Investigation of Rare Earth Element Extraction from North Dakota Coal-Related Feedstocks

2019 NETL Annual Crosscutting Technologies Meeting

Nolan Theaker, Institute for Energy Studies

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Project Team

Project Team Members

- Michael Mann, Brittany Rew, UND Institute for Energy Studies
- Steve Benson, Microbeam Technologies
- Dan Palo, Christine Lucky & Chad Haugen, Barr Engineering
- Shane Addleman, PNNL
- Mike Jones, MLJ Consulting
- Ned Kruger and Ed Murphy, NDGS

Project Sponsor Representatives

- Chuck Miller, NETL Project Manager
- Mike Holmes, Lignite Research Program
- Dennis James, North American Coal
- Sandra Broekema, Great River Energy
- Gerry Pfau and Dillon Wolf, Minnkota Power Cooperative
- Kai Xia, Great Northern Properties
- Rick Tonder, North Dakota University System
- Wesley Wintch, Valley City State University

Presentation Overview

- Project Background
- Summary of Phase 1
- Phase 2 Accomplishments
- Phase 2 Next Steps
- Commercialization Plans
- Questions

Project Background

<u>Project Title</u>: Investigation of REE extraction from North Dakota coal-related feed stocks (DE-FE0027006)

3-year Phase 1/2 effort

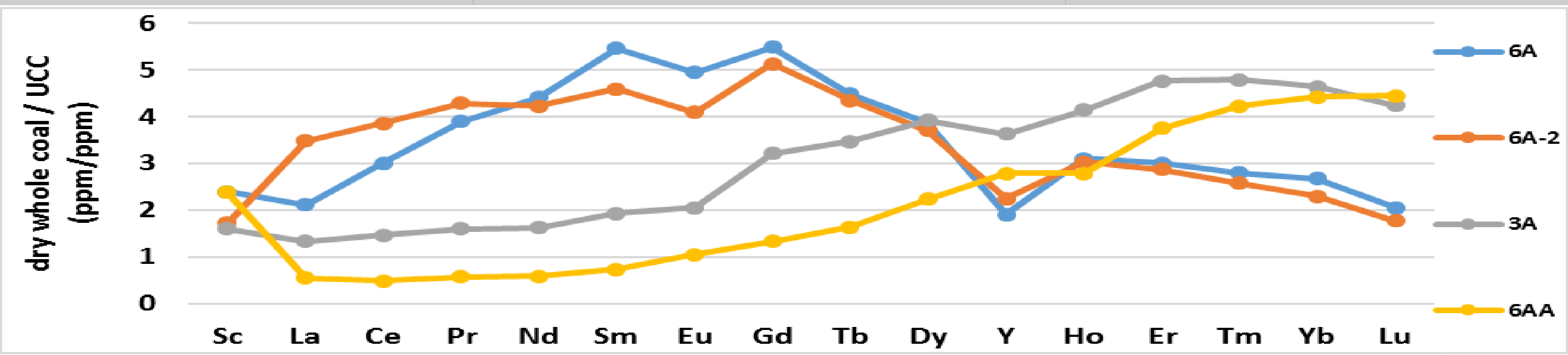
1. Sampling and characterization – Lignites with > 300 ppm REE
2. Laboratory-scale extraction/concentration development
3. Bench-scale extraction/concentration testing – current focus
4. TEA, market analysis and commercialization plan – next steps

Key Findings to Date

- REE primarily weakly associated with organics – easily leached with mild solvent from pre-combustion coal
- Process very similar to Chinese ion-exchangeable clays
  1. Leaching of REE from coal
  2. Hydrometallurgy to concentrate/purify REE in the solution
- Leaching process also a coal beneficiation process

Coal Resources – Phase 1

Sample ID	Ash Yield (wt%)	Total REE, ppm (dry mass basis)	Total REE, ppm (ash basis)	HREE/LREE	$ REE/MT Coal
6A-2	36.3	**642**	**1752**	0.28	437
6A	20.1	**564**	**2235**	0.35	599
6A-1	75.5	**449**	587	0.28	307
3A	40.5	**363**	892	0.89	400
3C	60.9	**322**	525	0.43	341
6AA	47.0	212	449	2.06	580
7F	20.9	194	924	0.76	147



