Evaluation of Novel Strategies and Processes for Separation of Rare-Earth Elements from Coal-Related Materials
Project FE-810-17-FY17

Project Team

Hakim Boukhalfa, *PI*

Biogeochemistry

Artaches Migdissov

Hydrothermal Geology

George Goff

Chemical Engineering

Giday WoldeGabriel

Geology

Steve Yarbro

Inorganic Chemistry

Iain May

Inorganic Chemistry

George Guthrie

Mineralogy & Geochemistry;

Ex officio: Coordination with LIBS-Based REE analysis Project

Los Alamos NATIONAL LABORATORY EST. 1943

April 9, 2019

Project Goals/Objectives & Tasks

Task 1: **Evaluation of current and enhanced actinide/lanthanide separation processes relative to identifying potential processes/strategies for REE separation from coal-related materials**

Deliverables: Report detailing an evaluation of existing actinides/lanthanides separation approaches developed for nuclear materials and their potential application for REEs extraction from coal-related products.

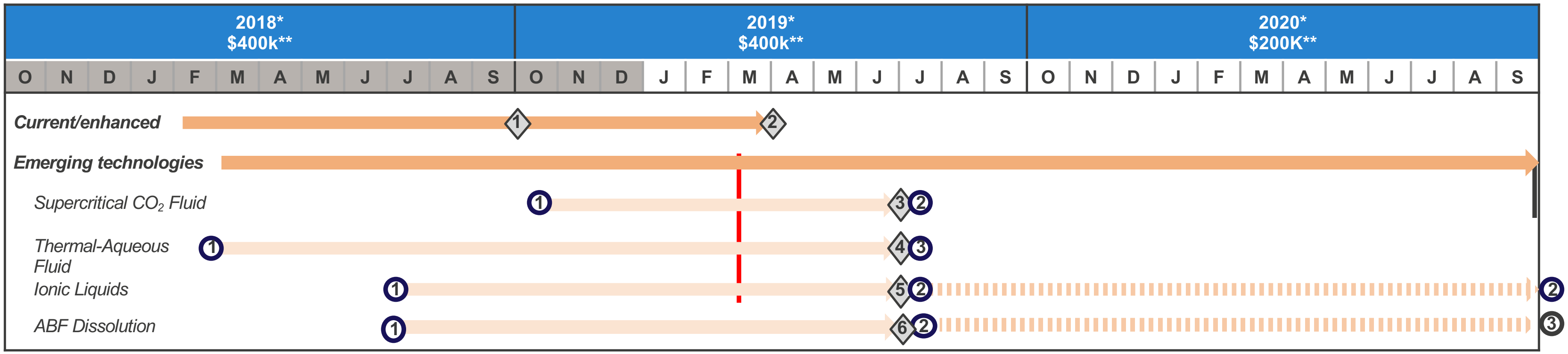
- ***Task 2:*** **Evaluation of emerging separations technologies processes/strategies for REE separation**
  - **Subtask 2.1: Supercritical CO_2, and soluble ligands application for simple and effective separation of REE**

    Deliverables: Report with a preliminary techno-economic evaluation of the potential use of supercritical CO_2, with selective ligand systems to develop REE separation processes from coal-related materials
  - **Subtask 2.2: Potential applications of ionic liquids and process intensification for** separation of Rare-Earth Elements from coal-related materials

    Deliverables: Report with a preliminary techno-economic evaluation of the potential use of ionic liquids and immerging process intensification techniques for REE separation from coal-related materials
  - **Subtask 2.3 :Hydrothermal approach for extraction and separation of Rare-Earth Elements from coal-related materials**

    Deliverables: Report with a preliminary techno-economic evaluation of the viability of the hydrothermal concentration approach for REE separation from coal-related materials

Evaluation of Novel Strategies and Processes for Separation of Rare-Earth Elements from Coal-Related Materials (LANL_FE-810-17-FY17)



Milestones

1. Review of current & enhanced separations for actinides/lanthanides relative to extension to coal-related materials
2. Assessment of current NETL REE separations portfolio relative current/enhanced separations for actinides/lanthanides
3. Preliminary technoeconomic assessment of supercritical CO_2 based separation
4. Preliminary technoeconomic assessment of geo-inspired thermal, aqueous-fluid based separation
5. Preliminary technoeconomic assessment of ionic-liquids based separation

Chart Key

\# TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Go / No-Go

Proceed with additional bench-scale R&D?
Decision based on proof of concept and of technoeconomic potential for a transformational path for REE separations from coal-related material.

Impact

Key Accomplishments/Deliverables	Value Delivered
2019: Assessment and transfer of learnings from actinide/lanthanide processes that could benefit current separations strategies for REE in coal-related materials **2019:** Preliminary technoeconomic assessment of several emerging technologies for REE/coal **2020:** Maturation and re-assessment of selected emerging technologies with potential for economically viable transformational option for REE separations from coal-related materials	• Improvements to existing DOE-FE/NETL portfolio for REE separations from coal-related materials based on learnings from LANL core-mission separations for actinides/lanthanides • Options for extraction/separation of REE from coal-related materials, with potential for transformational improvements in economics, efficiency, and/or environmental impacts

*FY of Performance **FY of funds

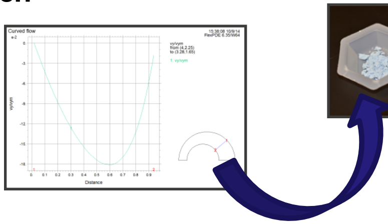
Subtask 2.1: Supercritical CO_2, and soluble ligands application for simple and effective separation of REE

Steve Yarbro, EES-14, LANL

Task objectives

- Use supercritical CO_2 with selected extractants and acids to recover lanthanides with high efficiency and low waste generation from coal and coal residues (fly-ash).
- Build on prior successful experience with using supercritical CO_2 to recover lanthanides from ore and oxides.
- Use data to provide experimental basis for a cost benefit engineering analysis to assess commercial scale operations to recover strategic materials as part of ongoing DOE missions.

Technical Approach



Velocity profile

One step dissolution from ore directly into a separation process capable of separating lanthanides will dramatically reduce the cost and facility footprint

Accomplishments to date against the objectives

Preliminary extractions with low acid concentration completed on both Alaskan coal and project fly-ash have been completed. Initial extraction efficiency was low for lanthanides, but high for lithium and medium for uranium. Low acid was used as a starting point for extraction tests to reduce the extraction of non-metallic elements such as carbon and silica. Initial tests did not show significant extraction of either carbon or silica.

Forecasted accomplishment at the end of FY2019

Additional extractions will be performed at higher acid and extractant concentrations to measure the influence of concentration on lanthanide extraction efficiency and selectivity.

