

New Sensing Mechanisms for REE Detection in Coal By-Products



Yoshiko Fujita, Idaho National Laboratory



Project Description and Objectives

Purpose of project:

- To develop the basis for a new simple, sensitive and rapid approach for screening complex environmental samples for the presence of rare earth elements. Looking for method capable of:



Image from Petoud, S. et al. (2003). JACS., 125 (44), 13324-13325.

- Application to a range of different chemical/mineral matrices
- Detection of REE in aqueous solutions at ≤ 1 ppm
- Discrimination between multiple co-occurring REE

Research objectives:

- *Take advantage of lanthanide luminescence*
- *Enhance luminescent signal by concentration of lanthanides and or chemical modification*
- *Demonstrate applicability to leachates of a variety of coal byproducts*

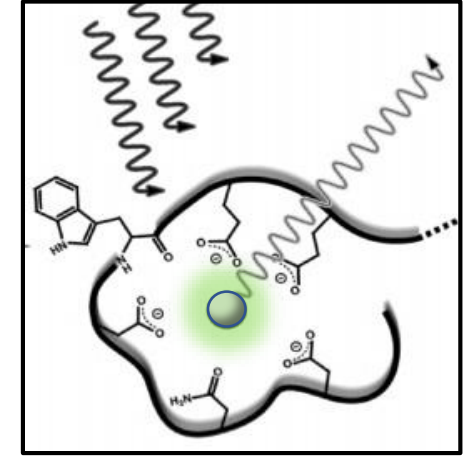
Project Description and Objectives

Original technical approach:

- Using peptide-based ligands (Lanthanide Binding Tags; LBT) as basis for sensing of REE: aimed to modify LBT structure to increase luminescence
- But we found that coal byproduct leachate matrix limited binding and luminescent signal

New approach:

- Immobilize the lanthanides in a solid host, which can both concentrate the Ln and reduce the quenching of luminescence by the solvent.
- With this approach, more of the lanthanides can be detected, and discriminated from each other.



Project Description and Objectives

Strategic Alignment with NETL's Rare Earth Elements Program:

- New rapid and simple approaches for REE detection and characterization will be useful for screening coal wastes for valuable content, monitoring during industrial REE processing, and rapid evaluation of extraction or separation techniques.
- Goal: to develop an approach suitable for field-deployable “test kits” for screening, or for in-line real time monitoring.
- **Status at beginning of project** → We knew that Tb or Eu bound to the LBT emitted visible light when excited with UV. But we didn't know how well this method would work with complex samples (e.g., coal ash leachates).



Project Description and Objectives

Technology Benchmarking:

- Inductively coupled plasma mass spectrometry (ICP-MS) is the most commonly used method for measuring REE in liquid samples.
 - Detection limits typically in low ppb
 - But analyses expensive, and time consuming
- X-ray fluorescence (XRF) can be used for surface or near surface REE in solids (or dried liquids), but calibration for complex samples is challenging.
 - Quantitation highly dependent on sample matrix
 - Detection limits typically in ppm range
 - Portable XRF not suitable for HREE
- A sensitive and rapid sensing method suitable for complex REE mixtures would be valuable

Project Description and Objectives

Current Status of Project

- Original milestone schedule based on LBT chemistry
- Changes in project goals/objectives:
 - Approach based on lanthanide precipitation in fluoride minerals is promising
 - ❖ Simple protocol allows REE detection at sub-ppm levels in leachate
 - ❖ Can simultaneously detect and discriminate between multiple REE by using unique excitation and emission wavelengths: Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm
- **Industry/input or validation –**
 - Aside from screening potential sources for value recovery, industry needs to monitor closure of coal ash disposal sites.
 - ❖ Detection of rare earths in groundwater or leachate monitoring samples could serve as proxy for release of other hazardous metals.

Project Update

Public Outreach

- Contribution to an invited chapter in a special American Geophysical Union monograph on rare earth elements
 - Chapter includes modeling of coal ash leachate chemistry
- Planned ACS presentation; plans upended by pandemic.
- Manuscript planned for submission by end Sept. 2020.

Technical Research Summary

- Coal ash characterization
- Leachate preparation
- Geochemical equilibrium model construction and application
- Testing of LBT-based approach for sensing
- Development of alternative sensing approach based on fluoride host precipitate formation

Project Update

Coal Fly Ashes Used for Leachates

- Appalachian coal ash from U. Alabama (“AL” ash)
- Wyoming Powder River Basin coal ash from U. Wyoming (“WY” ash)

Oxides	AL ash (%)	WY ash (%)
SiO ₂	49.3 ± 0.6	26.8 ± 0.3
Al ₂ O ₃	26.5 ± 0.3	14.9 ± 0.1
Fe ₂ O ₃	8.6 ± 0.1	3.9 ± 0.1
CaO	1.2 ± 0.0	26.9 ± 0.2
MgO	1.1 ± 0.0	3.3 ± 0.0
Na ₂ O	0.4 ± 0.0	2.0 ± 0.0
K ₂ O	2.9 ± 0.0	0.4 ± 0.0
Cr ₂ O ₃	0.0 ± 0.0	0.0 ± 0.0
TiO ₂	1.3 ± 0.0	1.0 ± 0.0
MnO	0.0 ± 0.0	0.0 ± 0.0
P ₂ O ₅	0.2 ± 0.0	0.6 ± 0.0
SrO	0.1 ± 0.0	0.3 ± 0.0
BaO	0.1 ± 0.0	0.4 ± 0.0
LOI*	6.8 ± 0.0	3.5 ± 0.1
Total	98.5 ± 0.3	84.1 ± 0.5

