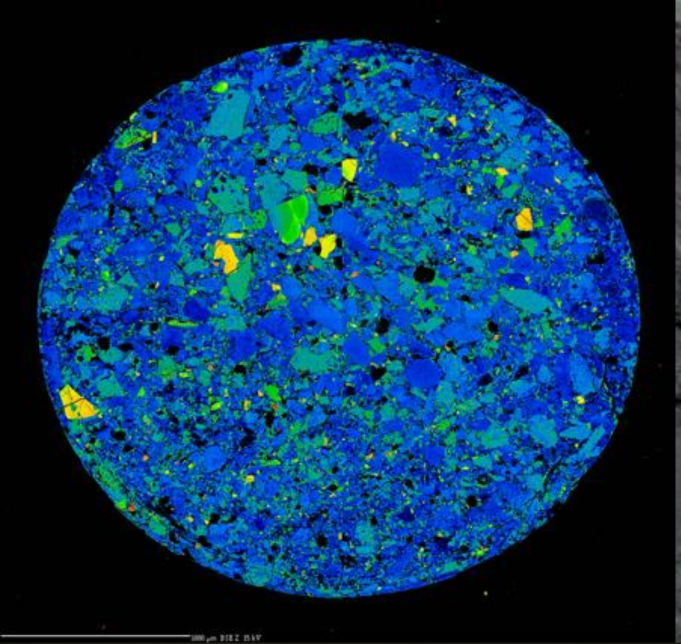

May 26, 2021

Yoshiko Fujita

New Sensing Mechanisms for REE Detection in Coal By-Products

DOE-NETL Rare Earth Elements and Critical Minerals Project Review meeting

Idaho National Laboratory

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Project Description and Objectives

Overall goal: to develop a new simple, sensitive, and rapid approach for detecting rare earth elements in any kind of solid or liquid sample

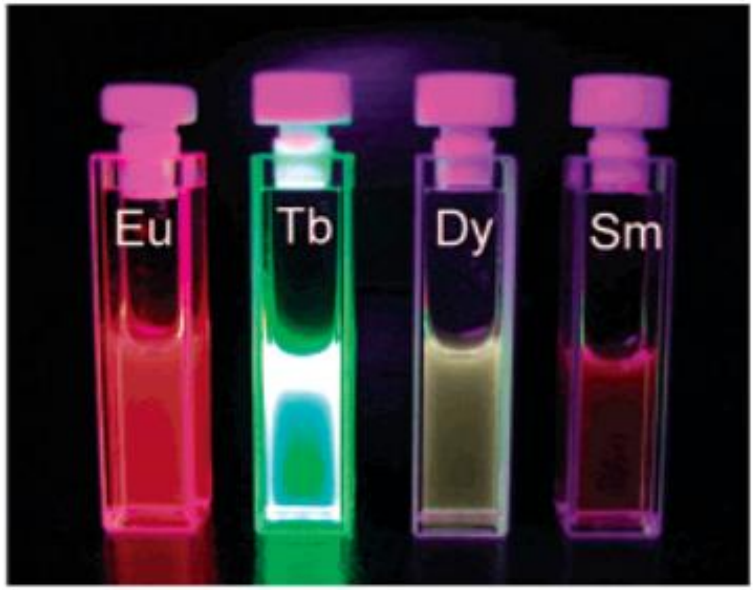


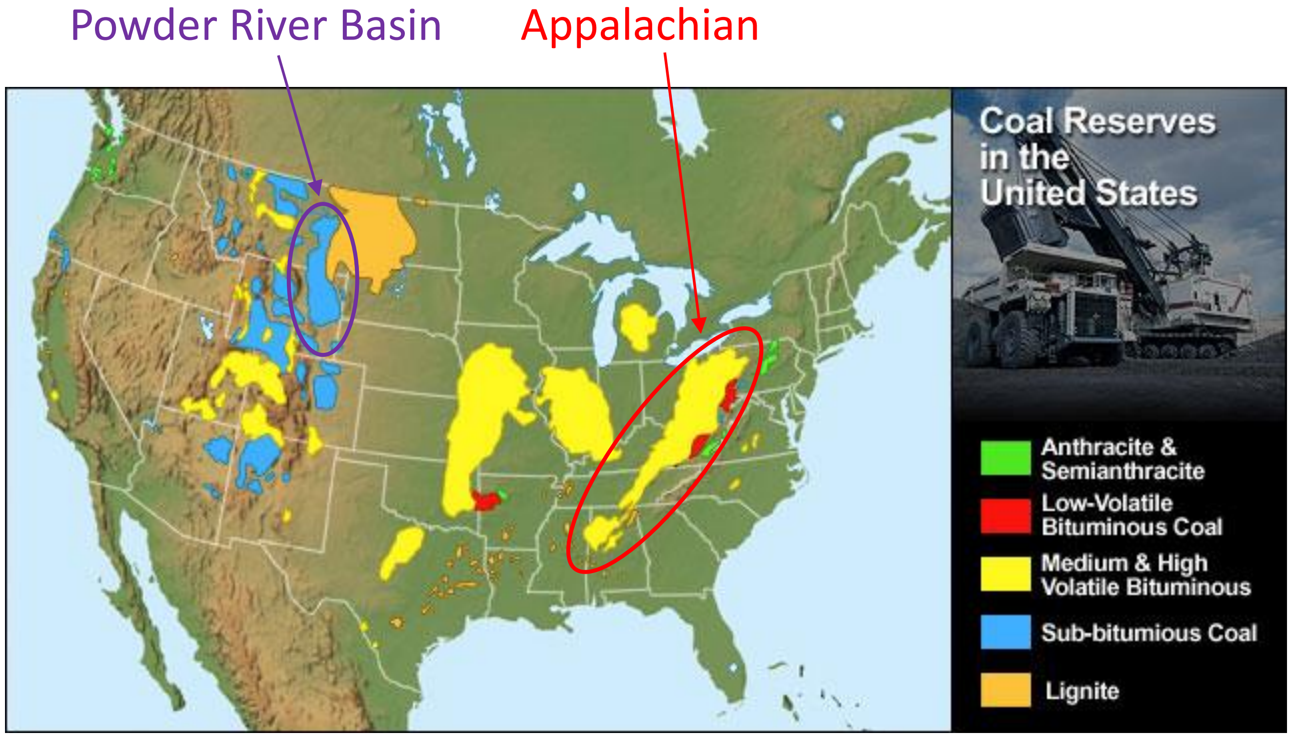
Image from Petoud, S. et al. (2003). JACS, 125 (44), 13324-13325.