Concerns or challenges

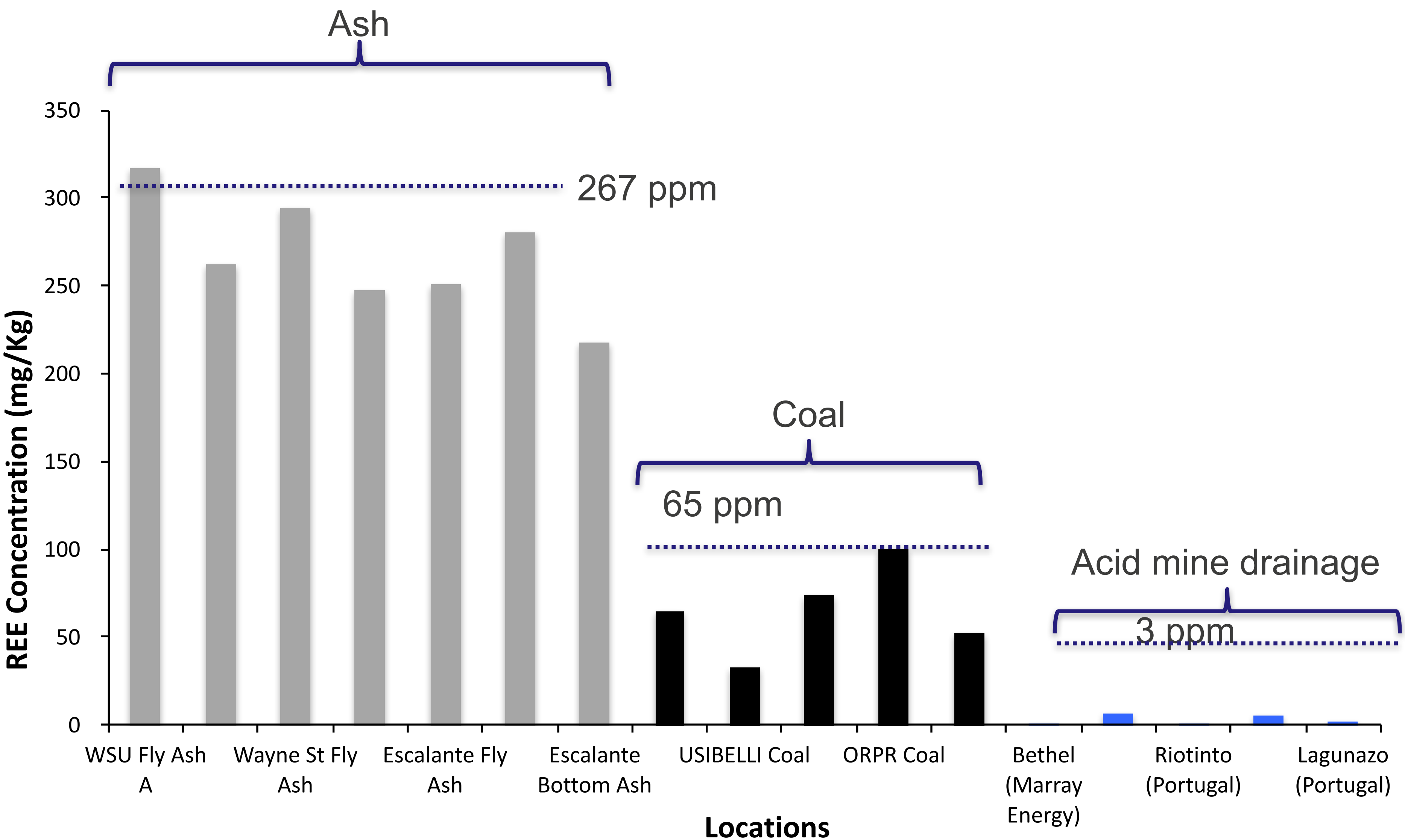
Prior work with lanthanide ores and oxides demonstrated essentially quantitative extraction of lanthanides. These tests were conducted with ore and oxide base materials. Main issue is understanding if the carbon and silica materials may interfere with efficiency and selectivity as acid and extractant concentrations are increased.

Subtask 2.3 :Hydrothermal approach for extraction and separation of Rare-Earth Elements from coal-related materials

Task objectives

- Develop an industrial technology mimicking natural systems (thermodynamic models), and permitting cost-efficient hydrothermal separation and concentration of REE from acid mine drainage (AMD).
- Advantages of this approach lies in the potential ability to selectively extract/concentrate M/HREE (market price $70-500/kg), leaving undesired LREE ($6/kg) in solutions or host rocks, and the possibility to of avoiding the involvement of highly concentrated acids and bases.

Introduction



REE concentrations in ash and coal and acid mine drainage

Introduction

Time	LIGHT RARE EARTH METALS	Last Price	Units
09 May 2018	Lanthanum metal ≥ 99%	6.00	US$/kg
09 May 2018	Cerium metal ≥ 99%	6.10	US$/kg
09 May 2018	Praseodymium metal ≥ 99%	128.00	US$/kg
09 May 2018	Neodymium metal ≥ 99.5%	70.00	US$/kg
09 May 2018	Samarium metal ≥ 99.9%	15.50	US$/kg
Time	**HEAVY RARE EARTH METALS**	**Last Price**	**Units**
09 May 2018	Gadolinium metal 99.9%	46.00	US$/kg
09 May 2018	Terbium metal ≥ 99.9%	665.00	US$/kg
09 May 2018	Dysprosium metal ≥ 99%	278.00	US$/kg
09 May 2018	Erbium metal ≥ 99.9%	111.85	US$/kg
09 May 2018	Yttrium metal ≥ 99.9%	37.50	US$/kg
09 May 2018	Scandium metal 99.9%	3,617.00	US$/kg
09 May 2018	Mischmetal ≥ 99%	6.00	US$/kg

Predominant REE, in order of median concentrations (range in µg/L):

La	0.005 – 140
Ce	0.01 – 370
Nd	0.006 – 260
Gd	0.005 – 110
Dy	0.002 – 99
Sm	<0.005 – 79
Y	0.11 – 530
Sc	1.0 – 36

Cravotta, C.A. (2008) Dissolved metals and associated constituents in abandoned **coal-mine discharges**, Pennsylvania, USA. Part 1: Constituent quantities and correlations. Applied Geochemistry 23, 166–202

Hydrochloric Acid, Technical: $77.00 / 2.5 l
Sodium hydroxide, Technical: $43.34/ 5 l
Sulfuric Acid, Technical: $92.04/ 2.5 l

Challenge: extraction/concentration technology needs to be economically competitive

Introduction

Motto: Nature does not use expensive reagents or strong acids to extract and concentrate REE to ore bodies– not much more than hot water and abundant ligands!

Known natural depositional (concentration) mechanisms:

Extremely low solubility of REE phosphates and fluorides

Just traces of F or PO_4 lead to REE precipitation
(e.g., ocurrence of F- or PO_4-bearing minerals in the rock with which REE-bearing solution contacts)

Solubilities are so low that REE precipitation is preferential to other elements (selective)

Solubilities are retrograde (decrease with increasing temperature)
most efficient at higher T

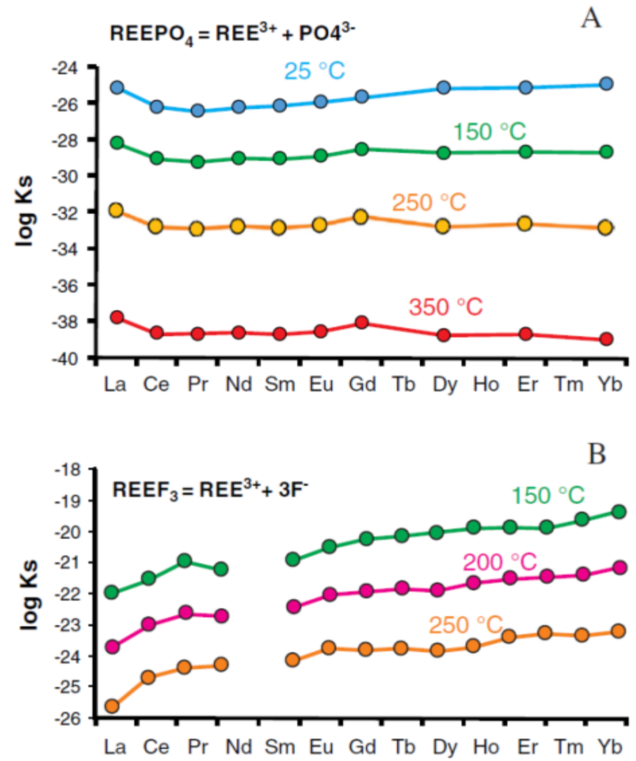
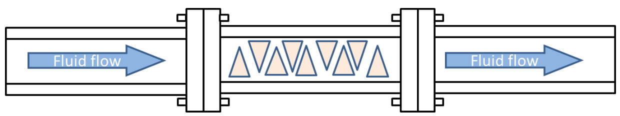
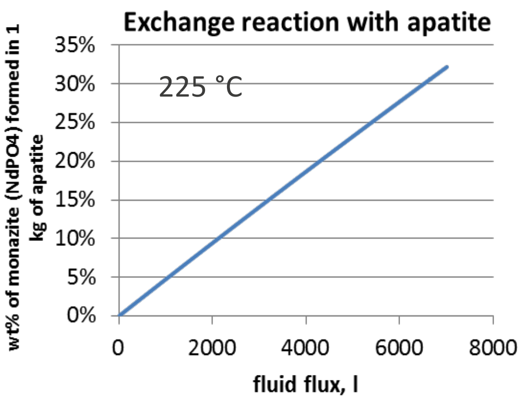


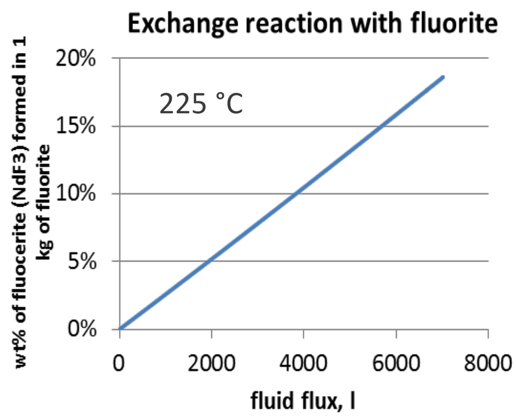
Fig. 26. The distribution of values for the solubility products of REE phosphates (A) and fluorides (B) at different temperatures.