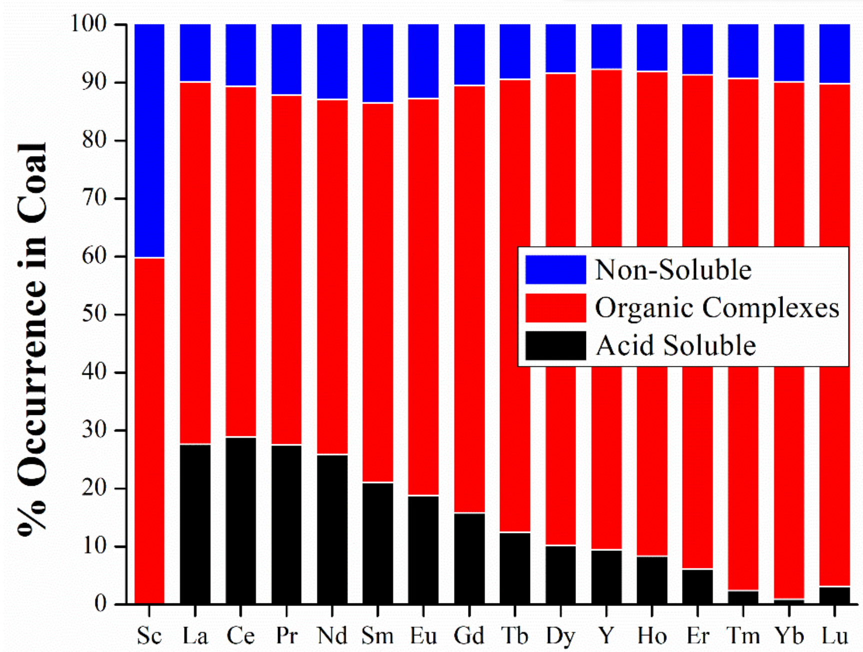
Unique Properties of Lignite

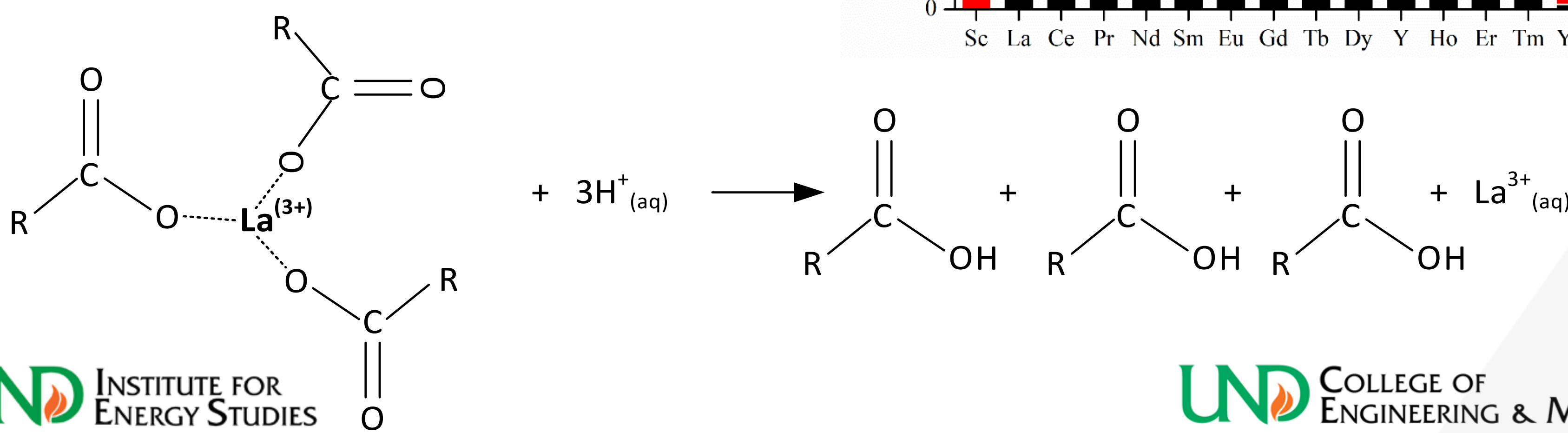
- Oxygen functional groups, which are uniquely prevalent in lignite, provide binding sites for inorganic cations such as REE
- But also a challenge: acid consumers (alkali and alkaline earth metals) are also organically associated

			High volatile bituminous			Bituminous		
	Lignite	Subbitu-minous	C	B	A	Medium volatile	Low volatile	Anthracite
% C (min. matter free)	***65-72***	72-76	76-78	78-80	80-87	89	90	93
% H	***4.5***	5-4	5.5	5.5	5.5	4.5	3.5	2.5
% O	***30***	18	13	10	10-4	4-3	3	2
% O as COOH	***13-10***	***5-2***	***0***	***0***	***0***	***0***	***0***	***0***
% O as OH	***15-10***	12-10	9	?	7-3	2-1	1-0	0
Aromatic C atoms % of total C	***50***	65	?	?	75	80-85	85-90	90-95
Avg. no. benzene rings/layer	***1-2***	?		2-3			5?	>25?
Volatile matter (%)	***40-50***	35-50	35-45	?	31-40	31-20	20-10	<10
Reflectance (%) of vitrinite	***0.2-0.3***	0.3-0.4	0.5	0.6	0.6-1.0	1.4	1.8	4

Organic Associations

- REE enriched in organic fractions of lignite
  - opposite of high-rank coals
- Primary form as organic complexes (i.e. carboxylic acid groups)
- Cations can be easily leached (stripped) using dilute acids





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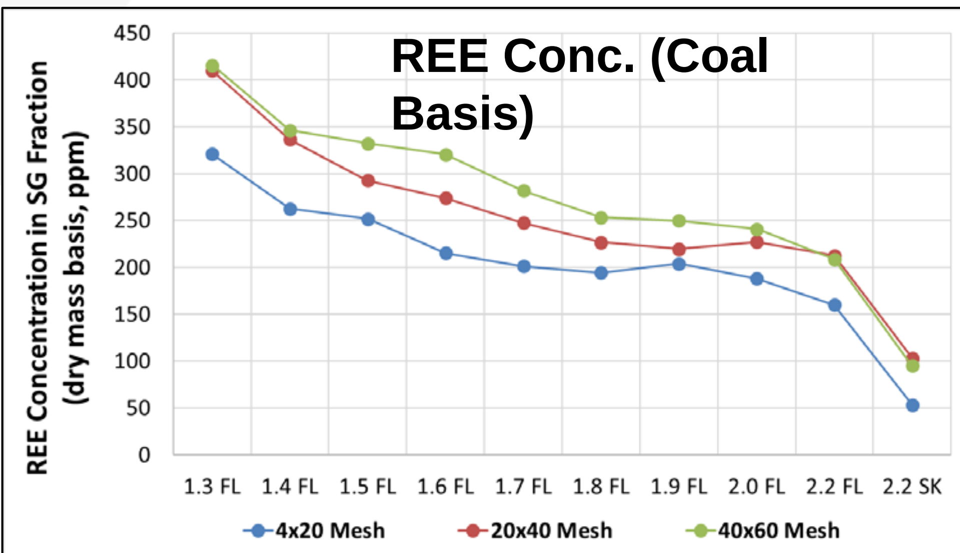
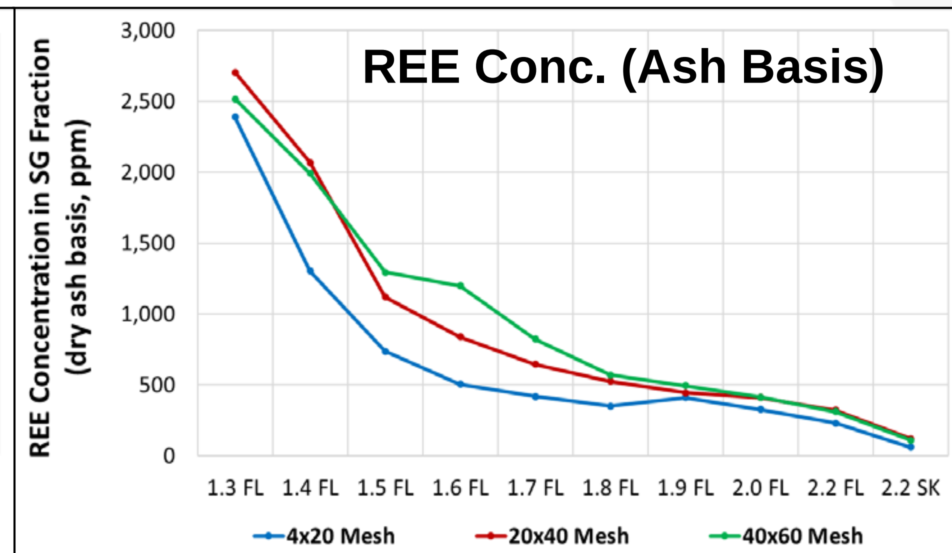
REE – Specific Gravity Correlations

