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

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2017 NETL Crosscutting Research & Analysis Portfolio Review

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Period of Performance
3/1/2016 to 8/31/2017

Goals and Objectives

- Goal:
  - To develop a high performance, economically viable, and environmentally benign concentrating technology for coal-related feedstocks to a mixed REE concentrate of > **2% by weight.**

- Objectives/Milestones:
  - Identify ND coal-related feedstock(s) with >300 ppm REE content
  - Identify the optimum methods to separate and concentrate the REEs to two percent by weight.
  - Perform a technical and economic analysis of the optimum methods.
  - Develop a design of a bench-scale system to concentrate REEs.

Presentation Outline

- Project Team
- Scope of Work – Description of tasks
- Schedule
- Accomplishments
  - Sampling and analysis results
  - REE concentrating results
  - Technical and economic analysis results
- Next Steps

Project Team

Technical Team:

- University of North Dakota – Institute for Energy Studies; Energy & Environmental Research Center
- Barr Engineering
- Pacific Northwest National Laboratory

Funding Support:

- U.S. Department of Energy – National Energy Technology Laboratory
- North Dakota Industrial Commission – Lignite Energy Council
- Great River Energy
- North American Coal Corporation

Advisory Support:

- North Dakota Geological Survey

Overview of Phase I Project – Scope of work

- Task 1.0 – Project Management and Planning
- Task 2.0 – Sampling and Characterization of Proposed Feedstocks
- Task 3.0 - Technical and Economic Feasibility
- Task 4.0 – Laboratory-scale Testing for Determination of Bench-scale Design Parameters
- Task 5.0 – Bench-scale System Design
- Task 6.0 – Final Report

Accomplishments

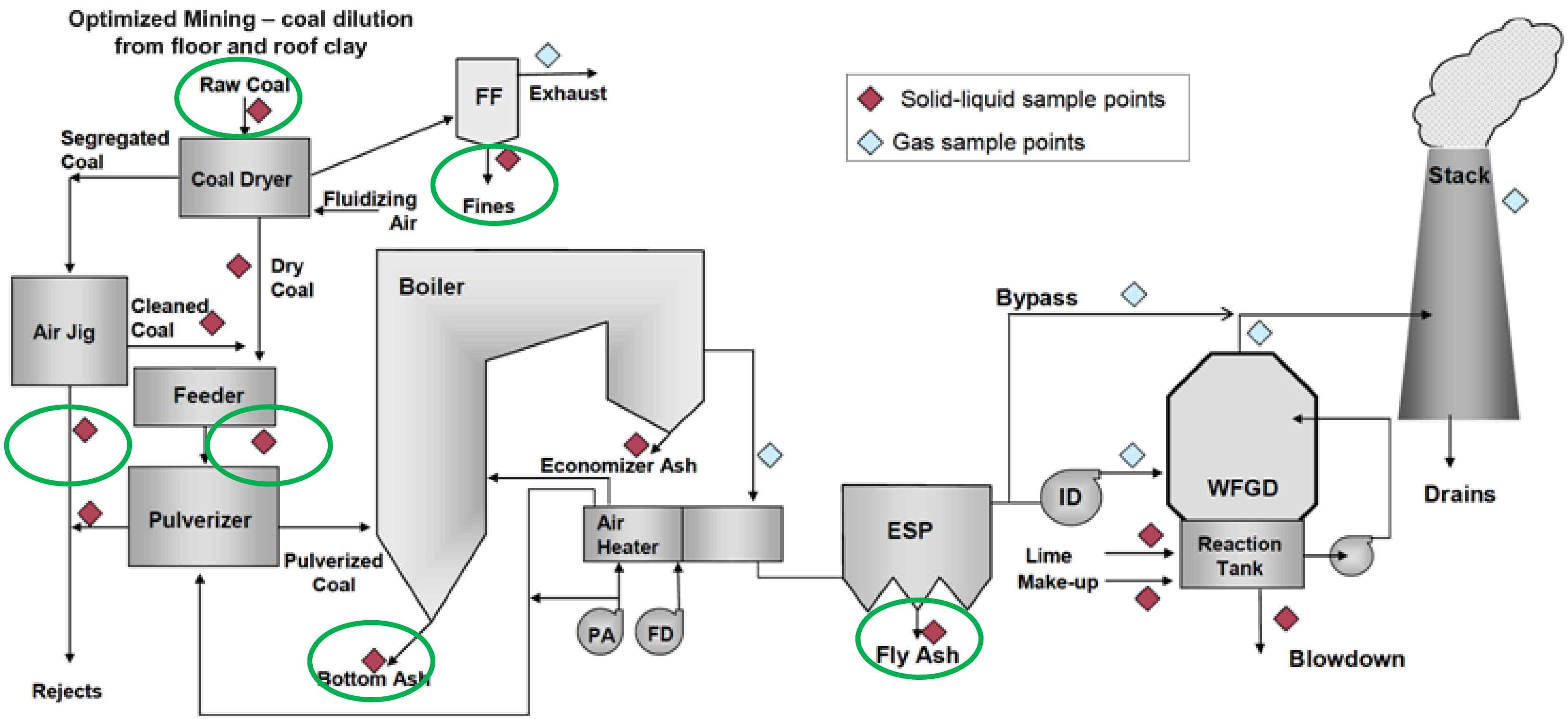
Overview of Task 2

- **Task 2.0 – Sampling and Characterization of Proposed Feedstocks**:
- This task involved extensive sampling and characterization of multiple potential feedstocks from NAcoal's Falkirk mine, GRE's Coal Creek station power plant in North Dakota, and other lignite related resources.
- Feedstocks from the mine included the lignite coal, roof, parting and floor materials.
- Feedstocks from Coal Creek Station plant included inlet coal, air jig outlet, feeder outlet and fabric filter fines associated with the DryFining™ system, and bottom ash and fly ash.