Mimicking nature:



A cartridge with fluorite or apatite chips

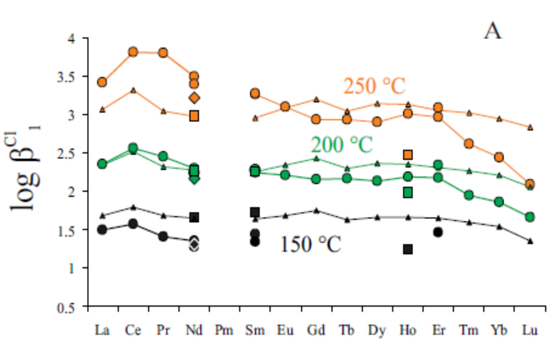


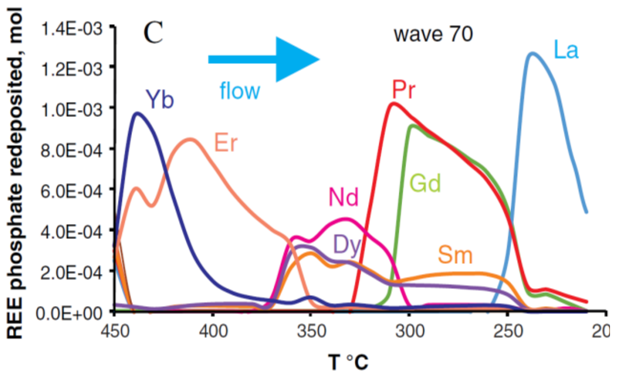


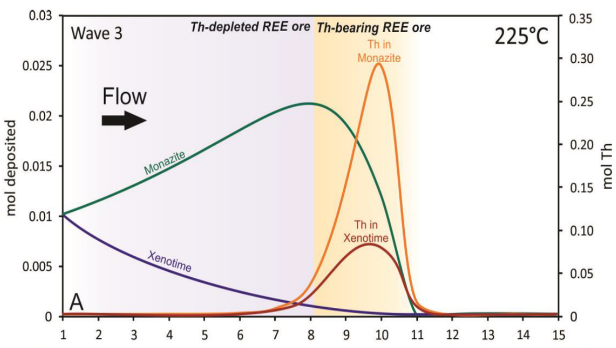
Thermodynamic model of the process:
interaction of 1 kg of apatite or fluorite with the solution having 250 ppb Nd (coal-mine discharges)

Assuming daily flux of 4000 gal (~15000 l) this technique can produce daily 7150 g of REE phosphate (monazite) or 3850 g of REE fluoride (fluocerite)

Additional bonus – LREE, HREE, and Th can be separated:







Proof-of-concept experiments: method

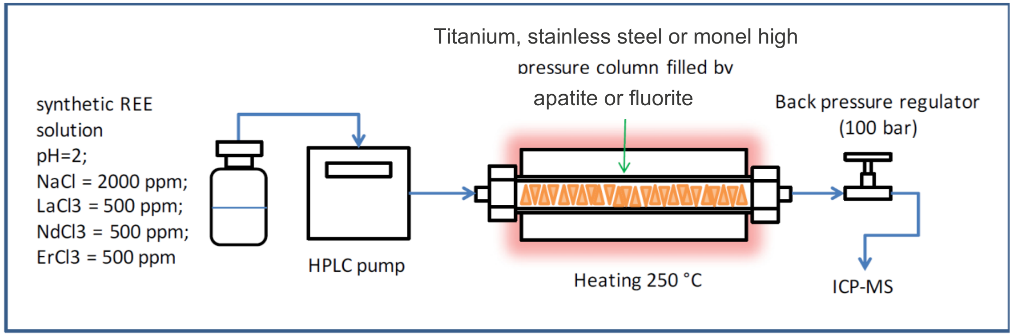
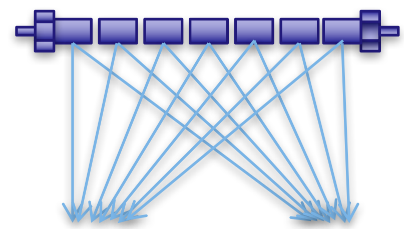


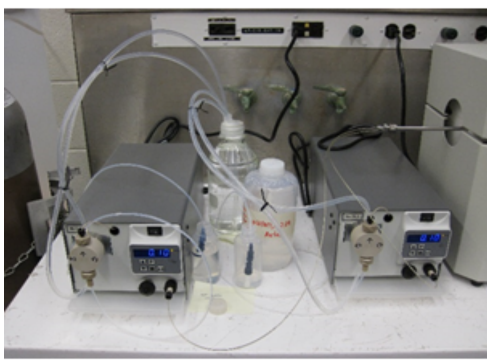
Figure 2. Design of the proof-of-concept experiments mimicking extraction and separation mechanisms illustrated in Figure 1.

Post-experiment treatment

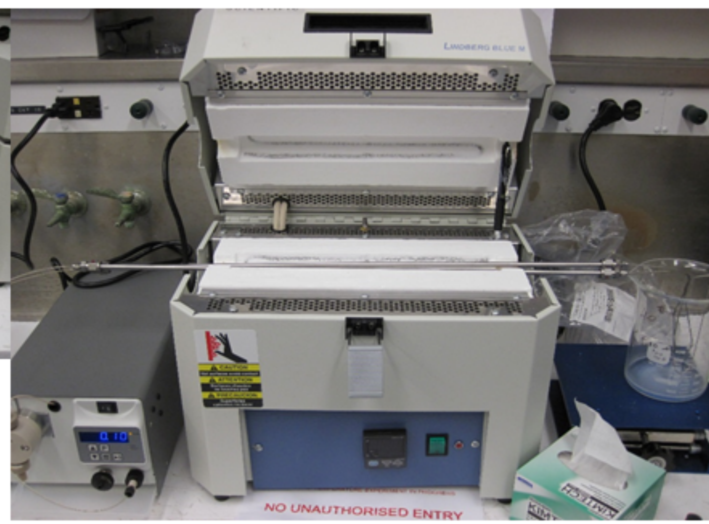


XRD
(mineral composition)

XRF
(chemical composition)



