High Yield and Economical Extraction of Rare Earth Elements from Coal Ash

Physical Sciences Inc., Andover, MA

UK/Center for Applied Energy Research, Lexington, KY

Winner Water Services, LLC, Sharon, PA

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Presentation to:

2021 AIChE Annual Meeting

November 7-12, 2021 - Boston, MA

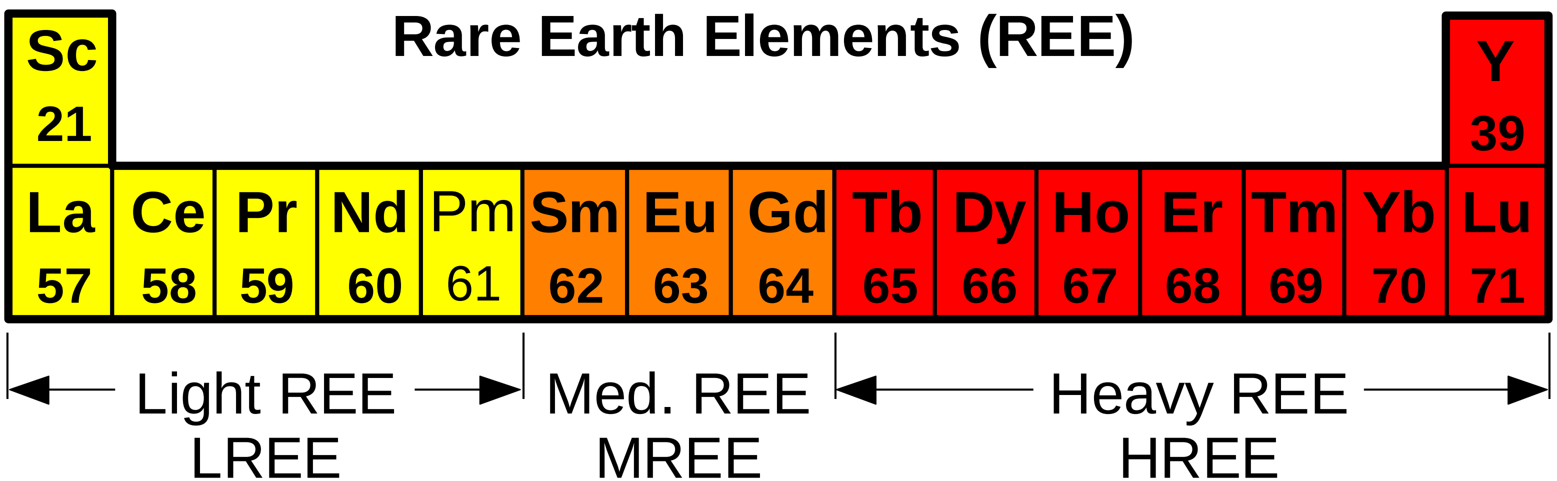
PROGRAM TOPIC: DESIGN, CONSTRUCTION AND OPERATION OF UNIT OPERATIONS LABS AND PILOT PLANTS

November 2021

Acknowledgement:
This material is based upon work supported by the U.S. Department of Energy under Award DE FE0027167.

Rare Earth Elements (REEs): Nomenclature

- **Group 3B Elements (Scandium, Yttrium) and lanthanides**
- **Classified into light (LREE), medium, and heavy (HREE)**



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Rare Earth Oxide Consumption Sectors

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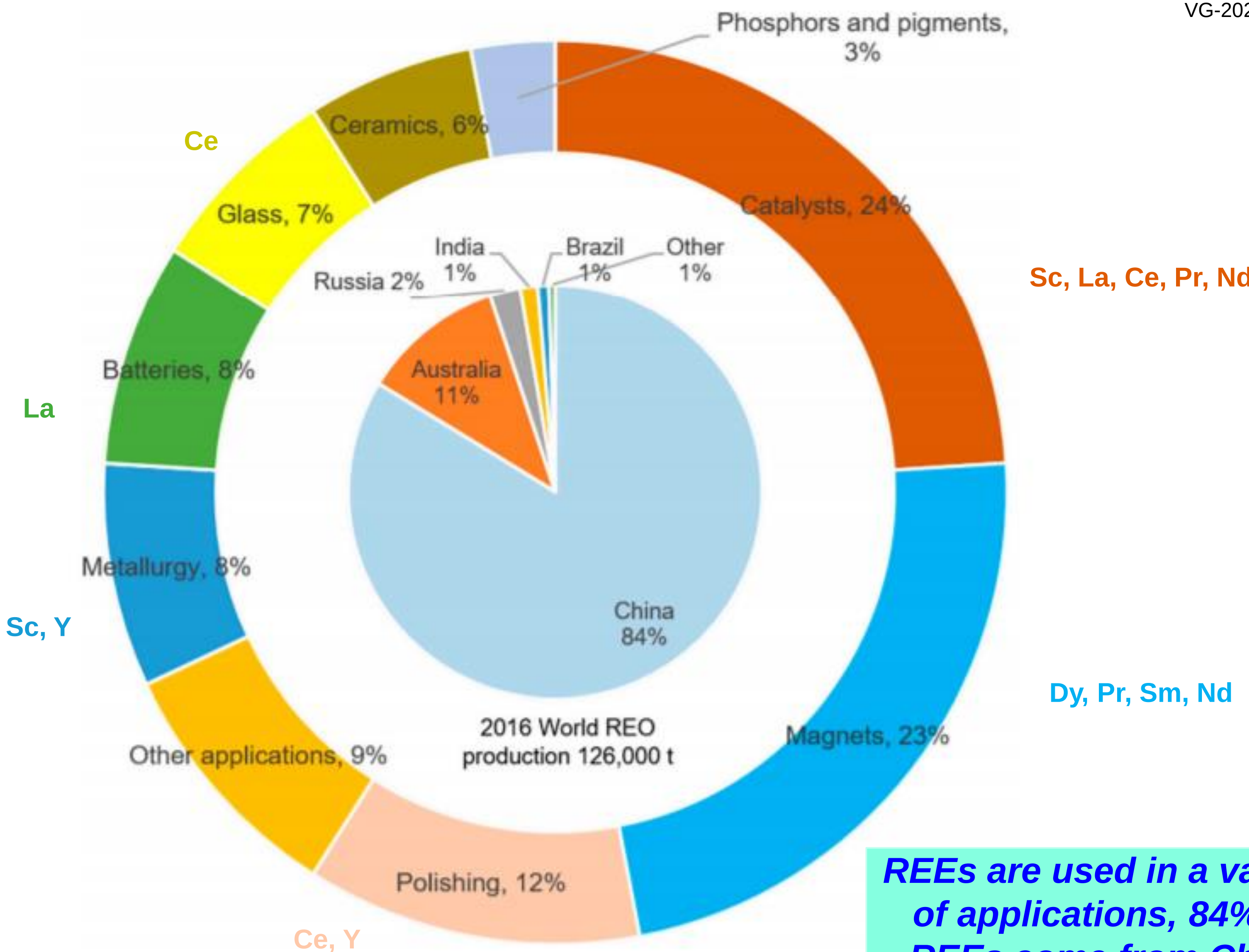

REEs are used in a variety of applications, 84% of REEs come from China

Source: Zhou et al., Minerals, 2017

Coal Ash: A Resource with Substantial REE Content

- **Russian and US literature:**
  - ~ 1 wt% (10,000 ppm) in Russian Far East coal ash*
  - Rich in HREE

➢ **Fly ash: An abundant waste product from coal-fired power plants in U.S. (~ 100M tons annually)**

*Seredin, V. V., "Rare earth element-bearing coals from the Russian Far East Deposits," *Int. J. Coal Geology*, 30, pp. 101-129 (1996).