Task 2 Analysis Methods

Category	**Equipment**	**Function**
Bulk chemical composition	ASTM standard analysis	Proximate analysis; Ultimate analysis; Ash composition
	X-ray Fluorescence	Bulk chemistry; major, minor and trace element
	Inductive Coupled Plasma-Mass Spectrometry	Abundance of trace elements including REE
Forms of REE	Scanning Electron Microscopy	Morphological analysis – imaging and chemical composition of minerals
		CCSEM – chemical composition, size and associations (included or excluded relative to coal particles)
	Chemical Fractionation	Quantitatively determine the modes of occurrence of the inorganic elements

Sampling Locations at Coal Creek Station



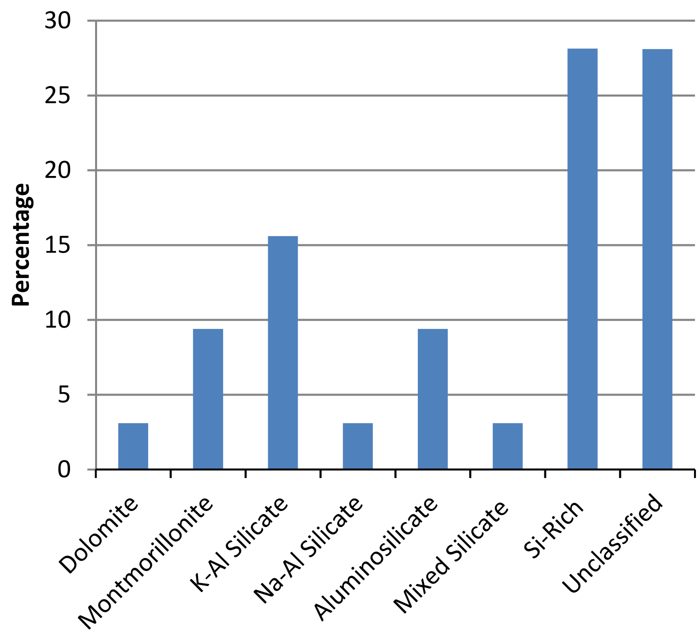
Coal Creek Station & DryFining™ Process Streams - REE content lower than expected

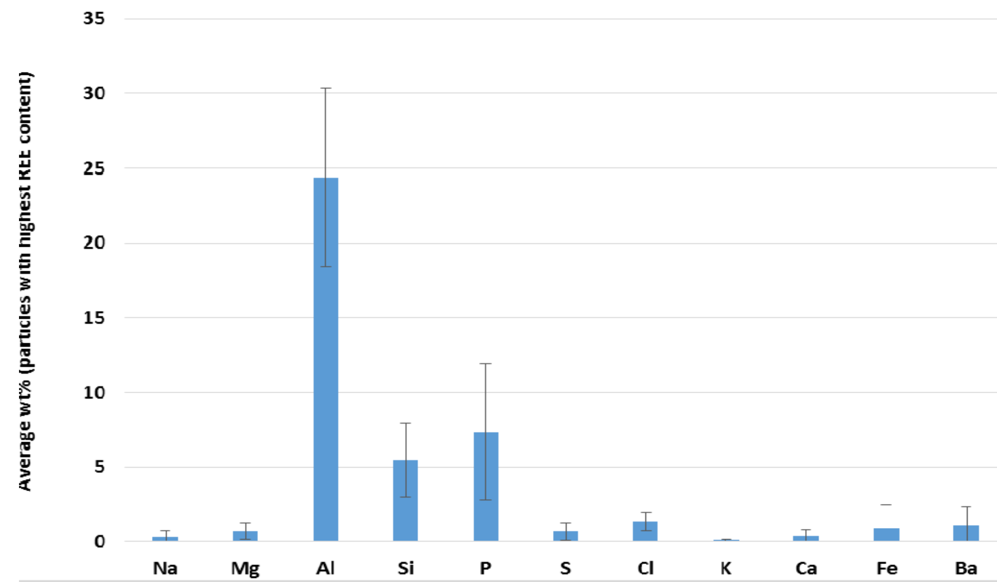
Sample Location	Average total REEs – dry whole sample basis, ppm	Average total REEs – dry ash basis, ppm
air jig rejects	36	105
coal dryer dust collector	66	199
Fly ash	240	240
Clean coal to feeder	25	234