High Pressure Pumps

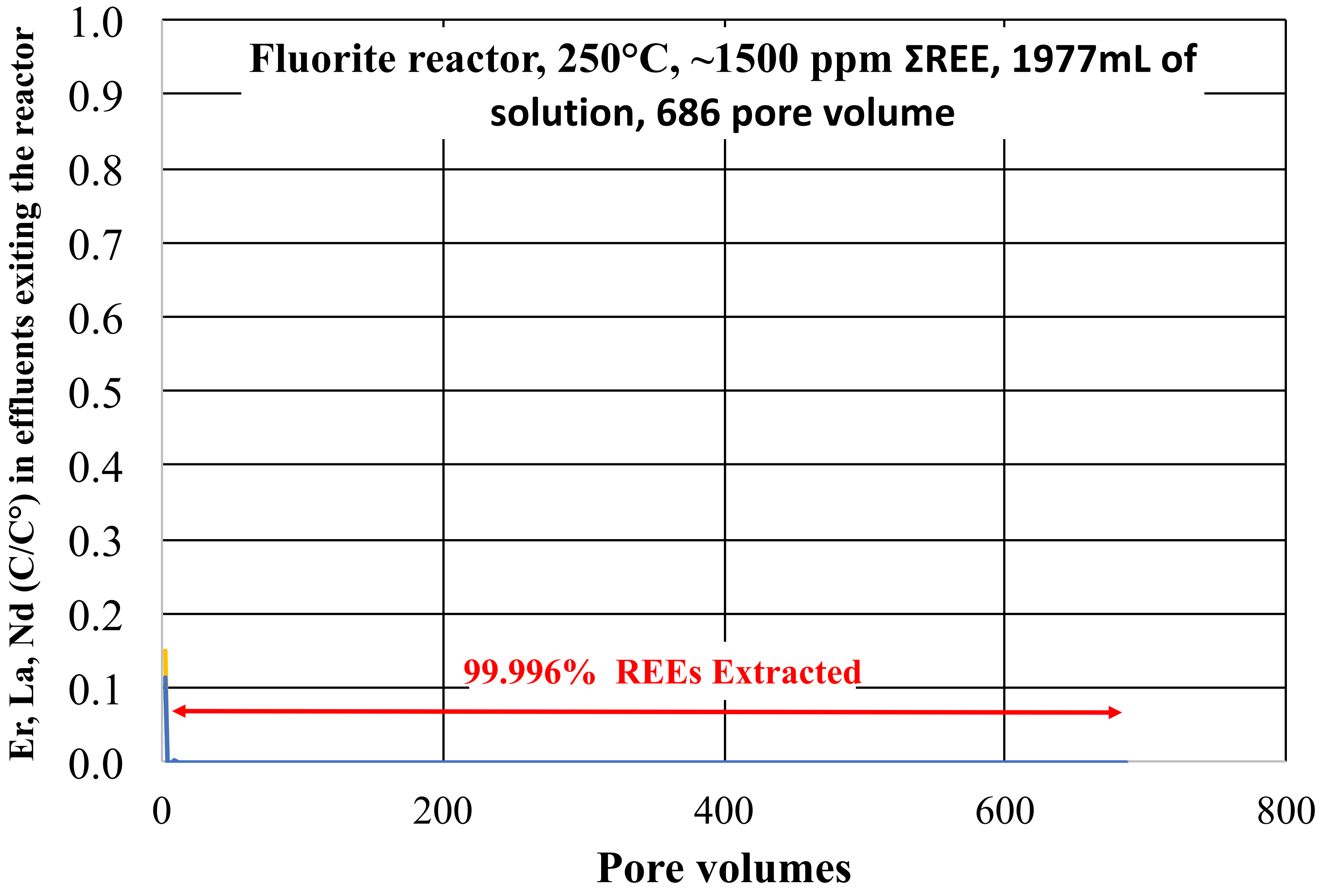


Oven

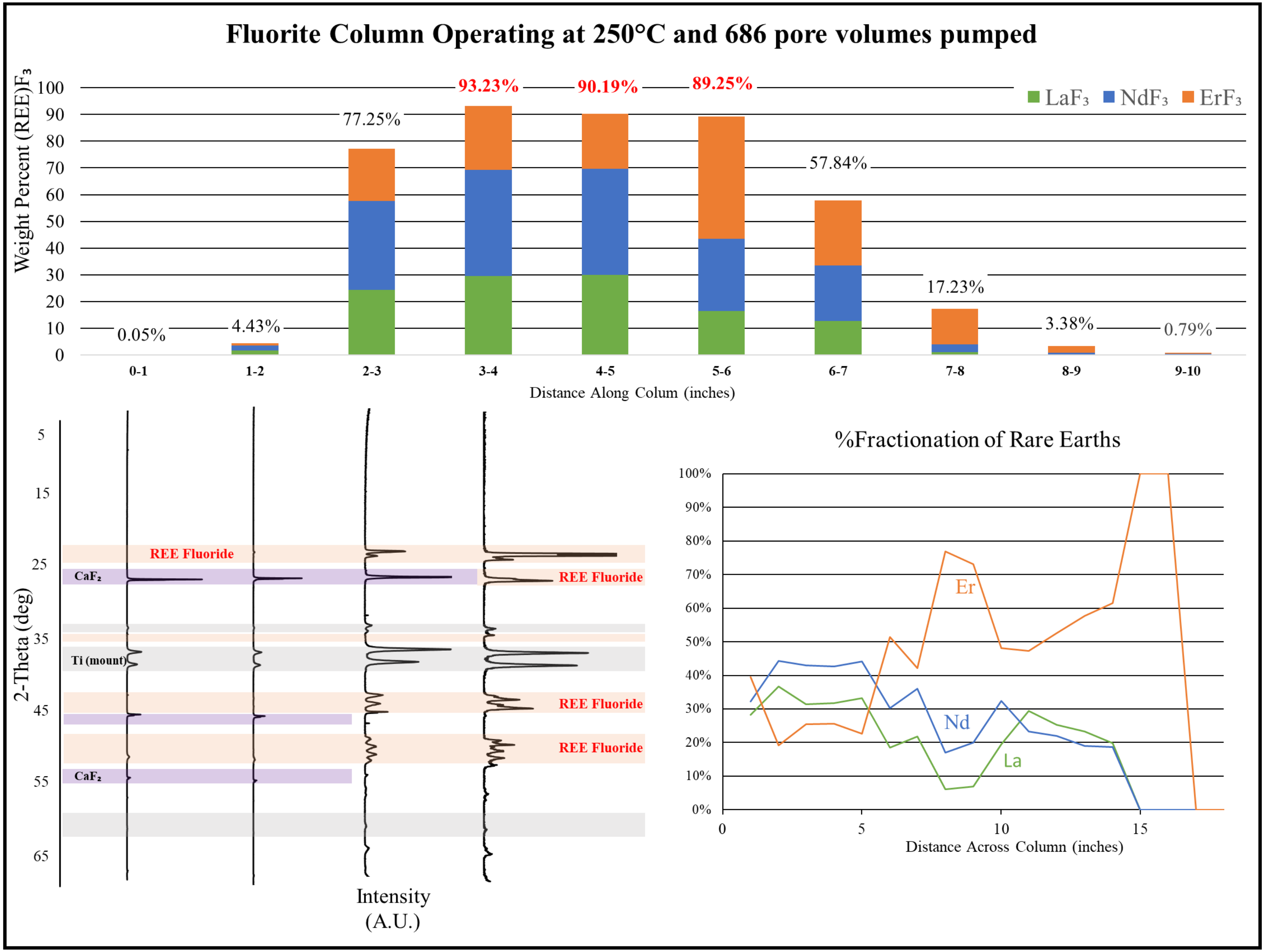
Fraction collector

Fluorite (CaF_2) - filled reactors

Fluorite (CaF_2) - filled reactors

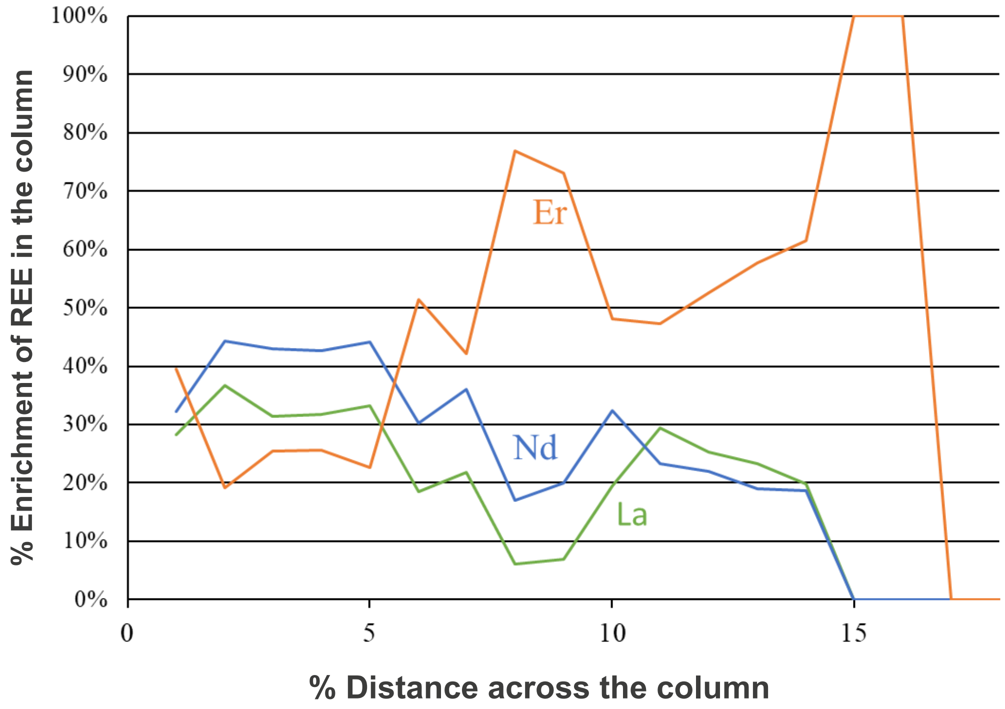


Fluorite (CaF_2) - filled reactors

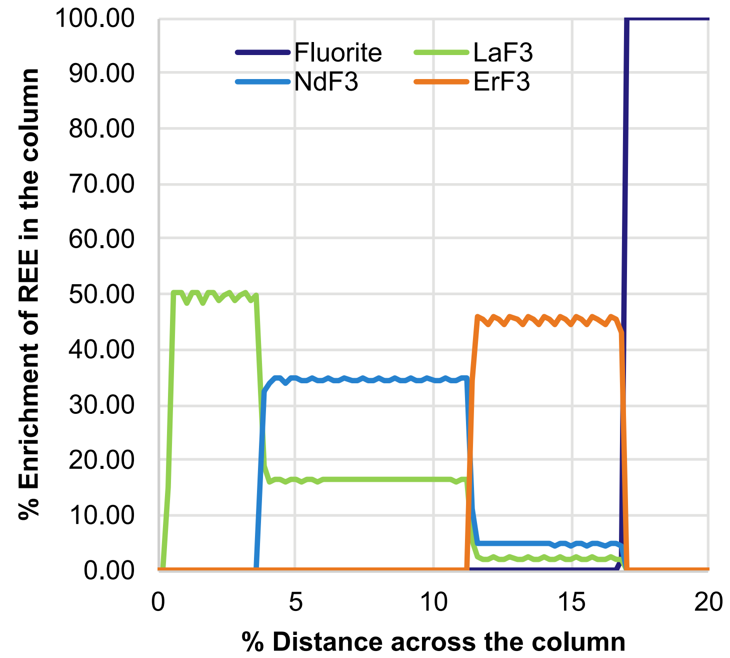


Comparison between experiments and model results for the composition of the fluorite filled reactor