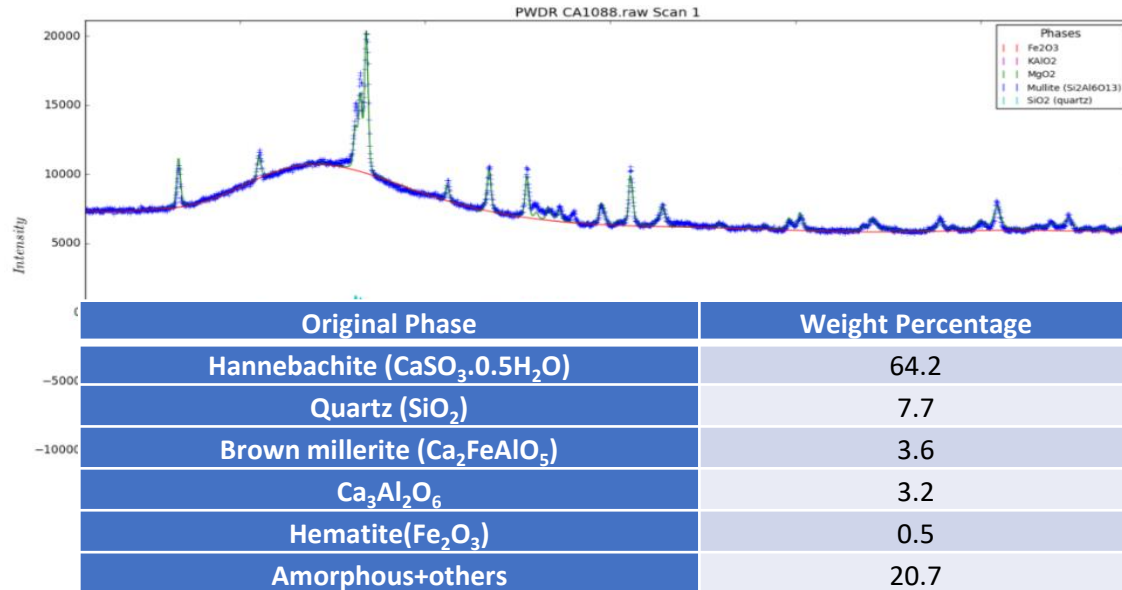
*LOI = Loss on Ignition (e.g., water, gases)

REE	AL ash (ppm)	WY ash (ppm)
La	94.6 ± 4.4	66.5 ± 1.1
Ce	184.8 ± 9.8	124.2 ± 2.1
Pr	22.1 ± 0.9	15.6 ± 0.2
Nd	84.7 ± 3.7	58.9 ± 1.0
Sm	18.8 ± 0.9	13.2 ± 0.2
Eu	3.8 ± 0.1	2.8 ± 0.2
Gd	16.4 ± 0.9	10.8 ± 0.2
Tb	2.6 ± 0.1	1.7 ± 0.1
Dy	16.0 ± 0.7	9.9 ± 0.3
Y	94.6 ± 4.1	53.6 ± 1.3
Ho	3.2 ± 0.2	1.9 ± 0.1
Er	9.3 ± 0.6	5.6 ± 0.2
Tm	1.4 ± 0.1	0.8 ± 0.0
Yb	8.7 ± 0.3	5.2 ± 0.2
Lu	1.2 ± 0.1	0.8 ± 0.0
Ave. Total REE	562	372