- Concentrated in lightest SG fractions
  - Able to be concentrated with standard coal cleaning techniques





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Phase 2 Accomplishments

Phase 2 Objectives and Work Scope

- Objective: Demonstrate technology at bench-scale (~10 kg coal/hr)
- Phase 1 Testing – batch parametric tests
  - Tune extraction chemistry/conditions to maximize REE selectivity/yield
  - Test additional unit operations to improve overall process and increase REE concentration
  - Optimize conditions and process configuration
- Phase 2 Testing – production testing (~1000 kg total feed)
- Techno-economic assessment
- Preliminary commercialization plan

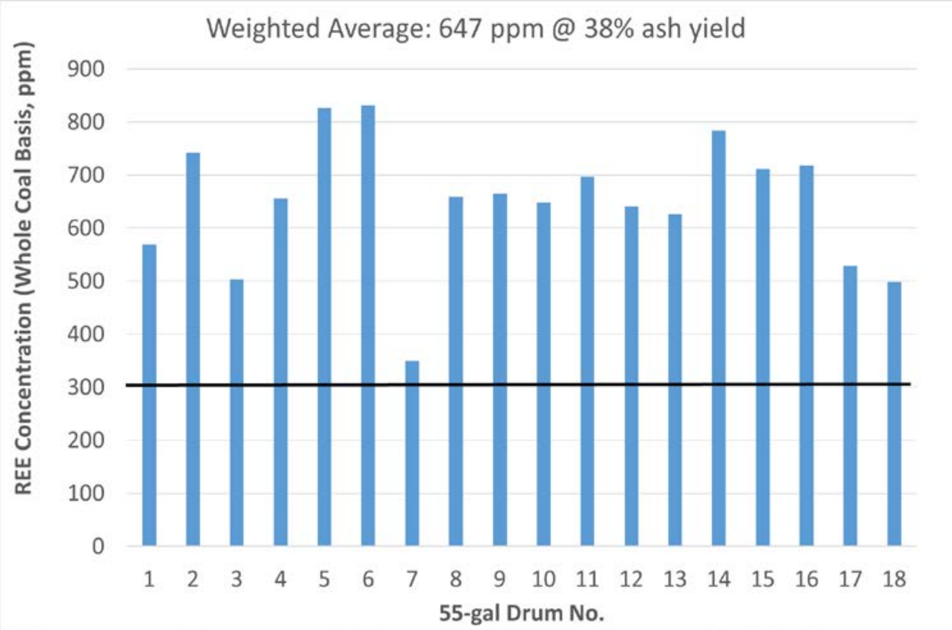
Feedstock Sourcing

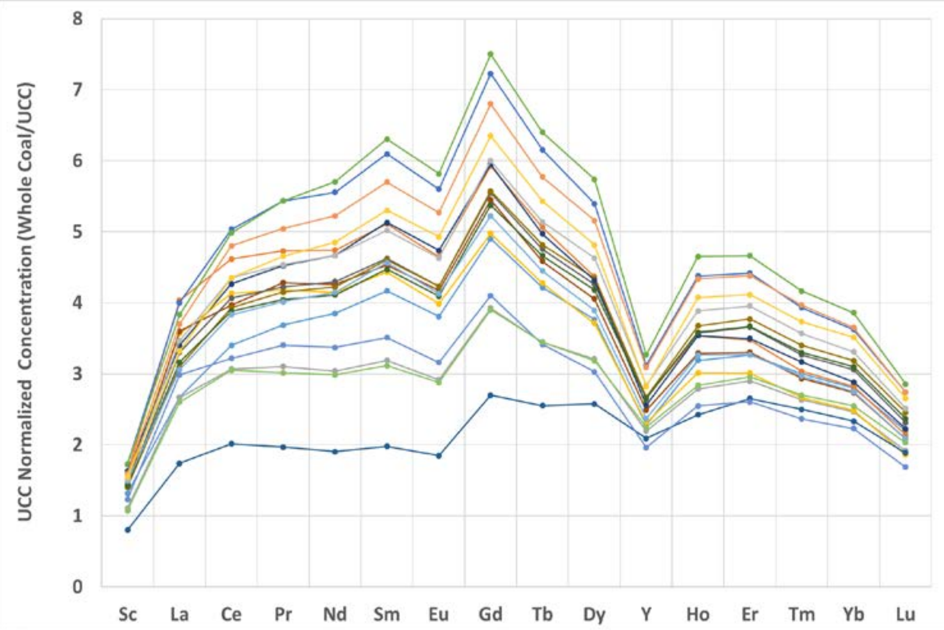
- New sample manually excavated in outcrop of H-Bed lignite
  - 18 55 gal drums extracted

Members of the UND and Barr team during collection of the H-Bed lignite in Slope County, ND (Nov, 2018) – approximately 7000 lbs excavated