On ash basis, fly ash REE content higher than mineral-rich reject stream

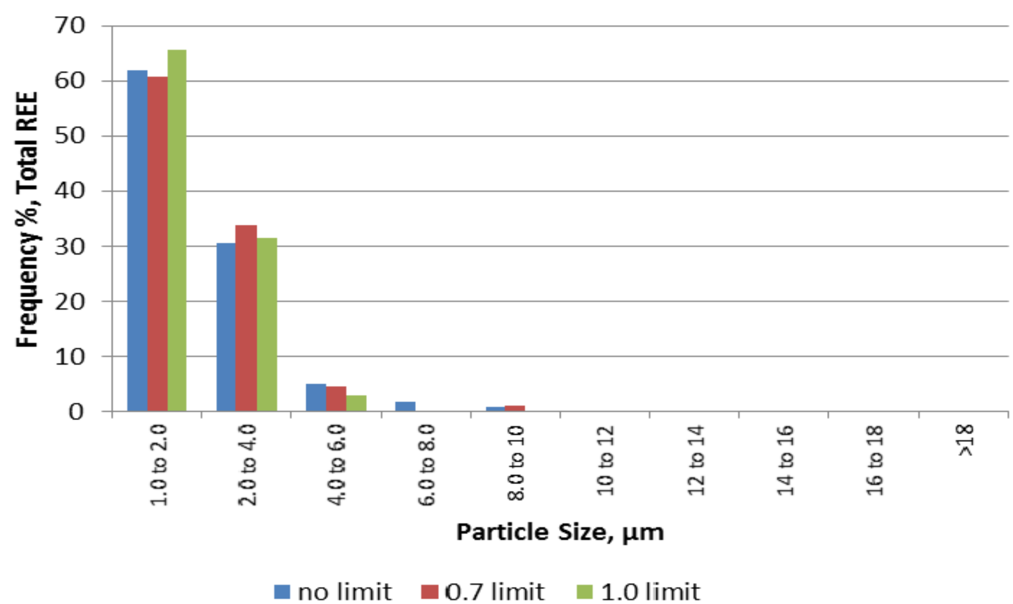
Low REE content in plant due to blending of coals/sediments

Evaluation of Roof/Floor Sediments at Falkirk Mine





- REEs mainly associated with phosphates, carbonates and clays
- REE-bearing minerals are very small: ~90% total REE in < 4 µm mineral grains
- Total REE content < 200 ppm (dry whole sample basis)

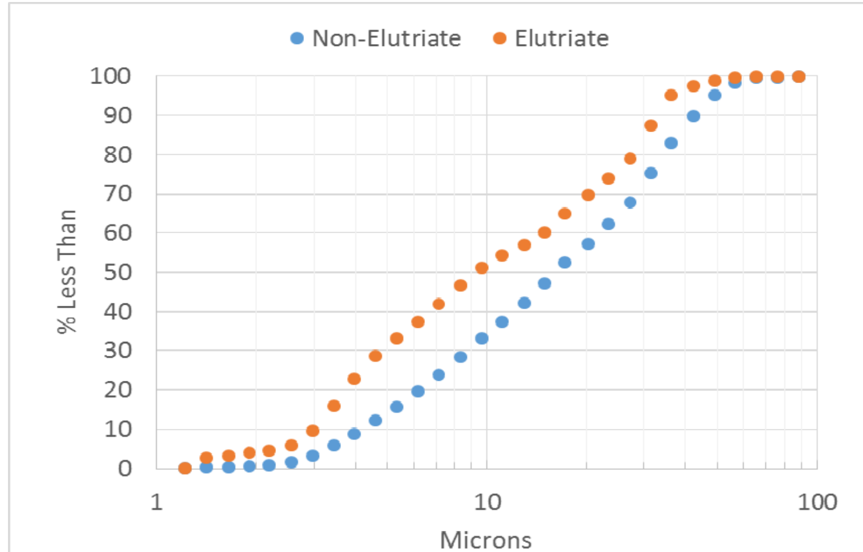


Physical Beneficiation Testing

- Size/density differences identified as possible separation drivers for REE enrichment
- UND is developing novel dry elutriation method for Chemical Looping Combustion
  - Method adapted and tested for REE enrichment in roof/floor sediments
- Simple wet screening evaluated to determine if enrichment by size naturally occurs with grinding or during combustion (flyash sample)
- Several samples with REE content above 150 ppm (whole sample basis) evaluated

Physical Beneficiation Testing Results

Sample ID (roof/floor sediments)		Dry ash basis	
		Elutriate Total REE (ppmw)	Non-Elutriate Total REE (ppmw)
IES	16024	178 & 172	170
IES	16025	194	201
IES	16026	213	210
IES	16035	202	204
IES	16036	186 & 172	182
IES	16037	171	169
IES	16047	175	179
IES	16048	179	179
IES	16053	150	146
IES	16054	178	168
IES	16056	185	182