Analysis Requirements

- Applicable to diverse chemical/mineral matrices
- Detection of REE in aqueous solutions at ≤ 1 ppm
- Discrimination between multiple co-occurring REE

Research Objectives

- Utilize lanthanide luminescence
- Enhance signal intensity with concentration and host variables
- Demonstrate applicability for a variety of coal and coal by-products
  - ➢ Different coal types/origins



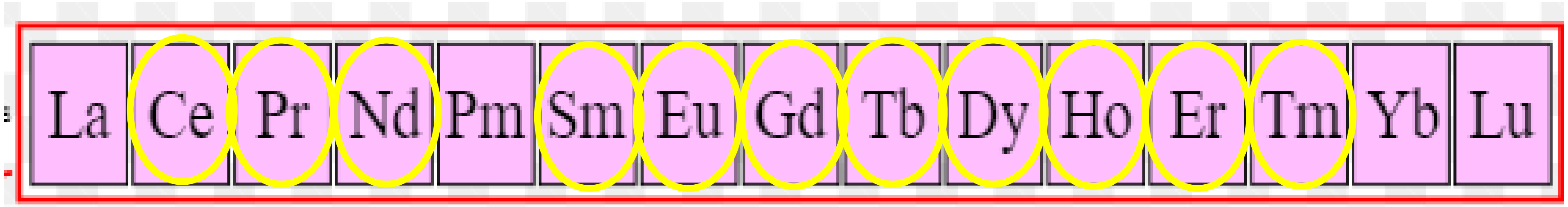
Original image from American Coal Foundation.

Motivation for project: need for simple, inexpensive REE sensing methods suitable for complex samples

- Inductively coupled plasma mass spectrometry (ICP-MS) for measuring dissolved REE
  - ➢ Detection limits typically in low ppb
  - ➢ Analyses expensive, and must be conducted inside laboratory
- X-ray fluorescence (XRF) for solid samples
  - ➢ Calibration for complex samples challenging
  - ➢ Quantitation highly dependent on sample matrix
  - ➢ Detection limits typically in ppm range
  - ➢ Portable XRF not suitable for HREE

Why luminescence?

- Most lanthanides:
  - Luminescent
  - Unique spectra excitation and emission lines
    - Easy to distinguish between any of the REEs below

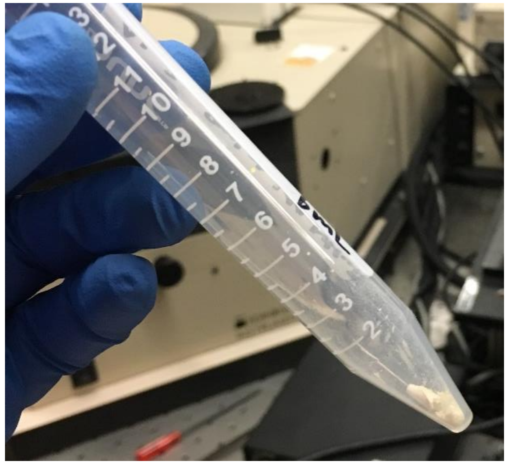


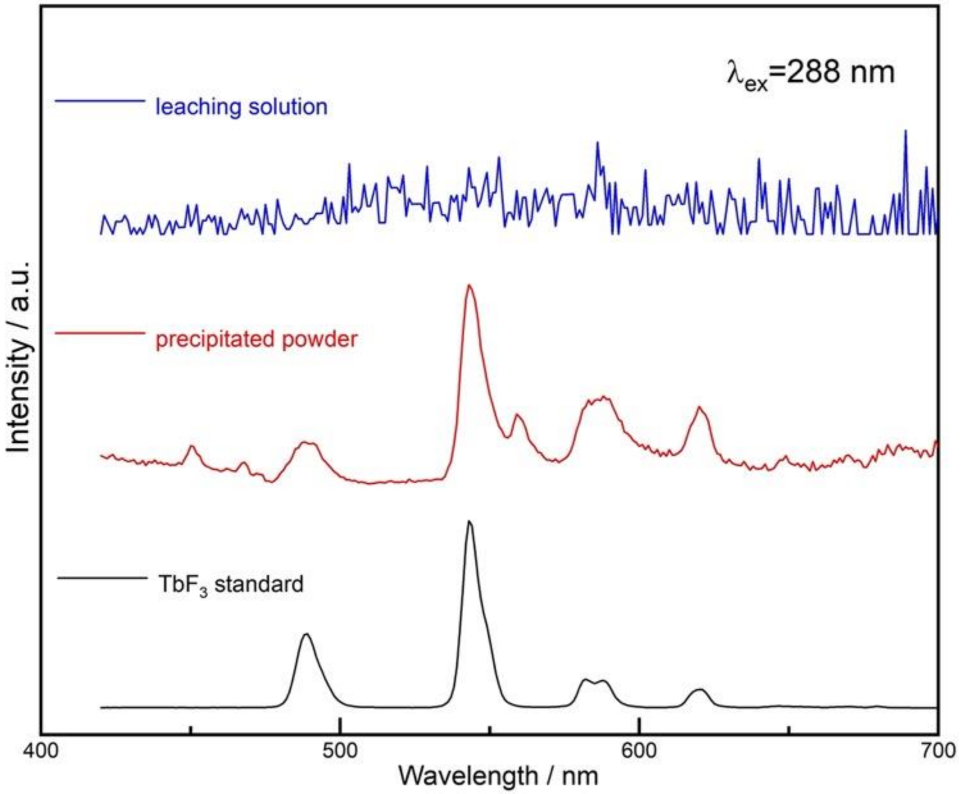
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

- Inexpensive semiconductors can be used for excitation and detection
- Lanthanide luminescence intensity can be enhanced by
  - Concentration
  - Choice of host

Approach: Precipitation of REE from leachates as mineral fluorides

- Fluoride mineral host is good for luminescence
  - ➢ Low phonon energy
- Quantitative precipitation of lanthanides from solution with NH_4F addition
  - ➢ All REE fluorides have low solubility
  - ➢ Independent of pH