Bench Coal Feedstock

- Eighteen 55-gal drums collected and measured to ensure REE concentration





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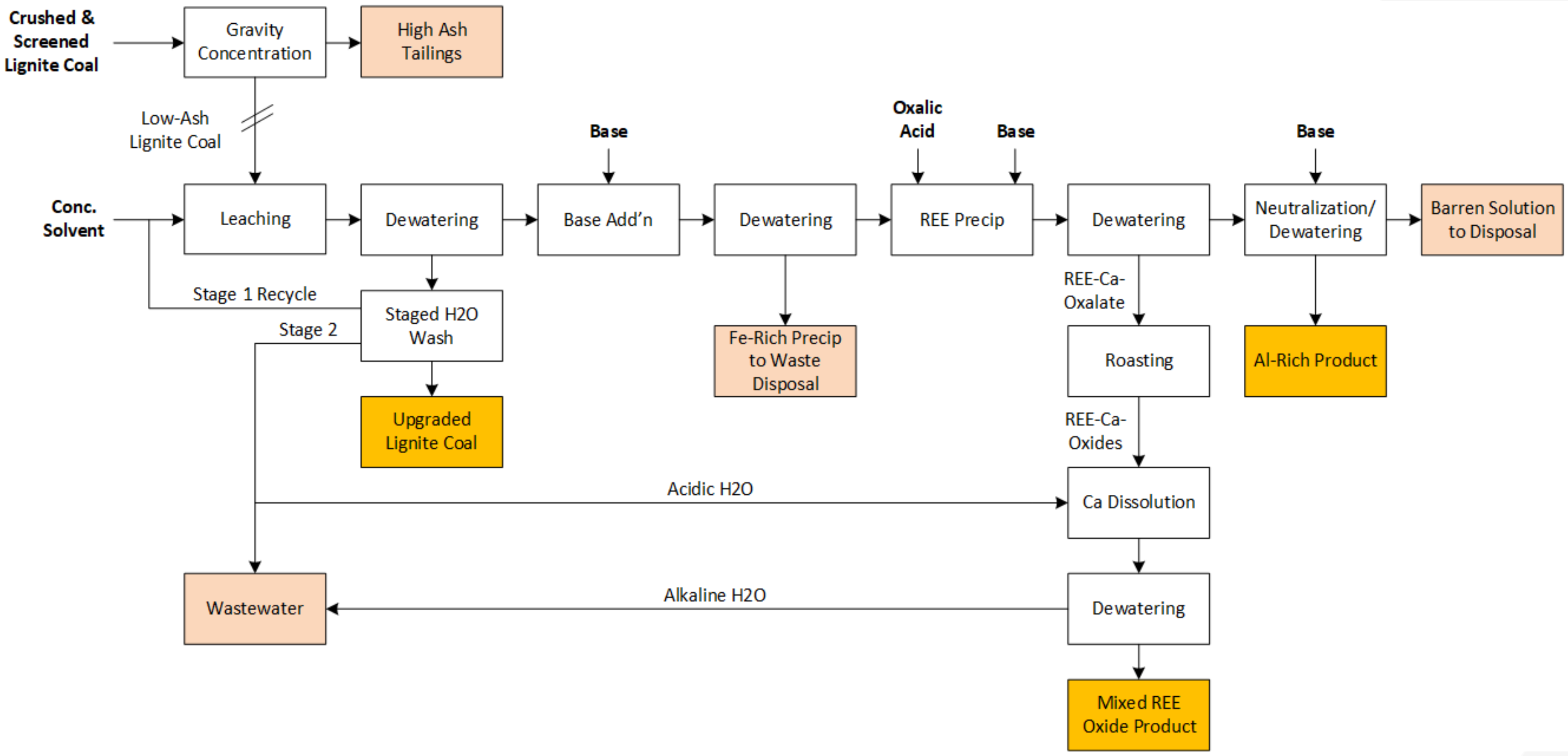
Bench-Scale System

- Multiple tank approach for testing multiple unit operations/conditions at once

Pictured for batch parametric testing

Process Schematic



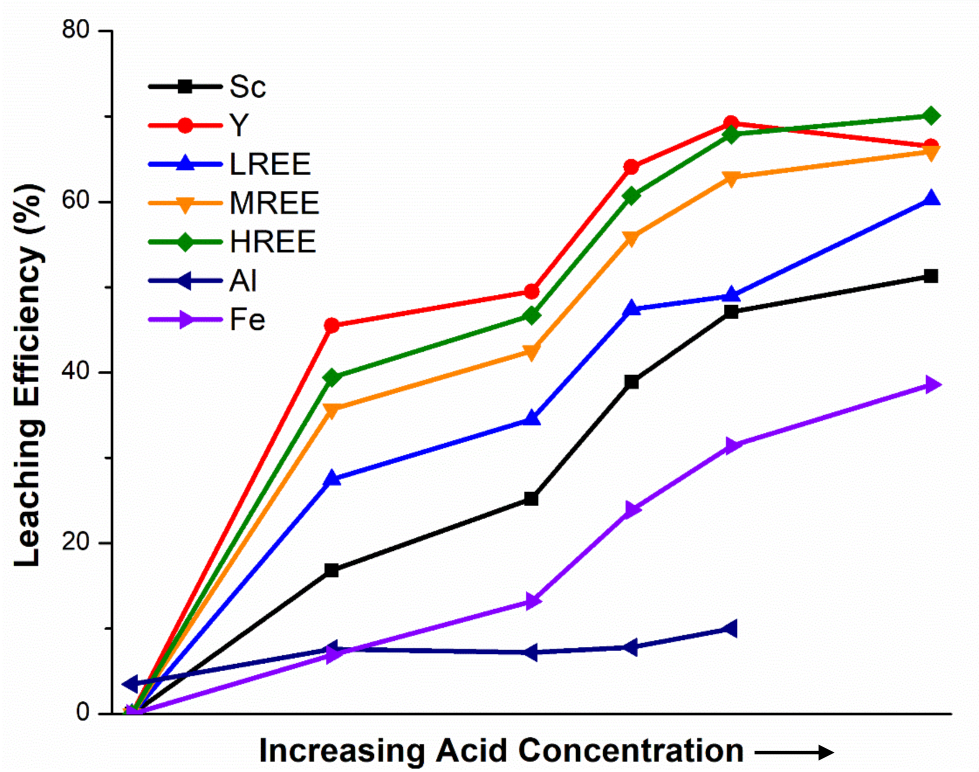
Physical Beneficiation Results

Coal Sample	Ash Content (wt%)	TREE (coal ppm)	TREE (ash ppm)	HREE/LREE Ratio
As Received	35.45	646	1822	0.28
Concentrate	15.09	657	4357	0.30
Tailings	70.31	353	502	0.26
Scav Conc	19.5	679	3483	0.30
Scav Midd	47.26	630	1333	0.28
Scav Tails	59.34	550	927	0.26
Blend	19.34	658	3881	0.30