Coal Combustion Enriches REE Content in Ash by ~ X10

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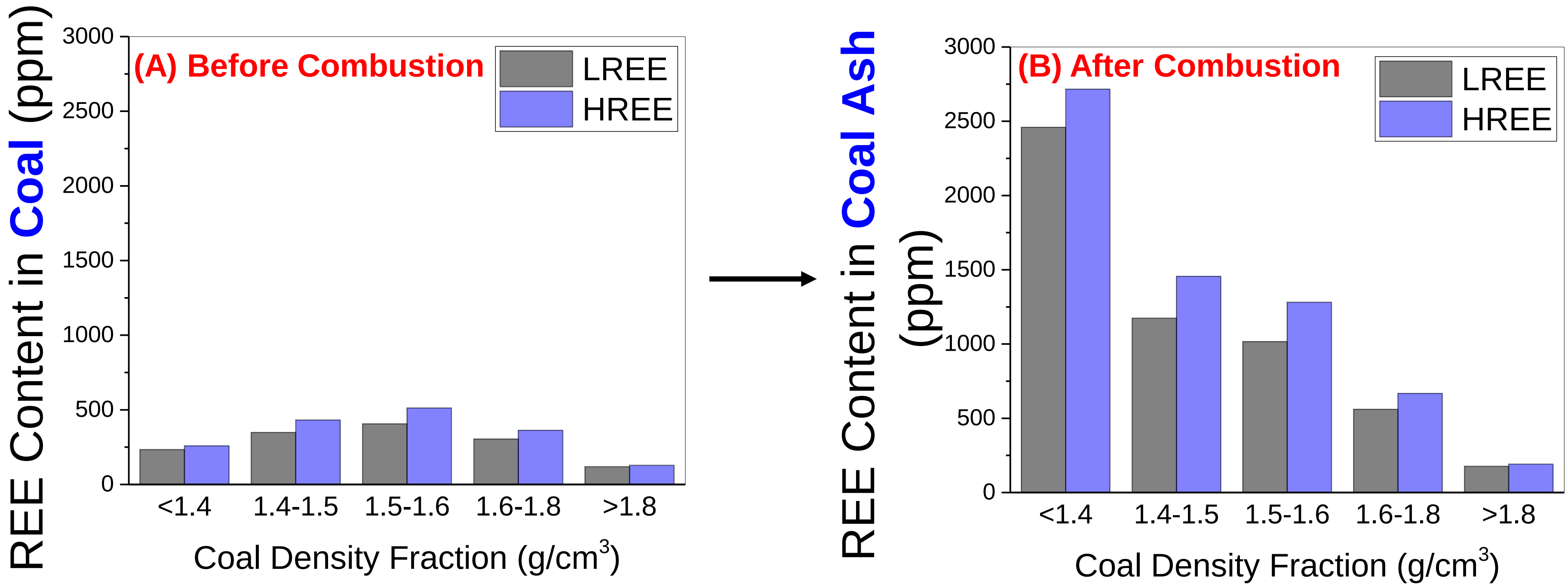
- **Example of Russian Far East Coal (Black Stone Deposit)**

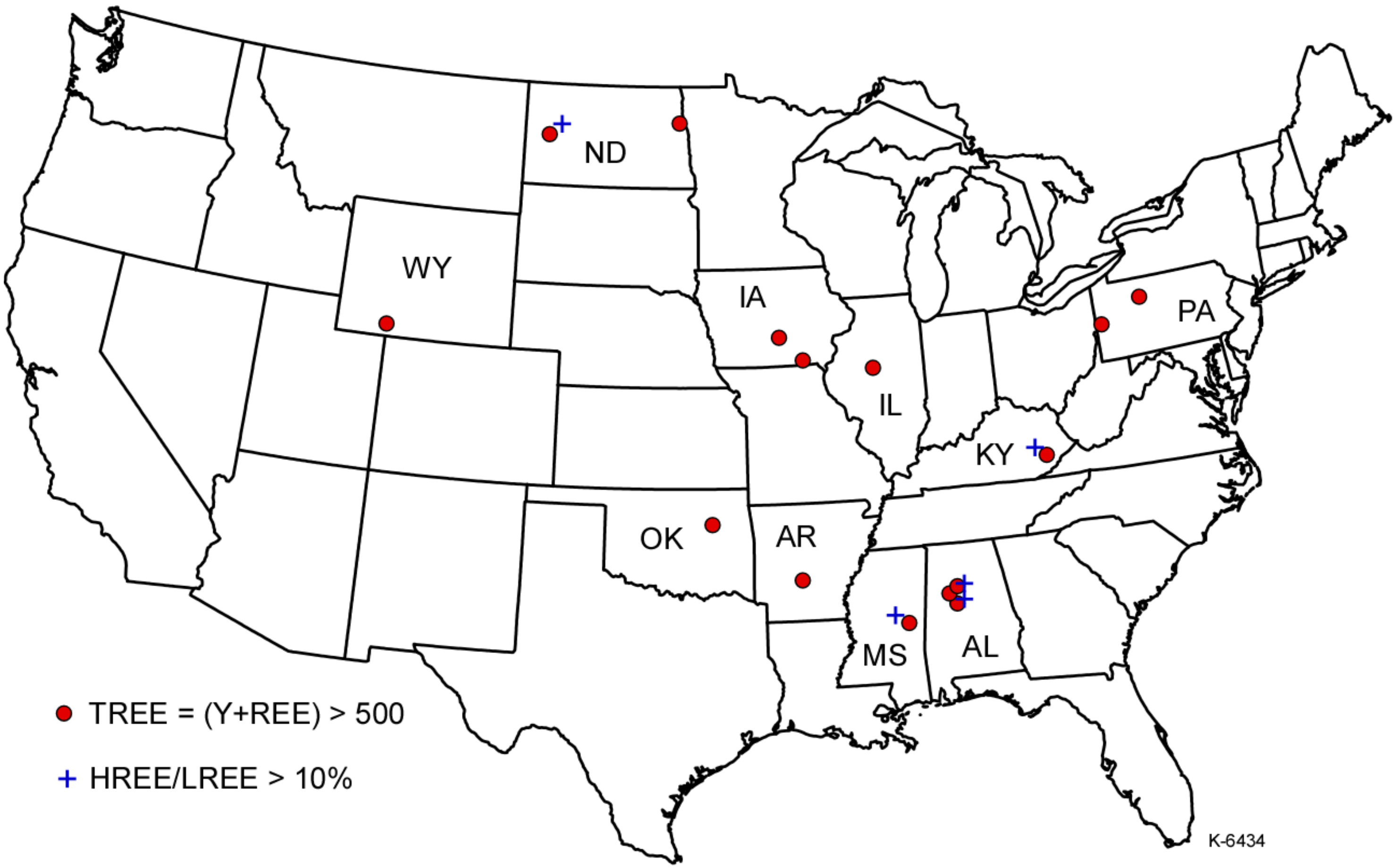


➢ **Coal Ash LREE + HREE Concentration = ~ 0.25 wt.%**

➢ **LREE/HREE ~ 1**

*Seredin, V. V., "Rare earth element-bearing coals from the Russian Far East Deposits," *Int. J. Coal Geology*, 30, pp. 101-129 (1996).

U.S. Coal Deposits with Total REE Content > 500 ppm and HREE/LREE Ratio > 10%



- **U.S. coals from PA, WV, <u>KY</u>, AL and ND meet threshold**

Source: USGS COALQUAL Database

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Project Description

- **Area Of Interest (AOI) 2 program: Pilot Scale Technology**
  - Phase 1 – Separation technology demonstrated successfully on bench scale
  - Phase 2 - Design, construction and operation of physical and chemical pilot plants to extract rare earth elements (REEs) from coal ash and additional CMs (Sc, Al)

- **Period of performance: 9/29/2017 – Fall 2021**

- **Team:**
  - Physical Sciences Inc. (PSI), Andover, MA
  - UK/Center for Applied Energy Research (CAER), Lexington, KY
  - Winner Water Services, LLC (WWS), Sharon, PA

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Key Functions

- ***The PSI, CAER, WWS team provides a complete integrated science, technology, engineering, technology transition, and commercialization solution for DOE/NETL***
  - **Physical Sciences Inc (PSI):**
    - PI/PM, Lead Chemist: Dr. Dorin Preda
    - Lead Chemical Engineer/Process Modeling/TEA: Dr. David Gamliel
    - Process Development, ICP-OES Analysis: Dr. Bryan Sharkey
    - Technical/Commercial Consultant: Dr. Prakash Joshi
  - **University of Kentucky Center for Applied Energy Research (CAER):**
    - Coal Geochemistry, Ash Source Selection, Materials Characterization: Dr. James Hower
    - Mineral/Ash Processing, Feedstock Logistics, Site Qualification: Dr. John Groppo
    - Pozzolanicity Testing: Dr. Robert Jewell
  - **Winner Water Services (WWS):**
    - Chemical & Pilot Plant Engineering, and Technology Commercialization: Mr. Todd Beers
    - Plant Design, Pilot Plant Operations: Mr. Michael Schrock

Phase 2 Project Objectives

- **<u>Overall Objective</u>: Demonstrate Phase 1 REE separation/enrichment technology at pilot scale in a plant(s) with *decoupled* operating capacities of ~ 0.4 tpd physical processing and ~ 0.5 tpd chemical processing**
  - Both pilot designs are modular and transportable
  - Demonstrate production of high purity REY product and of critical material products (Sc, Al)