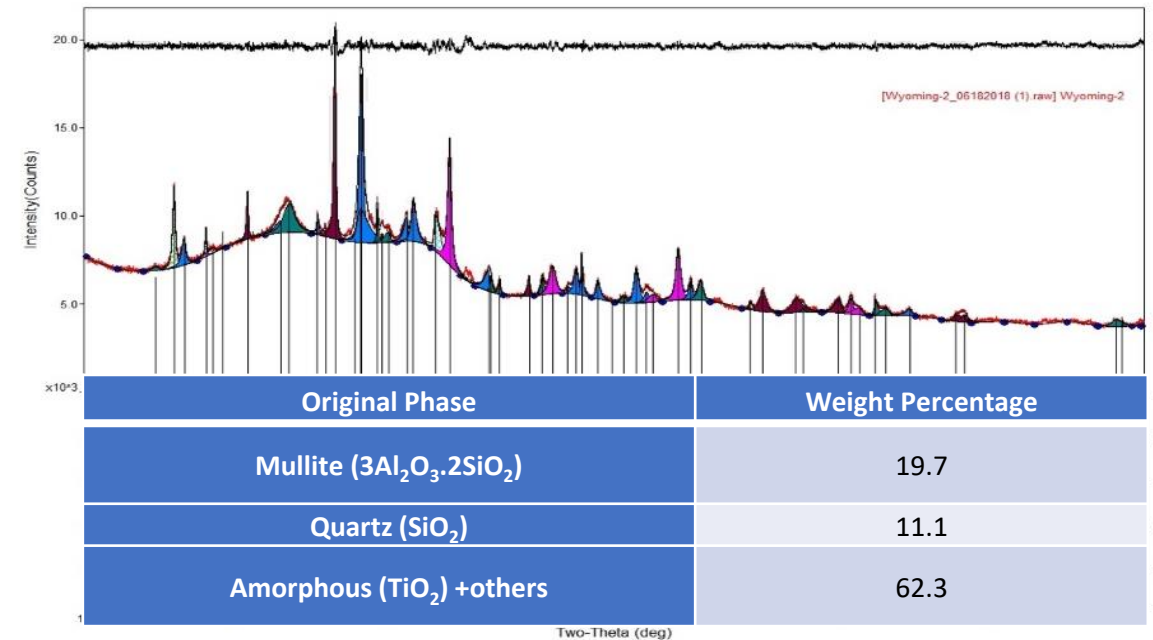
Project Update

Coal Fly Ash Mineral Characterization

XRD of Alabama ash



XRD of Wyoming ash

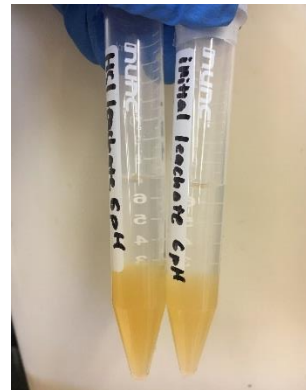
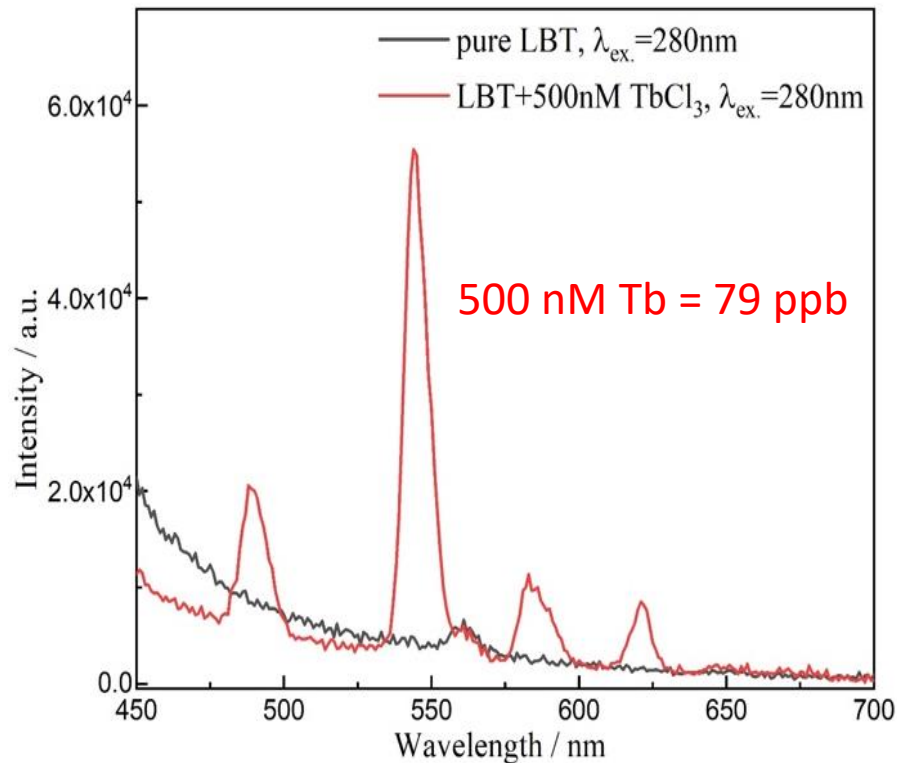


Wyoming and Alabama fly ashes have very different mineral composition—likely to affect leaching results