- Physical concentrating factor on ash basis (versus non-REE elements) of 2.13

Leaching Equilibrium

- Similar equilibrium behavior as ion-exchange resins
  - S-Curve



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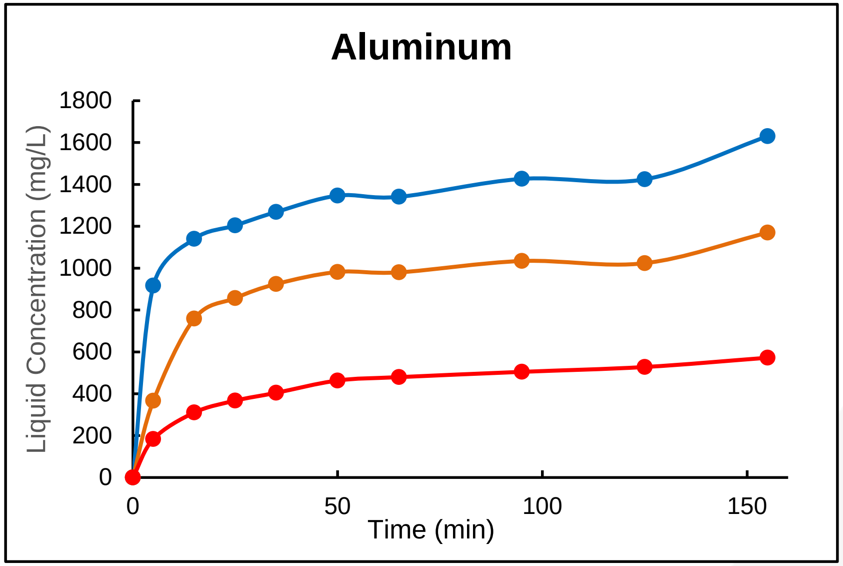
Leaching Kinetics

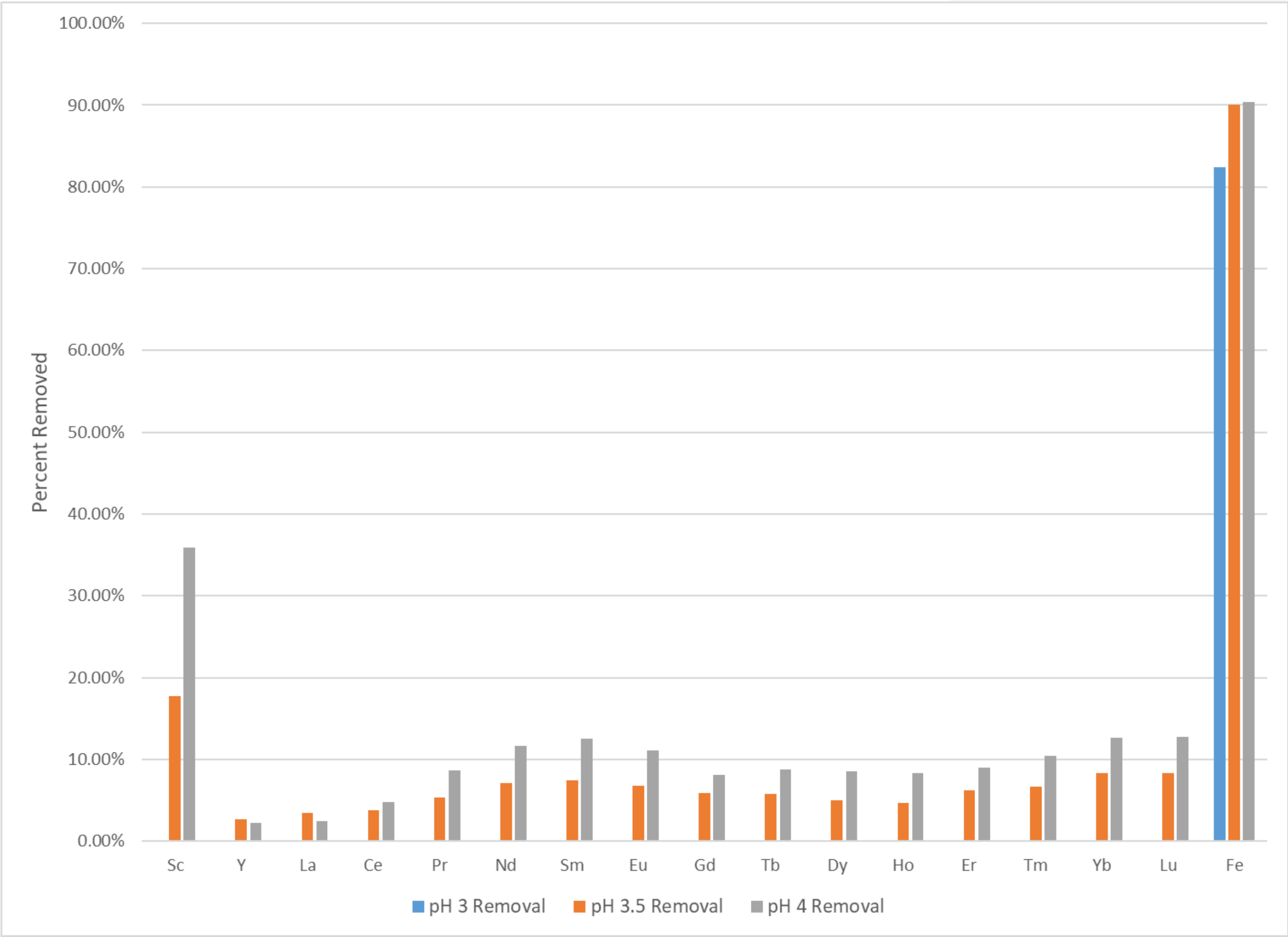
- Rapid kinetics at each pH level
  - Likely not mineral dissolution

- Aluminum used as tracer for trivalents
  - Similar kinetics for trivalents found in other coals



Impurity Removal

- Little-to-no REE loss under pH 3 conditions
  - Effective Fe removal
- Precipitate >90% Fe on oxide basis
  - Possible Fe ore for minimization of waste streams

