Energy & Environmental Research Center (EERC)

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

DOE CONTRACT DE-FE0031490

DOE NETL Annual Project Review Meeting, April 9–11, 2019

Crosscutting, Rare-Earth Elements, Gasification Systems, and Transformative Power Generation

April 10, 2019 – **SESSION C5: Transformational REE Separation**

Critical Challenges. **Practical Solutions.**

EXECUTIVE SUMMARY

Project Team

- **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

EXECUTIVE SUMMARY

Project Goals and Objectives

- The overall project goal is 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.
- Overall technology objectives:
  - Produce a domestic “green” source of REEs
  - Recover other valuable minerals/elements from coal fly ash
  - Remove toxic metals from the fly ash
  - Convert the fly ash into a value-added product
  - Generate a selective REE extraction not typical to existing approaches for REEs from coal 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)

EXECUTIVE SUMMARY

Project Tasks

- **Task 1. Management, Planning, and Reporting**
  – Perform overall project planning and management, and ensure all reporting requirements are met for the project.
- **Task 2. Sample Procurement and Characterization**
  – Coordinate sample procurement efforts with project participants and power generation stations, and perform all standard analysis methods in accordance with the requirements of the project.
- **Task 3. Laboratory-Scale Testing**
  – Develop the procedures and techniques for concentrating the REEs in ash material to greater than 2 wt%.
- **Task 4. Technical and Economic Analysis**
  – Prepare a high-level technical and economic analysis with the goal to estimate preliminary capital and operating expenses, which will serve to direct future process development.

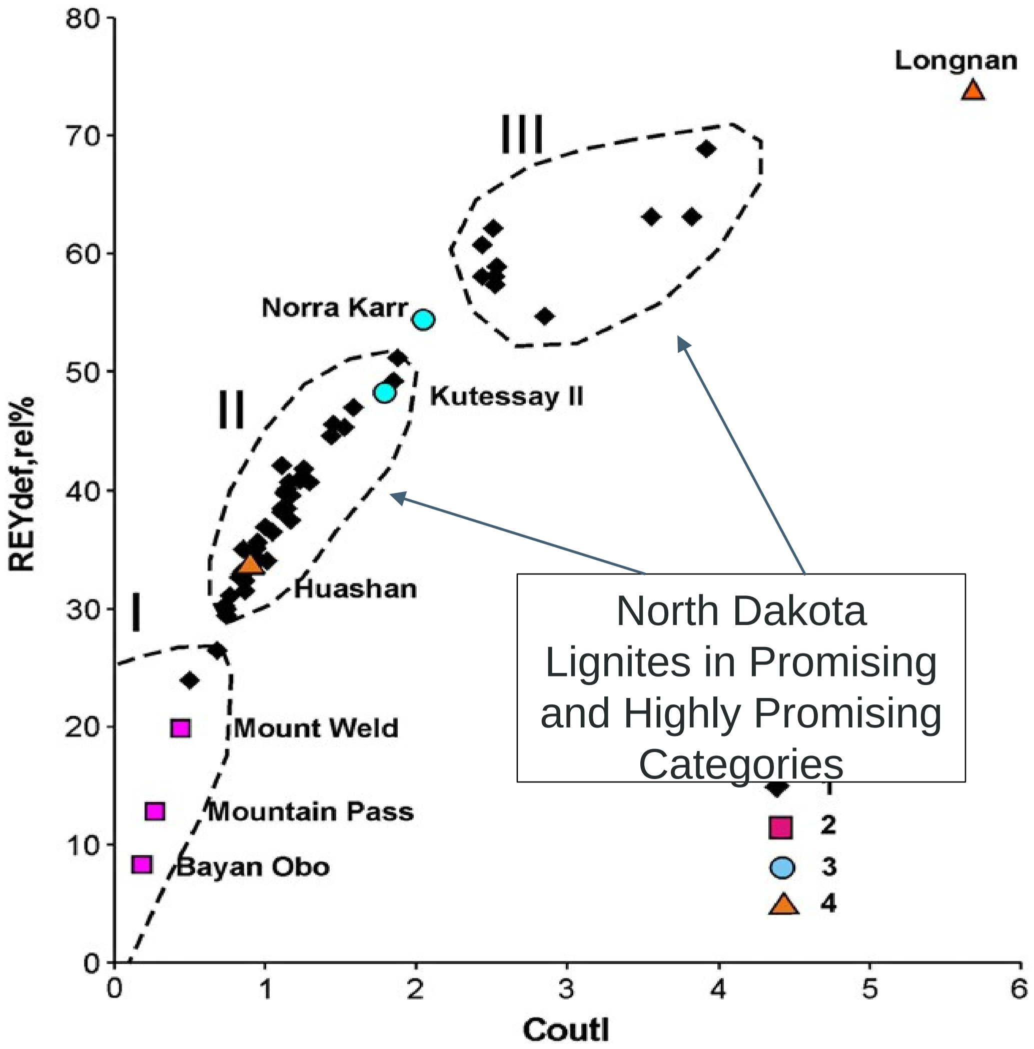
LRC ASH VALUE?

- *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.*

WHAT LOW-RANK COAL (LRC) 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 Harmon–Hanson coal seam in North Dakota has the potential to hold ~2 million tons of REEs.
- The Powder Rivr Basin (PRB) is the largest coal producing region in the United States.

WHY LRC ASH?



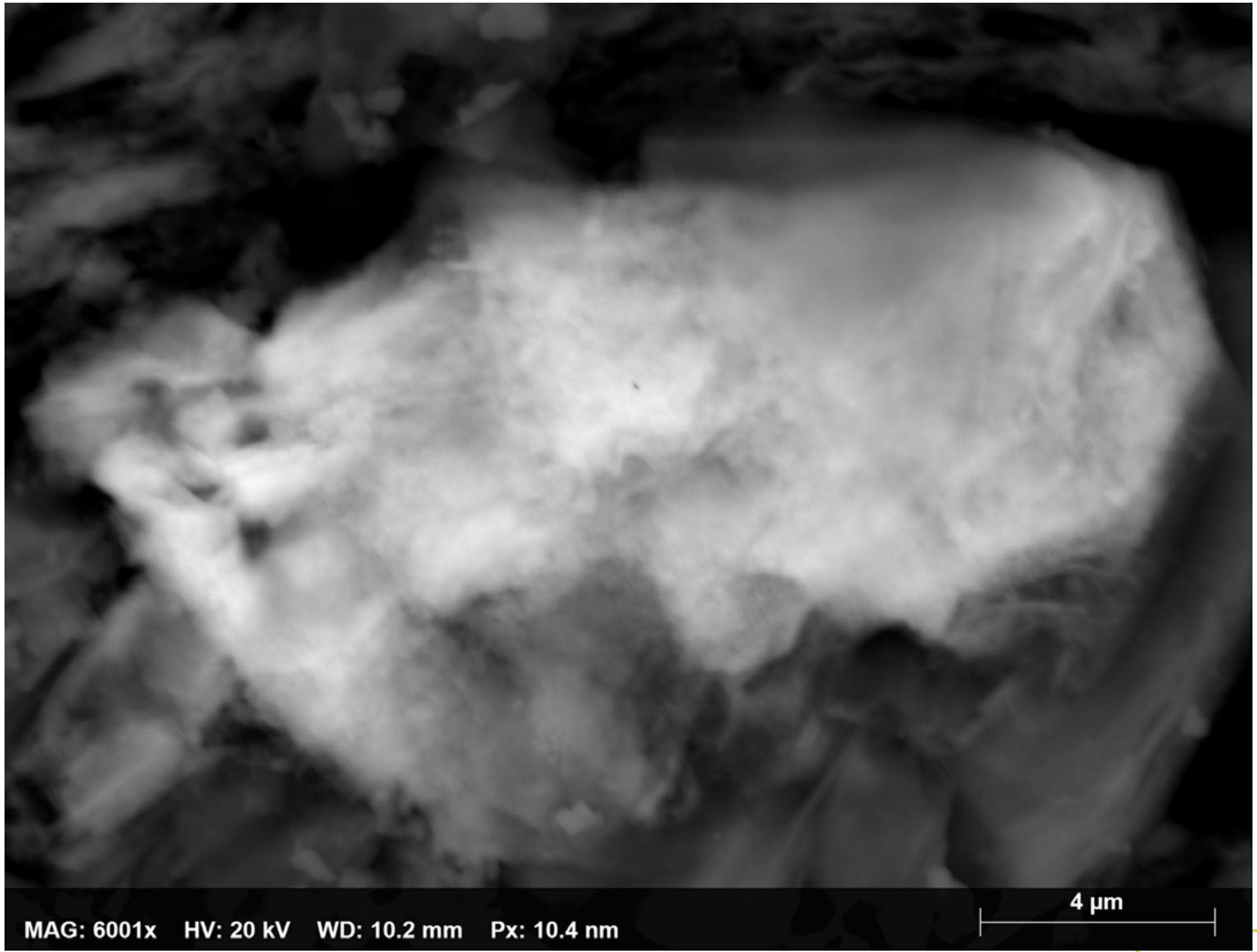
Group I – Unpromising
Group II – Promising
Group III – Highly Promising