Example with Alabama Appalachian bituminous coal leachate

Coal Fly Ashes Used for Method Development

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

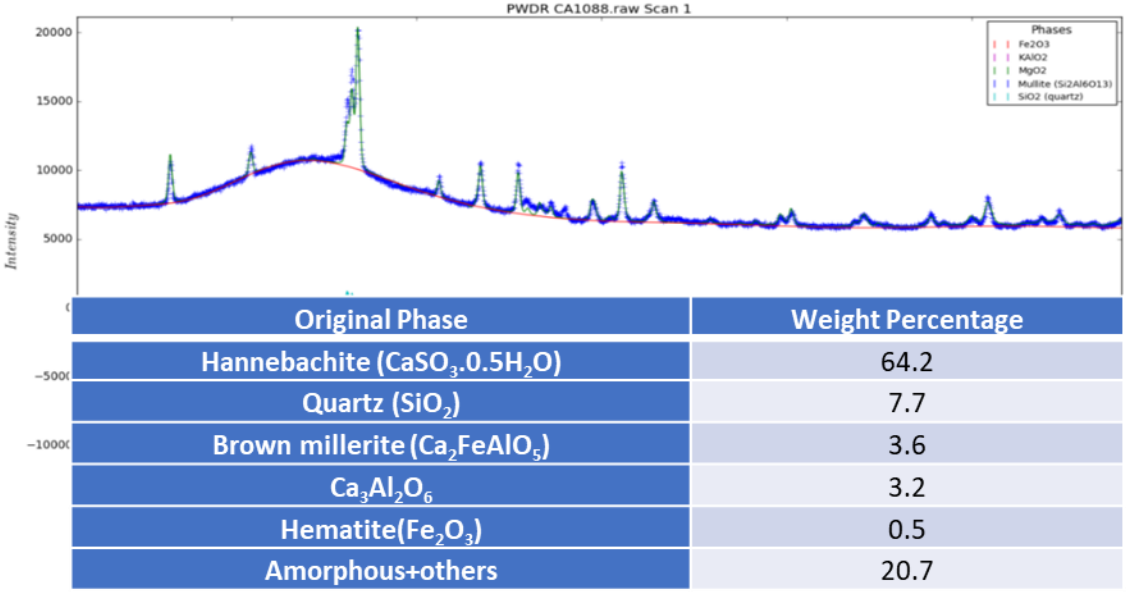
Oxides	AL ash (%)	WY ash (%)
SiO_2	49.3 ± 0.6	26.8 ± 0.3
Al_2O_3	26.5 ± 0.3	14.9 ± 0.1
Fe_2O_3	8.6 ± 0.1	3.9 ± 0.1
CaO	1.2 ± 0.0	26.9 ± 0.2
MgO	1.1 ± 0.0	3.3 ± 0.0
Na_2O	0.4 ± 0.0	2.0 ± 0.0
K_2O	2.9 ± 0.0	0.4 ± 0.0
Cr_2O_3	0.0 ± 0.0	0.0 ± 0.0
TiO_2	1.3 ± 0.0	1.0 ± 0.0
MnO	0.0 ± 0.0	0.0 ± 0.0
P_2O_5	0.2 ± 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

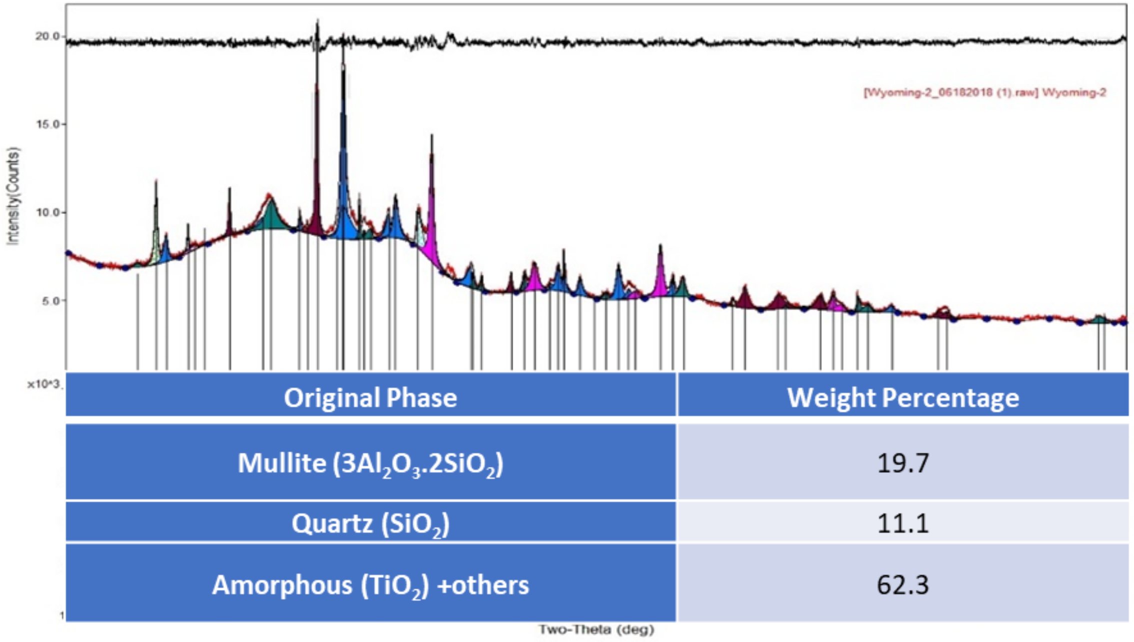
Mineral Composition of Coal Fly Ashes via XRD

Alabama ash



Original Phase	Weight Percentage
Hannebachite ($CaSO_3.0.5H_2O$)	64.2
Quartz (SiO_2)	7.7
Brown millerite (Ca_2FeAlO_5)	3.6
$Ca_3Al_2O_6$	3.2
Hematite(Fe_2O_3)	0.5
Amorphous+others	20.7

Wyoming ash



Original Phase	Weight Percentage
Mullite ($3Al_2O_3.2SiO_2$)	19.7
Quartz (SiO_2)	11.1
Amorphous (TiO_2) +others	62.3

Different ashes likely to yield different products (leachates and precipitates)