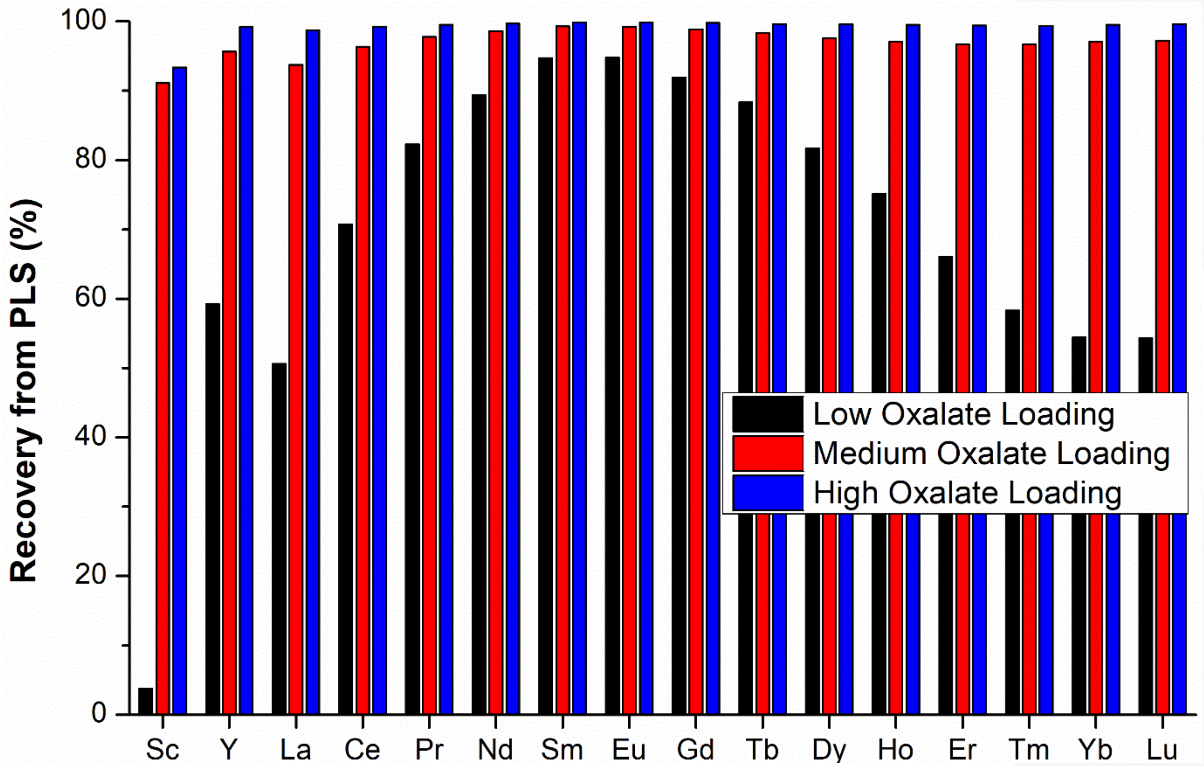


REEE Precipitation

- Control of precipitation conditions able to generate unique depositional environment

- Low oxalate loading resulted in high REE content (>80%) with high recovery of MREE

- Secondary product with high Sc, HREE



REE Precipitation – Low Ox Loading

- Product concentration from low oxalate loading

Sc	0.26%
Y	10.5%
La	9.23%
Ce	29.57%
Pr	4.09%
Nd	17.76%
Sm	3.84%
Eu	0.91%

Gd	3.56%
Tb	0.52%
Dy	2.58%
Ho	0.44%
Er	1.02%
Tm	0.12%
Yb	0.68%
Lu	0.09%

Current Status of Project

- Finalizing parametric testing on chosen coal blend
- Initiated semi-continuous modifications to the bench unit
  - Equipment acquisition
- Initiated commercialization plan discussions

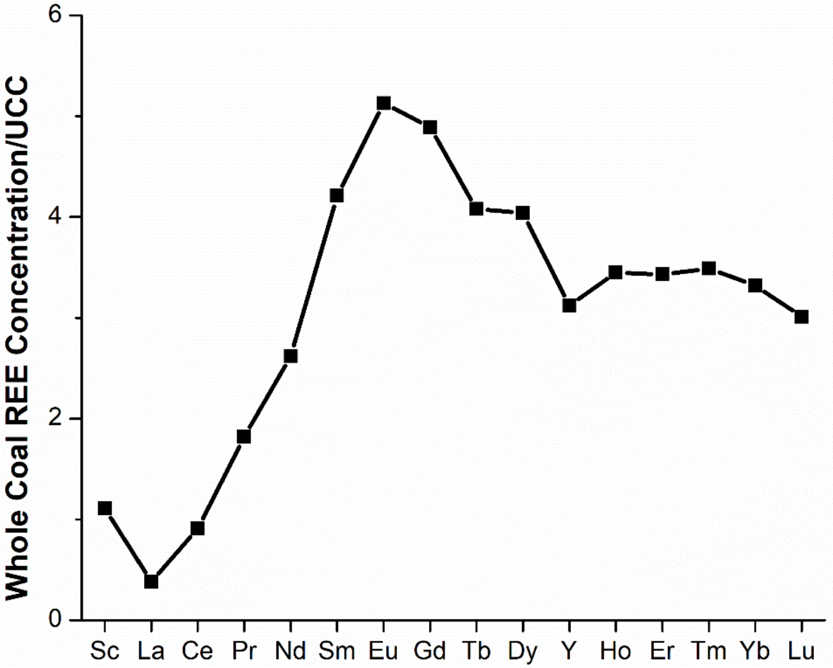
Next Steps

- Complete semi-continuous modification to system
  - Integration and shakedown
- Production testing
  - ~1000 kg of chosen coal blend from physical beneficiation
  - Produce sufficient mass of >2wt% REE concentrate suitable for further processing and detailed characterization
- Techno-economic analysis and commercialization plan development

