Energy & Environmental Research Center (EERC)

Economical Extraction and Recovery of REEs and Production of Clean, Value-Added Products from Low-Rank Coal Fly Ash

Tech Connect World* Innovation *Conference & Expo

Innovations in Rare Earths and Critical Minerals

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DISCLAIMERS

Project Team and Sponsors

- **U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL)**
  - Anthony Zinn, Contracting Officer's Technical Representative
    Mary Anne Alvin, Rare-Earth Element Technology Manager
- **Technical Team**
  - University of North Dakota (UND) Energy & Environmental Research Center (EERC)
  - Pacific Northwest National Laboratory (PNNL)
- **Partners**
  - Basin Electric Power Cooperative
  - Southern Company Services
  - Great River Energy
  - North Dakota Industrial Commission Lignite Energy Council

Project Goals and Objectives

- The overall project goal was to demonstrate at the laboratory scale a novel, economically viable, and environmentally benign process for recovery and concentration of rare-earth elements (REEs) from low-rank coal (LRC) fly ash.

lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and transition elements: scandium (Sc) and yttrium (Y)

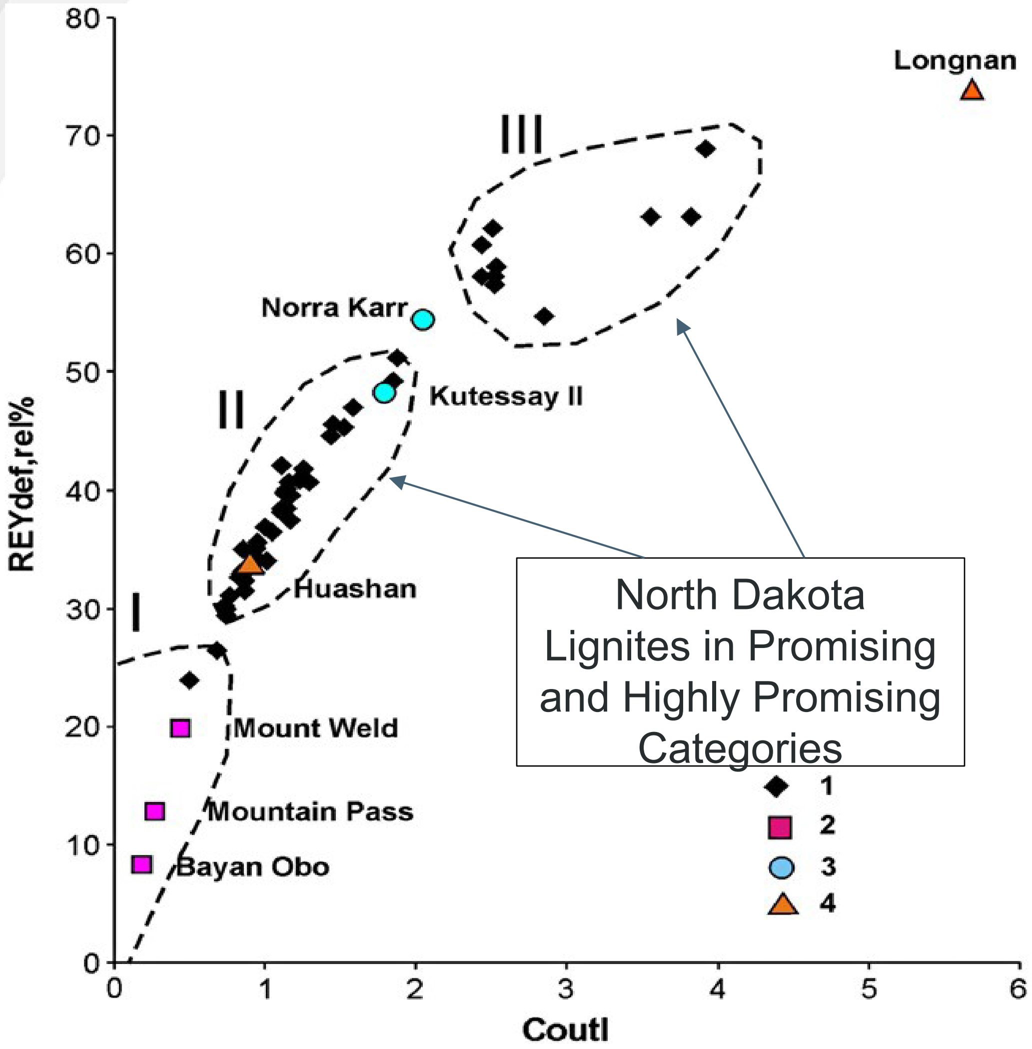
WHAT LRC HAS TO OFFER

- North Dakota is host to the world's largest lignite deposit – 350 billion tons.
- Work to date has identified coal seams in North Dakota with REE concentrations as high as anything ever measured in coal in the United States.
- The H-Bed coal seam in North Dakota has the potential to hold ~2 million tons of REEs.
- The Powder River Basin (PRB) is the largest coal-producing region in the United States.

LRC ASH VALUE?

- Fly ash from coal combustion is particularly promising because of its enrichment in REEs (loss of diluting organic material results in ~10× concentration over coal) and also its presence in fine powder form, eliminating or reducing high-energy fine grinding typically required for REE processing.

WHY LRC ASH?



Group I – Unpromising
Group II – Promising
Group III – Highly Promising

1 – REE-rich coal ashes
2 – carbonatite ore deposits
3 – hydrothermal ore deposits
4 – weathered crust elution-deposited (ion-adsorbed) ore deposits

Seredin, V.V.; Dai, S. Coal Deposits as Potential Alternative Sources for Lanthanides and Yttrium. International Journal of Coal Geology 2012, 94, 67–93.