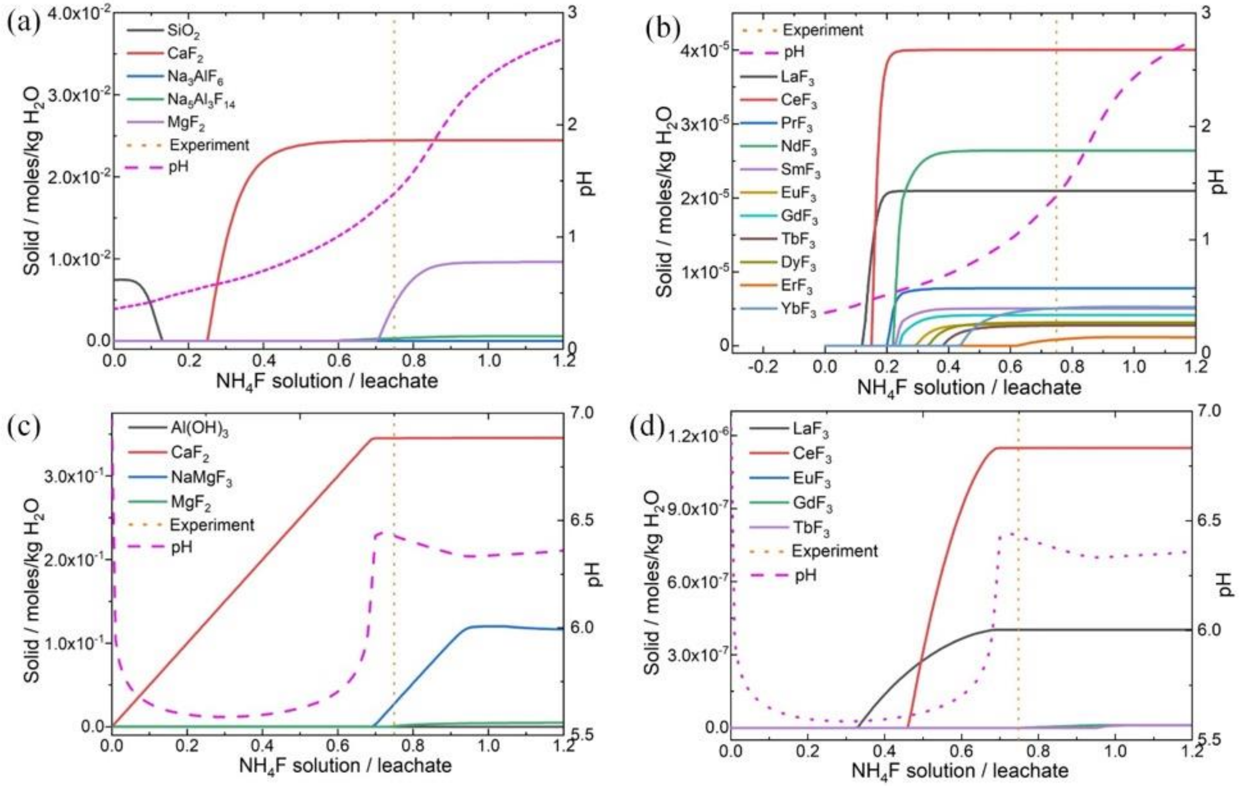
Thermodynamic predictions of reaction products

Primary minerals

LnF_3 minerals

Al leachate
(1M HCl)

WY leachate
(1M HCl)



- CaF_2 and MgF_2 are major phases
- All REEs precipitate

- CaF_2 and $NaMgF_3$ are major phases
- All REEs precipitate

Schematic of approach

Coal ash

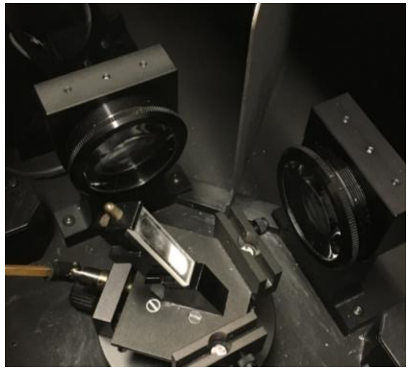
HCl →

Leachate

NH_4F →

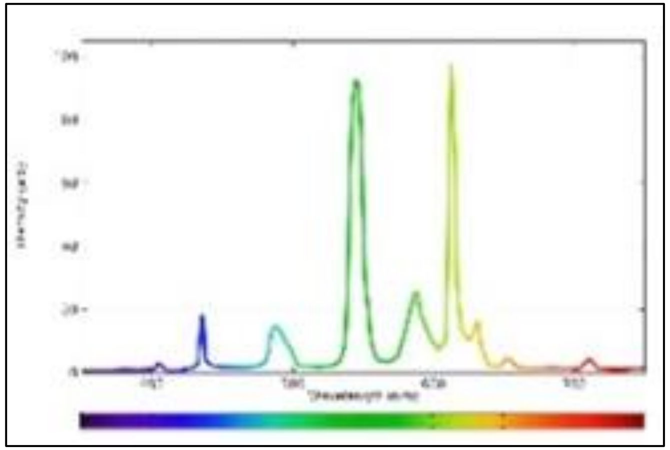
Precipitate

→



Luminescence measurement

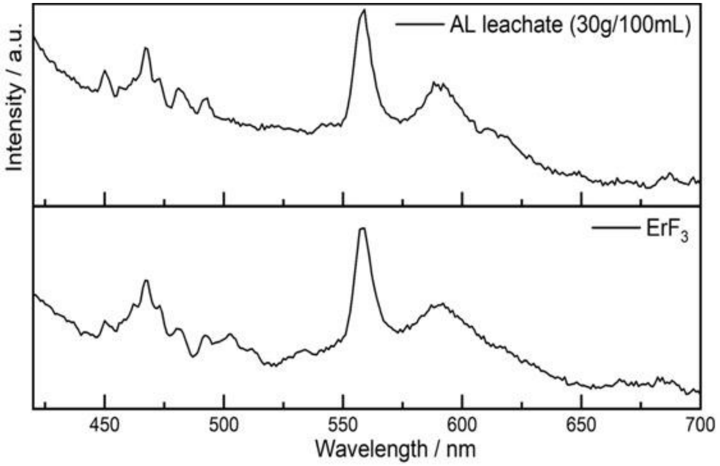
↑



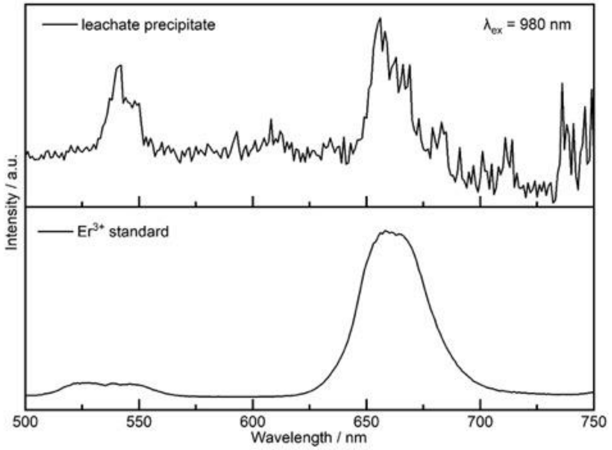
REE detected by “down- and up-conversion”

- Erbium can be detected by both conventional
  - ➢ Down-conversion = excite @ 980 nm; emit @ 1500 nm
  - ➢ Up-conversion = excite @ 980 nm; emit @ 550 nm

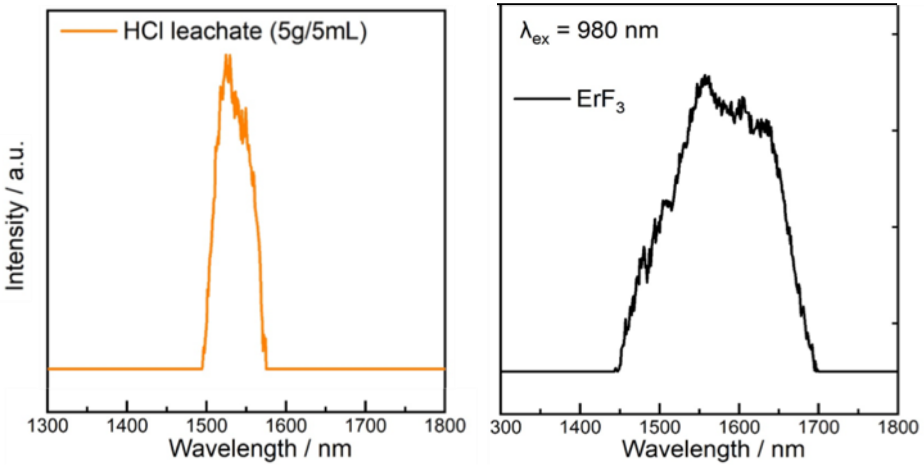
Down-conversion emits more efficiently and is brighter



Excitation Spectra @ 255 nm (UV)



Excitation spectra @ 980 nm (IR)



IR Emission Spectra (down conversion)

Which REE can be detected?