Commercialization Plans

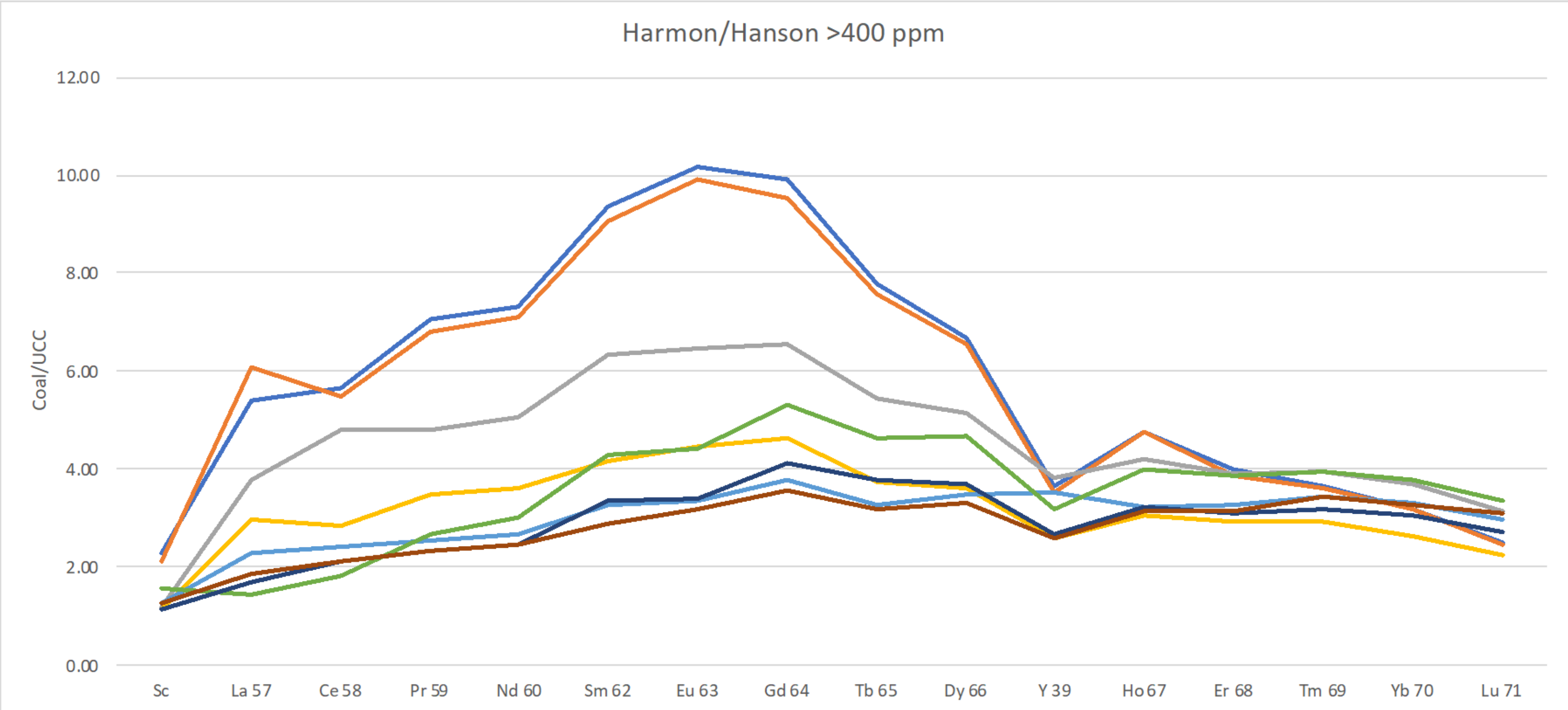
Additional Coal Options

- Coal in active mine in North Dakota was found to have >300ppm REE on whole coal basis
  - C_{outl} >2.5 in seam, HREE/LREE > 0.8



Comparison to Harmon/Hanson

- Highest in LREE



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Mining Considerations

- REE concentrated at margins of roof/floor, below partings and in thin seams
- ‘Selective’ mining likely needed to separate REE-rich coal from ROM coal – Wirtgen Surface Miner
- Coals near margins and/or thin seams often high ash and may be discarded during mining
- Recovery of REE via UND process can both provide value as well as reclaim and upgrade low-value coal
- Or, starting from lower-ash coal, opportunity to create high-purity carbon-based products with lower cost

ND University System Steam Generation Plants

- Valley City State University currently pursuing installation of activated carbon plant integrated with existing steam generation plant
- Basis of Phase 1 TEA…but really pilot or small demo-scale
- VCSU interested in being platform for pilot testing of fuel conversion technologies and REE
  - ~5 MW_{th} CHP facility: NG and Coal-fired boilers
  - Advanced turbine systems, carbon-based products, coal upgrading, biomass, emissions control systems, CO_2 capture…etc
- https://www.vcsu.edu/president/heat-plant-and-carbon-plant

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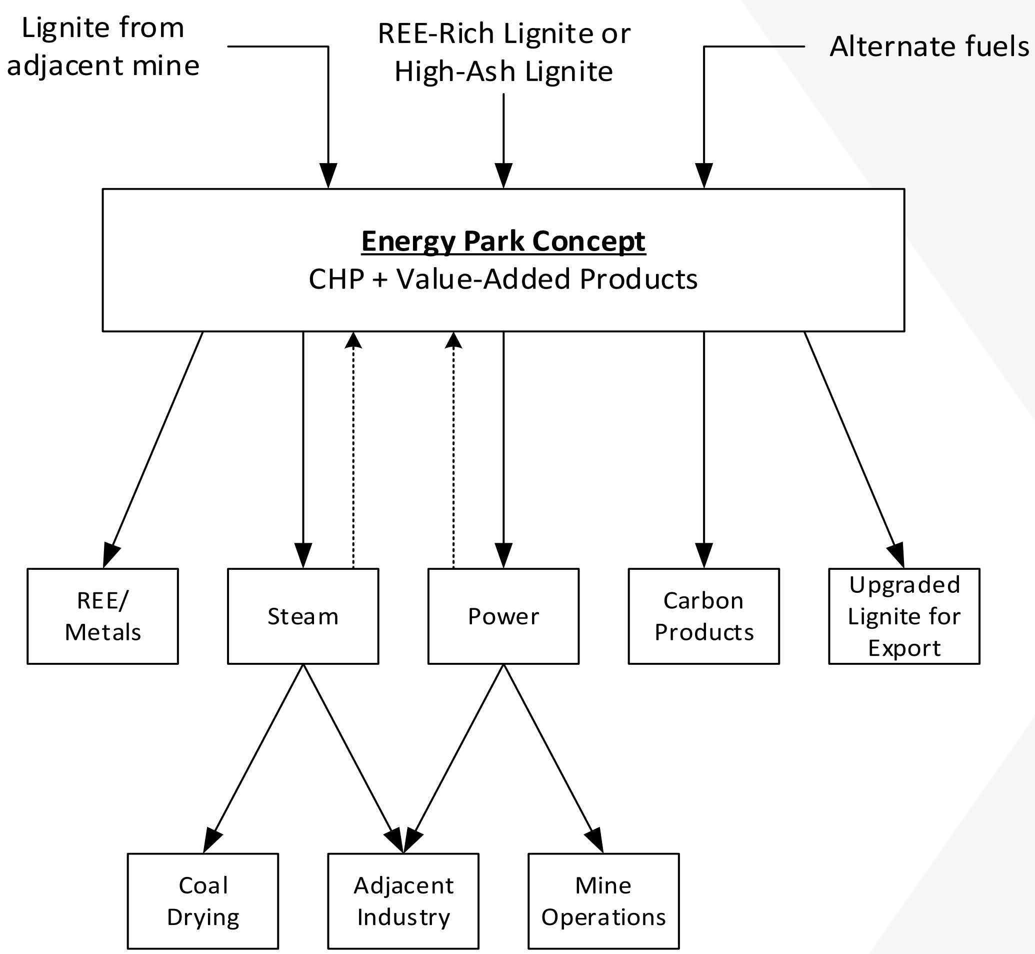
Integrated Facility Concept