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

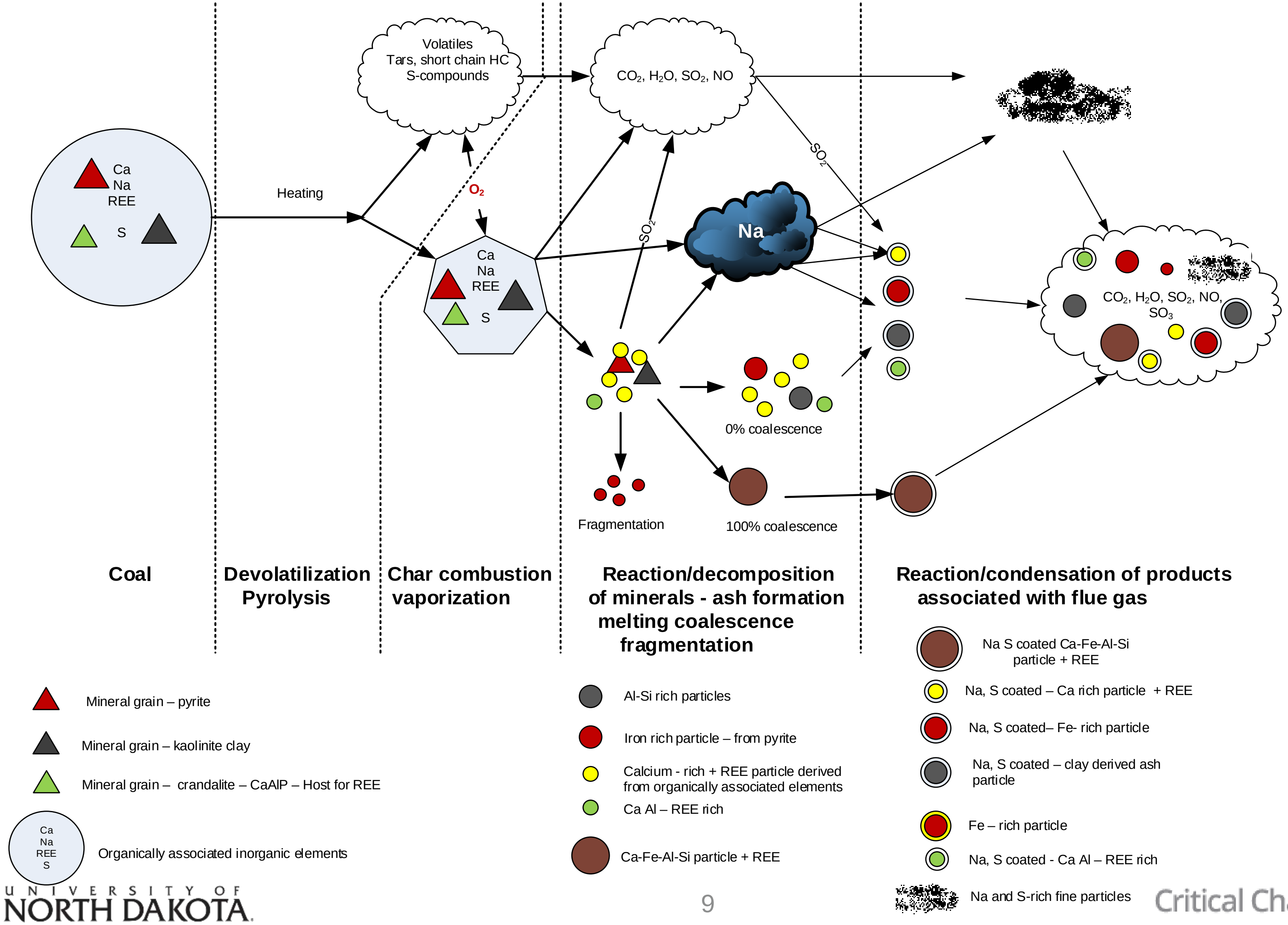
Seredin, V.V.; Dai, S. Coal Deposits as Potential Alternative Sources for Lanthanides and Yttrium. International Journal of Coal Geology 2012, 94, 67–93.

REEs IN LRC

- Rhabdophanes
- $XPO_4 \cdot nH_2O$ where X stands for REE, Y, Ca, Pb, Th, U, Fe
- Significant organically associated REEs



ASH FORMATION MECHANISMS IN LRC



TASK 2 - LRC ASH PROCUREMENT and ANALYSIS

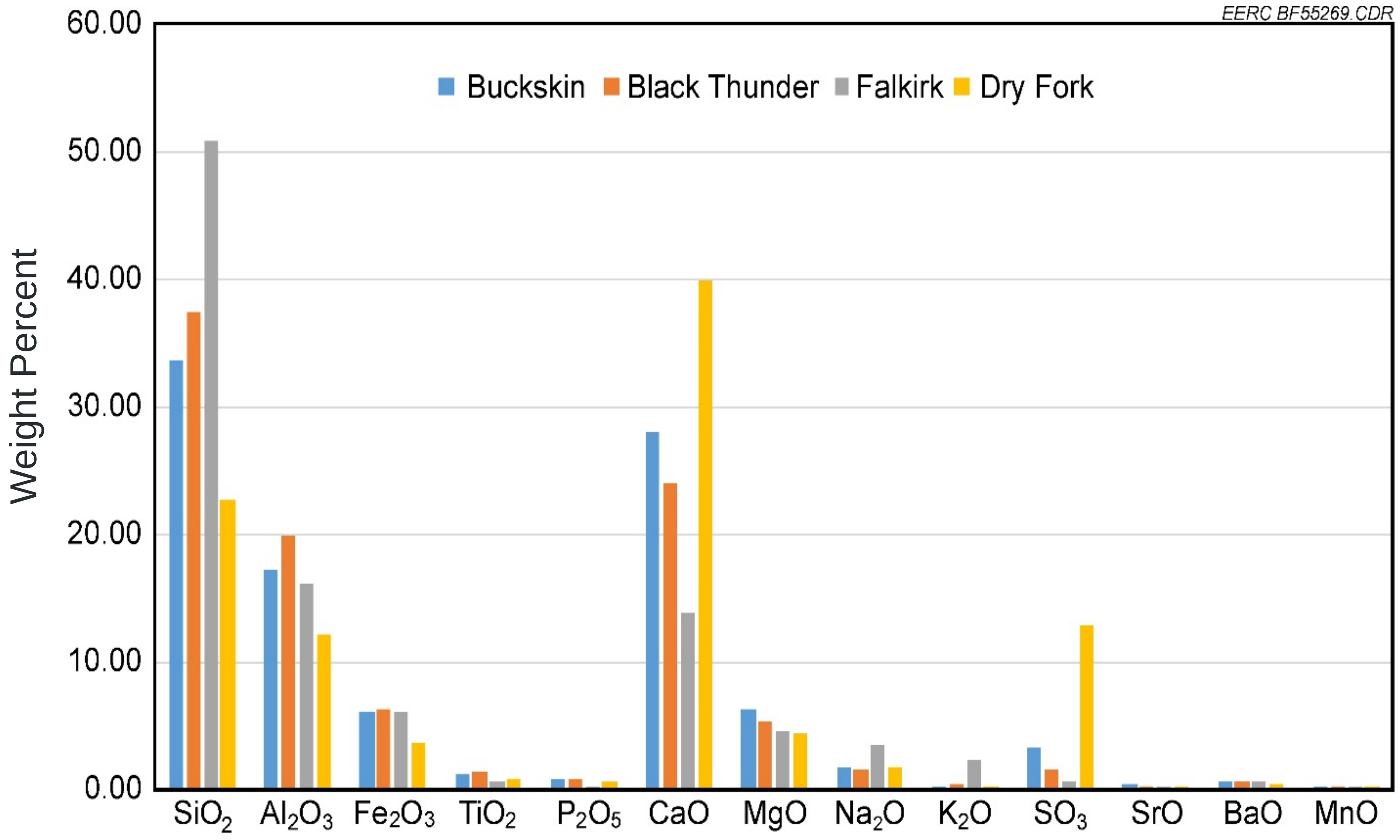
Description	Lanthanides	Lanthanides + Y	Lanthanides + Y +Sc	HREE/LREE ratio	Coutl
ND Lignite FBC Baghouse Ash	110	144	156	0.71	1.37
ND Lignite FBC Air Heater Hopper Ash	114	148	160	0.70	1.37
ND Lignite FBC Bottom Ash	121	144	155	0.46	0.98
ND Lignite FBC Bottom Ash Duplicate	125	148	160	0.47	0.99
ND Lignite pc-Fired Fly Ash – Falkirk	205	244	260	0.47	1.04
ND Lignite pc-Fired Bottom Ash – Falkirk	192	238	257	0.58	1.16
ND Lignite pc-Fired Station Fly Ash	159	191	204	0.49	1.04
ND Lignite pc-Fired Station Bottom Ash	135	163	174	0.51	1.05
PRB pc-Fired Dry Fork Station Fly Ash	227	267	282	0.43	1.06
PRB pc-Fired Station Fly Ash Duplicate	232	273	288	0.43	1.05
PRB Blend ESP Ash from CTF Antelope	269	319	345	0.49	1.04
PRB Blend ESP Ash from CTF Antelope Duplicate	264	312	337	0.49	1.04
ND Lignite Baghouse Ash from AF-CTS	174	207	223	0.48	1.00
ND Lignite Baghouse Ash from AF-CTS Duplicate	168	200	216	0.48	1.01
PRB pc-Fired Steam Plant Class C Fly Ash – Black Thunder	298	345	366	0.41	0.95
PRB pc-Fired Steam Plant Fly Ash Alpha Eagle Butte	288	338	358	0.43	0.99
PRB pc-Fired Fly Ash – Buckskin	321	380	401	0.45	1.06