REE ASH ANALYSIS

Sample Description	Lanthanides + Y +Sc	HREE/LREE Ratio	Coutl
ND Lignite pc-Fired Fly Ash – Falkirk	260	0.47	1.04
PRB pc-Fired Steam Plant Class C Fly Ash – Black Thunder	366	0.41	0.95
PRB pc-Fired Fly Ash – Buckskin	401	0.45	1.06
PRB pc-Fired Dry Fork Station Fly Ash	282	0.43	1.06
H Bed Lignite Coal – Ash from Downfired Combustor	1089	0.58	1.25

BET Surface Analysis of Ashes Selected for REE Analysis	Sample wt	BET Surface Area
	grams	m^2/g
ND Lignite pc-Fired Fly Ash –Falkirk	1.116	0.5
PRB pc-Fired Steam Plant Class C Fly Ash – Black Thunder	1.176	1
PRB pc-Fired Fly Ash – Buckskin	1.635	1.1
PRB pc-Fired Dry Fork Station Fly Ash	1.13	3.4
H Bed Lignite Coal – Ash from Downfired Combustor	1.229	1.6

Final Down Select from to 2 ash materials

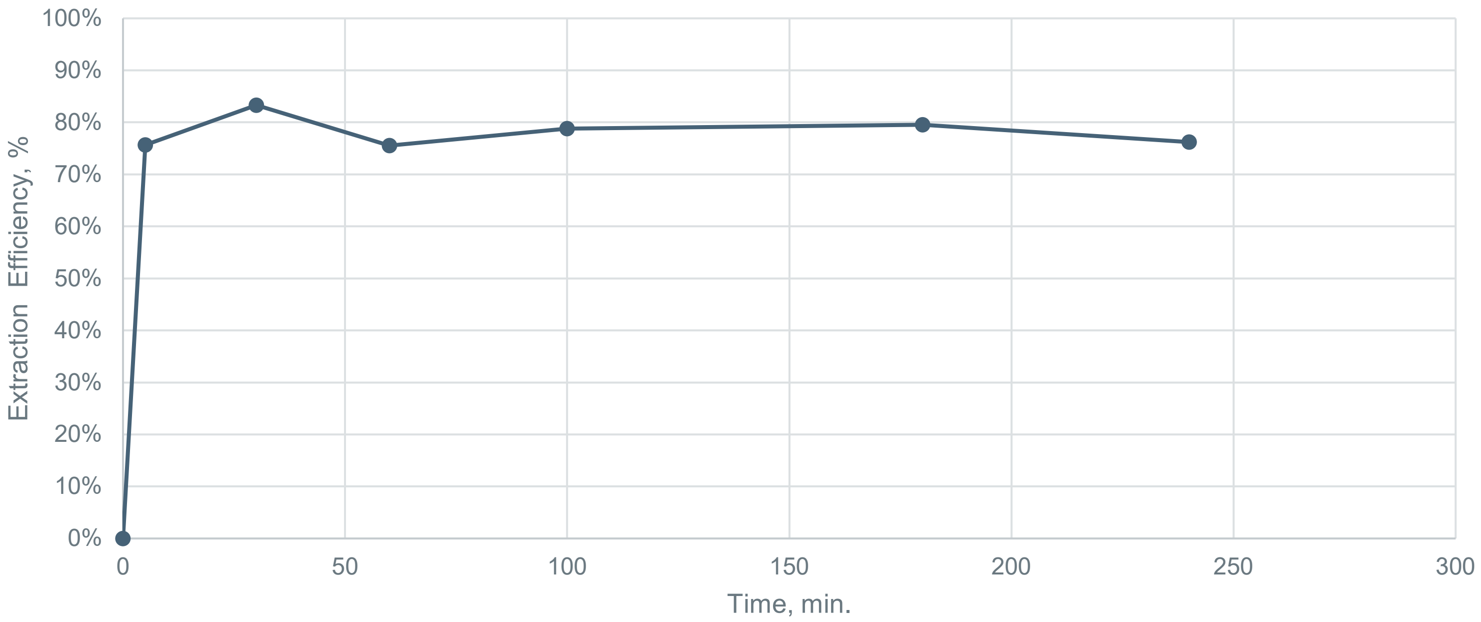
- Focus on 2 ash materials for extraction process
  - Suggested 2 ash materials – Dry Fork & Falkirk
    - ♦ PRB Dry Fork
      - Highest leach total
      - High calcium content
      - Smallest particle size
      - Highest surface area
    - ♦ Lignite Falkirk
      - Leach extraction from 3 extraction solvents
      - Organic/salt REE association in coal may lead to easier extraction in ash

LABORATORY-SCALE TESTING

- Fly ash pretreatment testing
  - Thermal pretreatment
  - Water leaching pretreatment
  - Carbonation pretreatment

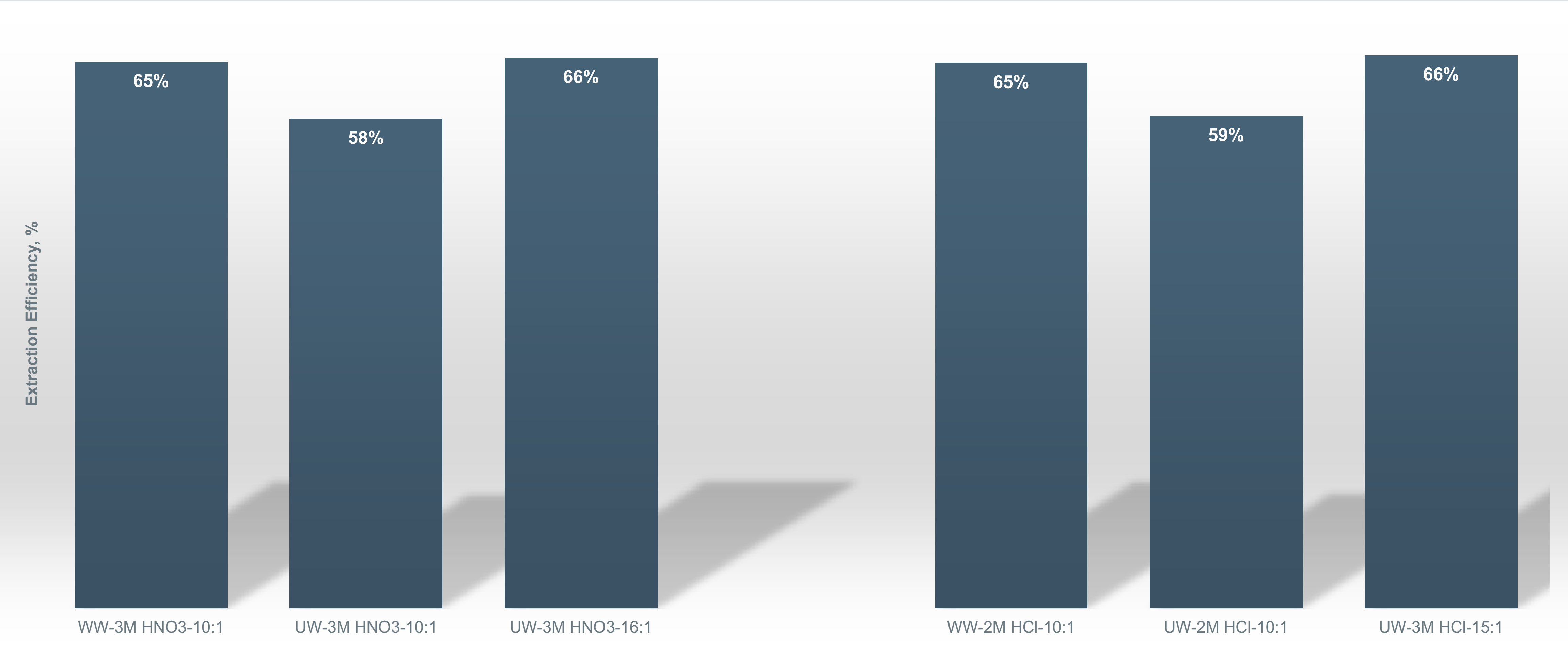
- Subcritical Liquid CO_2 extraction testing