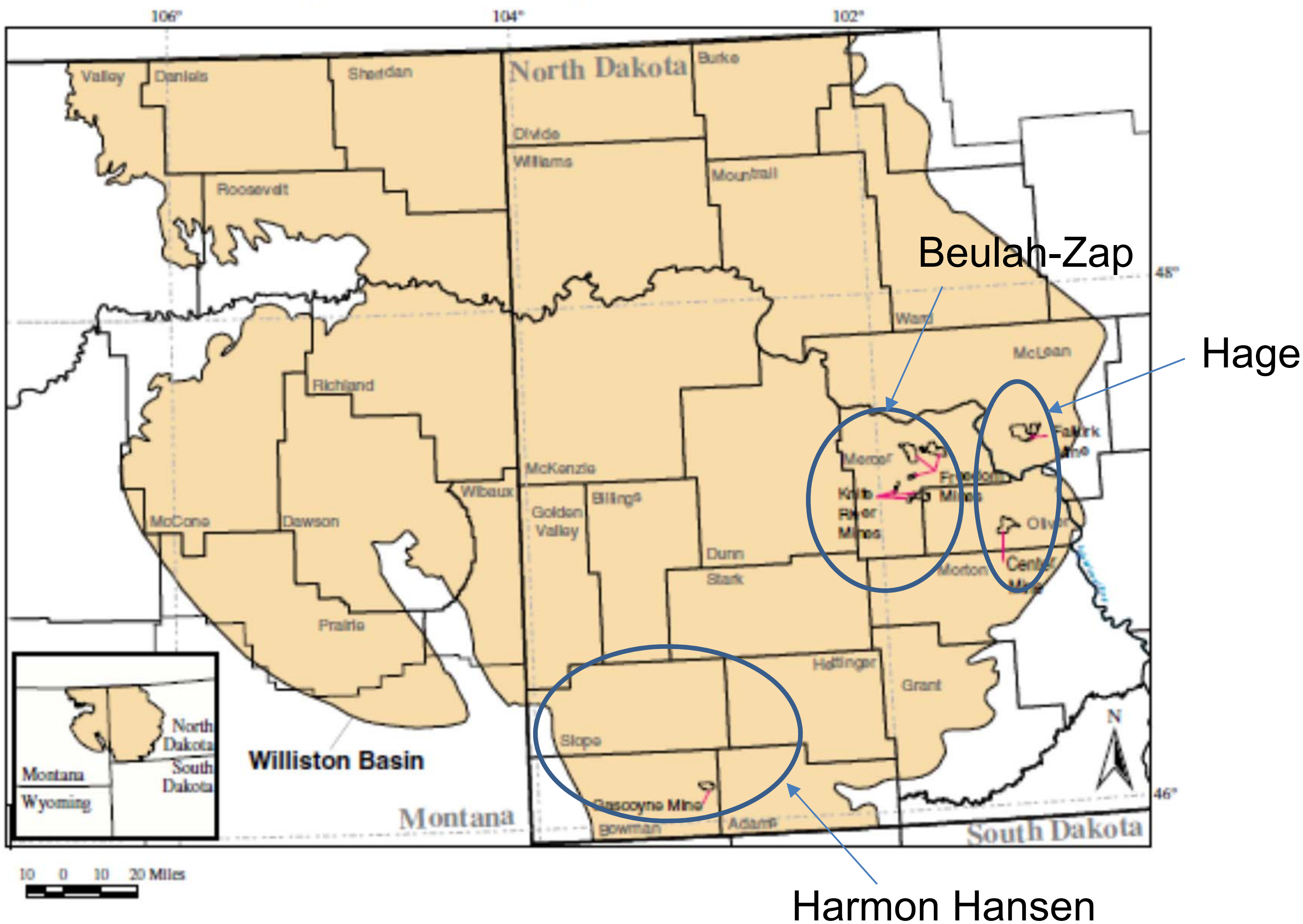
Sample ID	Size Fraction (microns)	Distribution (wt%)	Total REE (ppmw) Dry ash basis
IES16141 (Roof sediment)	+ 25	8.4	169
	25 x 10	15.8	139
	-10	75.9	186
IES16147 (Flyash from Plant)	+25	25.0	274
	25 x 10	40.2	244
	-10	34.8	243

Potentially some enrichment based on size…But, physical beneficiation extremely challenging due to fine particles – deemed not feasible for these samples