REE ASH ANALYSIS

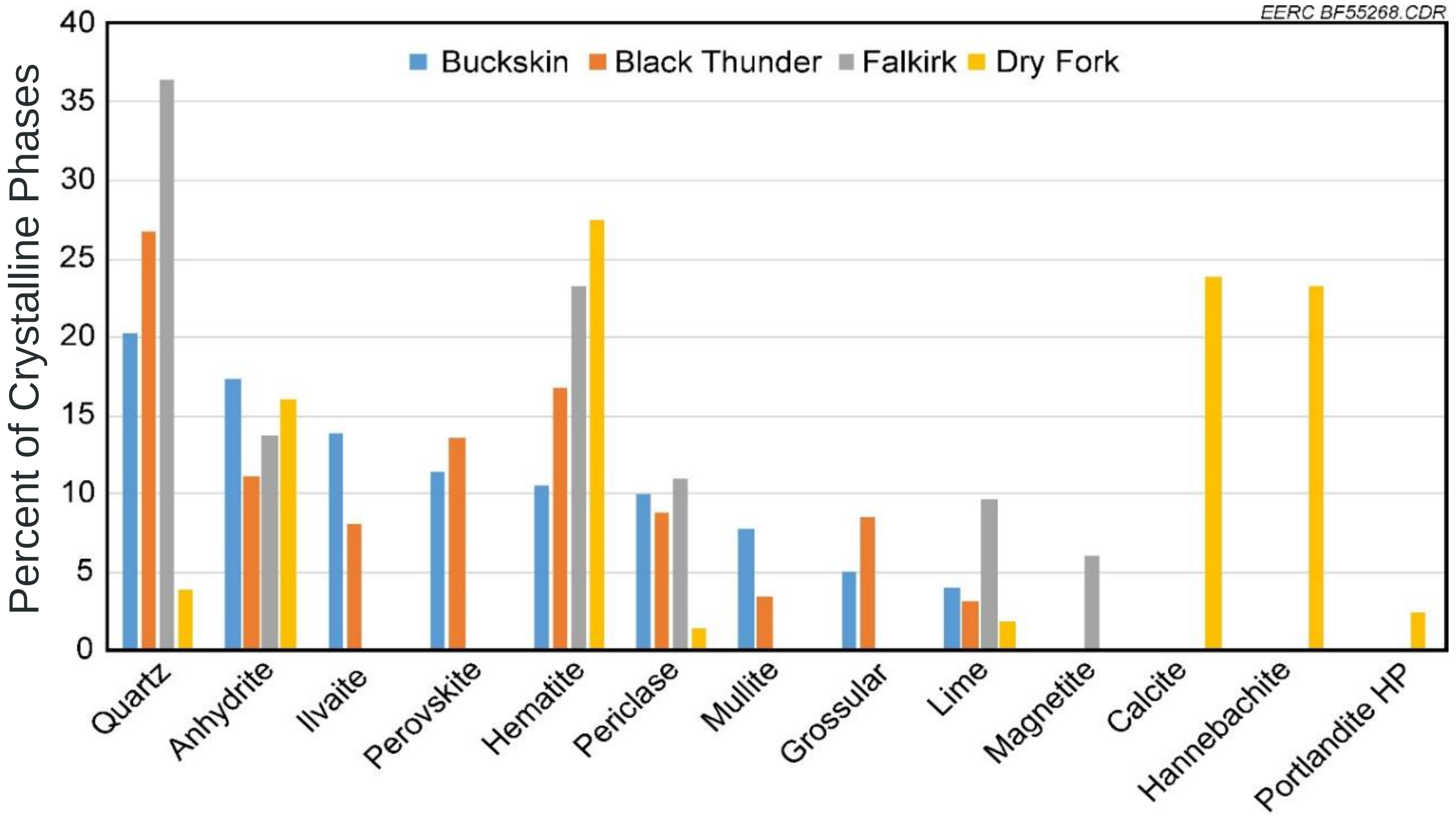
Sample Description	Lanthanides + Y +Sc	HREE/LREE ratio	Coutl
ND Lignite pc-Fired Fly Ash – Falkirk	260	0.47	1.04
PRB pc-Fired Steam Plant Class C Fly Ash – Black Thunder	366	0.41	0.95
PRB pc-Fired Fly Ash – Buckskin	401	0.45	1.06
PRB pc-Fired Dry Fork Station Fly Ash	282	0.43	1.06
H Bed Lignite Coal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

BET Surface Analysis of Ashes Selected for REE Analysis	Sample wt	BET Surface Area
	grams	(m2/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