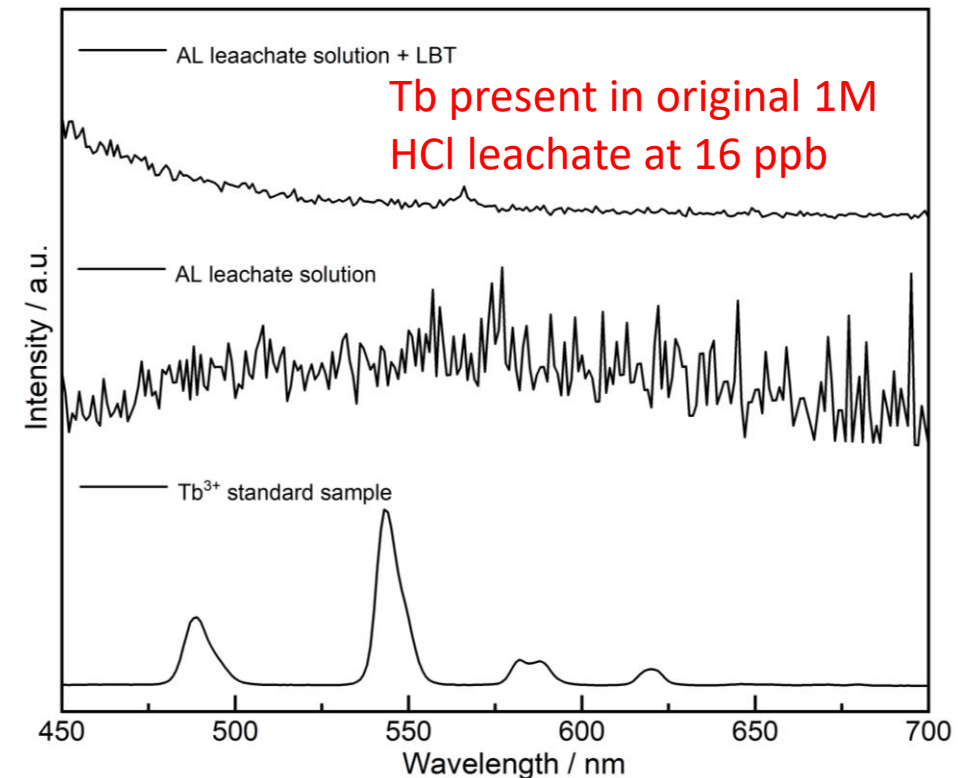
Project Update

REE Detection with LBT

- Tb bound to LBT can be detected in “clean” solutions, at 10 ppb Tb.
- However, quenching by water and complex chemical matrix interfere.



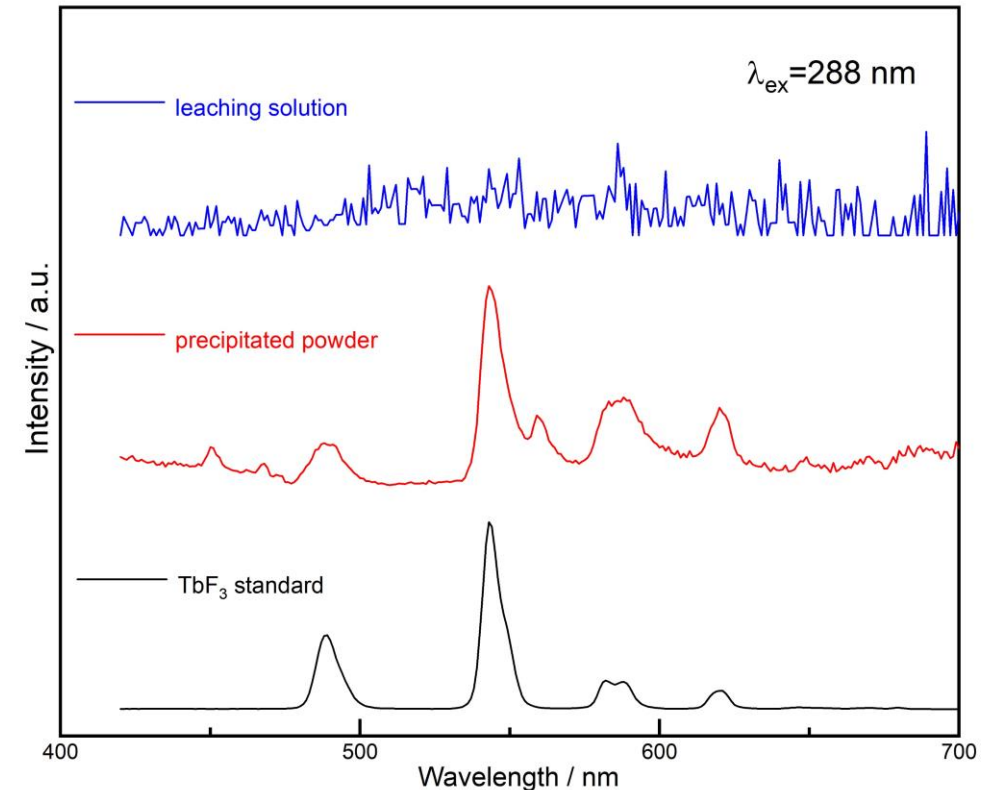
AL leachate after adjustment to pH 6—precipitate visible



Tried surface plasmon resonance approach to increase energy transfer, but not sufficient.

Alternative luminescence-based detection approach: Precipitation in mineral fluorides after leaching by HCl (1 M)

- Fluoride mineral host is good for luminescence—low phonon energy.
- Precipitation of Ln from solution also leads to concentration of the lanthanides.
- Can precipitate lanthanides simply by adding NH_4F to REE-containing solutions.
 - *No prior pH adjustment needed.*