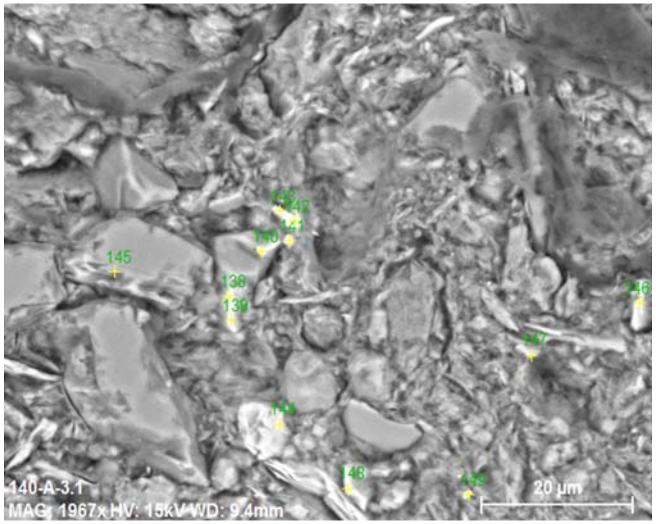
ND Coal Zone – Seam Sampling

- Lignite coal
- Roof
- Partings
- Floor materials

Coal Zones in North Dakota



Evaluation of Coal Samples – SEM-EDS

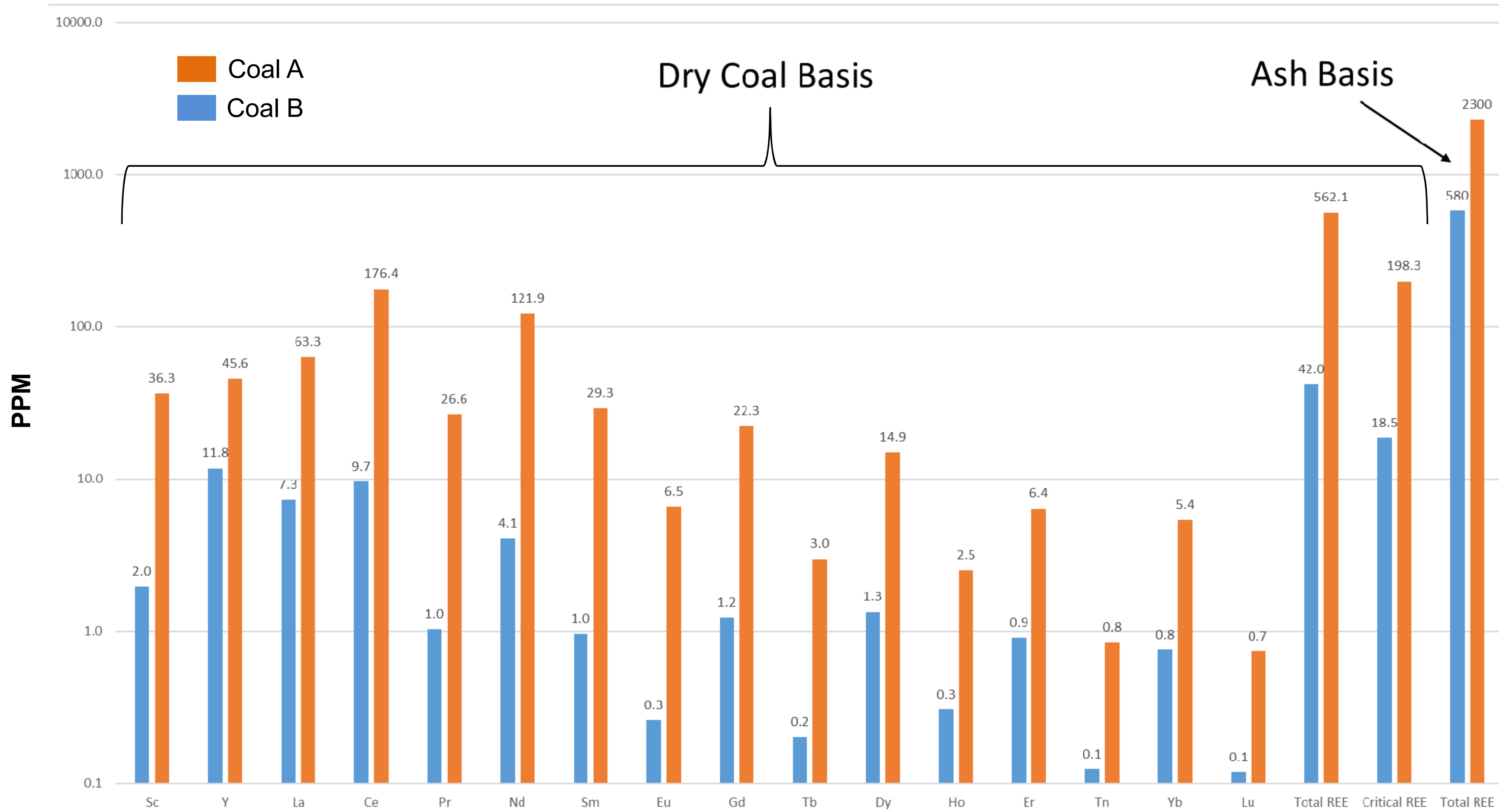


- REE minerals in raw coal difficult to detect via SEM – only La and Ce detected
- Mineral-bound REE appear to be associated with Zr, P and Fe in the raw coal

Norm. mass percent (%)

Spectrum	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Y	Zr	Nb	La	Ce
138	56.29	1.69	8.05	2.40	16.81	0.00	0.00	0.98	4.85	1.15	2.90	3.60	0.00	0.00	0.00	0.00	1.27
139	53.62	2.16	9.79	2.61	16.38	0.00	0.00	1.15	4.95	1.21	3.39	3.04	0.00	0.00	0.00	0.00	1.70
140	56.64	30.68	0.39	0.58	4.02	0.00	0.00	0.80	0.55	2.65	0.07	3.48	0.00	0.00	0.00	0.00	0.13
141	64.92	4.93	3.87	2.56	4.59	0.00	0.00	0.10	0.62	1.22	0.63	15.87	0.00	0.00	0.00	0.00	0.70
142	15.14	0.10	0.04	3.26	5.03	13.43	0.01	0.03	0.05	0.18	0.00	0.88	0.00	5.54	0.00	17.88	38.42
143	28.45	0.14	0.02	2.43	6.09	11.22	0.00	0.03	0.14	0.06	0.00	[illegible]	0.00	4.72	0.00	14.48	31.60
144	36.64	1.33	3.56	3.38	6.24	[illegible]	0.00	0.06	0.19	0.62	0.00	37.01	0.00	[illegible]	0.00	4.68	6.29
145	31.75	6.26	2.40	3.17	26.67	0.00	0.00	21.58	2.04	2.73	0.68	[illegible]	0.00	0.00	0.00	0.00	0.58
146	18.57	7.62	4.18	4.92	9.00	0.00	0.00	0.00	1.27	0.88	0.00	40.20	0.00	0.00	0.00	5.77	7.59
147	50.26	0.88	3.15	2.17	27.79	0.00	0.00	1.18	2.25	1.96	0.31	9.46	0.00	0.00	0.00	0.06	0.54
148	60.29	1.29	2.39	1.12	2.20	0.00	0.00	21.41	2.01	0.78	0.24	7.21	0.00	0.00	0.00	0.34	0.71
149	50.78	0.00	4.75	2.79	6.37	0.00	0.00	2.91	3.05	3.70	0.50	23.92	0.00	0.00	0.00	0.39	0.83
Mean value:	43.61	4.76	3.55	2.62	10.93	2.05	0.00	4.19	1.83	1.43	0.73	12.29	0.00	0.85	0.00	3.63	7.53
Sigma:	16.83	8.55	3.00	1.10	8.87	4.82	0.00	8.13	1.72	1.11	1.16	14.08	0.00	2.00	0.00	6.23	13.14
Sigma mean:	4.86	2.47	0.86	0.32	2.56	1.39	0.00	2.35	0.50	0.32	0.34	4.06	0.00	0.58	0.00	1.80	3.79

