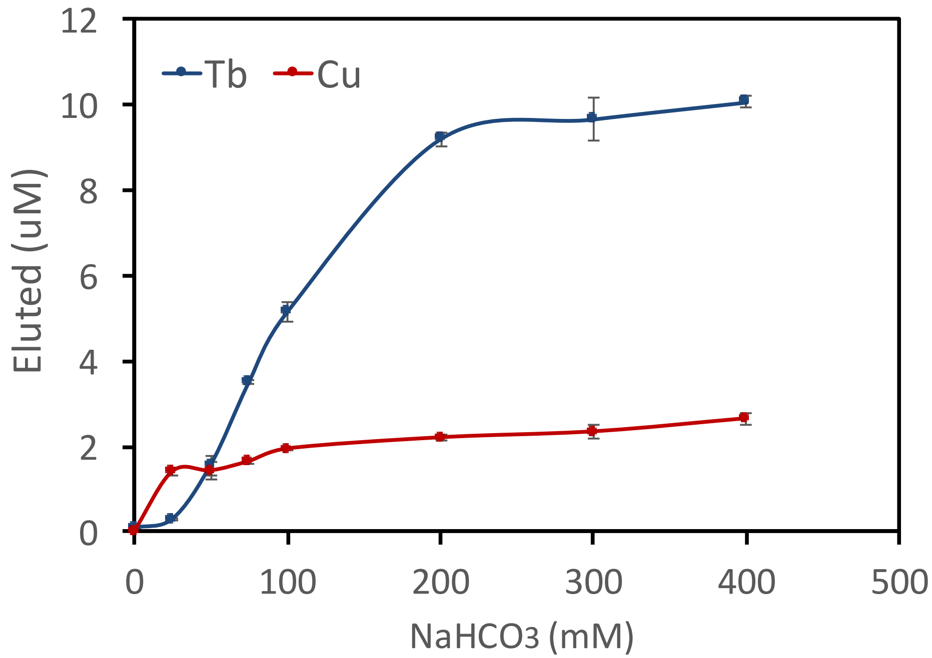
Surface displayed LBTs are specific for REE metal ions

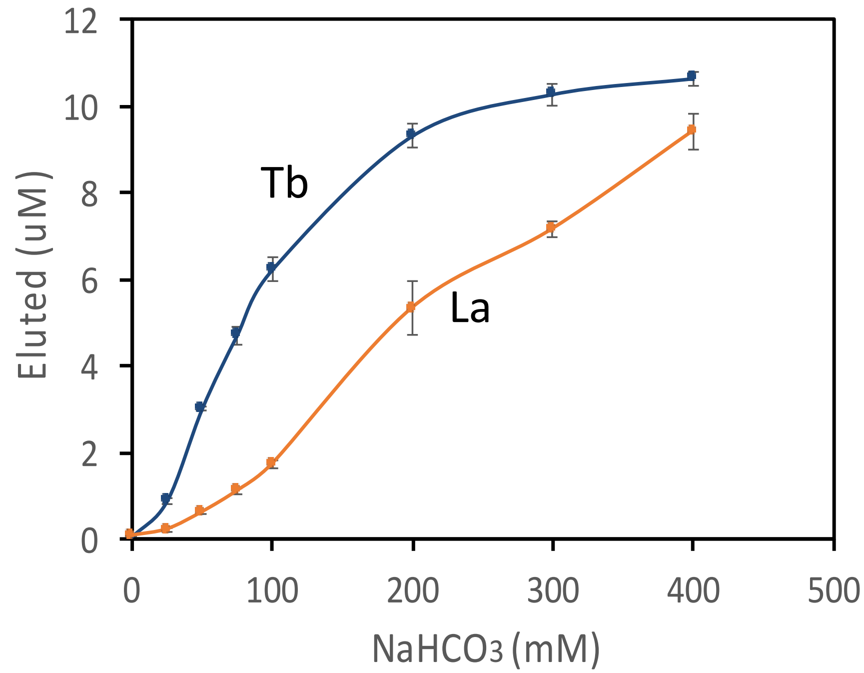
REE	K_D (μM)
Tb^{3+}	**3.8 (0.3)**
Al^{3+}	320 (80)
Fe^{3+}	210 (0.7)
Co^{2+}	976 (48)
Mn^{2+}, Ni^{2+}	>4000
Mg^{2+}, Zn^{2+}, Ca^{2+}	>>10,000
Cu^{2+}*	>300