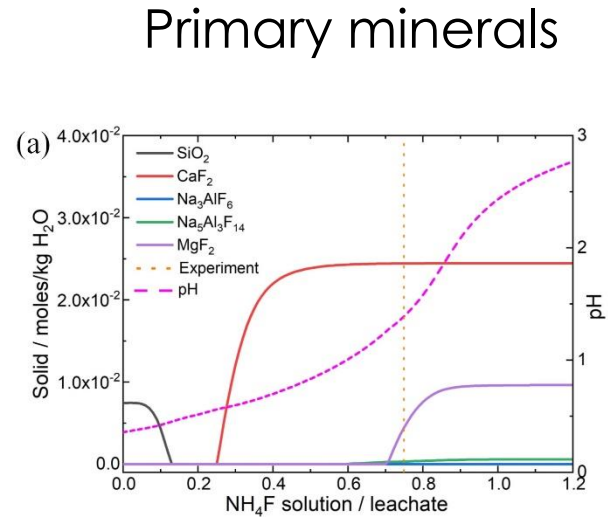


Example of AL leachate

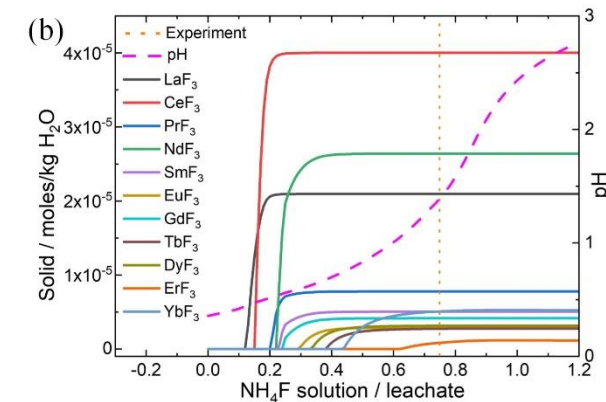
Project Update

Modeling of leachate chemistry to confirm propensity to form fluorides

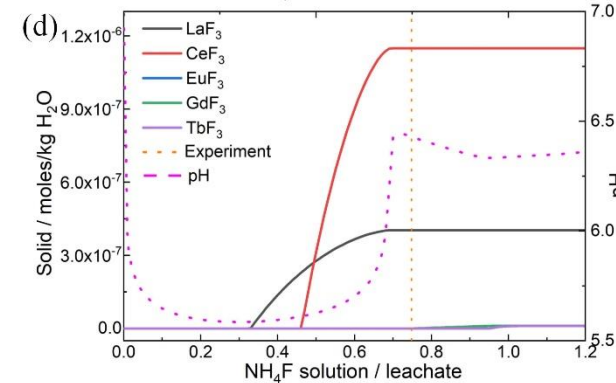
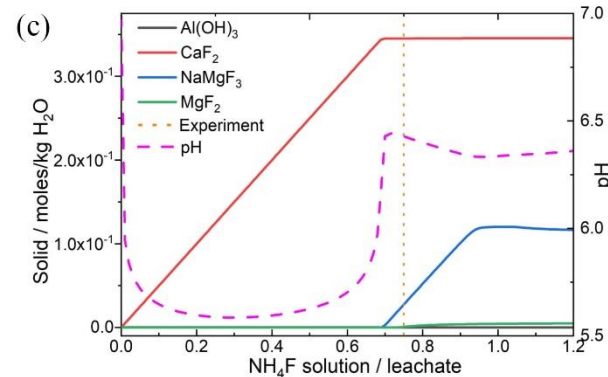
AL leachate



LnF₃ minerals



WY leachate

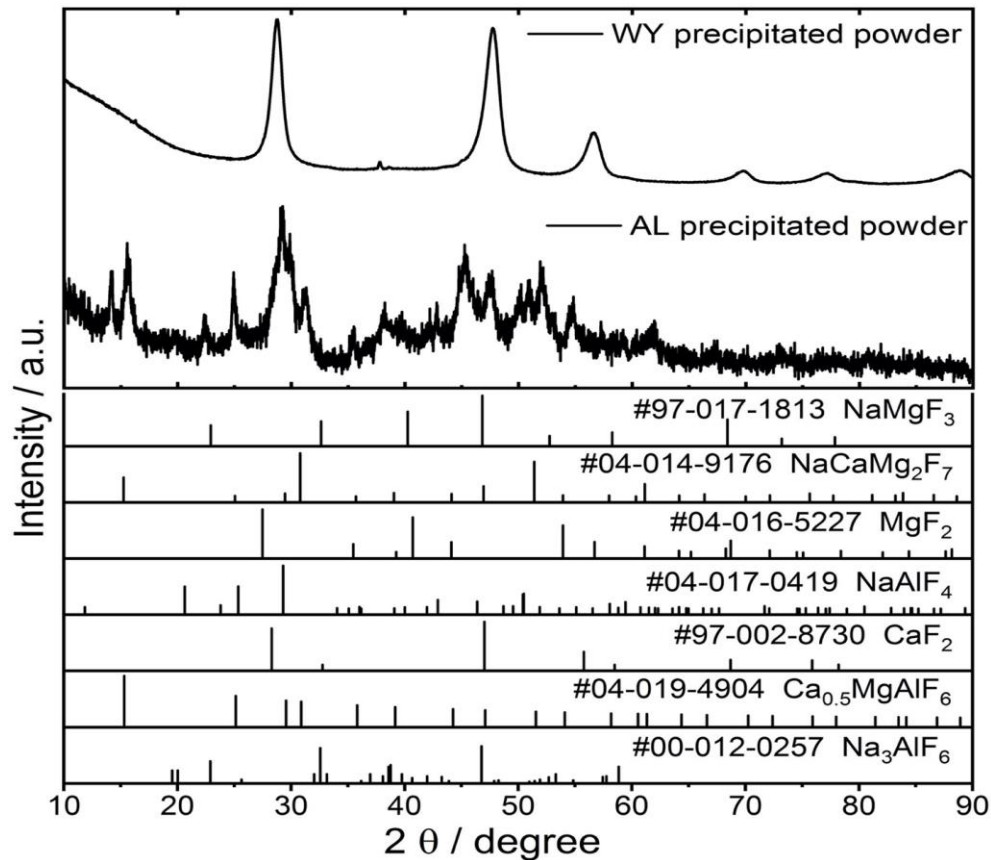


CaF₂ and MgF₂ predicted as major phases; all Ln present at detectable levels in leachate expected to precipitate