XRF ANALYSIS RESULTS

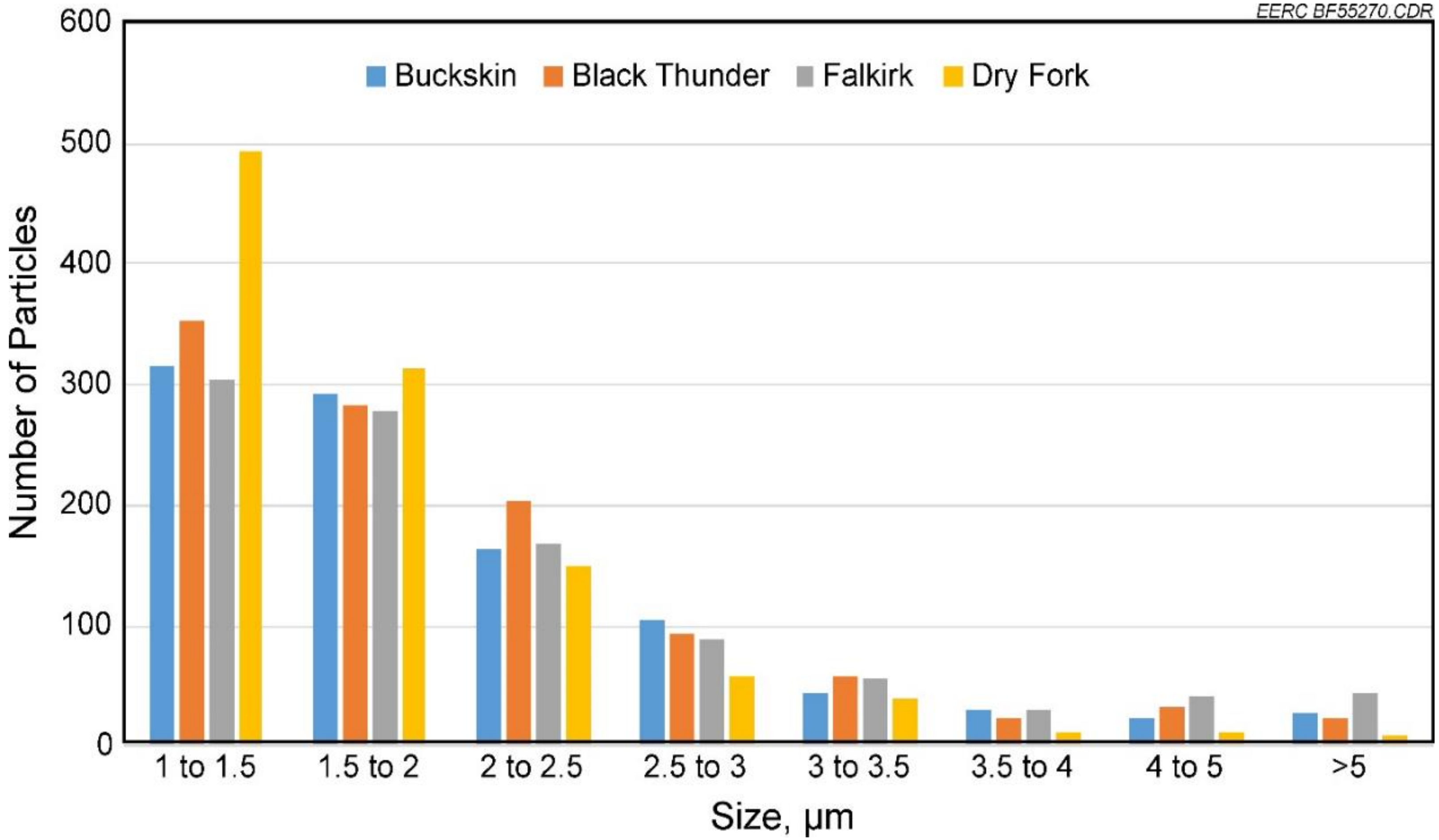


XRD ANALYSIS RESULTS

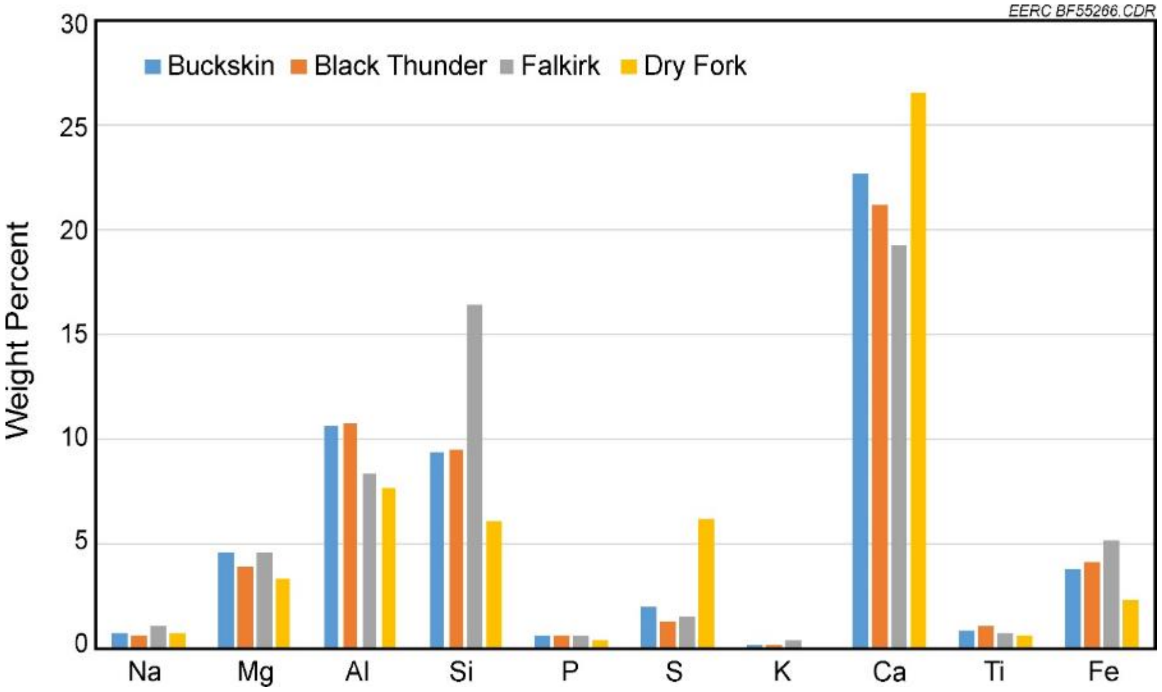


Anhydrite	$CaSO_4$
Ilvaite	$CaFe^{2+}{}_2Fe^{3+}Si_2O_7O$
Perovskite	$CaTiO_3$
Hematite	Fe_2O_3
Periclase	MgO
Mullite	$3Al_2O_32SiO_2$
Grossular	$Ca_3Al_2(SiO_4)_3$
Lime	CaO
Magnetite	Fe_3O_4
Calcite	$CaCO_3$
Hannebachite	2CaSO3•(H2O)
Portlandite	$Ca(OH)_2$