Performance Parameter		Threshold Value	Objective Value
Feedstock REY+Sc Content		>300 ppm	>500 ppm
Return on Investment		< 12 years	< 10 years
REY-enriched Product	Quantity (REY salts)	100 g	300 g
	REY-enriched Oxide Purity (total REY content - elemental basis)	*>85%*	*>90%*
Sc-enriched Product	Quantity (Salt/Oxide)	1 g	2 g
	Sc-enriched Oxide/Salt Purity (Sc content - elemental basis)	*>85%*	*>90%*
Aluminum Product	Quantity (oxide type material)	100 g	300 g
	Purity (Al content elemental basis)	*>50%*	*>68%*

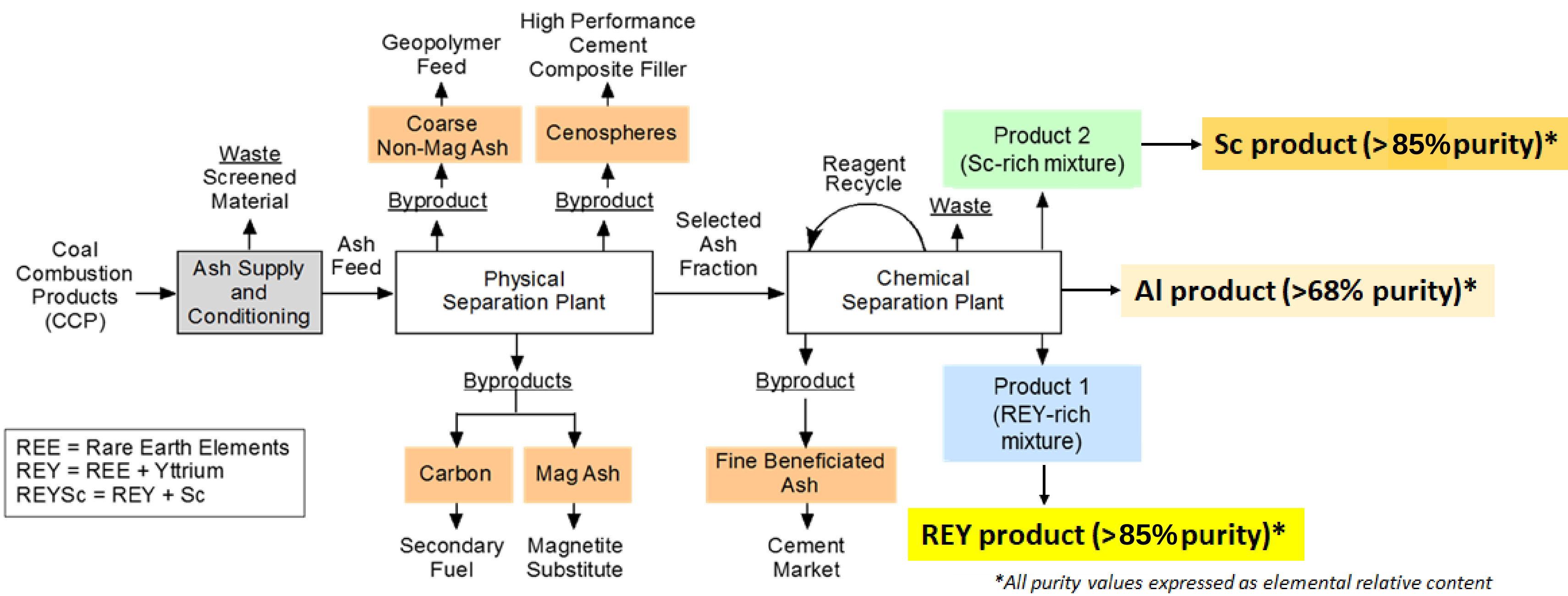
Current Program Status

- **Physical processing – completed:**
  - Collected ~15 tons of coal ash from two different KY plants for physical processing
  - 475 – 550 ppm ash REYSc content
- **Chemical processing operations – completed, material deliverables under evaluation:**
  - > 10 tons of coal ash processed to date
  - ~1.2 kg of REE concentrate produced
  - REY product:
    - Phase 2 REYSc product from LLX: ~10-68 wt.% (elemental basis)
    - Identified and implemented pathways to increase purity to >90 wt%
  - Sc-product produced using a PSI-proprietary LLX process
    - 12X enrichment obtained in a single cycle
    - Achieved target purity using two extraction cycles (>85 wt.%)
  - Al-product of >90 wt.% purity obtained in the scale-up runs

Key Results

Rare Earths Recovery Process Overview

- **Physical separation stage, followed by a chemical separation stage, followed by a post-processing stage**
- **<u>Proposed Products</u>: REY, Sc and Al products with high purity**
- **<u>Commercially Viable By-products</u>: Cement substitute, cenospheres, secondary fuel carbon, etc.**



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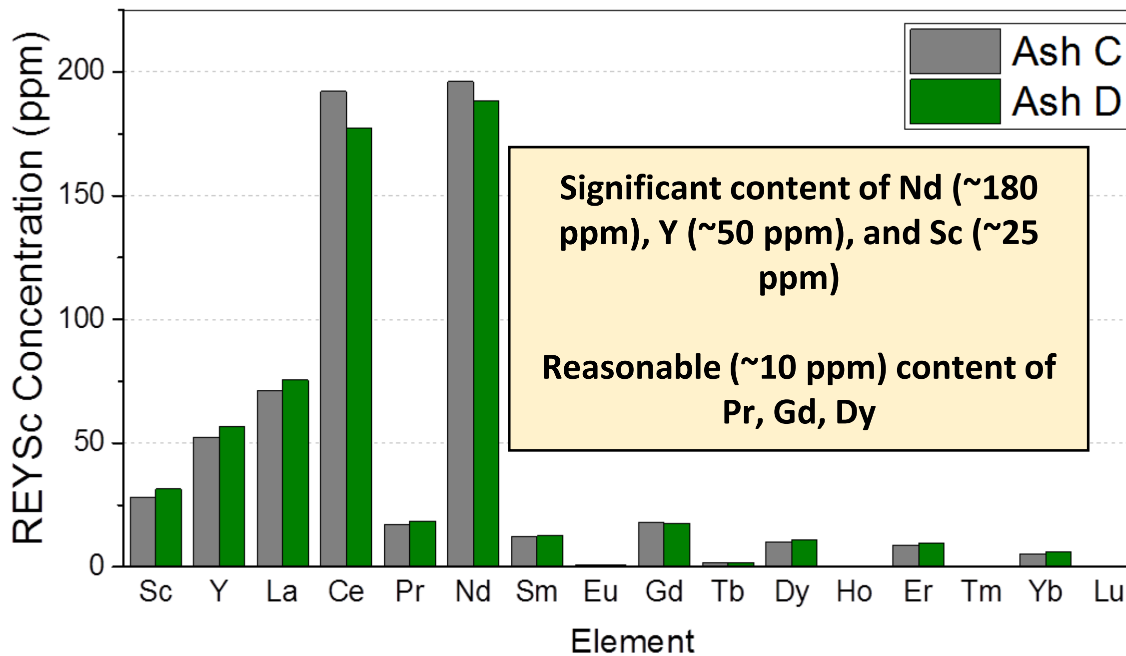
Feed Ash Material

- **Ash from 2 KY coal fired power plants was recovered and used as process feed**



Physical Processing Pilot

CAER physical pilot plant processed >15 tons of coal ash
>50% yield for ash mass fraction for chemical processing

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Output of Physical Processing

- **Physical processing creates an ash fraction that is a suitable feed to chemical pilot**
  - Low carbon content
  - Low magnetics content
  - Small particle size
- **Processed ash collected in super sacks, shipped to and processed in the chemical pilot in Sharon, PA**