Extraction Efficiency versus Time

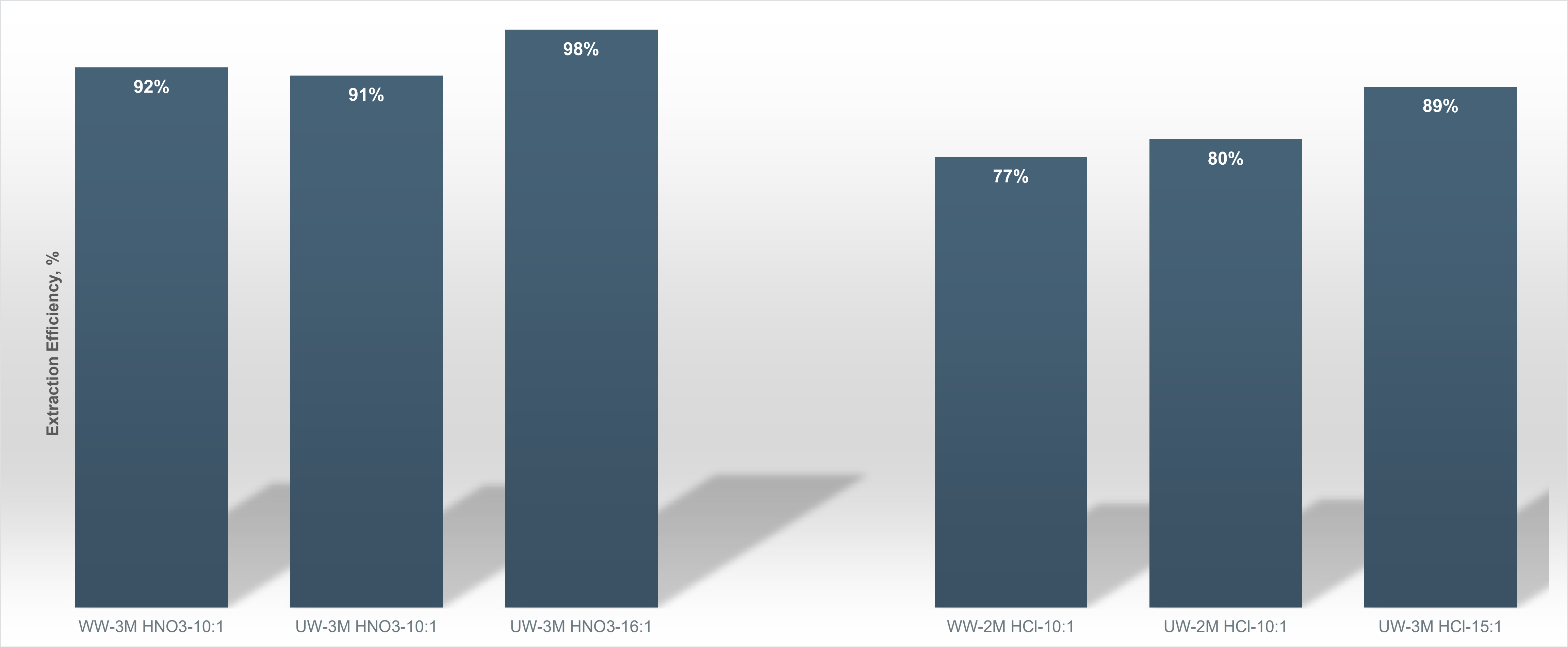


2M HNO_3 Extraction of REE from Lignite ash

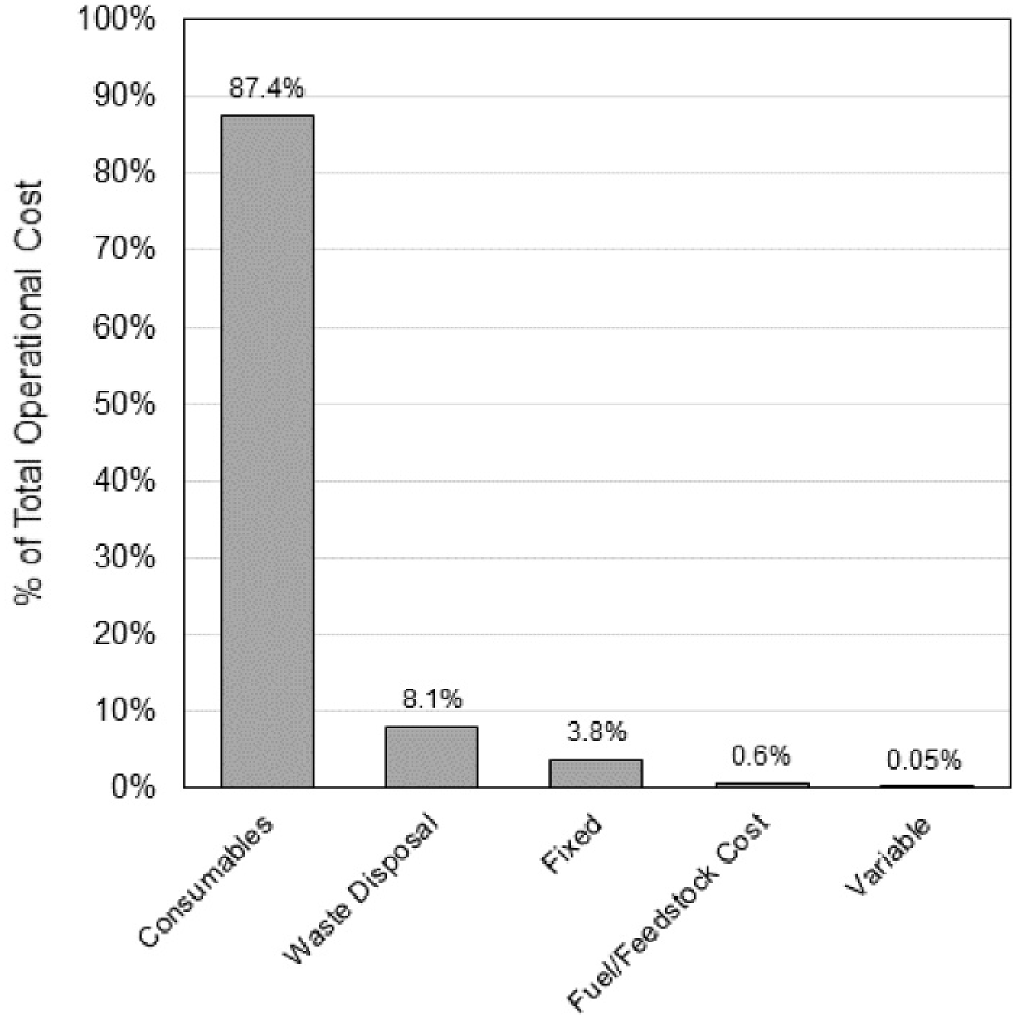
Lignite ash water pretreatment effect on extraction efficiency