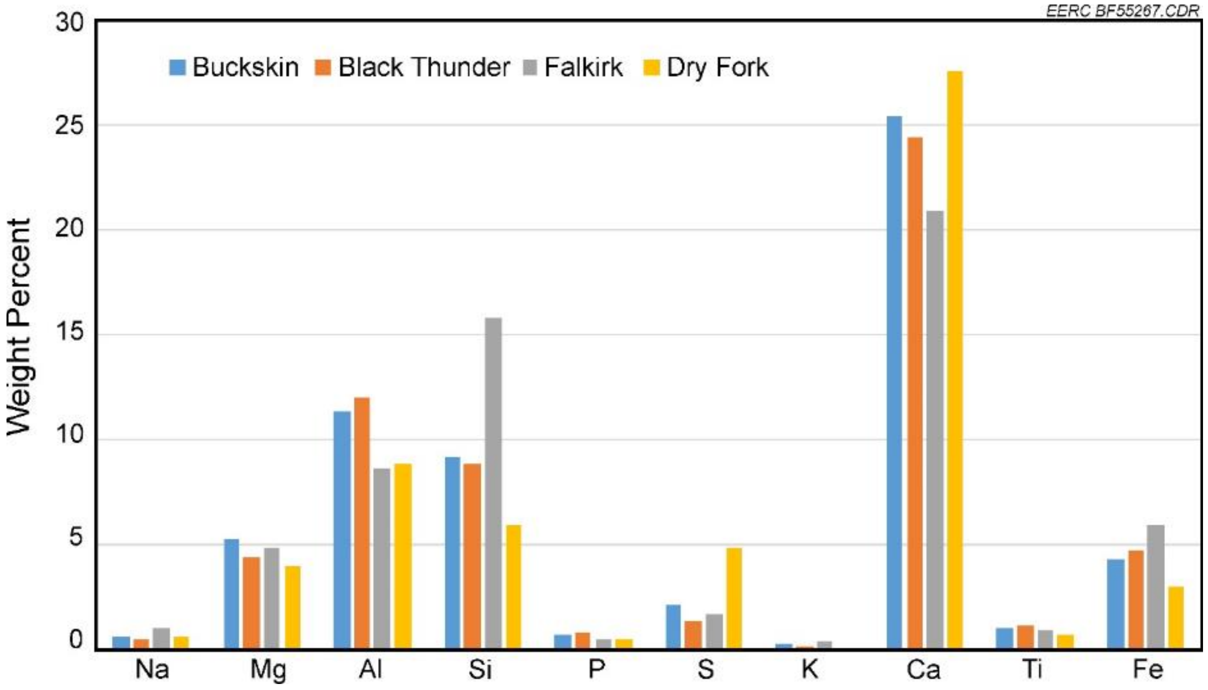
COMPUTER-CONTROLLED SCANNING ELECTRON MICROSCOPY (CCSEM) ANALYSIS RESULTS



CCSEM ANALYSIS RESULTS



Particle Size 1.0 to 1.5 µm vs. Chemistry

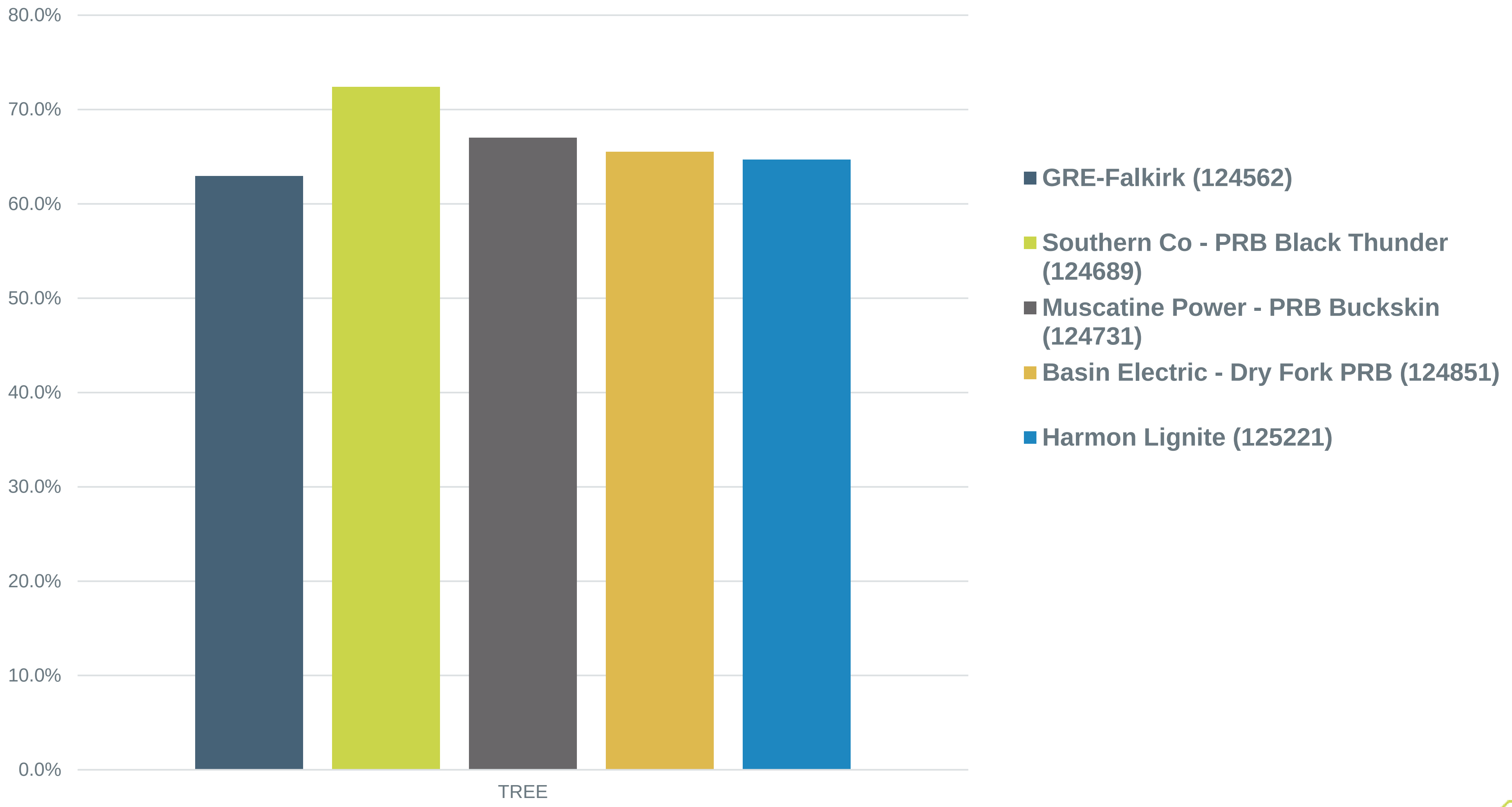


Particle Size 1.5 to 2.0 µm vs. Chemistry

TASK 3 – LABORATORY-SCALE TESTING

- **Subtask 3.2 – Fly Ash Pretreatment Testing**
  - Fly ash pretreatment methods
    - ♦ Thermal
    - ♦ Chemical alteration
  - Examine pretreatment impacts and efficacy

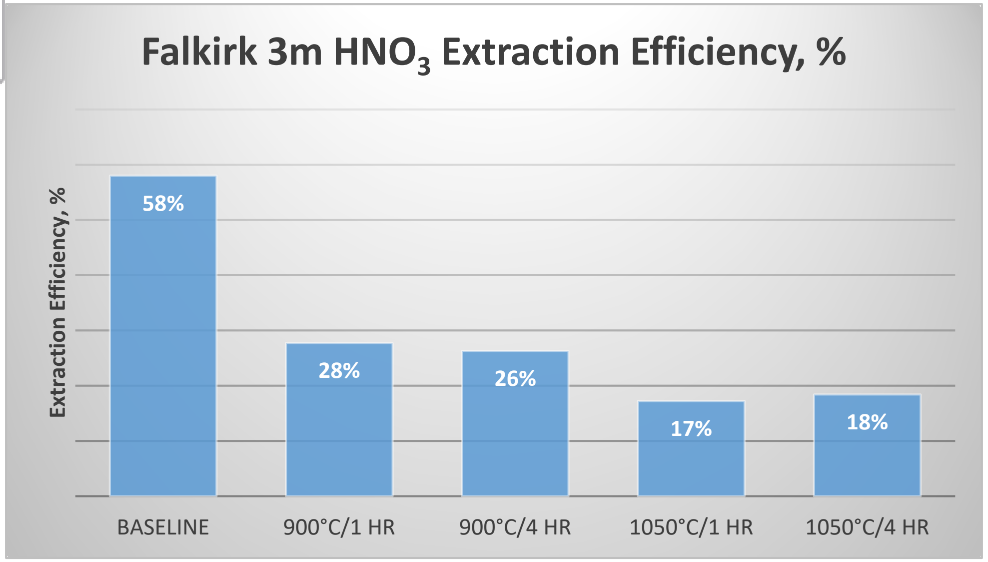
2 MOLAR NITRIC ACID – 16 HOURS – 10:1 L/S RATIO

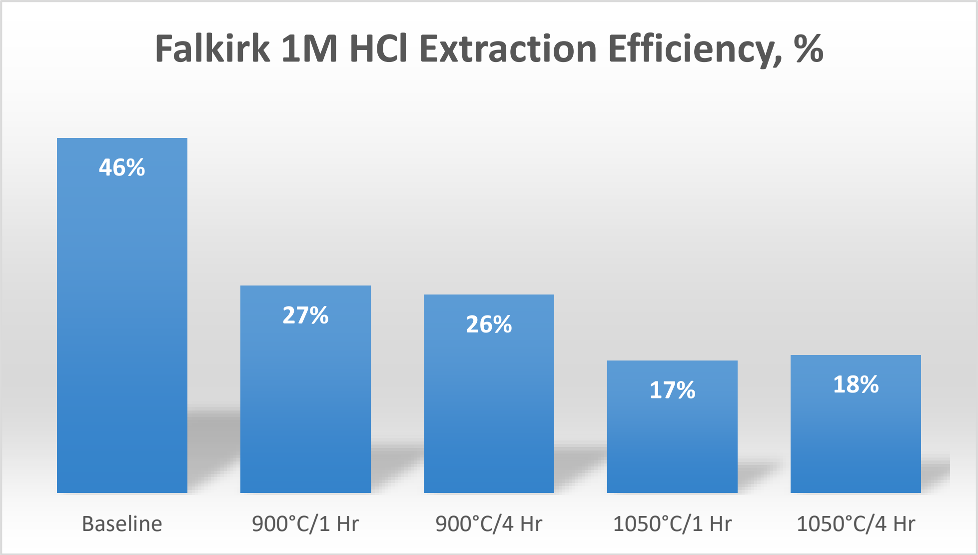


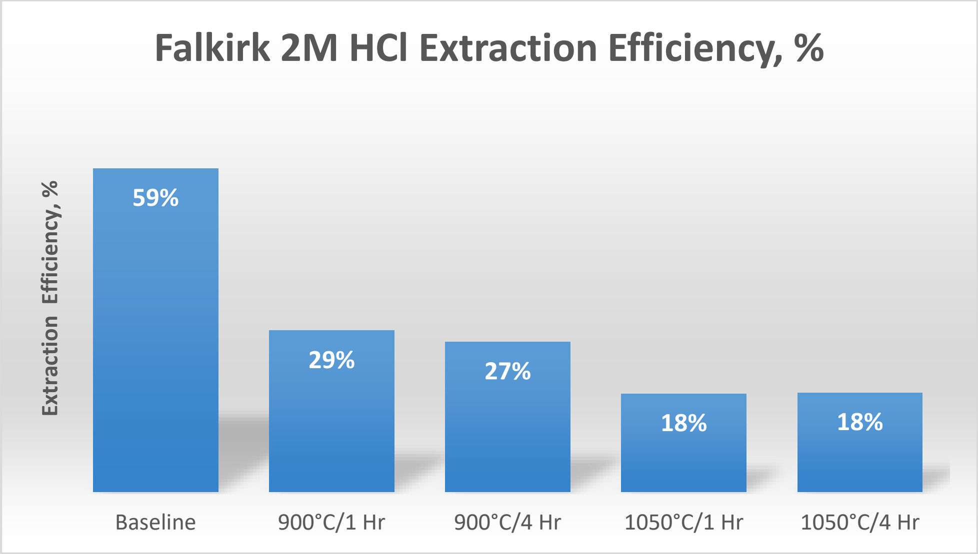
ACID MOLARITY AND LIQUID-TO-SOLID RATIO TESTING

Test Description	H+/kg Ash Ratio	Starting HNO_3 Molarity	Vol. Extract, mL	Mass Ash, g	Water Added	Liquid/Solid Ratio	Extraction Efficiency: GRE-Falkirk Lignite (124562)	Extraction Efficiency: Basin Electric - Dry Fork PRB (124851)
12-11-18 test - varying H+/kg ash ratios (5, 10, 20, 30) using 3 molar HNO_3 and varying the extractant liquid to solid ratio	5	3	20	12	0	1.7	32%	29%
	10	3	20	6	0	3.3	24%	0%
	20	3	20	3	0	6.7	44%	69%
	30	3	20	2	0	10	55%	80%
12-12-18 test - varying H+/kg ash ratios (10, 20, 30, 50) using fixed extractant liquid to solid ratio (10:1) and varying the HNO_3 molarity (1, 2, 3, 5)	10	1	20	2	0	10	45%	4%
	20	2	20	2	0	10	53%	53%
	30	3	20	2	0	10	58%	74%
	50	5	20	2	0	10	44%	61%
12-13-18 test - varying H+/kg ash ratios (10, 20, 30, 50) using 3 molar HNO_3 and varying the extractant liquid to solid ratio	10	3	20	6	0	3.3	40%	0%
	20	3	40	6	0	6.7	53%	68%
	30	3	60	6	0	10	58%	77%
	50	3	100	6	0	16.7	49%	85%
12-13-18 test - Fixed H+/kg ash ratios (30) using 60 mL of 3 molar HNO3 with 6g ash, but adding varying levels of water to vary the liquid to solid ratio	30	3	60	6	0	10	65%	78%
	30	3	60	6	40	16.7	66%	98%
	30	3	60	6	60	20	56%	74%
	30	3	60	6	120	30	56%	65%