Experimental Data

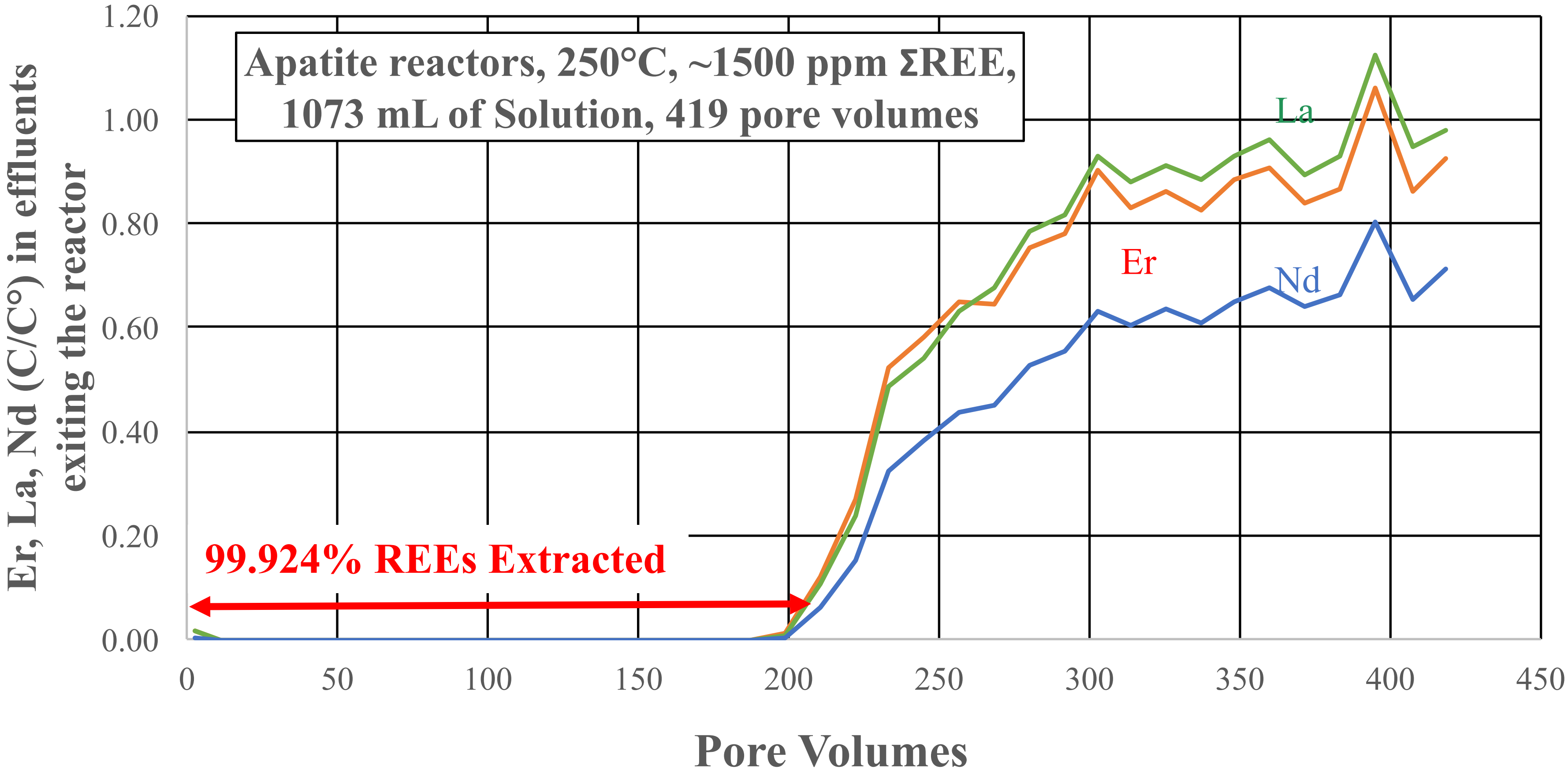


Model results

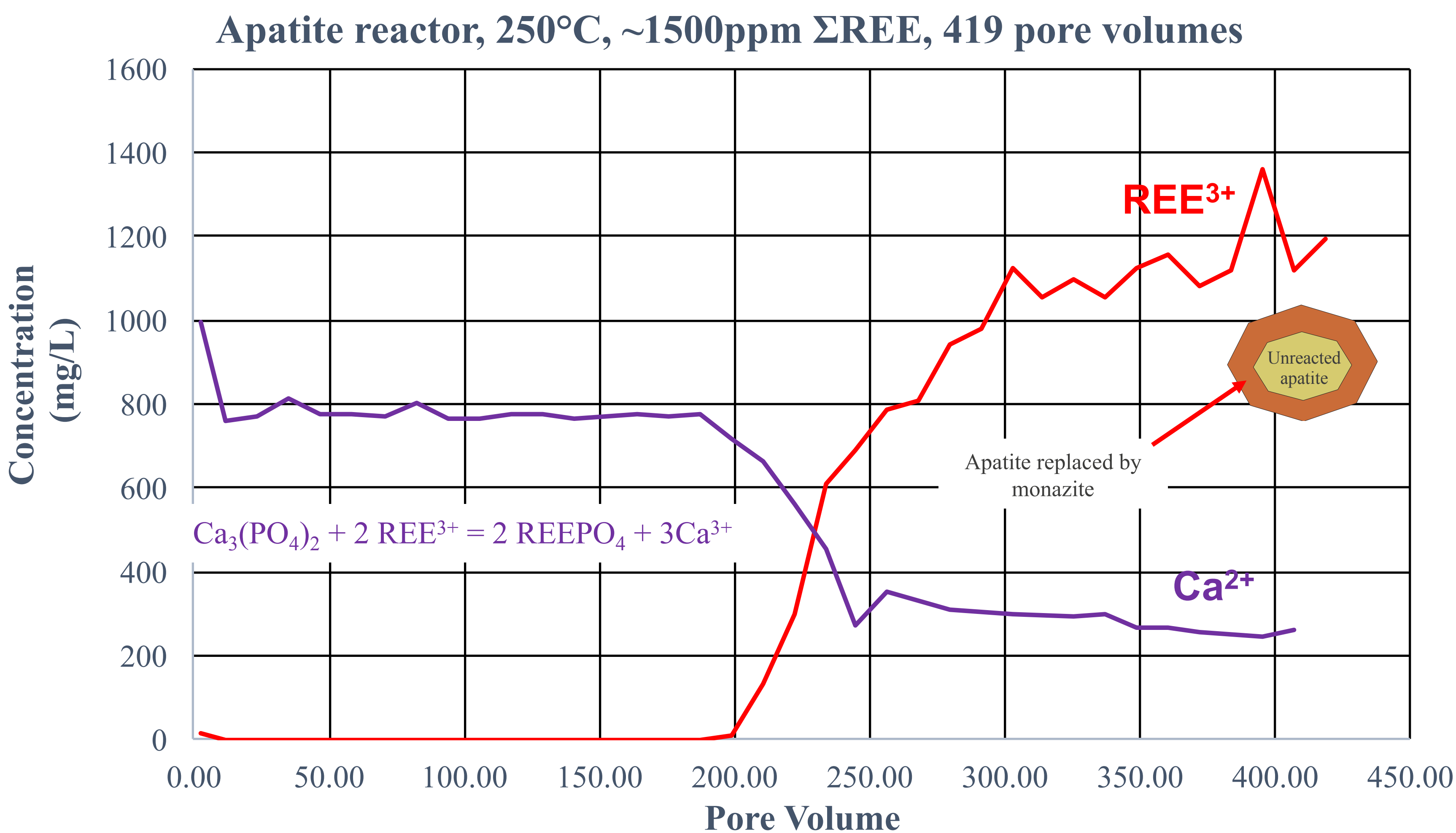


Apatite ($Ca_5(PO_4)_3OH$)/ Whitlockite ($Ca_3(PO_4)_2$) – filled reactors

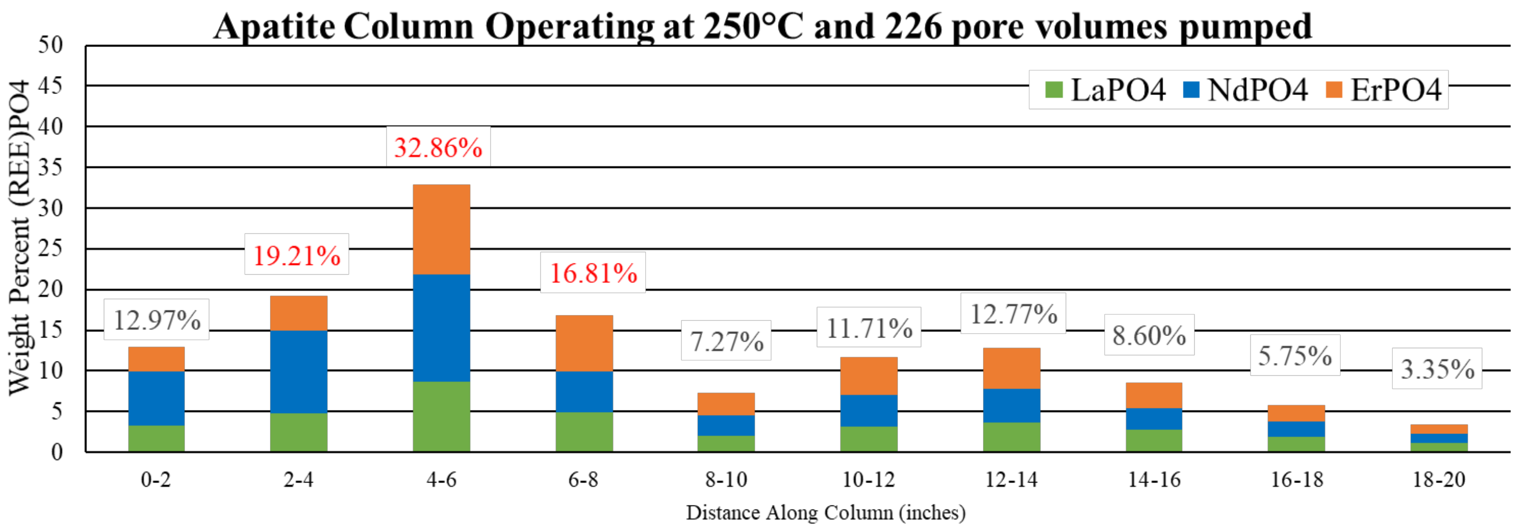