Comparison of Coal A and B Samples



Additional sampling of Coal A seam shows significant enrichment of the roof sediments as well – 450 ppm whole sample basis (595 ppm ash basis)

Content of Critical REE compared to global coal deposits and traditional mineral resources

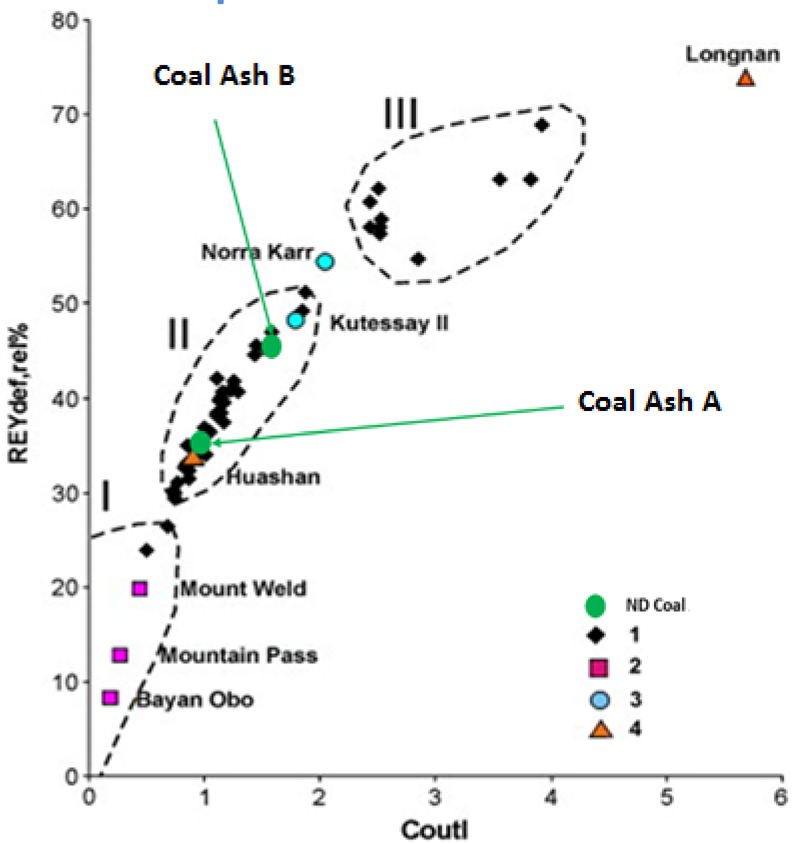


Fig. 6. Classification of REE-rich coal ashes by outlook for individual REY composition in comparison with selected deposits of conventional types.1 — REE-rich coal ashes; 2 — carbonatite deposits; 3 — hydrothermal deposits; 4 — weathered crust elution-deposited (ion-adsorbed) deposits. Clusters of REE-rich coal ashes distinguished by outlook for REY composition (numerals in figure): I — unpromising, II — promising, and III — highly promising.

Seredin, V.V., Dai, S. "Coal deposits as potential alternative sources for lanthanides and yttrium". International Journal of Coal Geology. 94 (2012) 67-93

- High REE-content coals are typically enriched in the heavy and critical REEs, more-so than traditional mineral resources (i.e. Mountain Pass USA)
- Coutl = ratio of critical to excessive elements
- REYdef,rel% = % critical REE in total REE
- ND Lignite fits nicely into Cluster II – Promising
- Coal ash represents a more promising resource than traditional carbonatite deposits

Task 2 Summary

- Sampling/analysis conducted on a range of ND lignite-related materials
- On ash basis, results indicate highest concentration of REEs exist in certain locations within certain coal seams
  - Lower content in the associated sediments
  - Lower content in the Coal Creek Station fly ash due to blending with lower REE content feed coals
  - Selective mining likely needed – maybe not feasible at large utility-scale?
- Ultrafine REE-bearing mineral particles make physical beneficiation very challenging/not feasible for roof/floor sediments
- Modes of occurrence testing has identified that the majority of REEs in lignite are associated with clays/phosphates or as organic complexes
- Two promising REE-rich resources identified:
  1. Feedstock A (Coal A): 2300 ppm REE in ash
  2. Feedstock B (Coal B): 580 ppm REE in ash