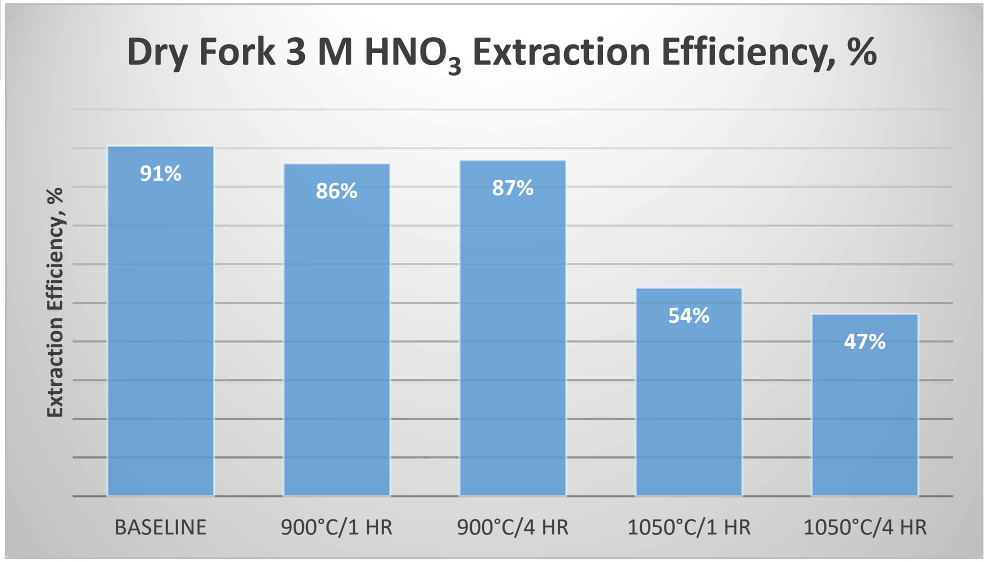
FALKIRK ACID EXTRACTION ANALYSIS

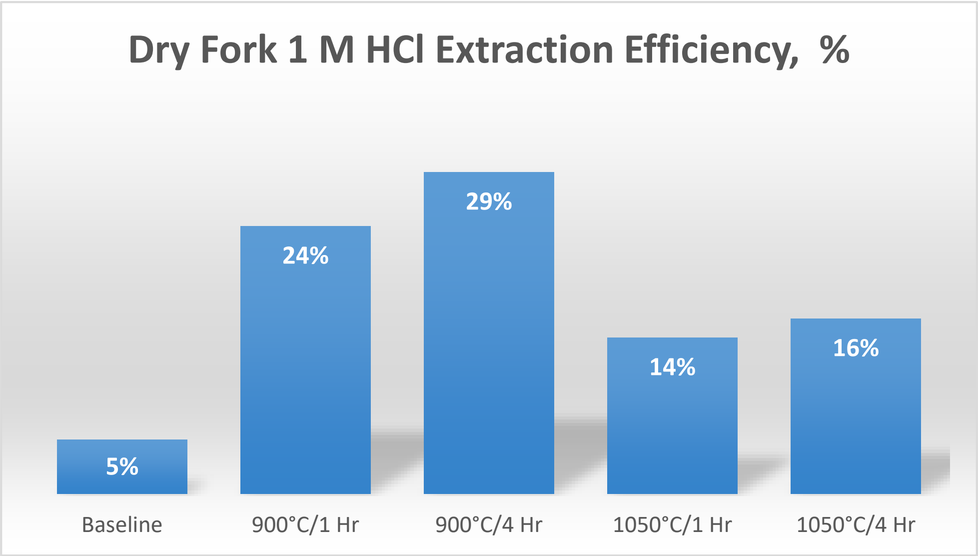


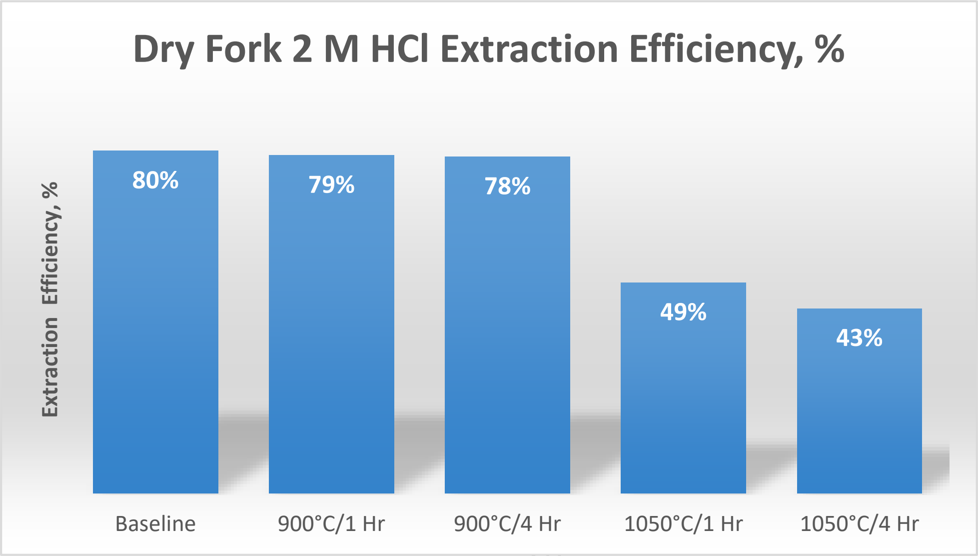




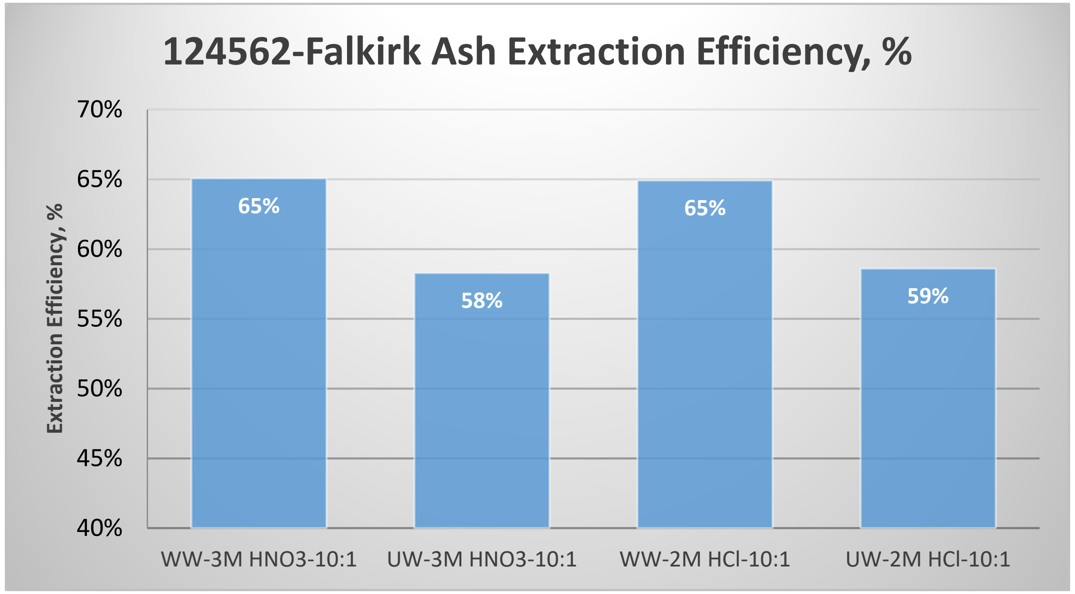
DRY FORK ACID EXTRACTION ANALYSIS

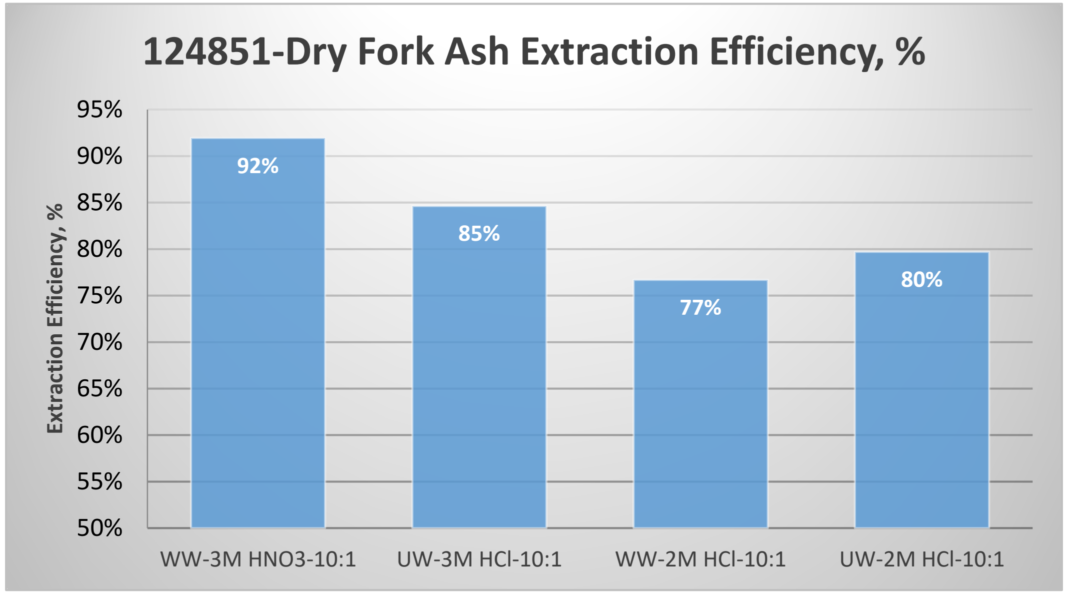


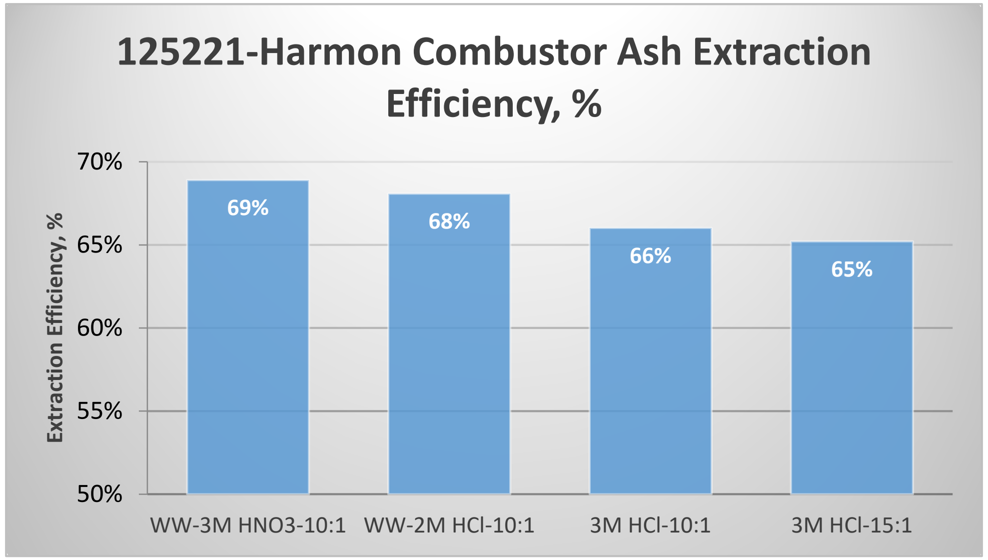