Chemical Processing Overview

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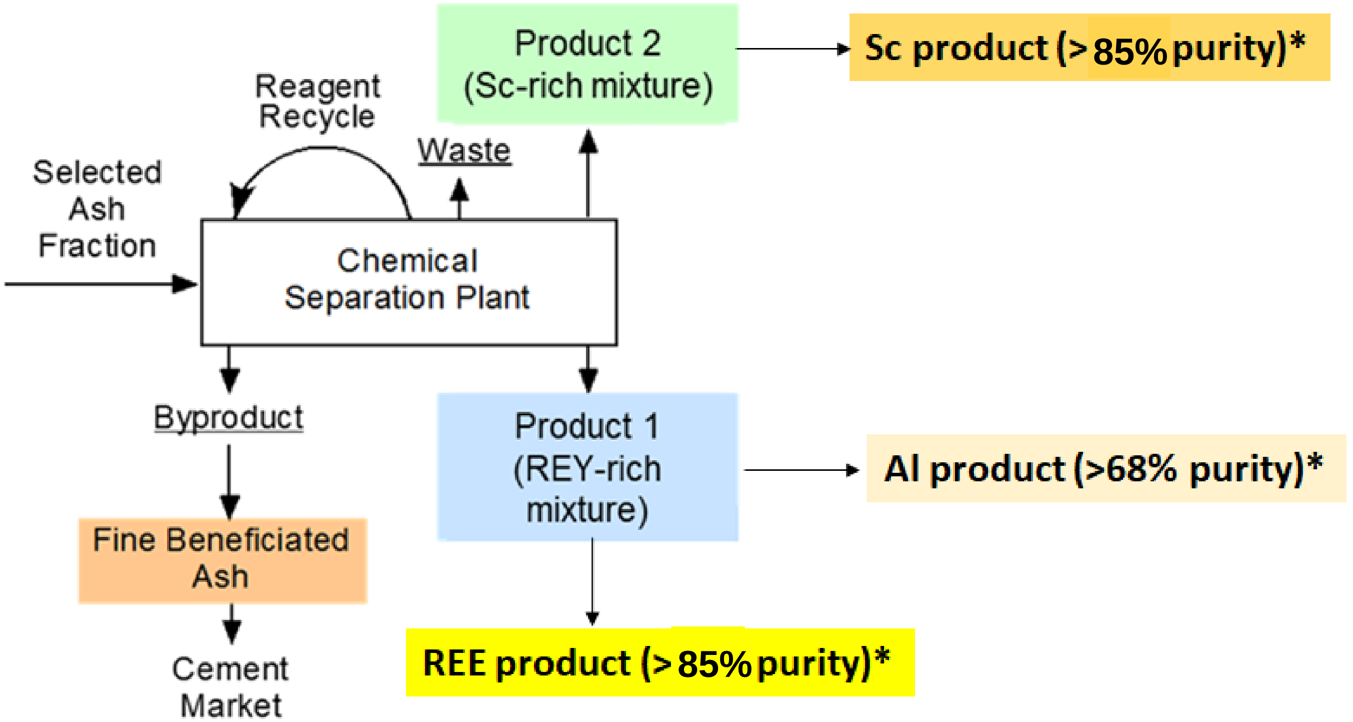

**All purity values expressed as relative elemental content*

REY-rich material, Sc-rich material and Al-product are produced from coal ash using simple and efficient process steps

PSI Micropilot Facility

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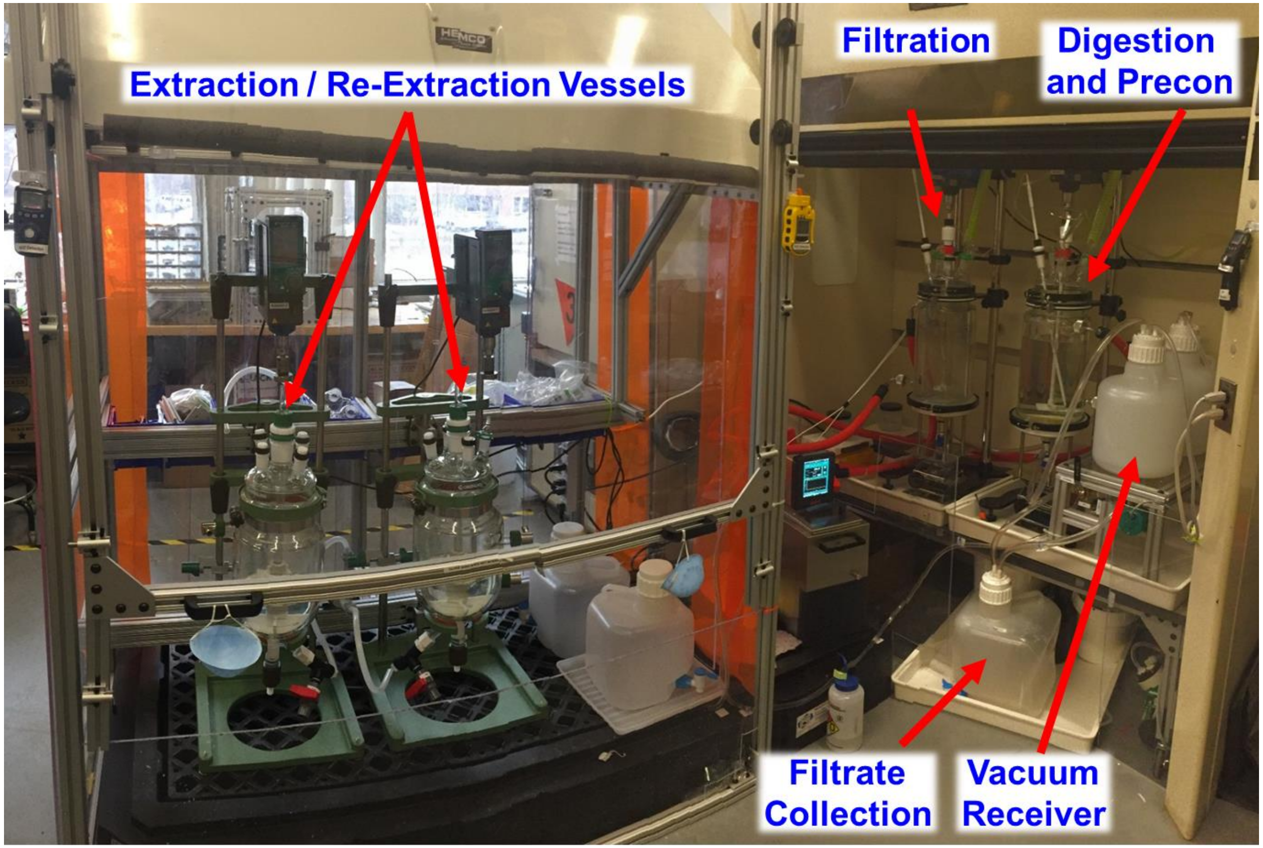
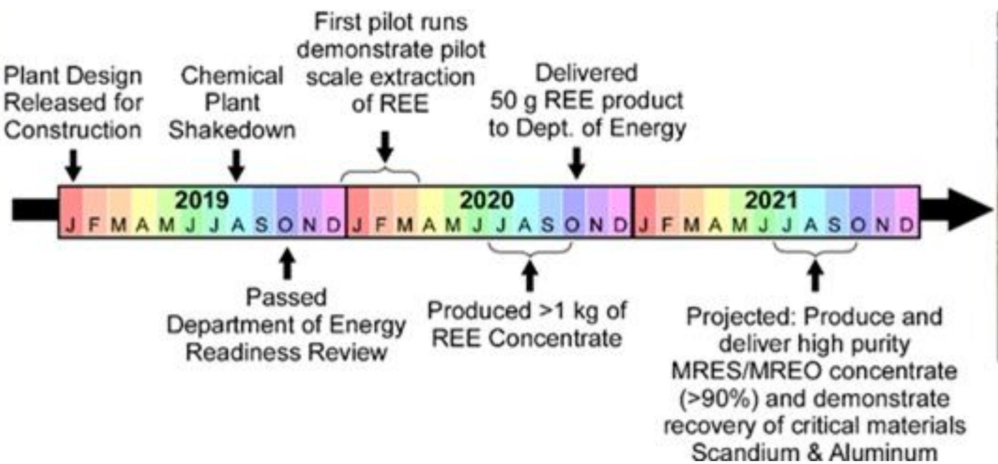
- **PSI micropilot is used to:**
  - Demonstrate target yields and enrichment
  - Determine ash suitability
  - Identify and troubleshoot processing challenges and bottlenecks for the pilot plant