PRB ash water pretreatment effect on extraction efficiency

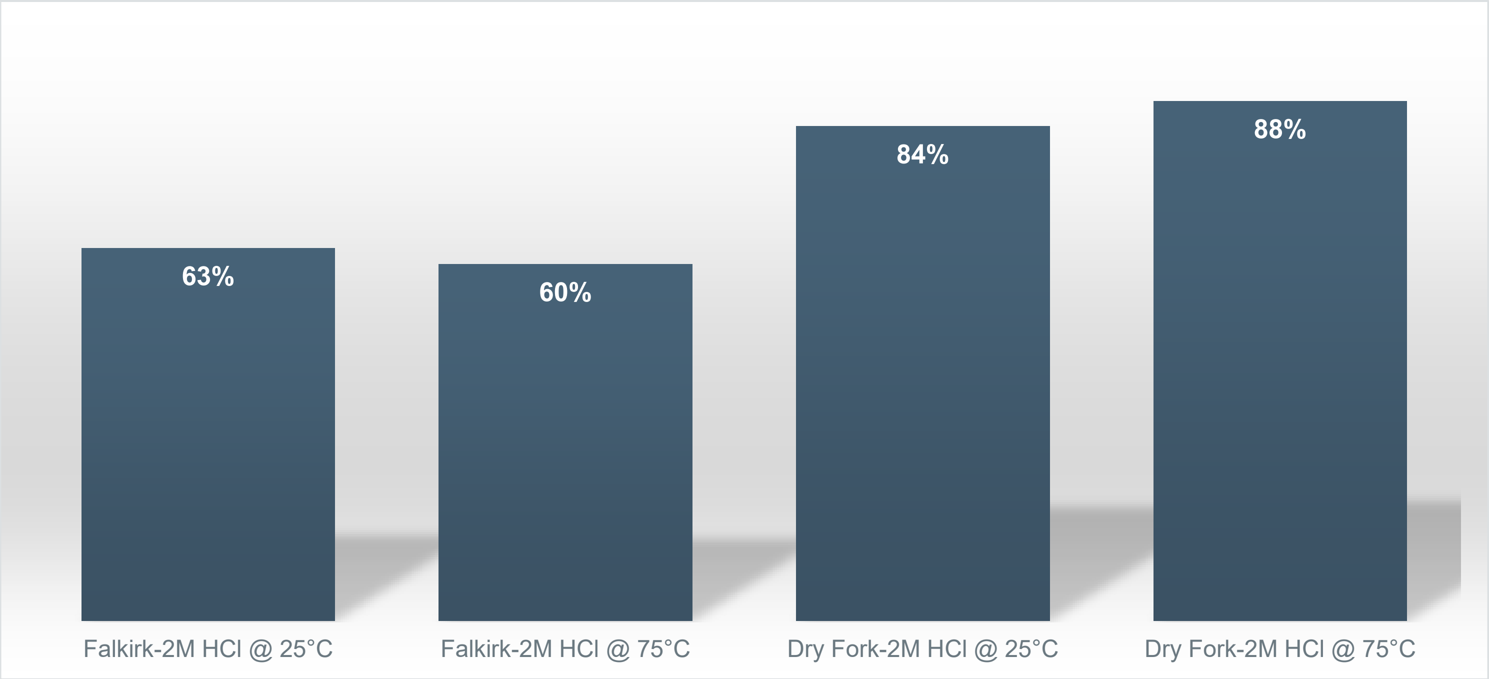


WHY NOT USE ACID TO EXTRACT REEs?



Temperature effect on extraction efficiency.

Literature showed temperature can reduce the amount of acid required for REE extraction