Surface displayed LBTs preferentially bind REEs with smaller atomic radii

REE	K_D (μM)
Eu*	2.5 (0.2)
Yb	3.1 (0.3)
Dy*	3.2 (0.7)
Tb*	3.8 (0.3)
Y*	5.7 (0.1)
Nd*	13.3 (3.8)
Ce	114 (53)
La	153 (55)

TCF: Cell encapsulation and column chromatography





Feedstock comparison of economic predictions for REE recovery based on biosorption technology

Feedstock Types	Coal ash	Mine tailings	Round Top	Bull Hill	Ion exchange clay	Geothermal brine
REE content (ppm)	337-603	178-232	633	2,800	131-293	0.6-3.2
Unit production cost ($/kg TREO)	136-227	318-410	142	25	256-546	130-574
Current TREO basket price ($/kg TREO)*	306-368	65-150	28	13	13	17-22
TREO price increase required for break-even (x-times)	**0.4-0.7**	**3-5**	**5**	**2**	**20-43**	**8-27**
Capital cost (in $ million) assumed life of 20 years	6	5	11	53	6-7	60

*We discounted our TREO price (at 95% or higher purity) by 30% from the 99+% pure individual REO prices. **Coal ash: 94-95% of the revenue is from Sc.

Ref: Jin et al, "Techno-Economic Assessment for Integrating Biosorption into Rare Earth Recovery Process". ACS Sustainable Chemistry & Engineering, 2017

Patent and Publications

- A US patent (application #15400948, pending) entitled "Engineered Microbes for Rare Earth Element Adsorption" was filed in January, 2017.
- Park *et al*, Recovery of Rare Earth Elements from Low-Grade Feedstock Leachates using Engineered Bacteria. *Environ Sci Technol**, 2017.*** DOI: 10.1021/acs.est.7b02414
- Jin *et al*, Techno-Economic Assessment for Integrating Biosorption into Rare Earth Recovery Process. *ACS Sustainable Chem. Eng.*, **2017**, 5 (11), pp 10148–10155.
- Park *et al*, Bioadsorption of Rare Earth Elements through Cell Surface Display of Lanthanide Binding Tags. *Environ Sci Technol,* **2016,** *50* (5), 2735-42