Chemical Pilot Operations

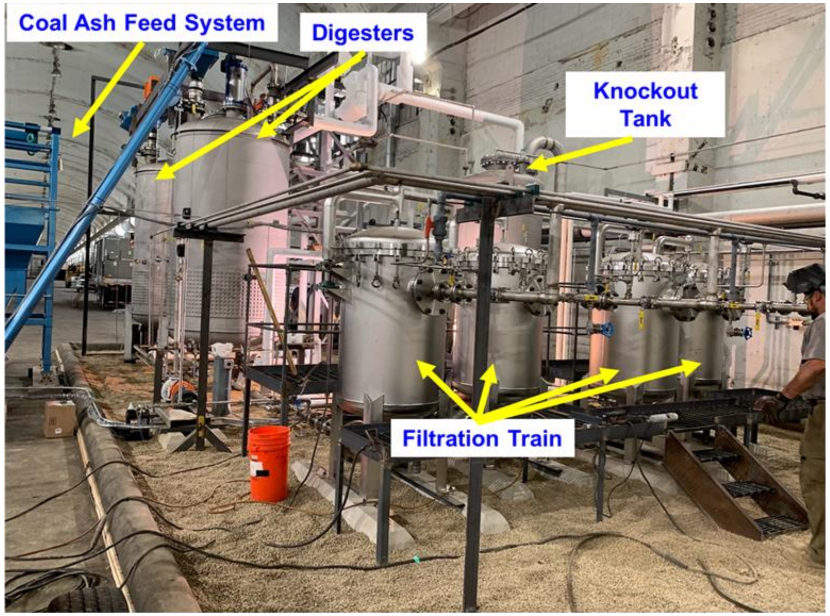
- **Chemical pilot designed to process 0.5 tons/day of coal ash**
- **Situated on the floor of a former torpedo factory**
- **All unit modules are currently operational**

Former Westinghouse Torpedo Manufacturing Facility (Dec 2018)

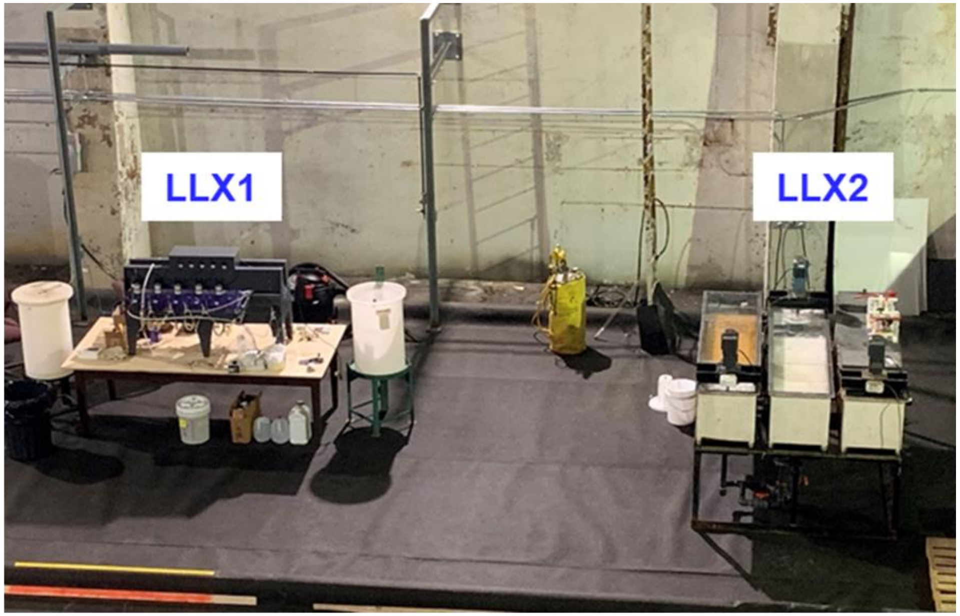


REE Recovery Pilot Plant (Jan 2021)