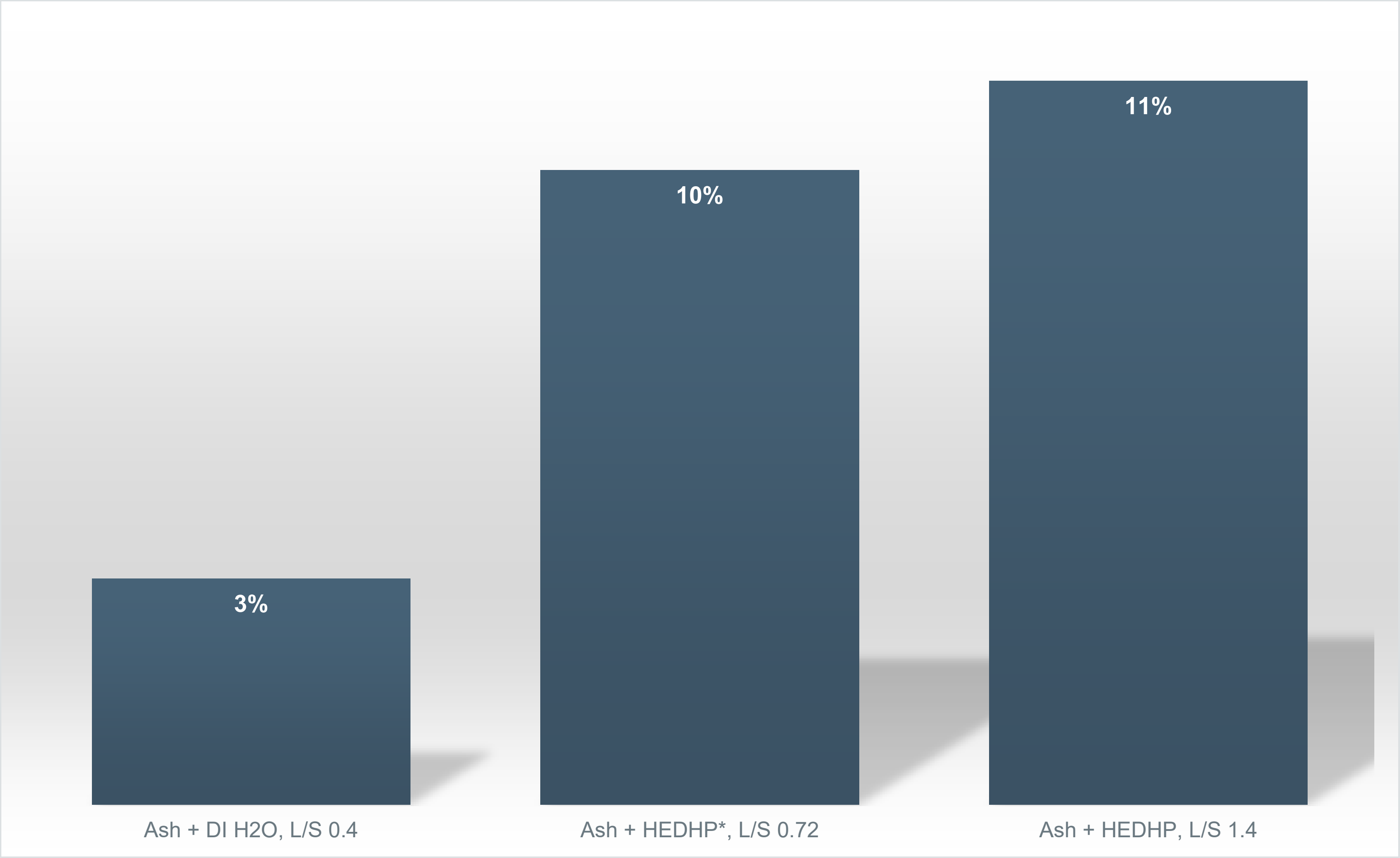


Subcritical Liquid CO_2 Extraction Testing

9 grams of ash and 6.5 grams of a 50:50 solution of HDEHP:Hexane - 1:1 by volume ratio of L/S

9 grams of ash and 13 grams of a 50:50 solution of HDEHP:Hexane - 2:1 by volume ratio of L/S.