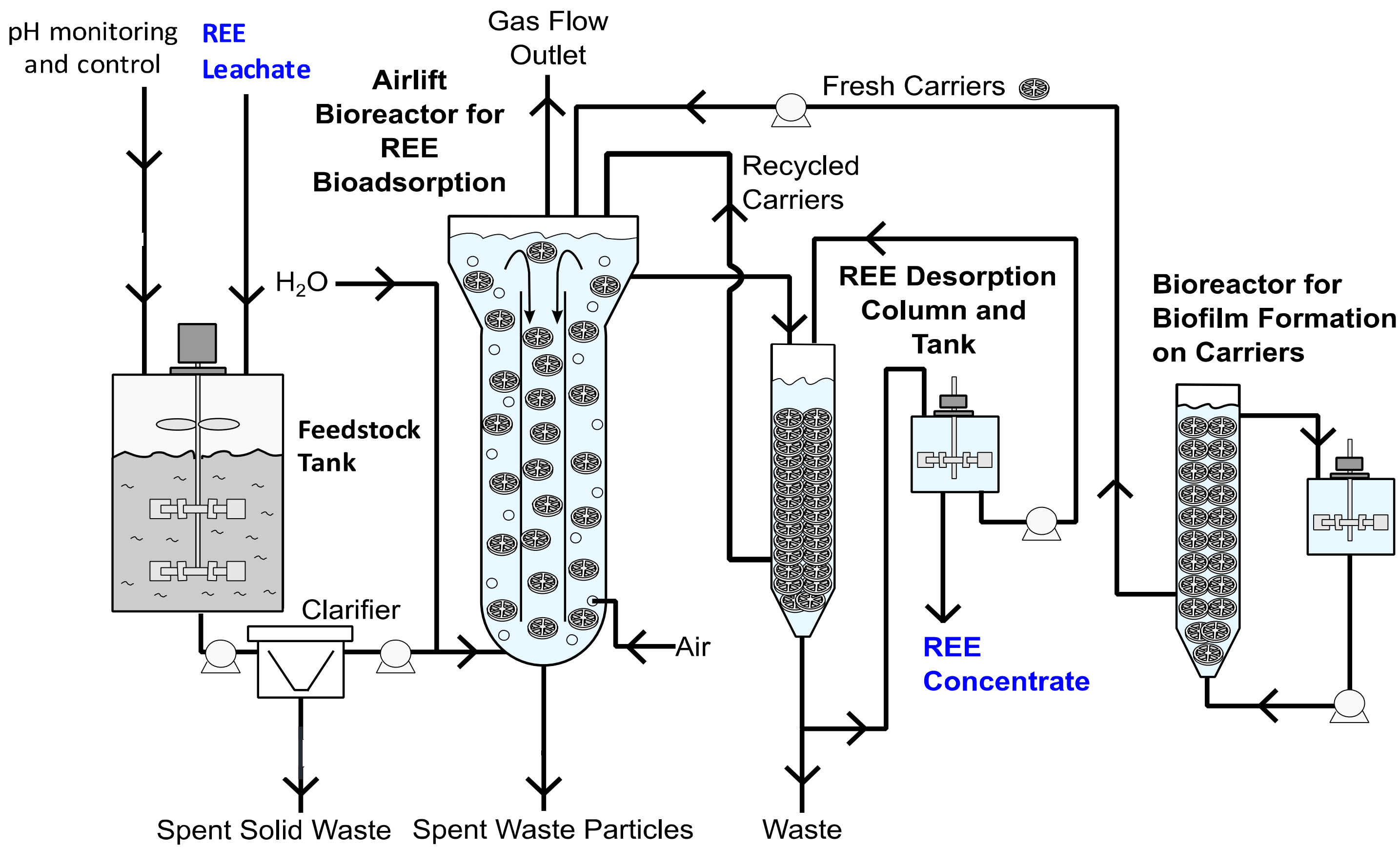
Major tasks for FWP and TCF

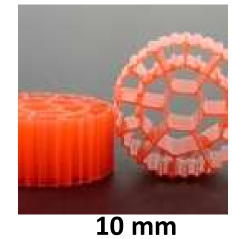
	FY18	FY19	FY20
Duke U.	• Characterize feedstocks • Compare different leaching methods • Leachate compatibility with biosorption	• Select best-performing feedstock from each category • Improve on leaching efficiency	• Scale the preferred REE leaching method • Supply REE-containing leachates for bioreactor runs
LLNL	• Bioengineering E. coli multi-functional *E. coli* biofilm • E. coli biofilm stability test • *Caulobacter* biofilm on carriers (TCF) • Cell encapsulation and column chromatography (TCF)	• REE biosorption with biofilm coated carriers • Performance test with a bioreactor	• Performance test of an airlift bioreactor • Design and operational parameters for pilot scale
Purdue U.	Perform techno-economic analysis	Perform life cycle assessment	Reiterate TEA and LCA with data from bioreactor

Breakdown of LLNL REE Recovery Effort

	Microbial System Engineering	Chemical Engineering	Primary Focus	Feedstock Type
CMI (ends June 2018)	• *Caulobacter* S-layer • *E. coli* OmpA	• Couple bioleaching with biosorption	• REE recovery • Individual REE separation (CMI-Phase 2)	• Mines and tailings • Leachate of e-wastes
TCF (FY18)	*Caulobacter* S-layer	• Biofilm carriers • Beads encapsulation	REE recovery	Coal byproducts
NETL (FWP)	*E. coli* curli	• Airlift bioreactor	REE recovery	Coal byproducts Mine Tailings Acid Mine Drainage
NETL (FY18-20) (INL led)	Cell free system	Biotic and abiotic ligand-based REE detection via luminescence	REE sensing and detection	Coal byproducts