- Potential new mine in Harmon-Hanson coal zone offers next generation opportunities
- Highest value utilization of lignite
- Multiple products
- Potential for export – 800-year supply at current mining rates
- Opportunity to deploy advanced boiler/turbine systems (small coal plant/REMS concepts)
- REE/metals, activated carbon, battery electrode materials, metallurgical coal, carbon fibers…etc
- UND is currently commercializing integrated CHP and activated carbon production system with Valley City State University – **potential host site for pilot-scale demonstrations**



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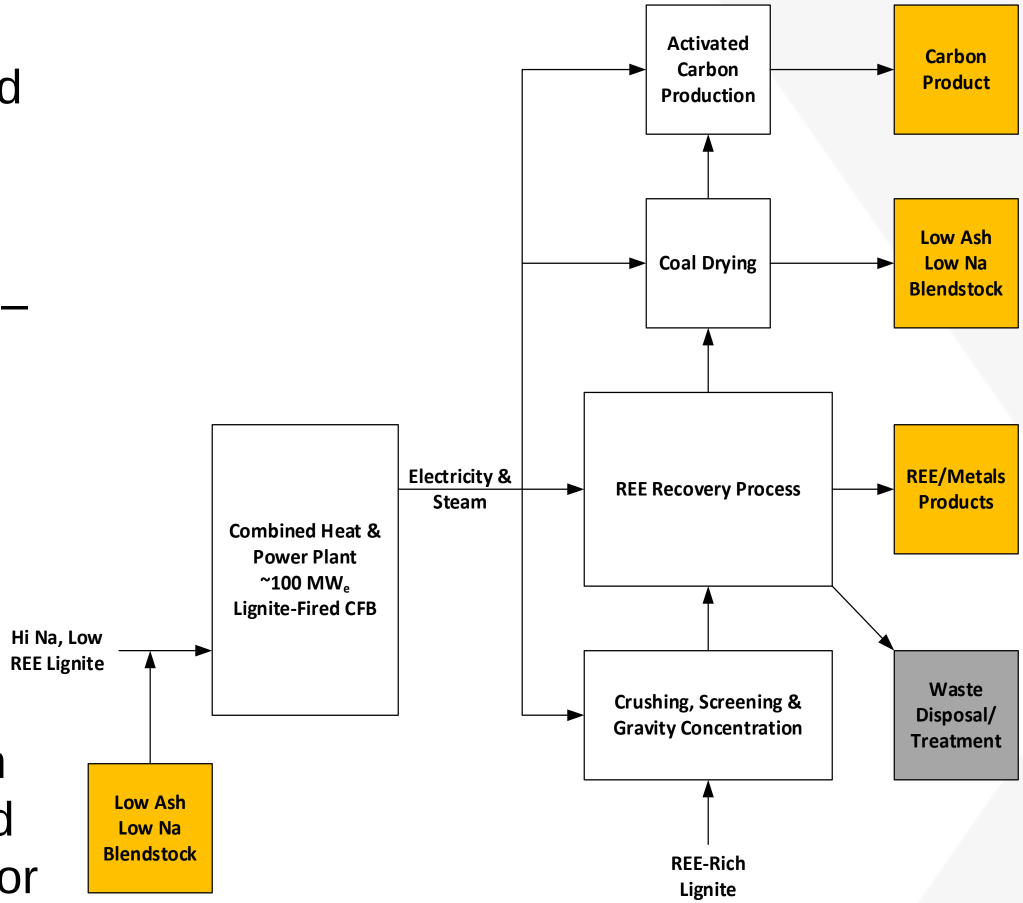
Spiritwood CHP Station

- Update the Phase 1 TEA with a larger-scale commercial facility and based on experimental data in Phase 2
- Same overall concept as Phase 1 – integrate REE recovery with CHP and Activated Carbon
- Project co-sponsor Great River Energy has agreed to consider integrating the concept into its Spiritwood Station Plant
- Project co-sponsor Great Northern Properties interested in Coring and providing core samples of H-Bed for testing



Summary

- Discovered high REE concentrations in ND lignite
- REE weakly bound – primarily as organic complexes
- Pre-combustion extraction permits sale of upgraded coal products
  - REE concentration through selective precipitations
- Preliminary parametric testing complete
  - Finalizing operating parameters and equipment for semi-continuous testing
- Commercialization pathways
  - Multiple products for synergistic economic approach
  - VCSU/GRE Spiritwood for pilot/commercial demo opportunities

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Questions?

CONTACT INFORMATION

Nolan Theaker, Co-Principal Investigator
Research Engineer, Institute for Energy Studies
nolan.theaker@und.edu
701-777-6298

Dr. Steven Benson, Co-Principal Investigator
President, Microbeam Technologies Inc.
sbenson@microbeam.com
701-213-7070

Dr. Michael Mann, Project Manager
Director, Institute for Energy Studies
michael.mann@und.edu
701-777-3852

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