Laboratory REE Concentration Results

Laboratory REE Recovery Tests – Stage 1 Concentration

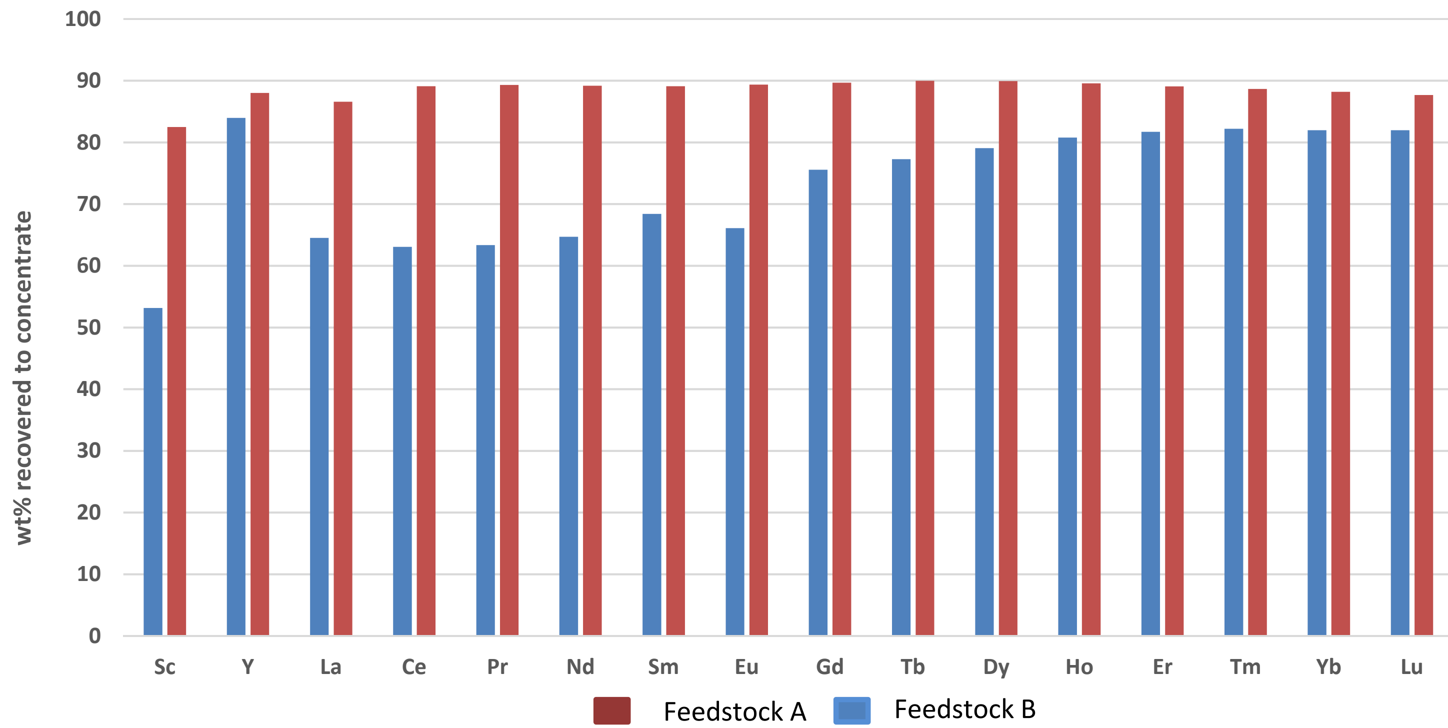
element	wt% rejected to tailings
Sc	0
Y	9.2
La	2.7
Ce	1.7
Pr	0.6
Nd	0.7
Sm	1.3
Eu	2.1
Gd	3.7
Tb	4.1
Dy	4.6
Ho	5.5
Er	6.9
Tm	6.8
Yb	6.3
Lu	7.8
IMPURITIES	68
	42
	57
	80
	80
	80
	10
	57

- Minimal loss of REE to tailings
- Effective removal of some of the impurities

Laboratory REE Recovery Tests – Stage 2 Concentration Screening Tests

	wt% recovered in REE concentrate					
	Condition 1	Condition 2	Condition 3	Condition 4	Condition 5	Condition 6
Sc	11.8	26.7	4.0	53.2	12.4	69.9
Y	10.6	92.6	5.3	84.0	8.7	74.1
La	10.8	90.4	4.5	64.5	7.5	61.1
Ce	11.2	88.2	4.8	63.1	7.2	58.0
Pr	11.0	87.0	3.8	63.3	7.2	57.5
Nd	11.4	86.4	3.9	64.7	6.7	57.7
Sm	11.7	86.4	3.7	68.4	6.9	64.0
Eu	10.9	85.0	0.6	66.1	7.7	59.5
Gd	11.4	89.4	2.6	75.6	7.5	67.7
Tb	12.1	90.0	2.4	77.3	7.9	67.2
Dy	11.8	90.1	2.9	79.1	7.2	66.4
Ho	11.4	90.3	3.5	80.8	7.6	65.1
Er	11.4	90.0	3.8	81.7	7.7	62.8
Tm	11.6	89.1	4.1	82.2	8.5	61.5
Yb	10.9	87.7	3.1	82.0	7.6	61.4
Lu	11.3	87.4	3.4	82.0	7.7	62.0
Total wt% recovered	11.0	86.8	4.5	70.9	7.9	64.6
LREE % recovered	11.2	83.9	4.3	63.8	7.6	60.4
HREE % recovered	10.8	91.8	4.8	83.1	8.4	71.7
critial REE % recovered	10.9	90.8	4.7	79.0	8.1	69.2
non-critical REE % recovered	11.1	83.7	4.4	64.6	7.7	60.9

Stage 2 Concentration - Optimized Results



- Recovery of Feedstock B REEs lower, but good selectivity to critical/heavy REEs
- Scandium (highest price ~$2000/kg oxide) has excellent recovery from Feedstock A
- Results also showed high recovery of other valuable elements
  - Co, Cu, Ga, Ge…others – substantially improves economics