CaF₂ and NaMgF₃ predicted as major phases; all Ln present at detectable levels in leachate expected to precipitate

Project Update

Experimental characterization of precipitates consistent with model predictions



← NaMgF_3

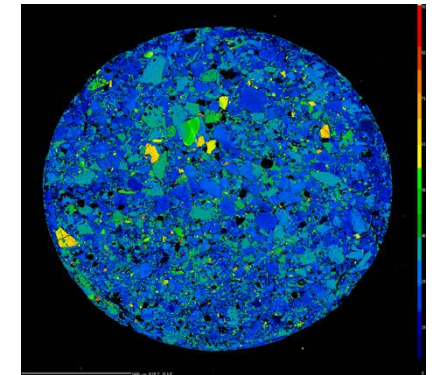
← MgF_2

← CaF_2

Major phases predicted by modeling were detected by XRD.

But other more complex phases also detected that were not predicted—likely due to lack of required thermodynamic data.

Crystalline LnF_3 not detected in either precipitate—concentrations too low for XRD, but Ln seen with electron microprobe



Project Update

Schematic of overall approach



Coal ash

HCl
→



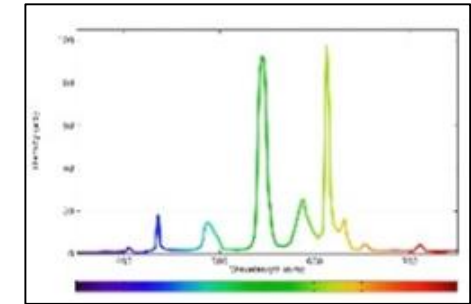
Leachate

NH₄F
→

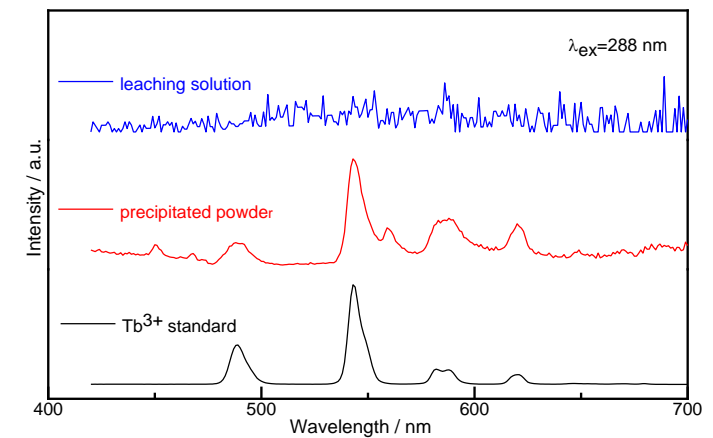
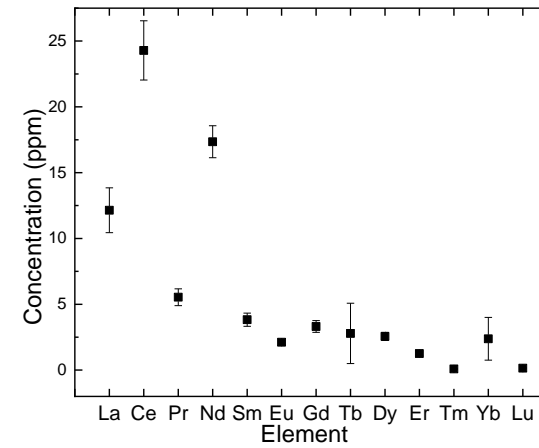
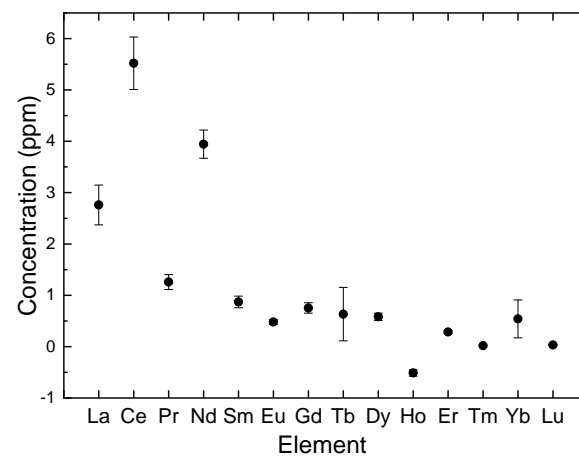
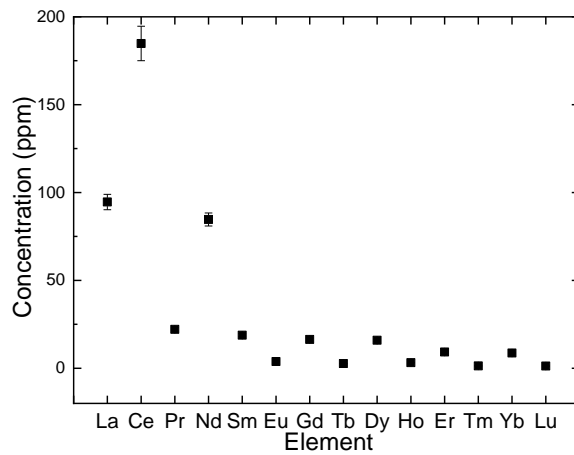