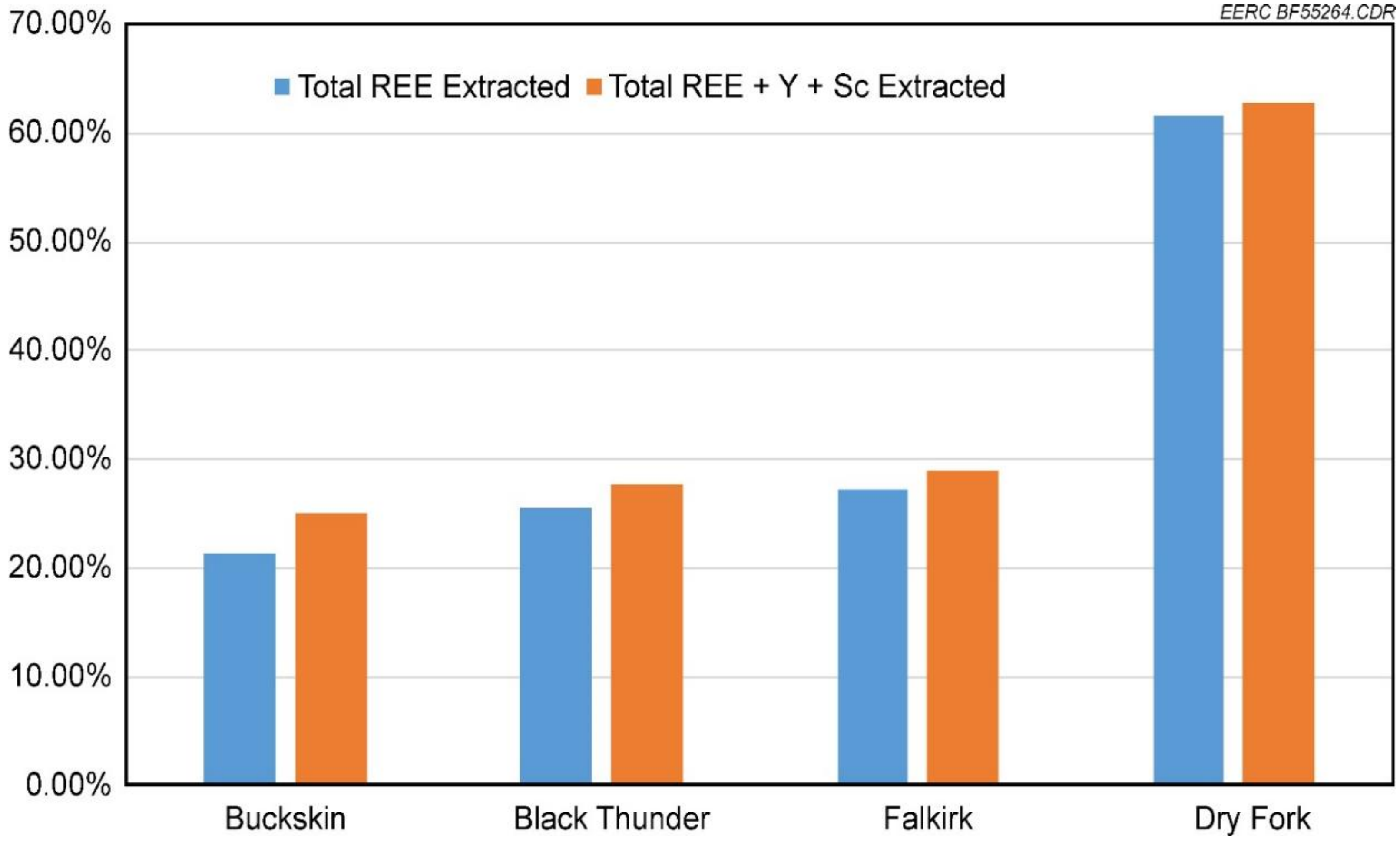
ACID EXTRACTION ANALYSIS WATER WASH





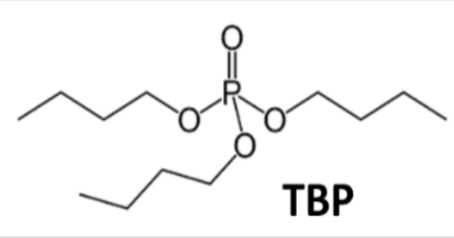


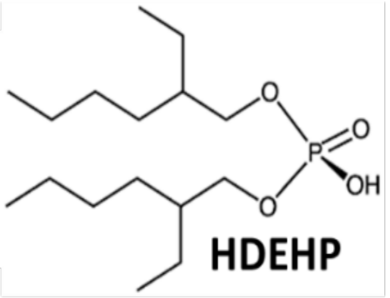
MILD SOLVENT LEACHING ANALYSIS

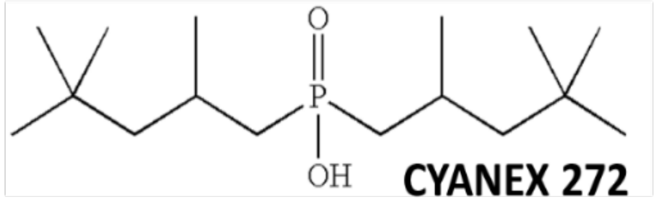


TASK 3 – LABORATORY-SCALE TESTING

- **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.