Hot and Cold Side Operations



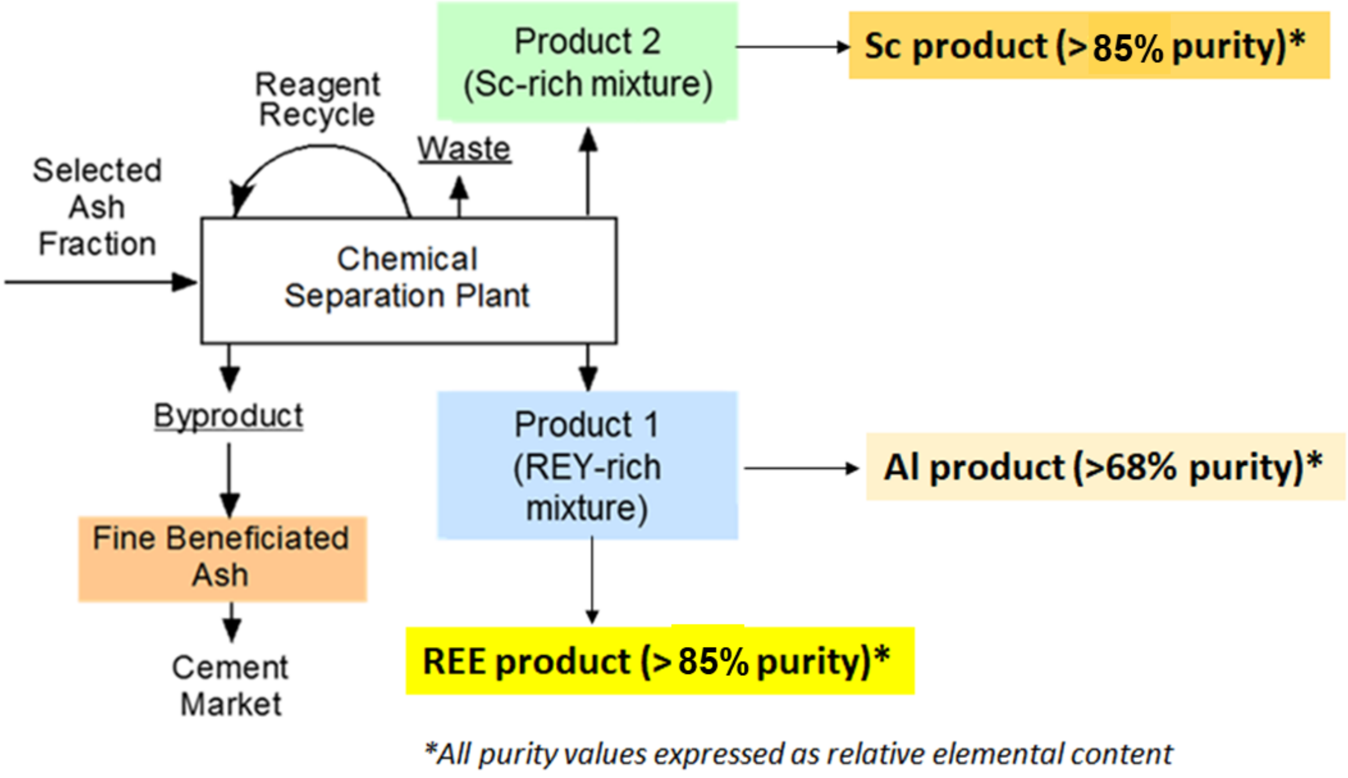
Hot Side Operation



Cold Side Operation

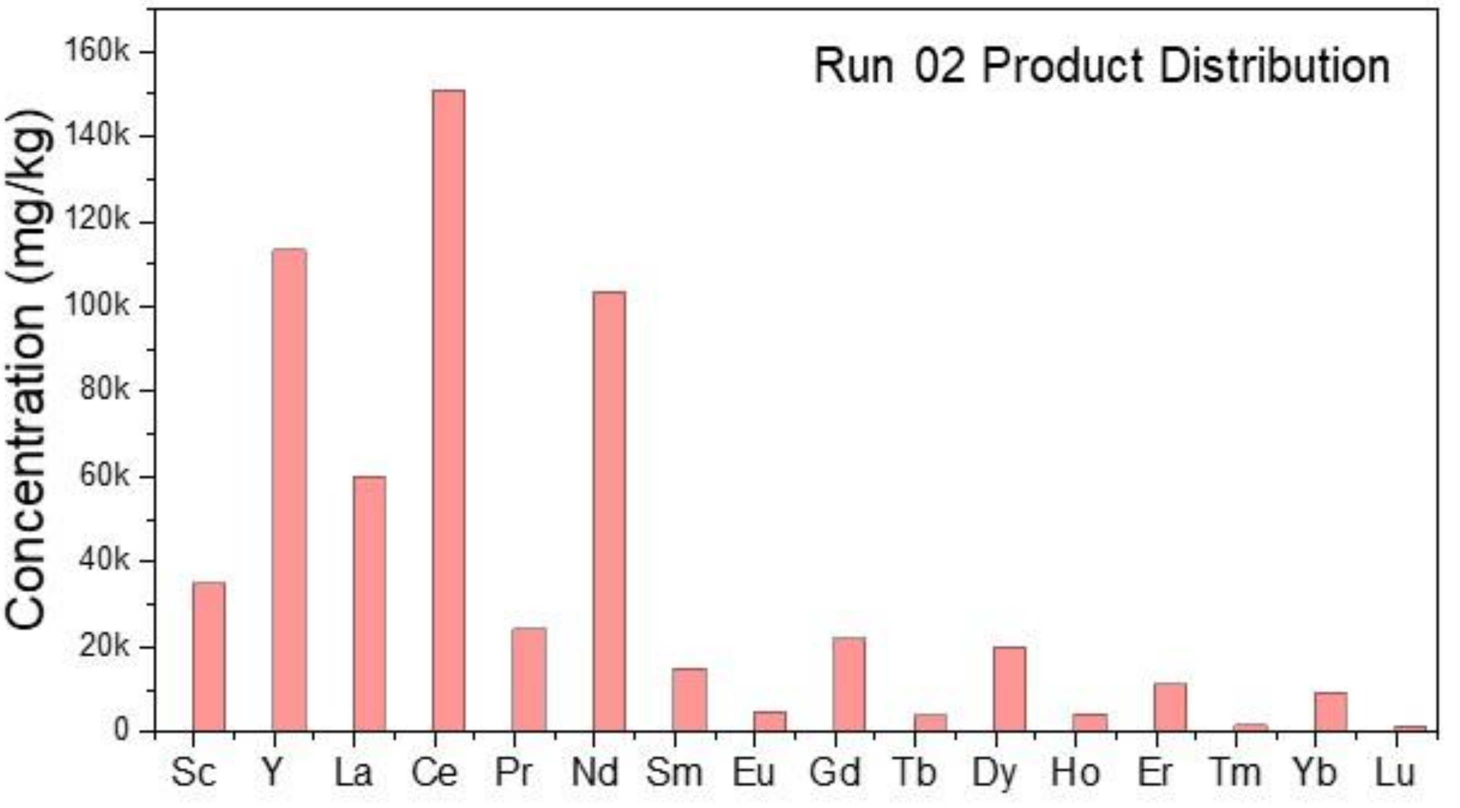
WWS chemical pilot plant operational: ~10 tons of coal ash processed to date.
>20% yield for REYSc concentrate, >50% purity (elemental basis).
Produced REYSc concentrates delivered to Department of Energy.

Generation of Program Deliverables



Processes were developed at the bench scale to generate the Sc, Al, and REE product program deliverables from the pilot scale LLX products

LLX - Dried Product Composition (Initial Program Phases)



Product compositions exceed initial objective key performance parameter (>20 wt.%).Significant quantities of Nd, Y, Sc and HREE in product material.

Generation of REY Deliverable

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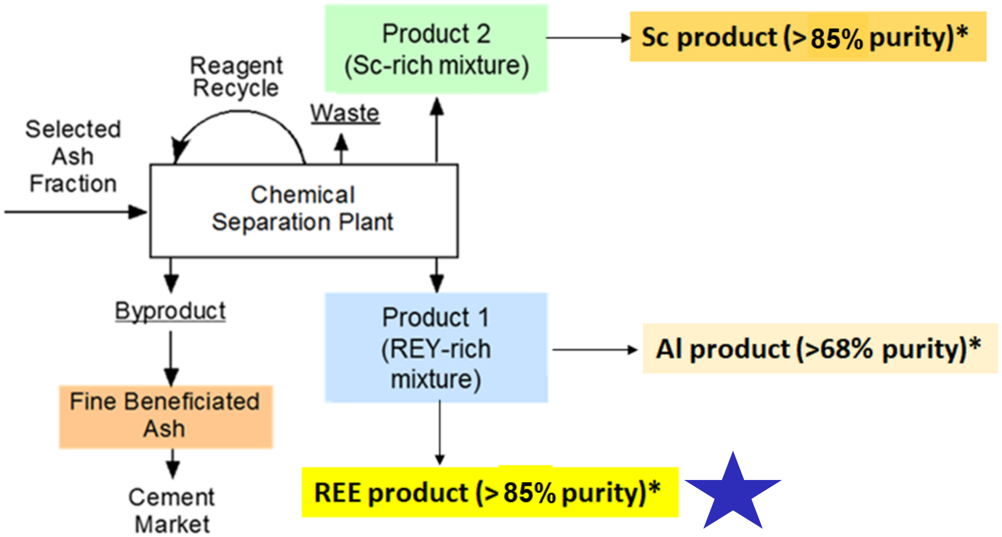
- **LLX optimization and feed normalization resulted in an LLX product with an REE purity consistently above 40-60% relative content**
- **PSI developed and characterized a process capable of consistently generating >85% relative content REE oxide material from the LLX products**



All purity values expressed as relative elemental content

REE Oxide Product

Process was normalized to the feed and used to produce deliverable quantity of REE oxides with >85% purity

Sc Recovery Process: Summary

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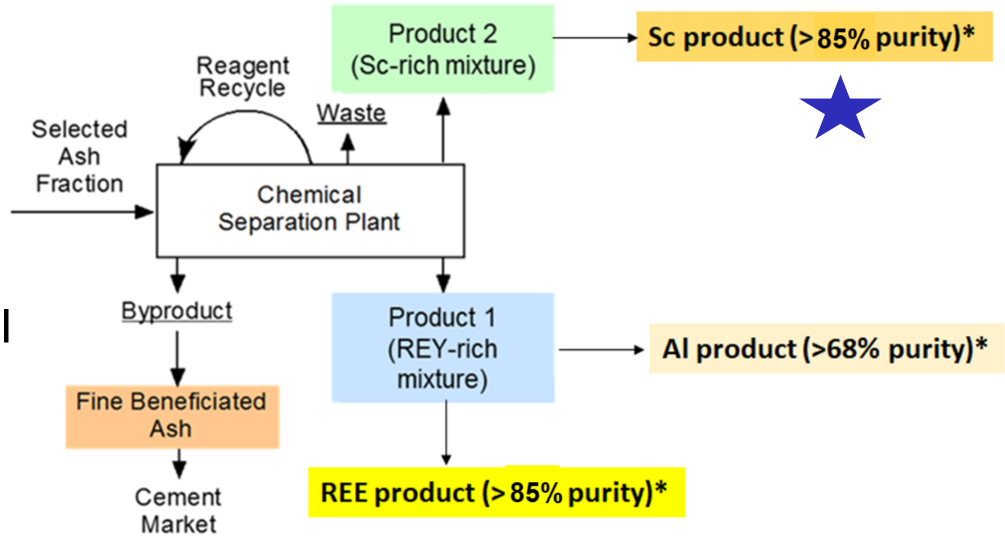
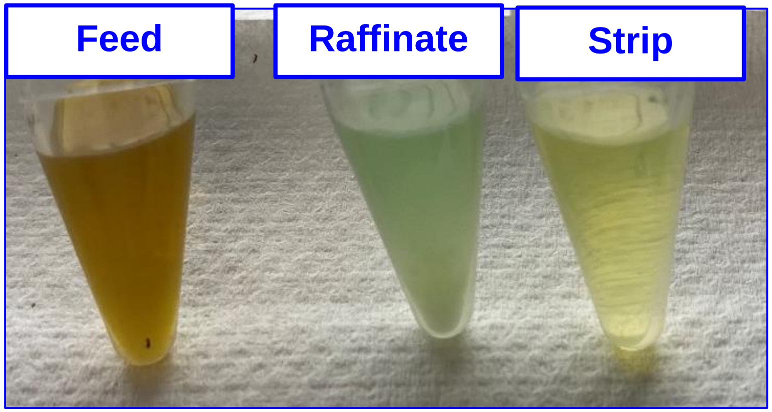
- **Methodology:**
  - Validated a company proprietary LLX process for selective recovery of scandium, a high value product
    - Process developed under PSI IRAD project
- **Bench-Scale Results:**
  - Using this LLX process we were able to increase Sc relative content from 3.3 wt.% in the feed to 41 wt.% in the strip phase
  - Indicates over 12X enrichment in scandium content for a single cycle
  - 51% Sc yield using 2 stripping stages