Precipitate

→

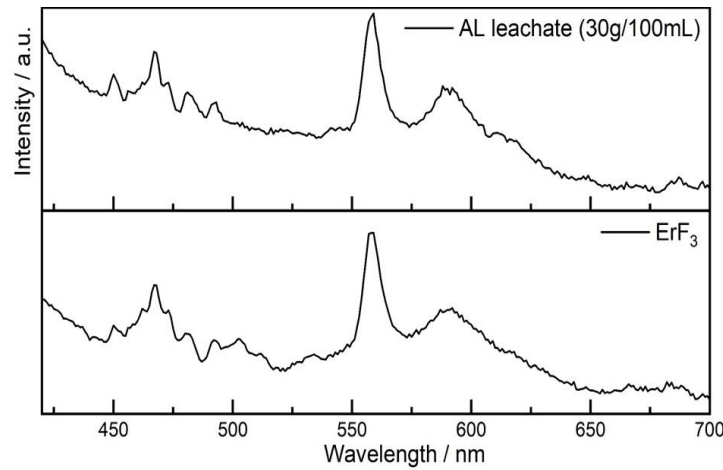


Luminescence
measurement

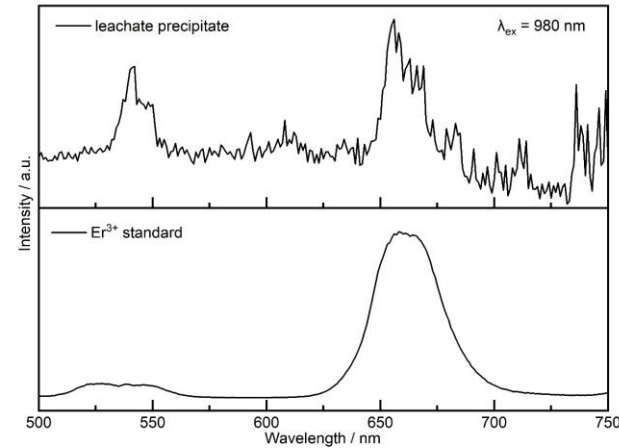


Project Update

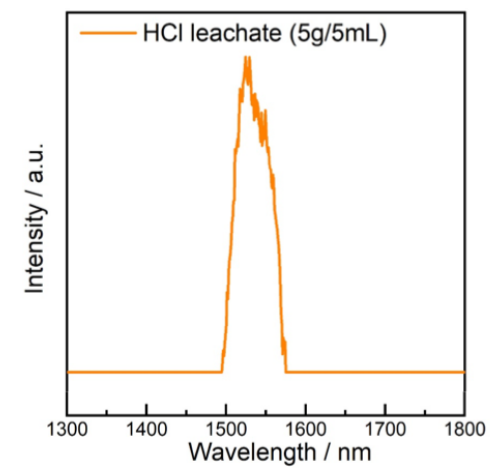
Most lanthanides detected by “conventional” luminescence, but some can be detected by upconversion



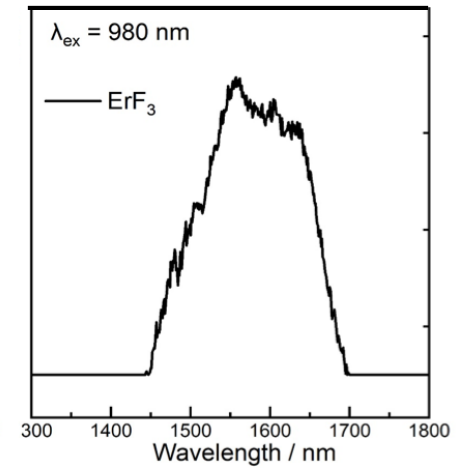
Excitation by 255 nm



Excitation by 980 nm (near IR)
Upconversion



Excitation by 980 nm (near IR)



Er can be detected by both downconversion and upconversion

Project Update

Multiple lanthanides can be detected simultaneously, and distinguished from each other by distinct wavelengths (excitation and or emission)

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Does LnF_3 fluoresce?	N	Y	Y	Y	N	Y	Y	Y	Y	Y*	Y*	Y*	Y*	N	N
Detected in AL leachate?	na	N	Y	Y	na	Y	Y	Y	Y	Y	N	Y	N	na	na

Y = Yes. N = No. na = not applicable.

*Detected by upconversion.