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

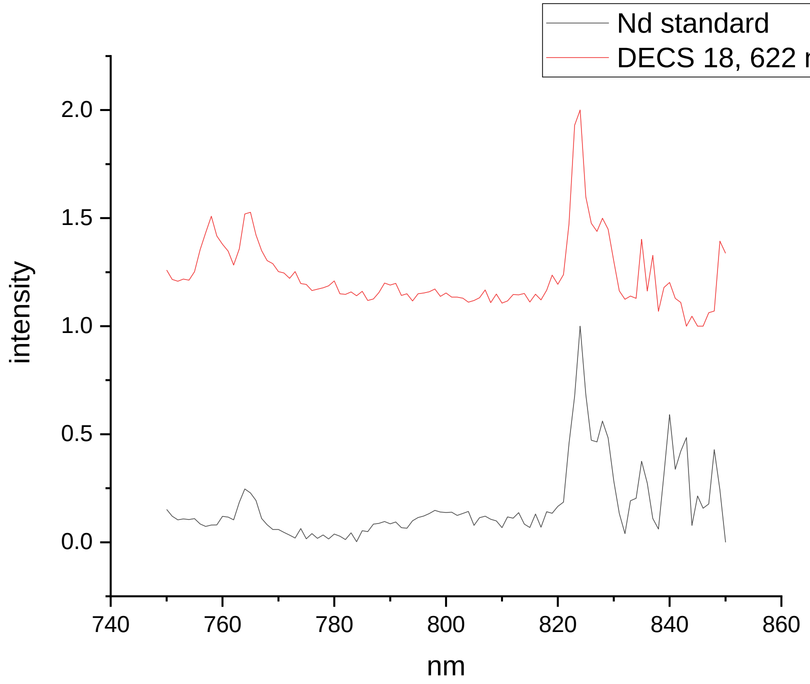
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Does LnF_3 fluoresce?	N	Y	Y	Y	N	Y	Y	Y	Y	Y*	Y*	Y*	Y*	N	N
Detected in AL leachate?	na	N	Y	Y	na	Y	Y	Y	Y	Y	N	Y	N	na	na

Y = Yes. N = No. na = not applicable.
*Detected by upconversion.

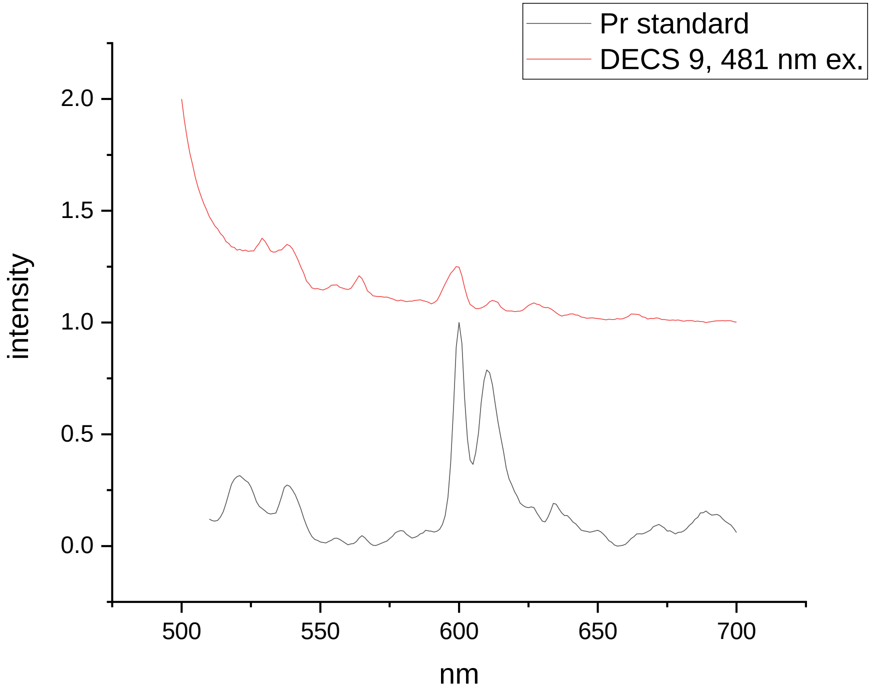
What about other types of samples?

Coal feedstock (bituminous coal)

Penn State coal bank sample DECS-18 (from Union County, Kentucky)