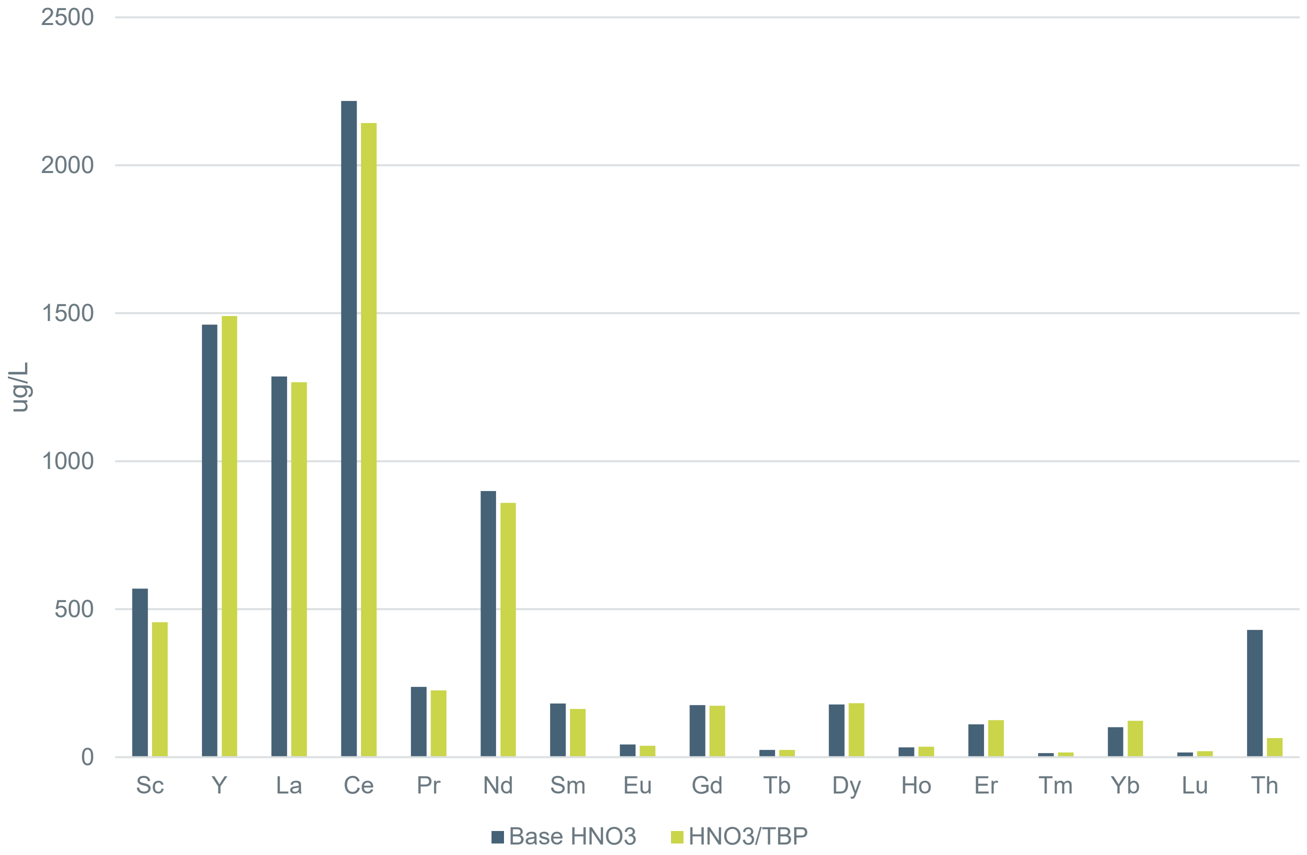
1100 psi of CO_2 at 22 °C



Aqueous and Aqueous/TBP extraction

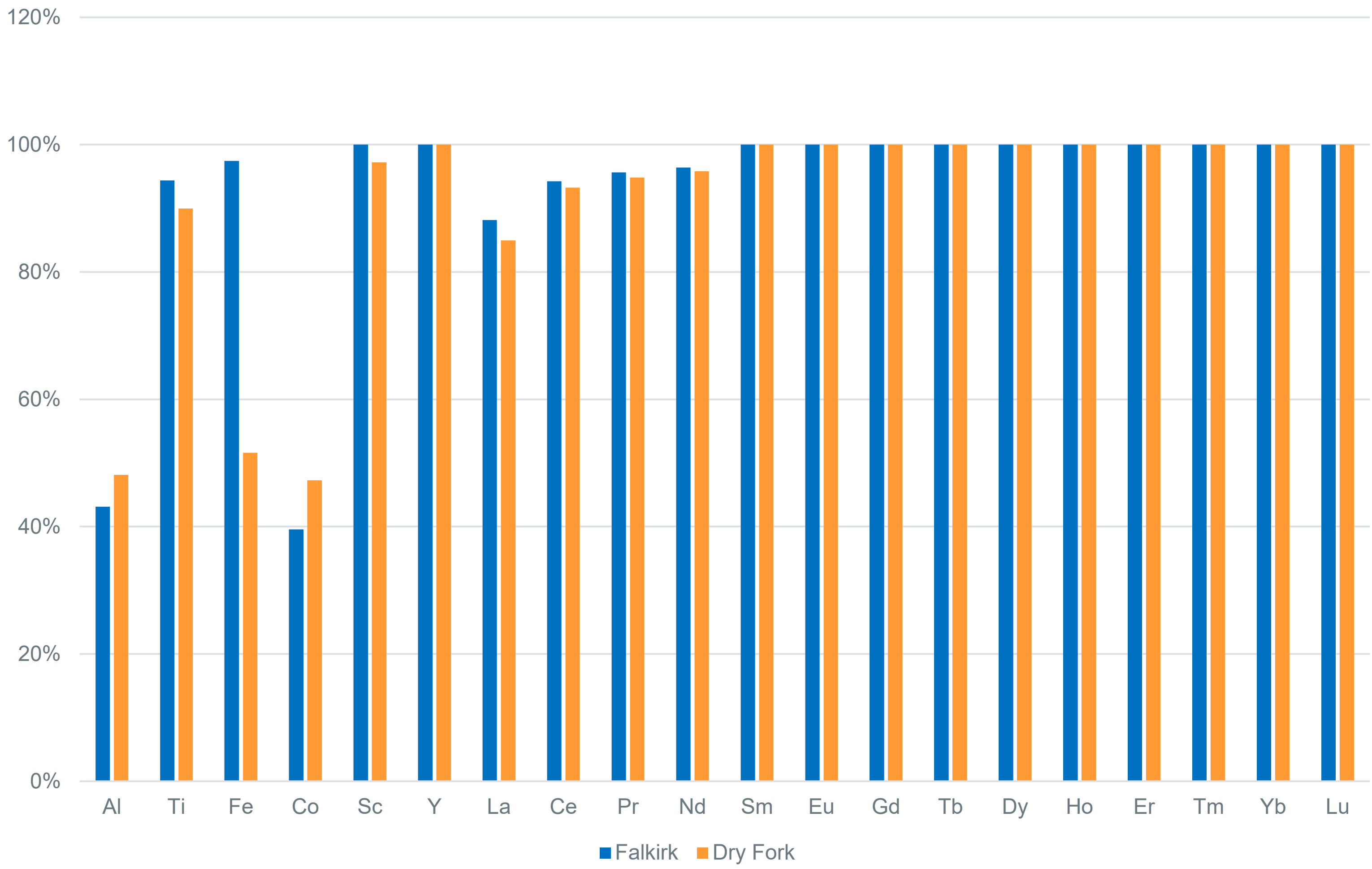
~85% of the Th transferred into the organic TBP phase from the aqueous phase