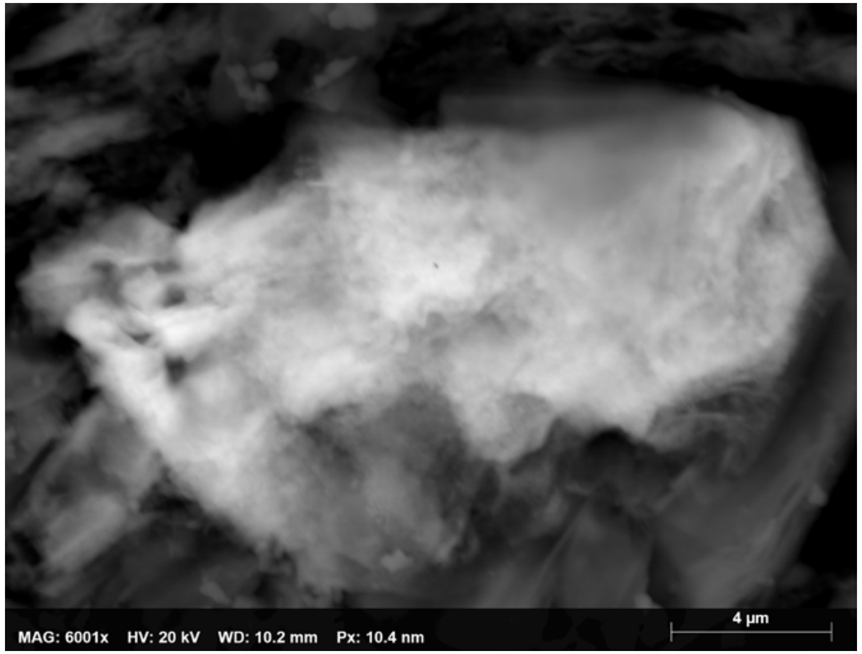


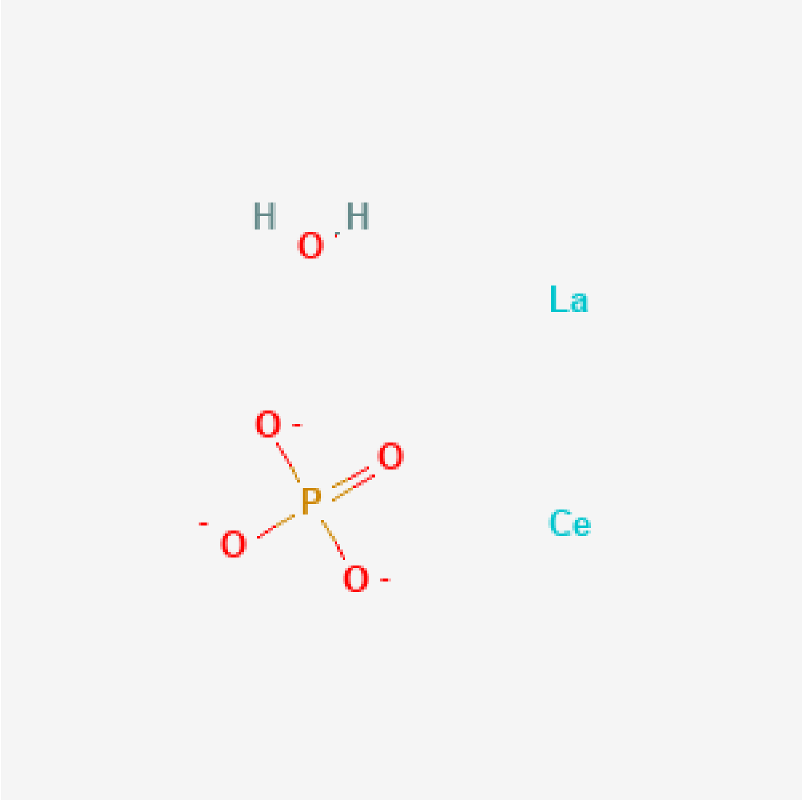


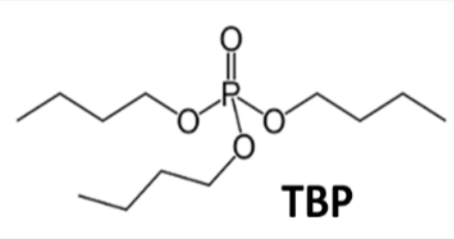
REE EXTRACTIVE SOLUTIONS

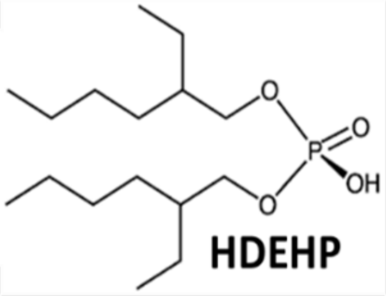
Substitutions for La and Ce:

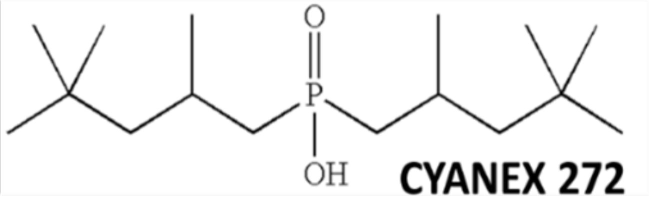
REE, Y, Ca, Pb, Th, U, Fe



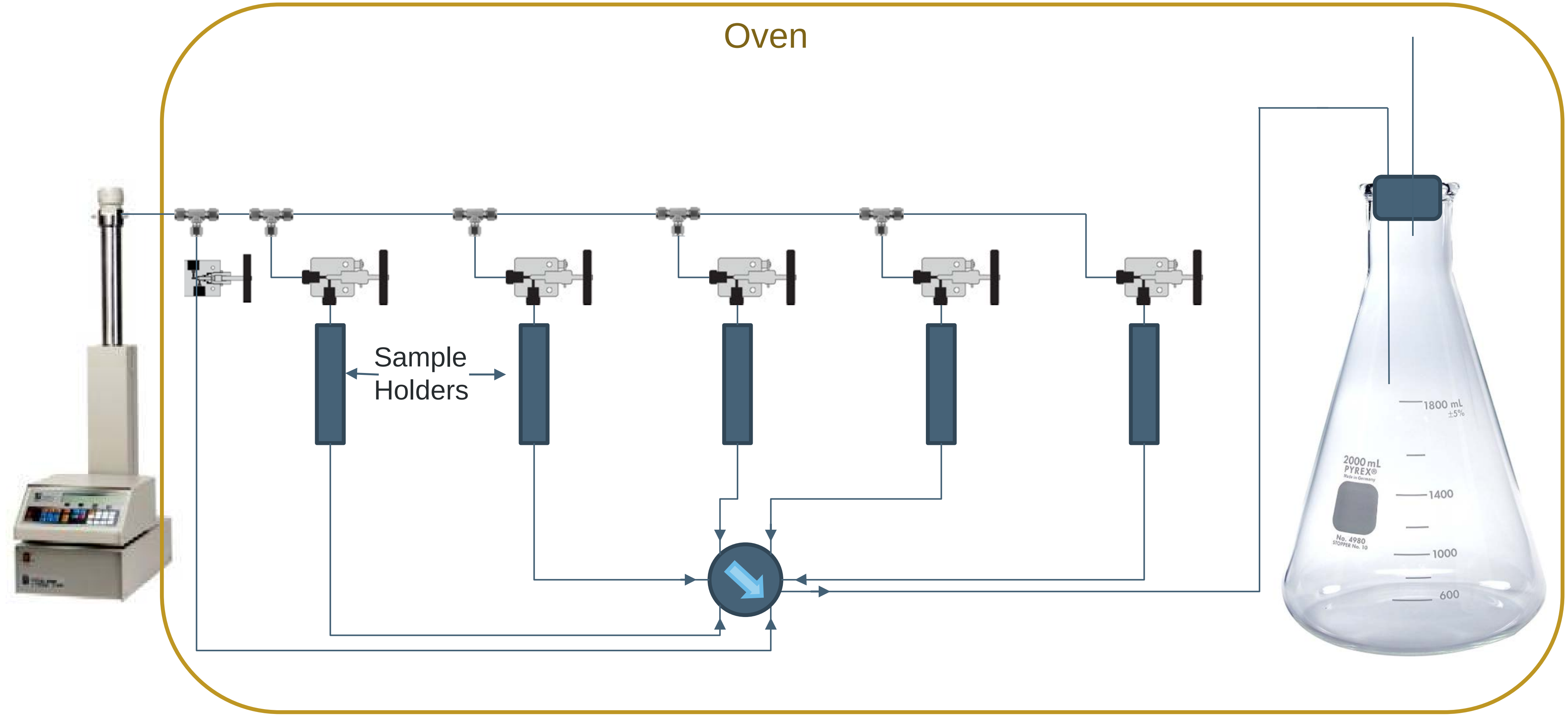








HIGH-PRESSURE EXTRACTION SETUP



CURRENT SETUP FOR PRESSURIZED EXTRACTION

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THANK YOU

Critical Challenges. Practical Solutions.