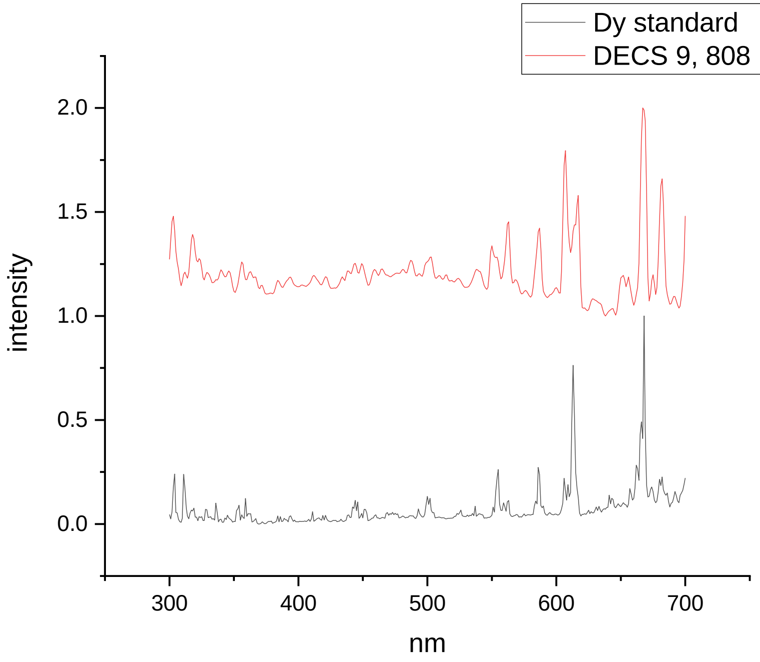
Nd at 445 ppb in HCl leachate



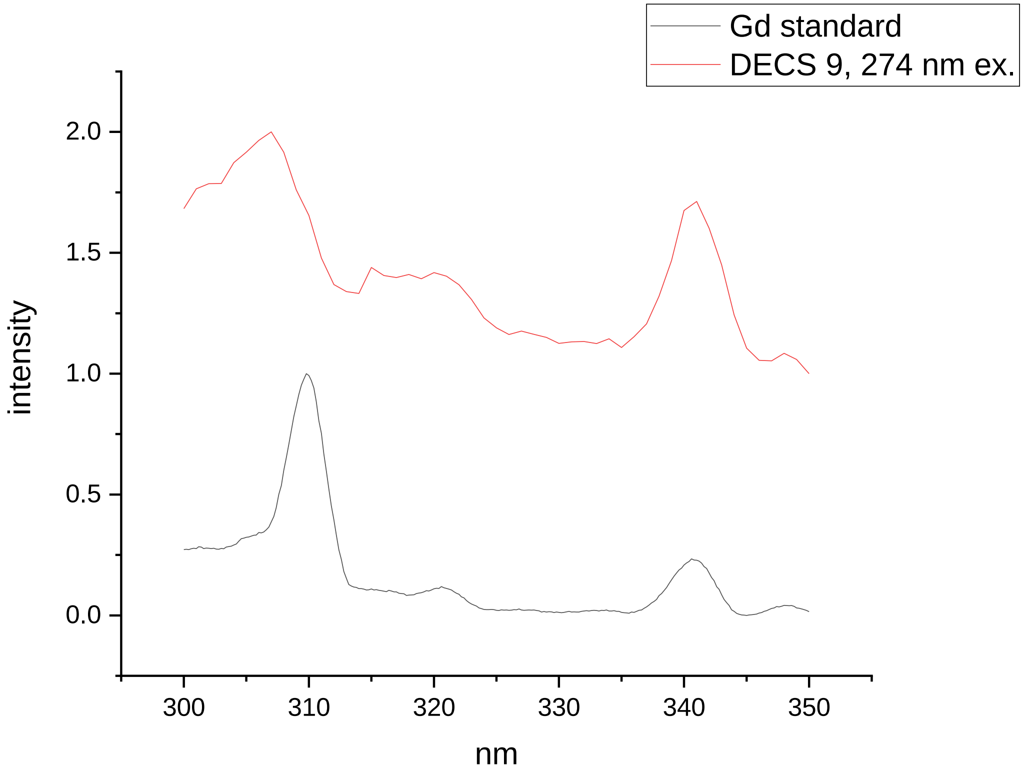
Pr at 114 ppb in HCl leachate

Another coal feedstock (lignite coal)

Penn State coal bank sample DECS-9 (Fort Union region, MT)



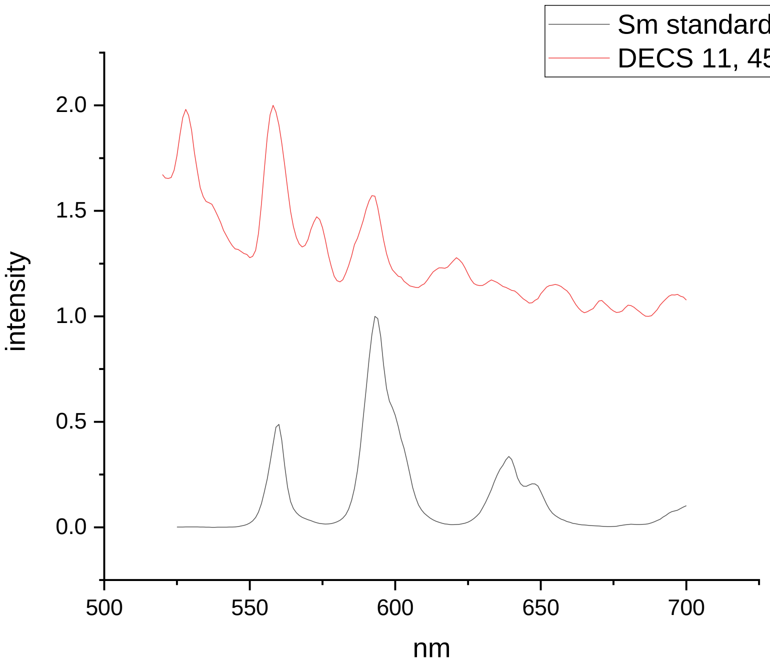
Dy at 2.5 ppb in HCl leachate

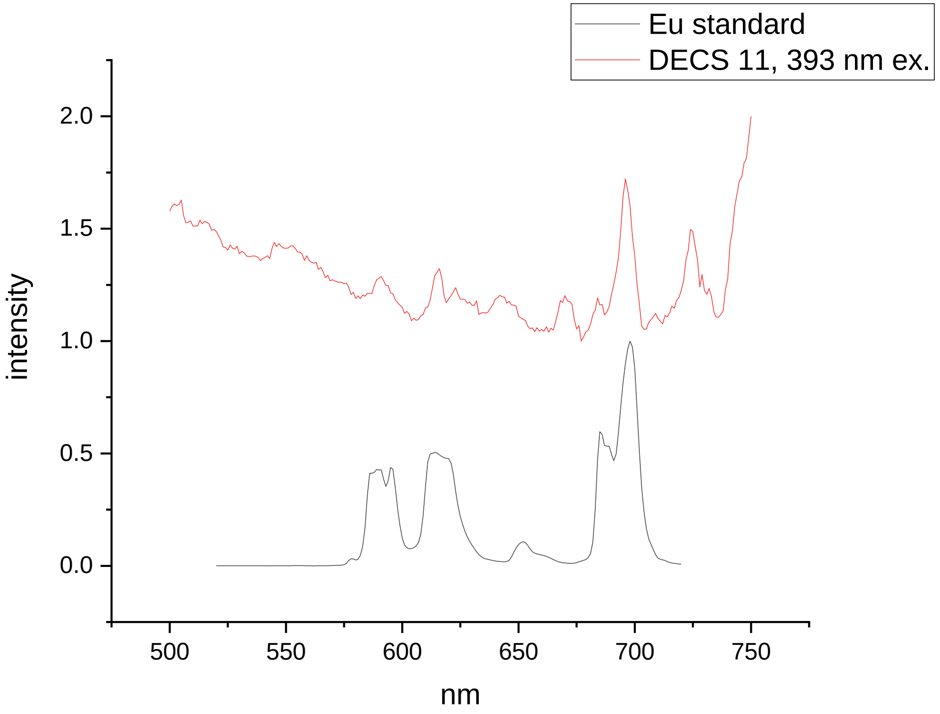


Gd at 61 ppb in HCl leachate

Another lignite coal

Penn State coal bank sample DECS-11 (from Fort Union Region, ND)