Apatite ($Ca_5(PO_4)_3OH$)/ Whitlockite ($Ca_3(PO_4)_2$) – -filled reactors

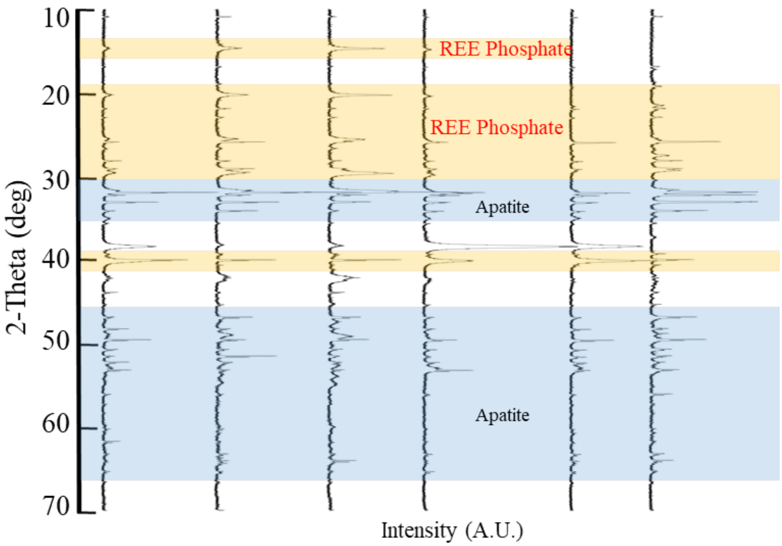


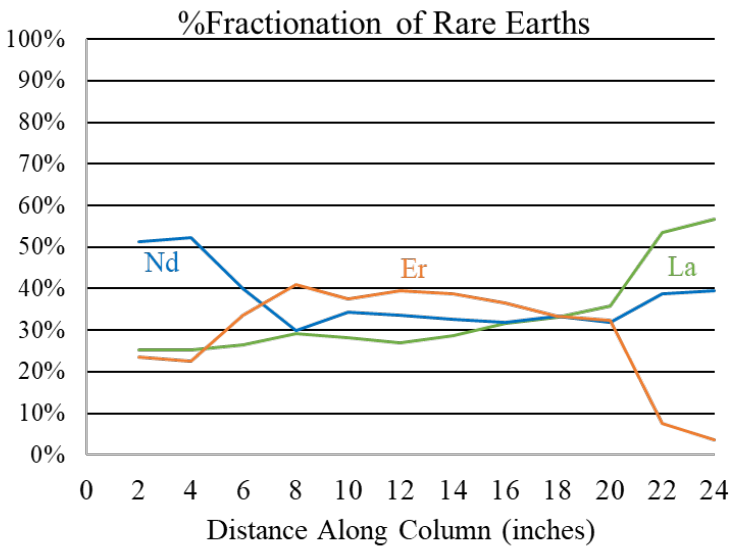
Apatite ($Ca_5(PO_4)_3OH$)/ Whitlockite ($Ca_3(PO_4)_2$)-filled reactors