Possible Th removal step



Elements transferred to the organic ligand HDEHP from aqueous, no pH adjustment

Almost all the REE available



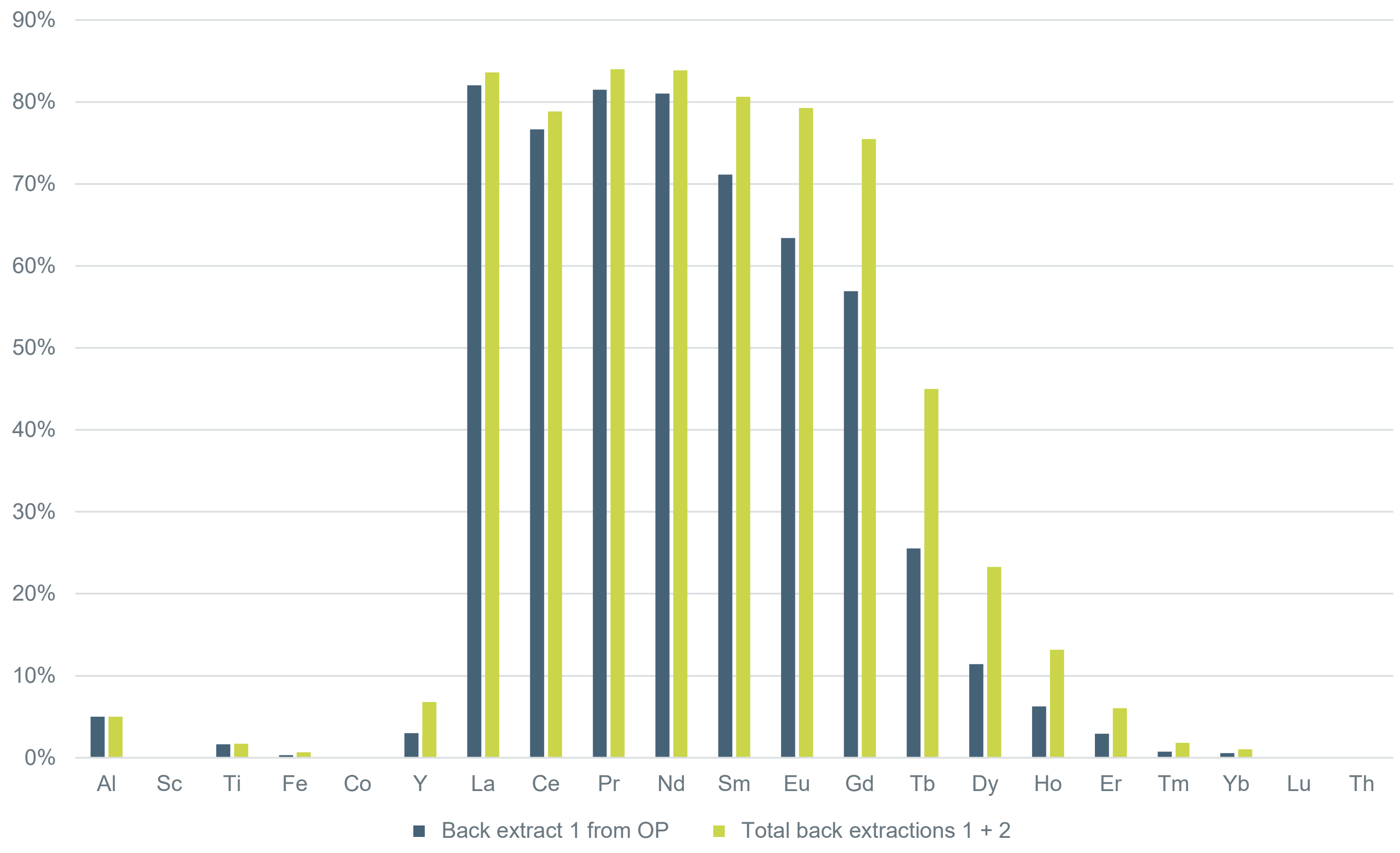
Back Extraction Purification Step

Large fraction of the LREE

Almost none of the problematic elements Al, Fe, Ti

No Sc or Y

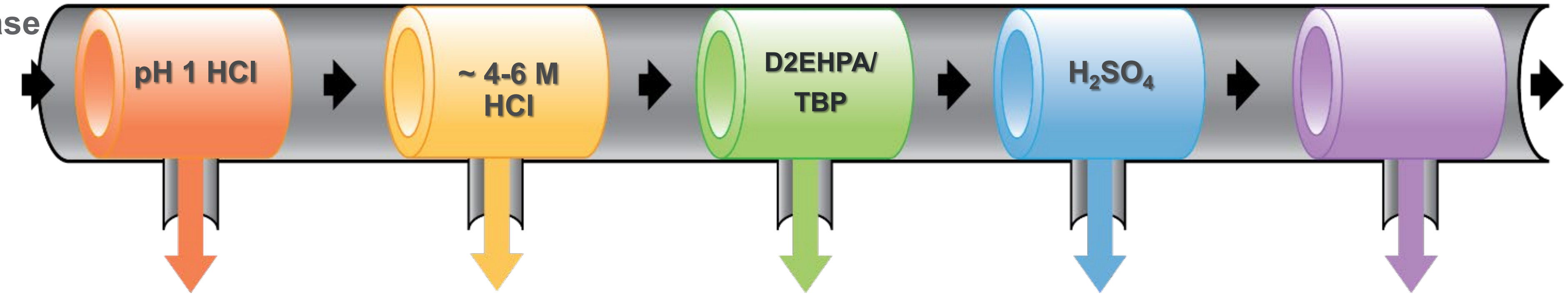
33% wt% concentration of REEs



INTEGRATED SEQUENTIAL PROCESS FOR MINERAL RECOVERY

Coordinated recovery conditions increase product concentration and purity

REE-Rich Organic Phase From Acid Extraction



Rejuvenated Organic Phase Ready for Reuse

Light REEs

Heavy REE

Sc
pH TBD

Ligand Cleanup
Th, Fe, Al, Ti
Reprotonate HDEHP

Raffinate
Reuse

Optimal process conditions to be determined

Key Take Aways

- Demonstrated concentration of mixed REEs to Greater than 2 wt%
- Developed Valid "Tunable" pathway to economic extraction process

  – needs further validation and scale up
- All ash materials different and will require specific extraction process – Tunable Process
- Water wash pretreatment can reduce required amount of acid for initial REE extraction from Lignite
- pH is key to extraction efficiency process and solutions re-use
- Many literature examples of REE concentration processes but few that use LRC ash.

  – Literature methods need to be validated with actual ash because of impurities and multitude of species present
- Extraction of Th with TBP shows great promise for purification
- More work needs to be performed to reduce extraction purification steps,

  - can we get to one back extraction step from HDEHP

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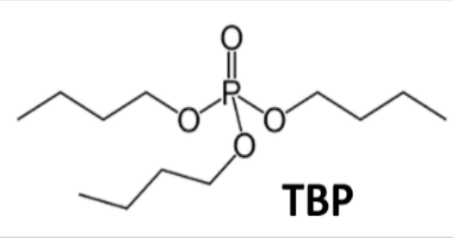
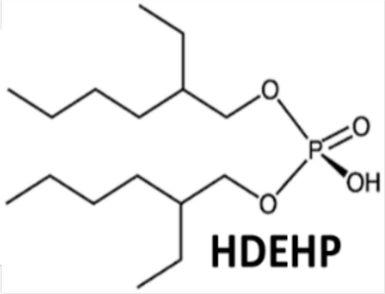
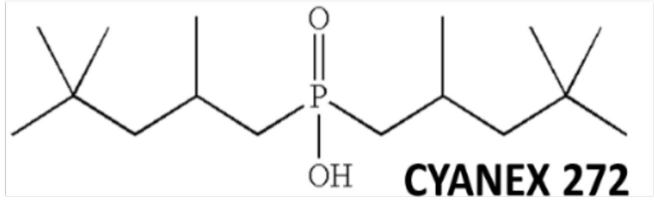
TASK 3 – LABORATORY-SCALE TESTING