FWP: Test of an airlift bioreactor for REE recovery



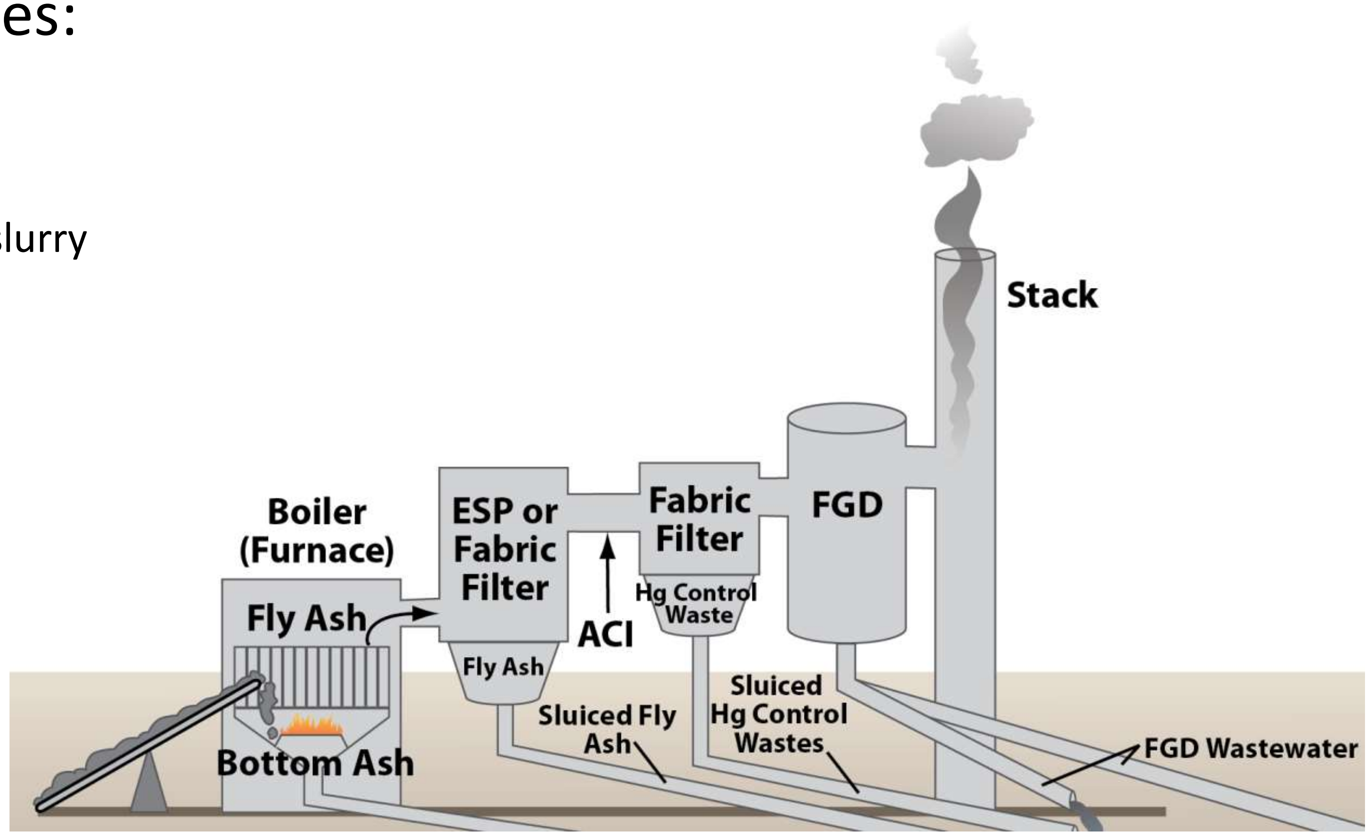


Relevance to Industry Needs and FE objectives

Coal combustion residues:

- Bottom Ash
- Fly Ash
- Flue Gas Desulfurization (FGD) slurry wastes

- Pre-combustion coal



Secondary usage of coal byproducts

Production rate:

- ~120 million tons yr^{-1} in U.S.
- (>400 million t yr^{-1} in China)

Coal Combustion Residues:

Selenium	Radium
Mercury	Vanadium
Arsenic	Boron
Chromium	Strontium
Lead	**Rare Earth Elements**

~45% for beneficial use
fly ash - concrete
gypsum - drywall

~55% must be disposed as solid waste

Application of Biosorption for REE Recovery from Coal Byproducts

Collaboration among 3 institutions

- LLNL: Curli biofilm engineering and REE recovery in airlift bioreactor
- Duke U: Feedstock characterization and leaching; ICP measurements
- Purdue U: Techno-economic analysis and life cycle analysis

Industry engagement

- Navajo Transitional Energy Company
- North American Coal Corporation
- Native American Mining Solutions LLC
- Innovation Metals Corporation
- Thor ORE

TCF: Tasks and deliverables

Tasks	Deliverables
• Test and compare surface attachment vs polymer embedding for cell immobilization; • Conduct and compare basic economic predictions of the 2 methods for REE recovery	• REE loading capacity per unit volume is measured and compared between the 2 methods • REE adsorption/desorption kinetics is measured and compared • Material cost is compared • Bottlenecks and areas for optimization are identified • Preliminary economic predications are derived and compared

FWP: Tasks and deliverables

Tasks	Deliverables
• Leaching method development • Perform curli engineering • Perform REE recovery in an airlift bioreactor • Perform TEA and LCA	• Biofilm engineering is completed and patented. • Biofilm stability is tested • REE adsorption per unit area is measured • Performance of an airlift bioreactor is tested • Design and operational parameters for pilot scale bioreactor are predicted. • TEA and LCA for pilot and large scale bioreactor operation is completed.

Progress to date:

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