Apatite ($Ca_5(PO_4)_3OH$)/ Whitlockite ($Ca_3(PO_4)_2$) –filled reactors



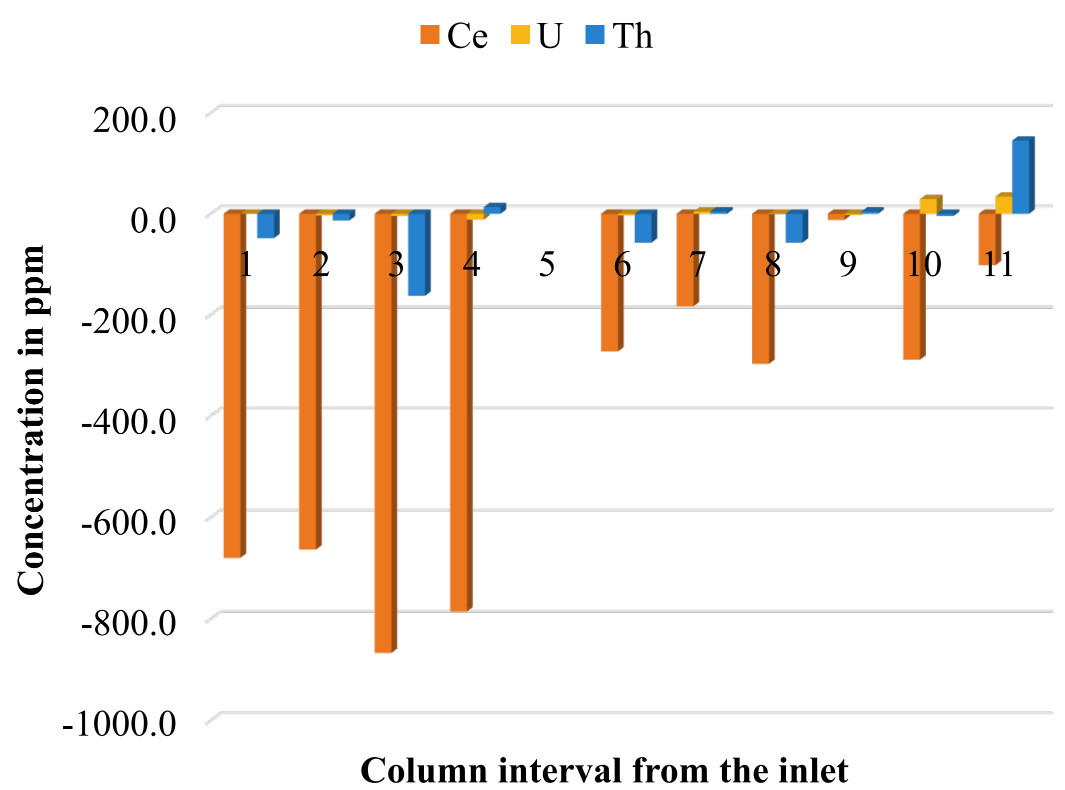




Behavior of other elements originally present on apatite (U,Th) – first clues

Table 2. Detailed elemental composition of apatite used as column fill material.

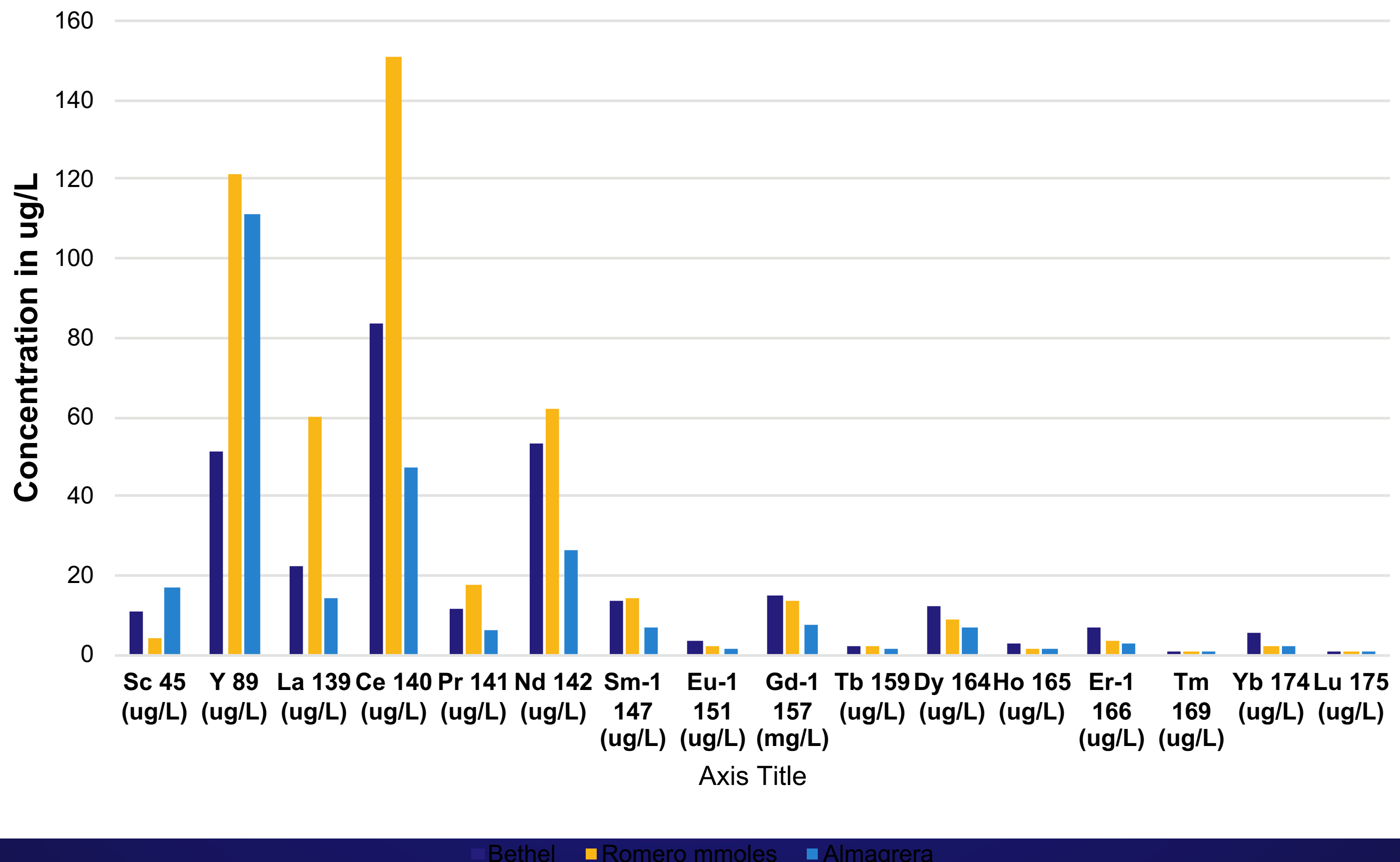
Element I.D.	% or PPM
Na_2O %	0.222
MgO %	0.07
Al_2O_3 %	0.196
SiO_2 %	9.1
P_2O_5 %	33.8
CaO %	54.7
V ppm	20
Cr ppm	179
NiO	0.004
Ni ppm	30
Cu ppm	15
Sr ppm	631
Y ppm	449
Zr ppm	150
Pb ppm	53
La ppm	2404.5
Ce ppm	5120.6
Pr ppm	452.0
Sm ppm	119.0
Gd ppm	138.7
Nd ppm	1594.7
Er ppm	82.201
Th ppm	2144.3
U ppm	71.2
LOI %	0.18
Total %	100.2