*All purity values expressed as relative elemental content



Scale Up and Generation of Sc Product

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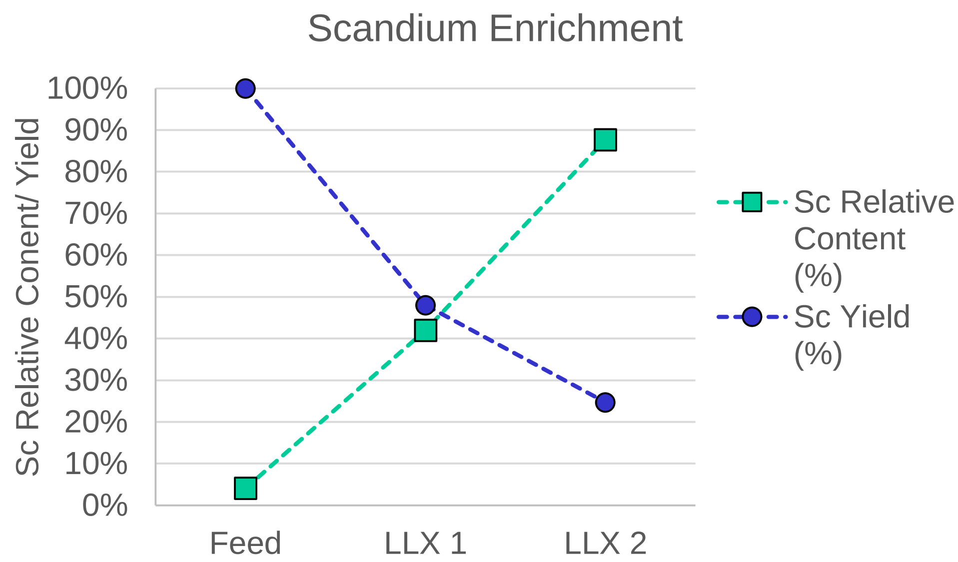
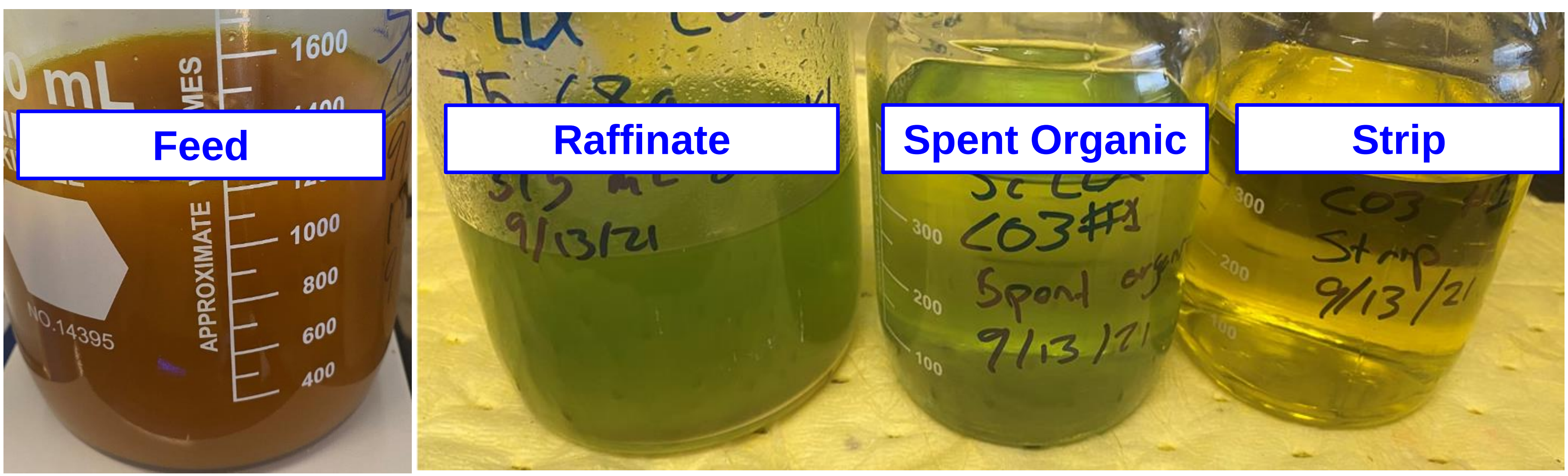
- **Process was scaled up to liter scale**
- **Using two LLX extraction cycles, overall Sc yield was ~25%**

>1 g of Sc product with >85% Sc relative content was generated





Al Recovery Process: Summary

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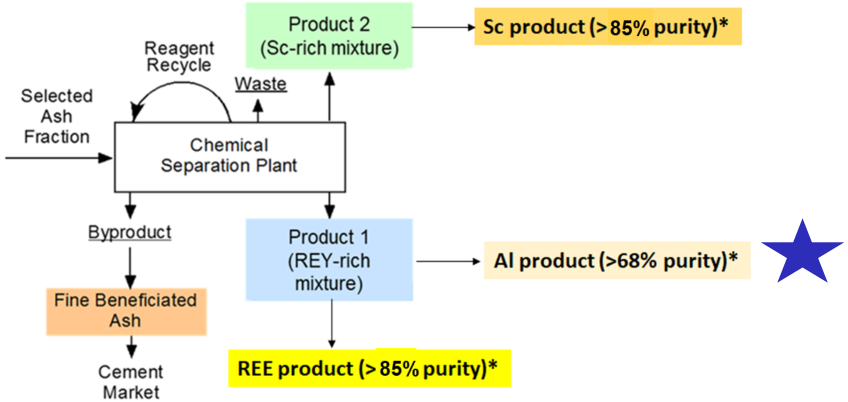
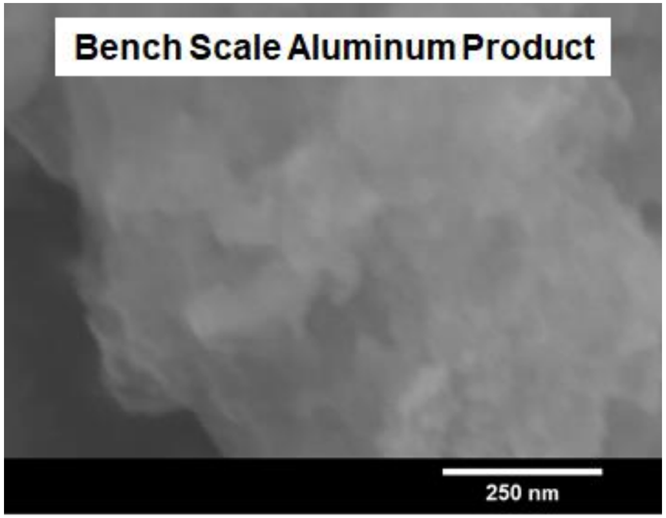
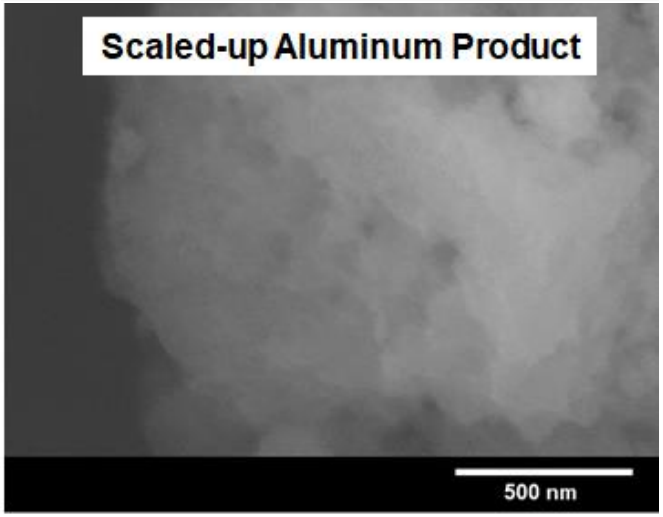


**All purity values expressed as relative elemental content*





- **The LLX raffinate is highly enriched in aluminum**
  - Sample raffinate contained (elemental content) 45% Al relative content
- **Recovery of aluminum represents an additional potential value stream from the raffinate waste product**
- **Key Results:**
  - Developed and demonstrate a bench scale process to selectively recover aluminum from LLX raffinate waste stream
  - Optimized, scaled up process and produced >100 g of material with 90% purity
  - SEM Analysis indicated similar morphologies of the bench scale and scaled-up materials