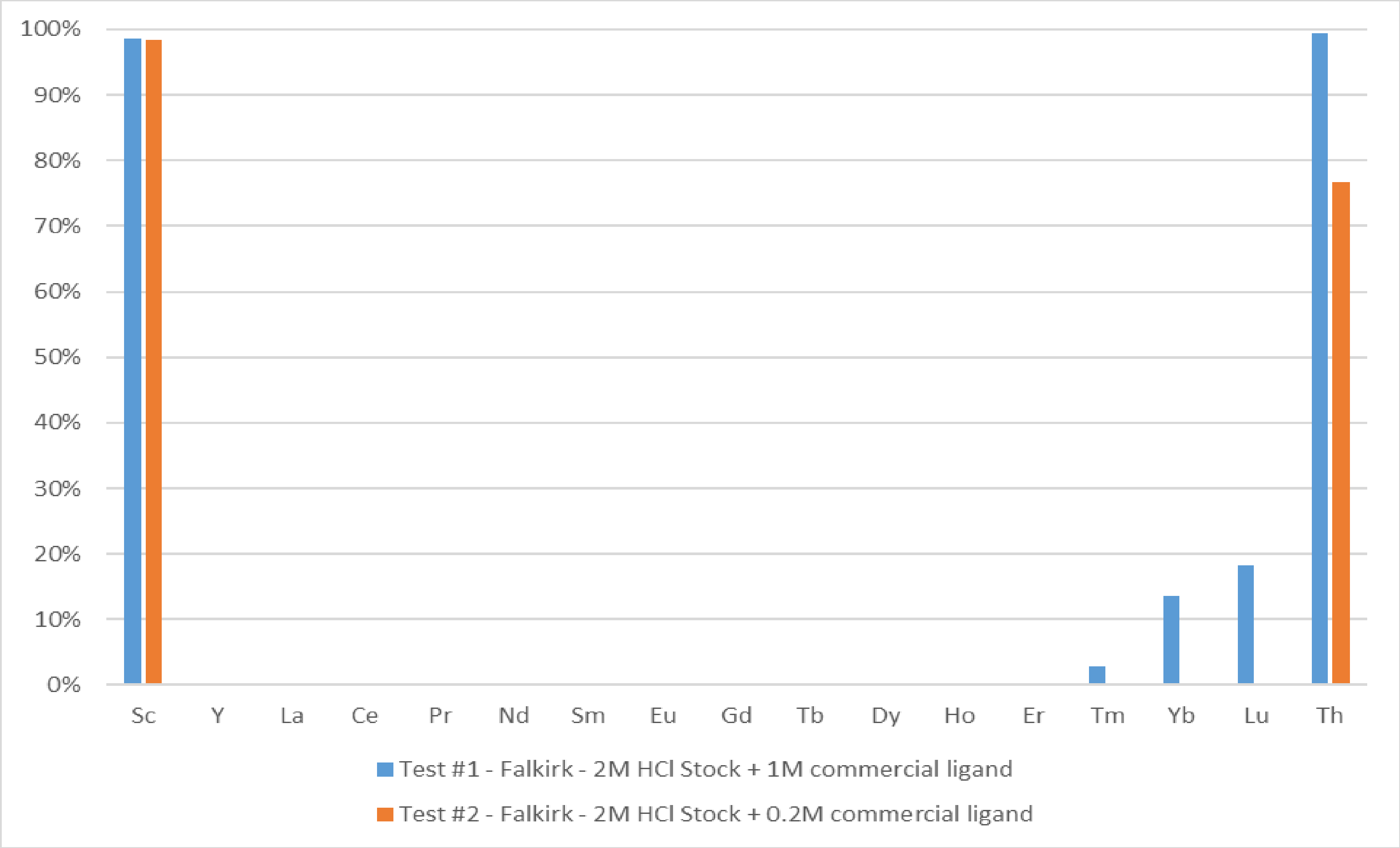
- **Solvent extraction testing**
  - Goal to identify the most effective conditions (the combination of organic ligands, cosolvents and proportions, contact time) required to achieve the highest level of REE extraction.
  - Organic ligands commonly employed with the solvent extraction system.
  - Novel low-cost ligands currently being developed.



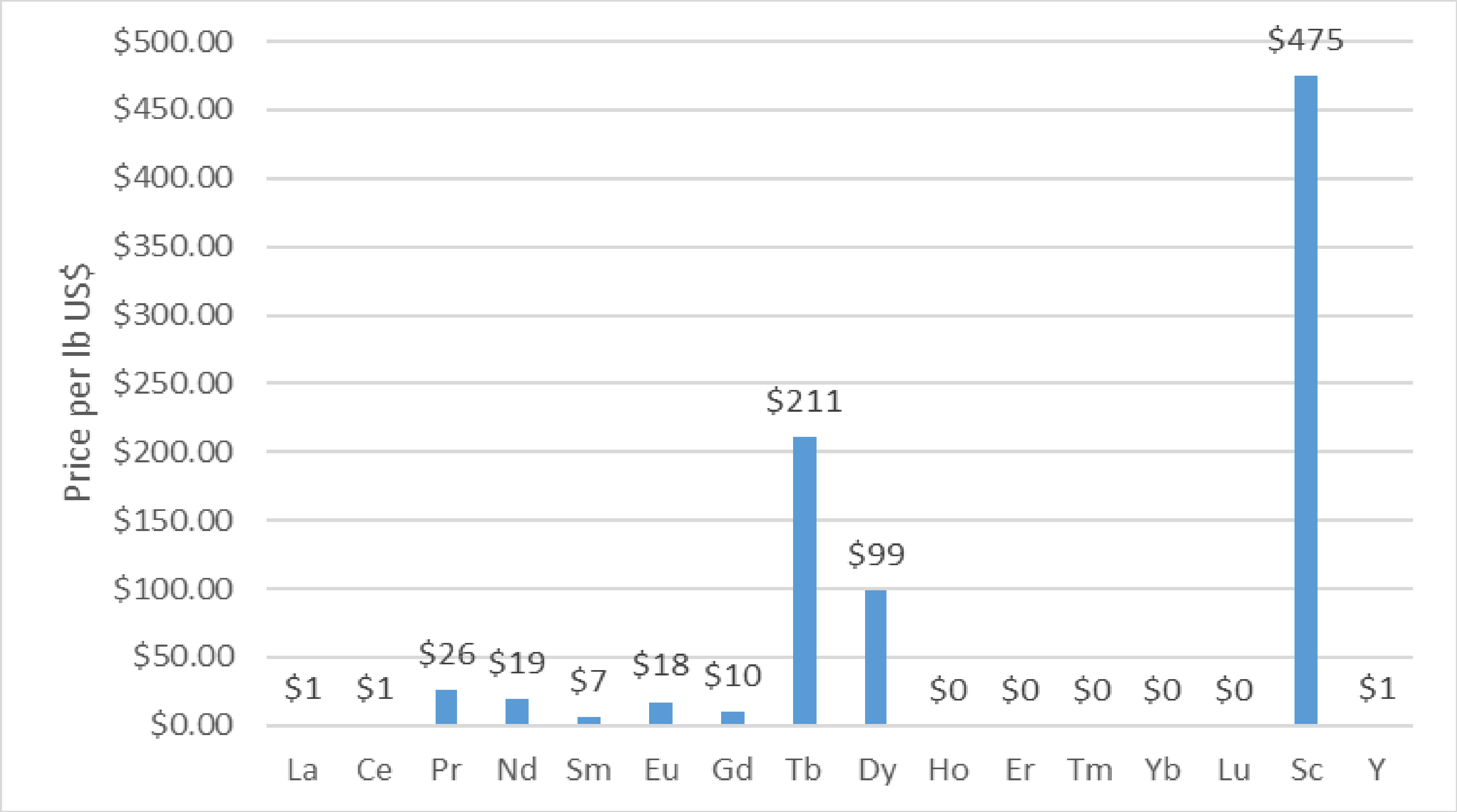




EXTRACTION WITH LIGAND



PRICE OF REE PER LB



CURRENT SETUP FOR PRESSURIZED EXTRACTION