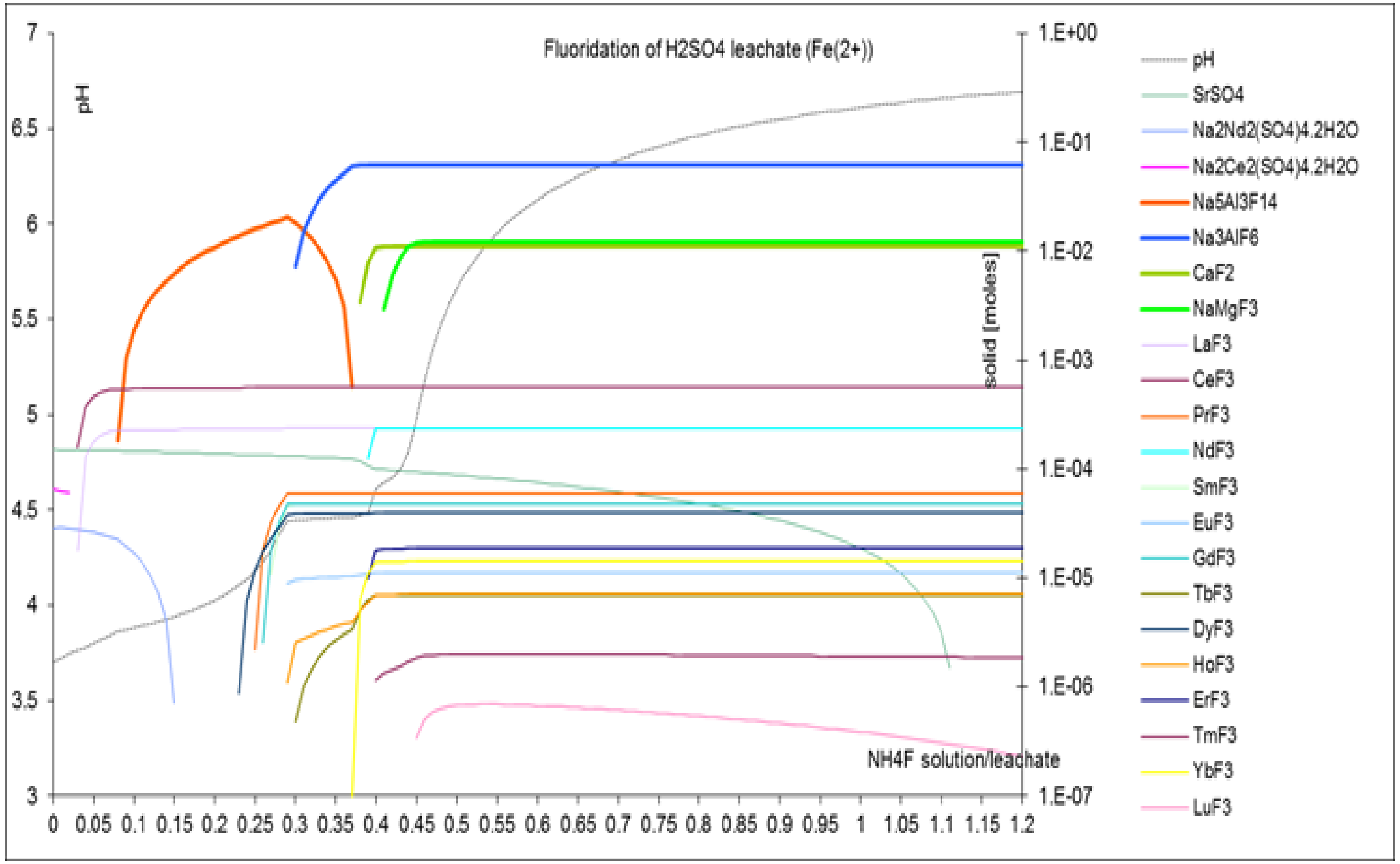


Sm at 486 ppb in HCl leachate

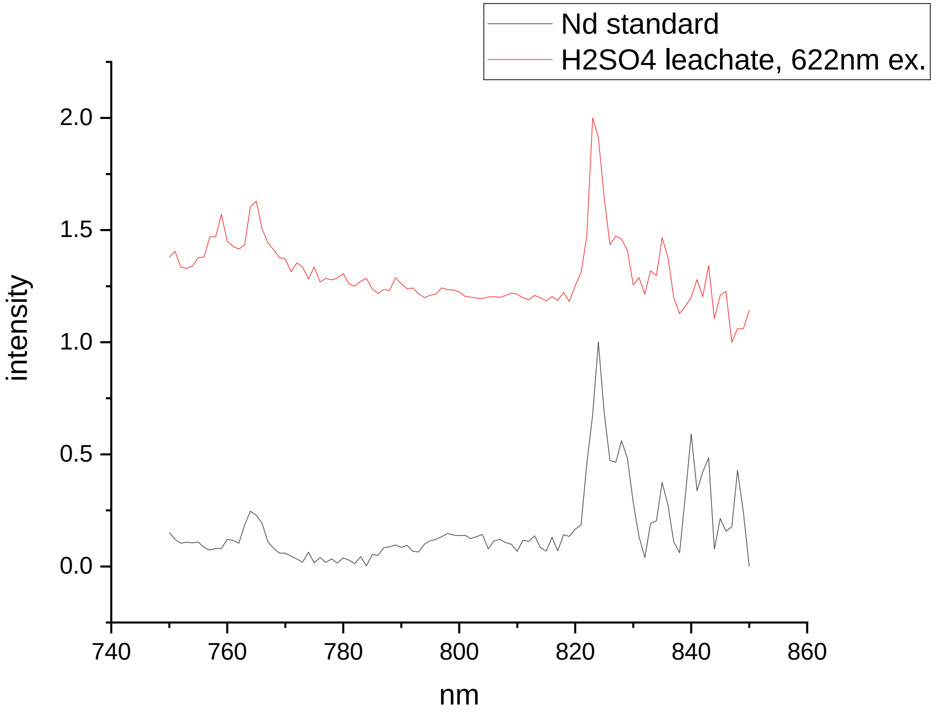
Eu at 28 ppb in HCl leachate

Different acid: H_2SO_4 leachate of AL coal fly ash

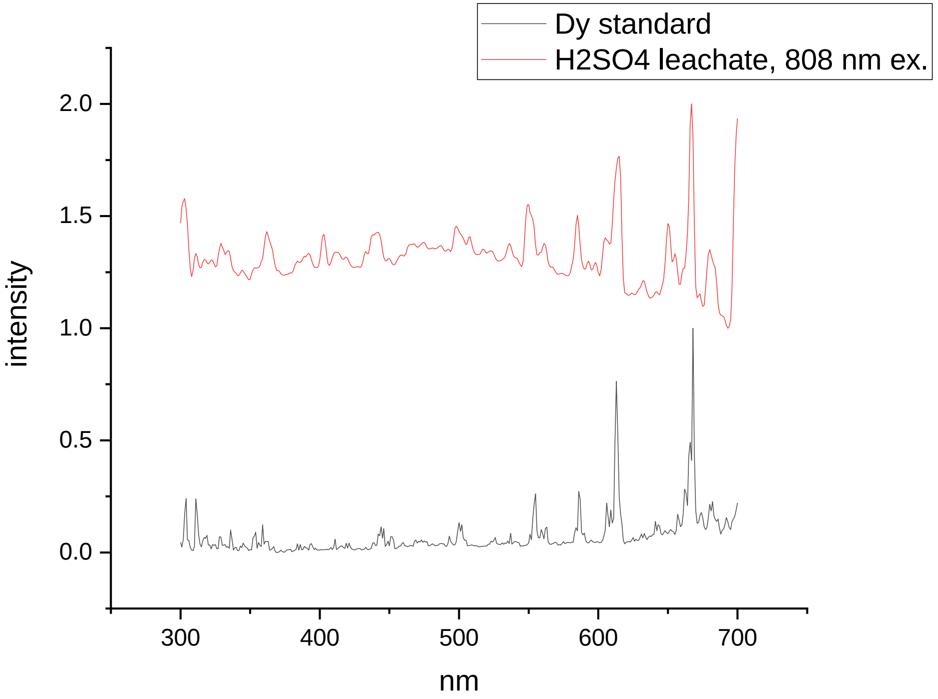
- Thermodynamic simulations predict saturation of leachate with Na-Nd and Na-Ce sulfate double salts
  - $Nd_2Na_2(SO_4)_4 \cdot 2H_2O$ limits REE solubility in leachate
- After NH_4F addition:
  - Remaining REE converted to fluorides
  - Host matrix composed of mixed Na-Al and Na-Mg fluorides as well as CaF_2



REE luminescence in precipitates derived from H_2SO_4 leachates



Nd at 3005 ppb in H_2SO_4 leachate

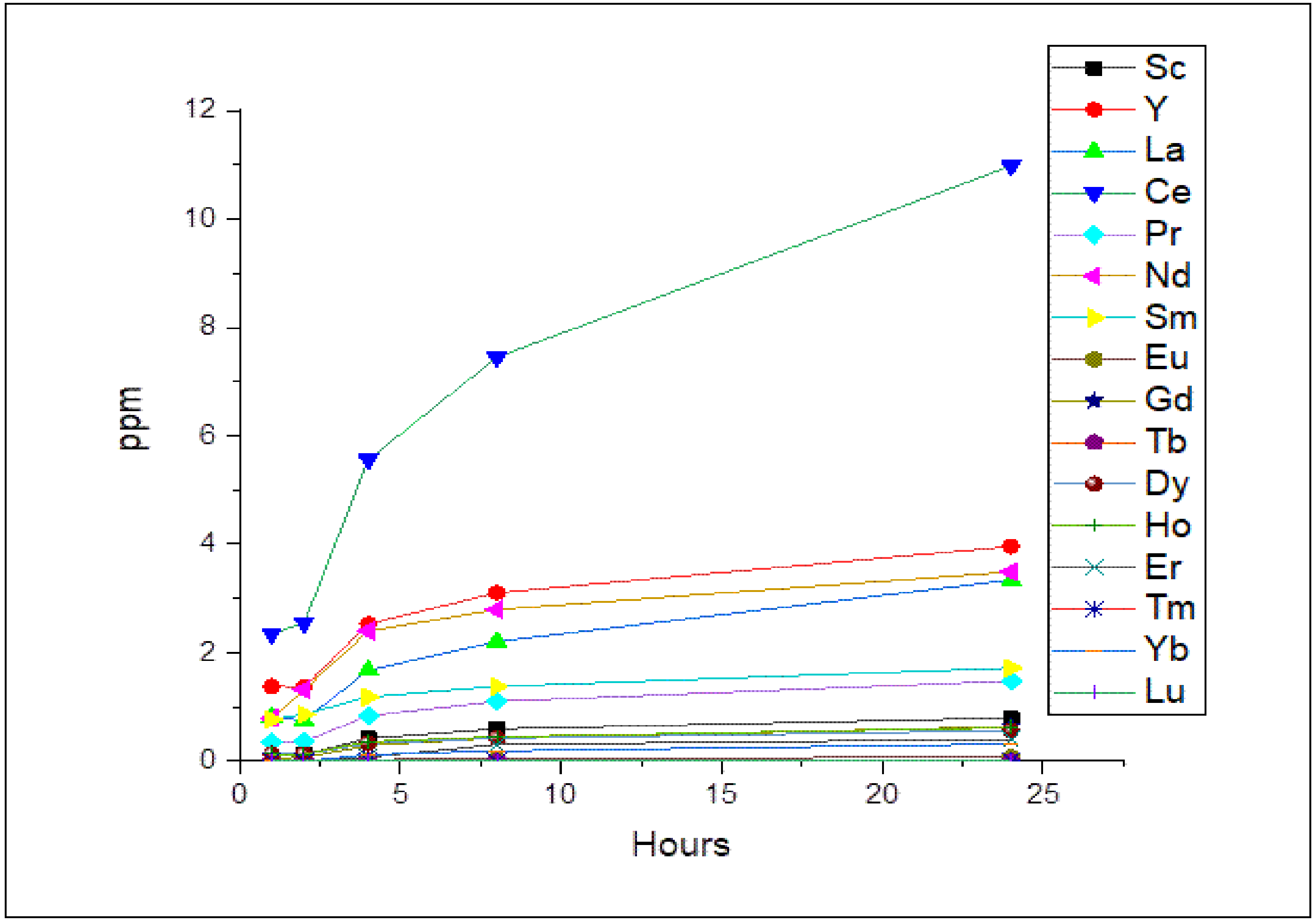


Dy at 461 ppb in H_2SO_4 leachate

How long does the process take?

- Leaching time used in method development 24 h
  - ➢ 30% pulp density, 1 M HCl, room temp (22°C), 500 rpm
- Leaching kinetics studies:
  - ➢ Time could be shorter
    - By 4 h, Sm and Nd reach ~70% of 24 h value
    - But even 1 h likely sufficient
- Precipitation kinetics:
  - ➢ Rapid; ≤ 1 h sufficient

Total time could be ≤ 1 h



Summary and next steps

- Fluoride precipitation allows luminescent REE detection in complex samples
- Unique excitation and emission spectra allow discrimination of individual lanthanides at leachate concentrations as low as 1 ppb
- Generation of fluoride precipitates is rapid and simple
- Future work:
  - ➢ Optimization of protocol (faster, simpler)
  - ➢ Field test kit using portable vials and syringe filters; detection w/smartphone coupled with battery powered LED excitation light source

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