Al Recovery Process: Results

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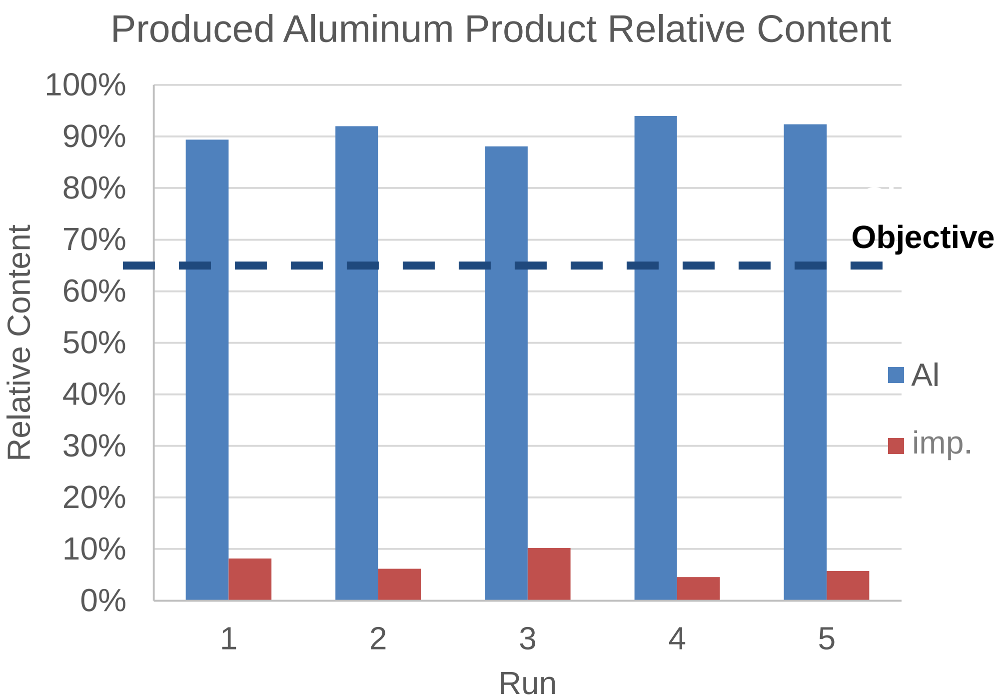
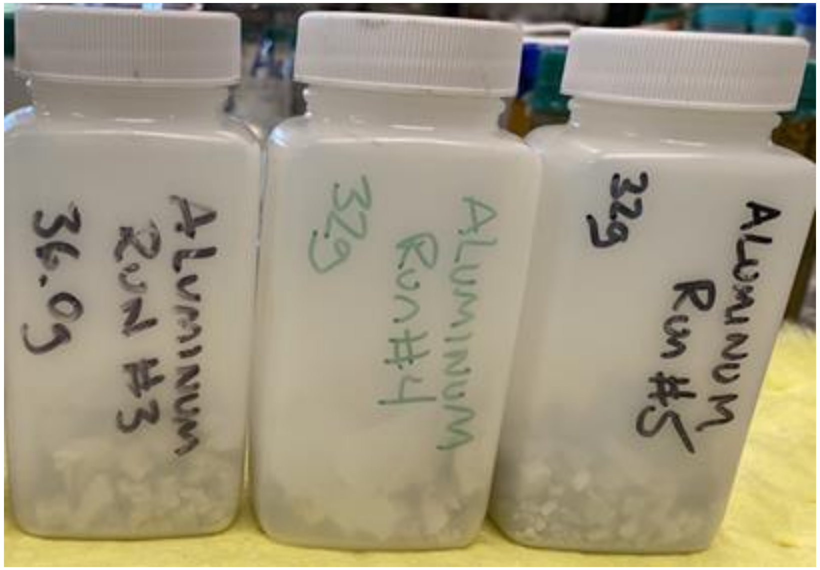
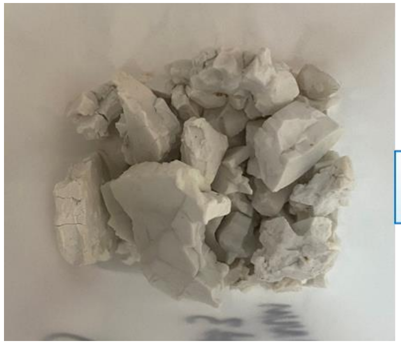




As-produced aluminum product consists of large chunks



Aluminum product ground to a powder

Produced aluminum product over 5 pilot scale runs with ~90% relative content (objective: >65%)

Pozzolanicity Testing – Strength Activity Index

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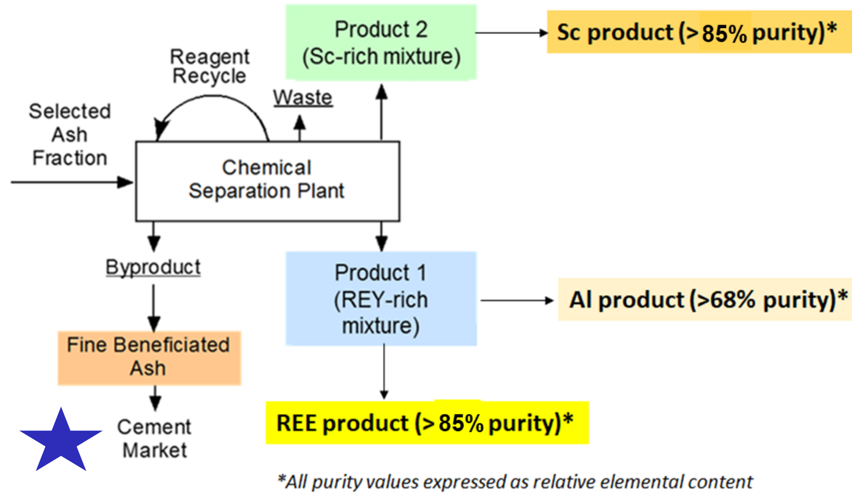
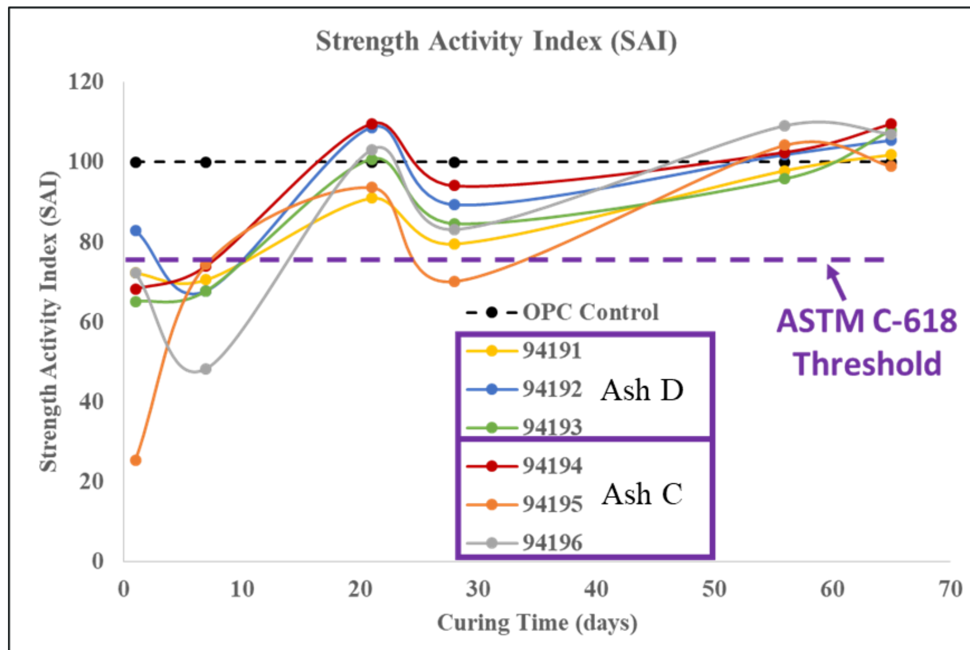
- **Strength Activity Index or SAI: how the coal ash contributes to the strength of concrete.**
- **Typically measured as the compressive strength of a standard mortar mix with fly ash substituting for 20 wt% Portland cement; a defined period of curing.**
- **SAI is then compared as a ratio (%) to a mortar with 100% Ordinary Portland Cement (OPC).**
- **ASTM C-618 SAI threshold passing criterion is 75% at 7 days or 28 days (Purple line).**
- **The processed fine ash utilized at 20% replacement of OPC achieved a strength index greater than 75 by 28 days of curing in 5/6 cases.**





Concluding Remarks

- **U.S. fly ash is an attractive feedstock with rare earths content sufficient for economical recovery of REYSc, particularly, the heavy rare earth elements**

- **Demonstrated operational pilot plant (0.4 tpd) for physical separation processes**
  - Optimized processes to produce selected ash fraction as feedstock for the chemical processing
  - Valuable by-products: cement substitute, cenospheres, secondary fuel carbon

- **Pilot plant for chemical processing (0.5 tpd) fully operational**
  - Optimized processes validated in micropilot plant operations
  - REY concentrate as main product
  - Critical mineral recovery (Sc, Al)
  - Beneficiated ash as valuable by-product

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Acknowledgements

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Thank You!