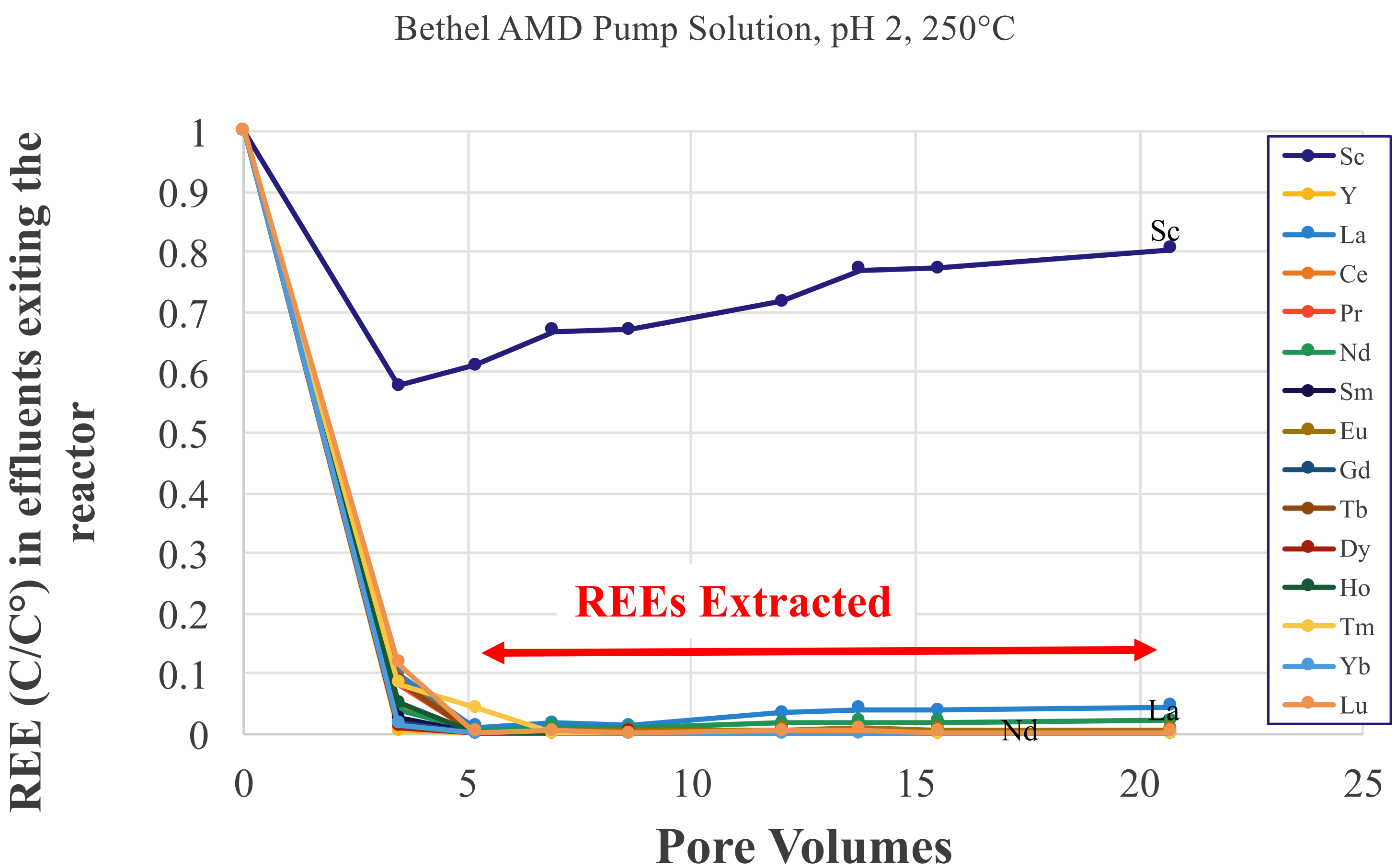
Application of fluorite Ca(F_2) filled reactors for the recovery REE from an acid mine drainage (AMD) sample obtained from a Murrary Energy coal mining site

REE measured value in the acid mine drainage sample

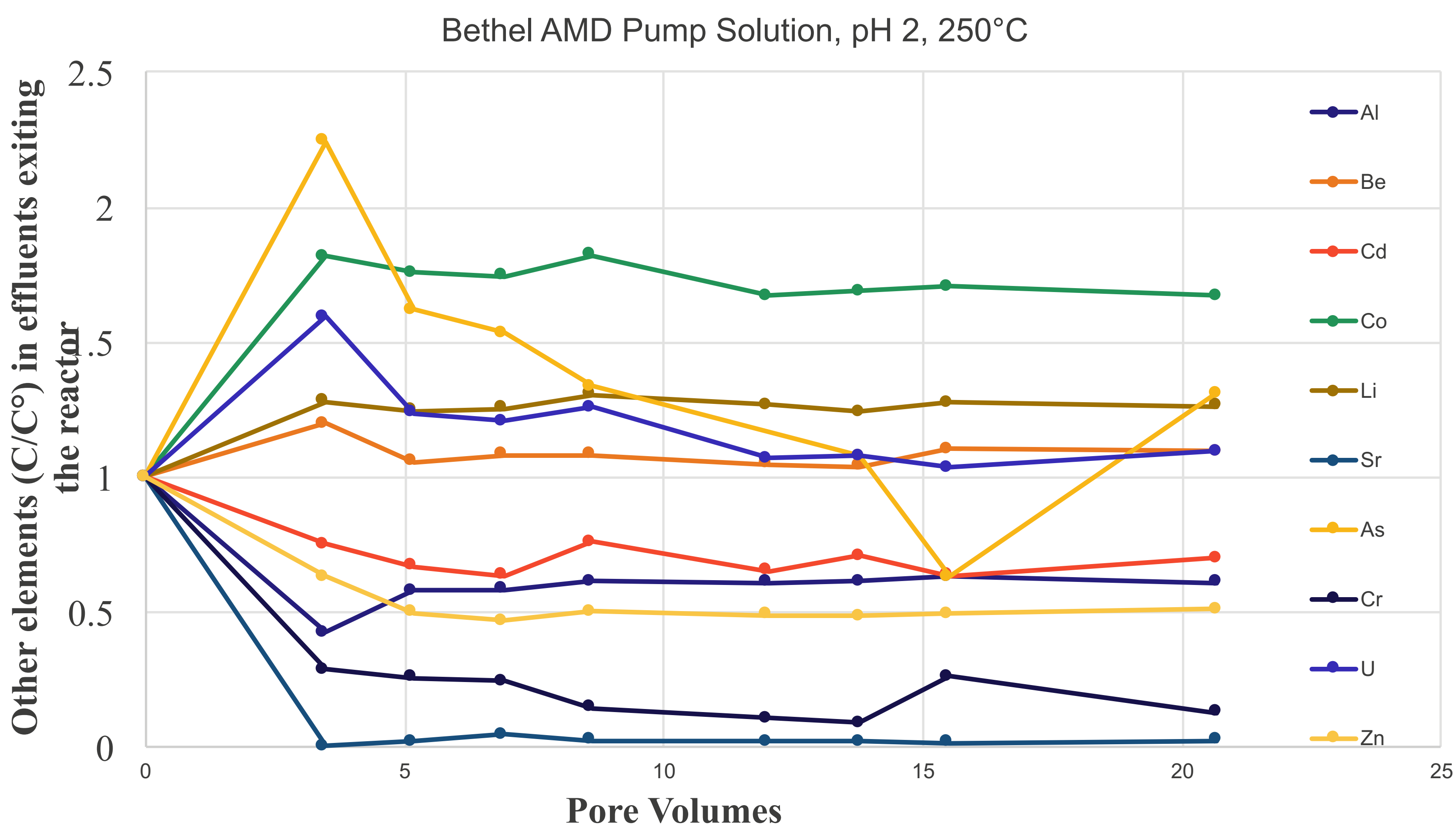
Sample Id	Sc 45 (ug/L)	Y 89 (ug/L)	La 139 (ug/L)	Ce 140 (ug/L)	Pr 141 (ug/L)	Nd 142 (ug/L)	Sm-1 147 (ug/L)	Eu-1 151 (ug/L)	Eu 153 (ug/L)	Gd-1 157 (mg/L)	Tb 159 (ug/L)	Dy 164 (ug/L)	Ho 165 (ug/L)	Er-1 166 (ug/L)	Tm 169 (ug/L)	Yb 174 (ug/L)	Lu 175 (ug/L)	pH	TDS
hagens pump	-1.446	-0.005	0.025	-0.011	-0.009	-0.013	-0.011	-0.009	-0.007	0.002	0.001	-0.003	0.002	0.011	-0.020	-0.008	-0.002	6.900	4,601 mg/L
Bethel sample	7.504	57.445	24.302	82.068	12.007	56.823	15.623	3.604	3.472	16.699	2.542	13.645	2.597	7.254	0.901	5.531	0.818	2.910	3,399 mg/L



Extraction of REE elements from an acid mine drainage sample from a coal mining plant



Behavior of other elements originally present in the acid mine drainage sample



Summary of results

Fluorite

- Extracts 99.99% of REE from synthetic solutions containing 1500 ppm of a mixture of REE's.
- Concentrates REE to 93.2% of REE fluorides in final product
- Eliminates U, Th, Al, Fe, Mg
- Reaction occurs with volumetric effect (grains are cracked): no inhibition
- Partial fractionation of REE along the reactor length
- Extracts 95 % of REE from AMD samples containing 0.2 ppm of REE

Apatite

- Extracts 99.92% of REE from synthetic solutions containing 1500 ppm of a mixture of REE's.
- Concentrates REE to 32.8% of REE phosphates in final product (likely can be improved)
- Eliminates U, Th, Al, Fe, Mg
- No fractionates REE !!!
- Extracts of REE from AMD has not been tested

Future work

- The first stage techno-economic assessment of this method is currently in progress.
- The next steps is to see if scaling the experiment up from the benchtop scale will still be as effective.