Detection limits

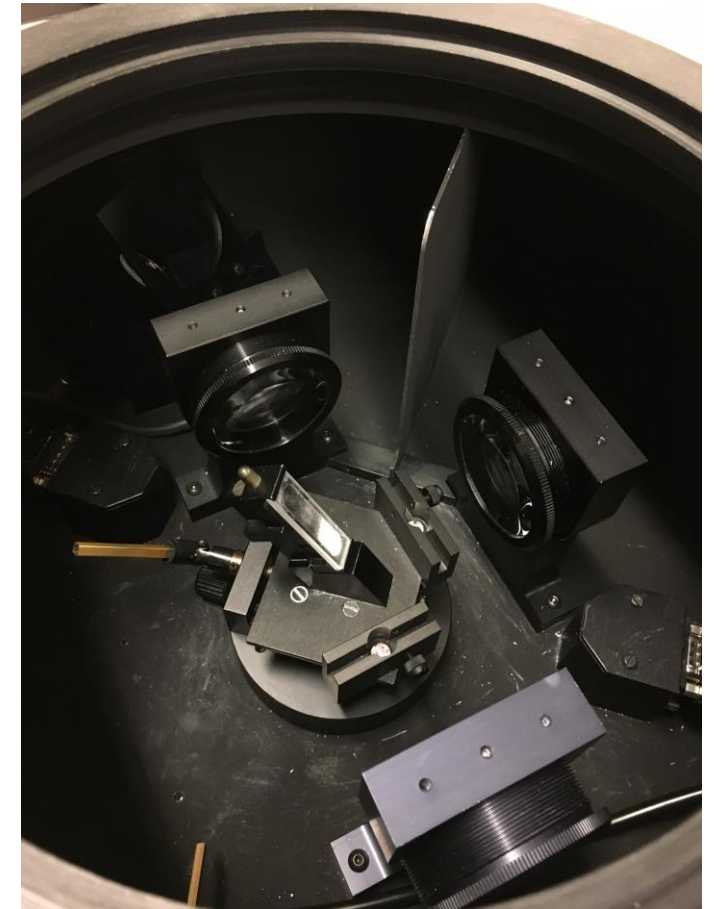
- **Highly dependent on the chemistry of the leachate, because that determines the host mineralogy.**
- **But our experience indicates that a concentration of 1 ppm of an individual lanthanide in the *precipitate* can be readily detected.**
- **Using the AL precipitate yields as a guide, we estimated that the *leachate* can contain sub-ppm levels (~0.2 ppm)**

Element	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er
Concentration (ppm)	0.226	0.221	0.189	0.227	0.223	0.227	0.227	0.201

Project Update

Applicability of approach to other sample types

- **Recently tested approach with an acid leachate of a lignite coal (North Dakota)**
- **Also with 1M HCl leachates of coal from:**
 - N. Dakota, Mercer County
 - Virginia, Buchanan County
 - Montana, Bighorn County
 - Kentucky, Union County
 - Pennsylvania, Columbia County
- **Could detect Dy and Er by upconversion in all but Pennsylvania sample**
 - Unfortunately Xenon laser for UV/Vis excitation could not be used at the time, but based on chemistry of leachates, expect other REE detectable.



Challenges and Next Steps

Technical Challenges

- Additional work (empirical and modeling) needed to confirm applicability of approach to different solution chemistries.
- Thermodynamic data for mixed fluoride phases needed, since they are likely to be dominant for precipitation of fluorides from complex samples.

Next Steps

- Adapting protocol (to be faster, simpler) to be compatible with a field test kit design, or portable sensor design.
 - A number of designs reported in the literature that use smartphone cameras to record spectra, coupled with LED light sources for excitation

Market Benefits/Assessment

- Conventional methods of REE measurement are expensive and time consuming, or rapid and cheaper but less sensitive.
- The ability to rapidly assess REE content, in total and as individual REE, will be valuable for screening of potential REE resources, monitoring during REE processing, and rapid evaluation of extraction or separation technologies.

Technology-to-Market Path

- Remaining technology challenges include integration with a spectrometry system.
- Follow-on research would include design of a system to integrate the reaction chemistry with direct detection using a portable spectrometer.
- Need collaborators in analytical instrumentation industry.

Concluding Remarks

- The identification of a new sensing approach that can be applied for rapid characterization of promising coal-based REE resources and or for monitoring of REE concentrations during industrial processing advances FE's goal of accelerating the advancement of commercially viable technologies for the extraction and recovery of REE from U.S. coal and byproduct resources.
- Next steps and current technical challenges:
 - Further assessment of whether this approach is applicable for detection of REE in a wider range of sample types than coal fly ash.
 - Working with experts in detection device instrumentation to adapt our approach to a rapid portable detection format.

Project team



- Yoshiko Fujita
- David Reed
- John Klaehn



- Alexandra Navrotsky
- Lili Wu
- Jayanthi Kumar



- Andre Anderko
- Margaret Lencka
- Gaurav Das
- Ali Eslamimanesh
- Jerzy Kosinski



- Rik Riman
- Chenshuo (Melody) Ma
- Paul Antonick
- Paul Kim



- Yongqin Jiao
- Dan Park

Acknowledgments



- Rona Donahoe lab at University of Alabama and Fred McLaughlin lab, at University of Wyoming, generously shared coal fly ash samples.
- We thank Jacob Fisher, undergraduate intern from Brigham Young University-Idaho, for performing some initial leaching studies. Jacob's internship at INL was supported by the DOE-SC Science Undergraduate Laboratory Internship (SULI) program.
- Deborah LaCroix at Center for Advanced Energy Studies performed ICP-MS analyses of some of the leachates.
- Funding was provided by DOE-FE, National Energy Technology Laboratory, via the DOE Idaho Operations Office Contract DE-AC07-05ID14517.