Feedstock A Concentration Results

- 3-stage approach
- Stage 1 focus on impurity rejection
- Stage 2 focus on REE recovery
- Stage 3 primary focus on impurity rejection

Feedstock A - Initial Feedstock at 0.23 wt% (ash elemental basis)		
Concentration Stage	**% REE Recovery to Concentrate**	**wt% REE in Concentrate (elemental)**
1	**97**	**0.3**
2	**89**	**1**
3	**84**	**2.9 to 6.1**

Technical and Economic Feasibility Study

Commercial Concept: Integrated CHP+REE - NDUS

- North Dakota University System (NDUS) campus heating plants need to be re-powered
- Concept includes recovery of REE from next generation design of NDUS combined heat & power plants
- NDUS systems use smaller quantities of fuel than utility-scale plants
- Opportunity to selectively mine REE rich seams
- Integration with existing facility results in cost-saving synergies
- Multiple revenue streams to augment REE economics

TEA Mass Balance

<u>Valley City State University – Coal Feed Rate of 2.5 tons/hour</u>

Basis: Feedstock A – 2300 ppm REE in Ash

- Total REE, Y, Sc production (pure oxides): ~12 tons/year
  - ~85% recovery into 2wt% REE concentrate product
  - ~80% recovery from the 2wt% concentrate during final purification

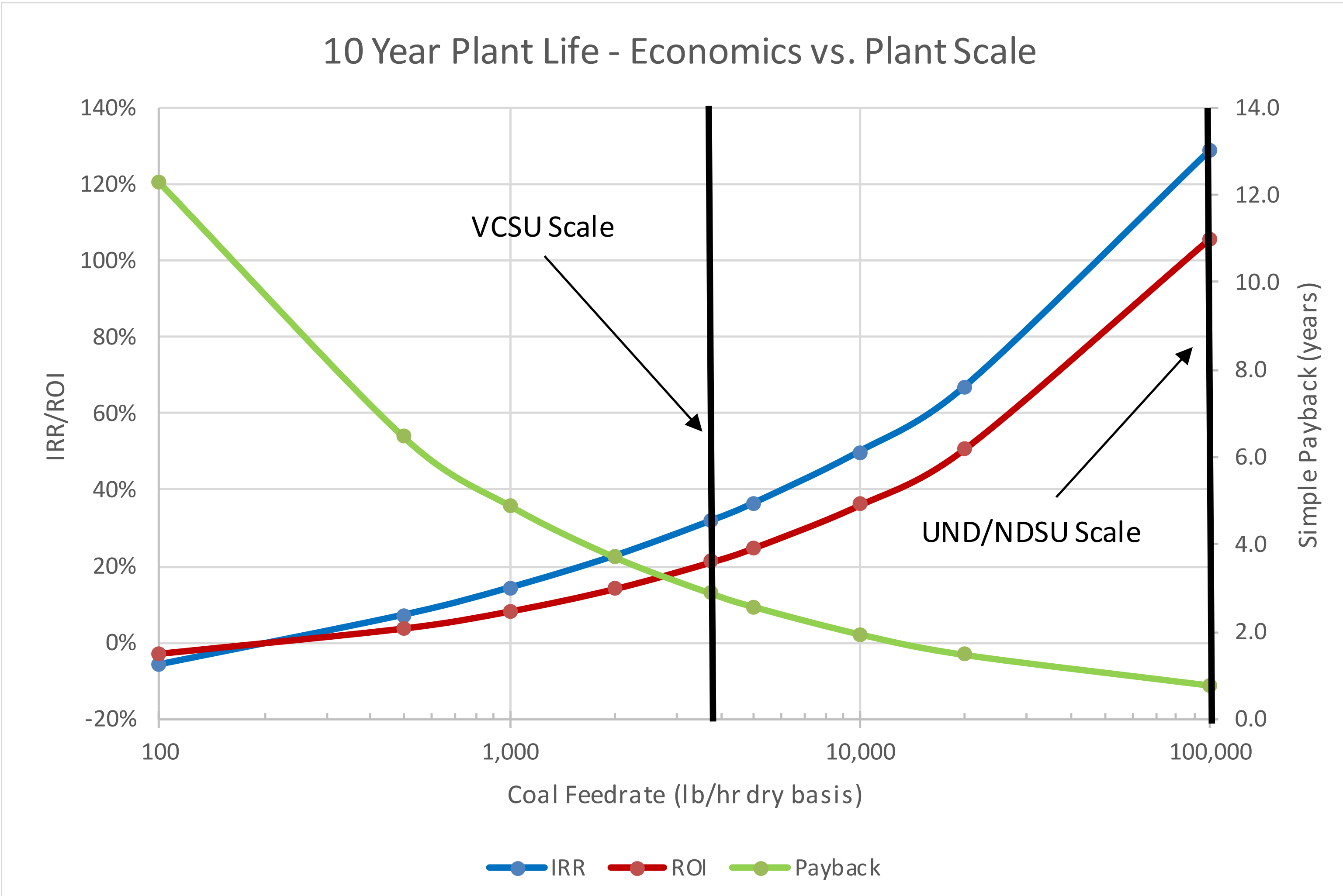
For future reference: If concept installed at largest NDUS facilities (UND & NDSU)

- UND = 20X scale-up
- NDSU = 15X scale-up
- Total REE, Y, Sc production (pure oxides): ~440 tons/year

TEA Results and Conclusions

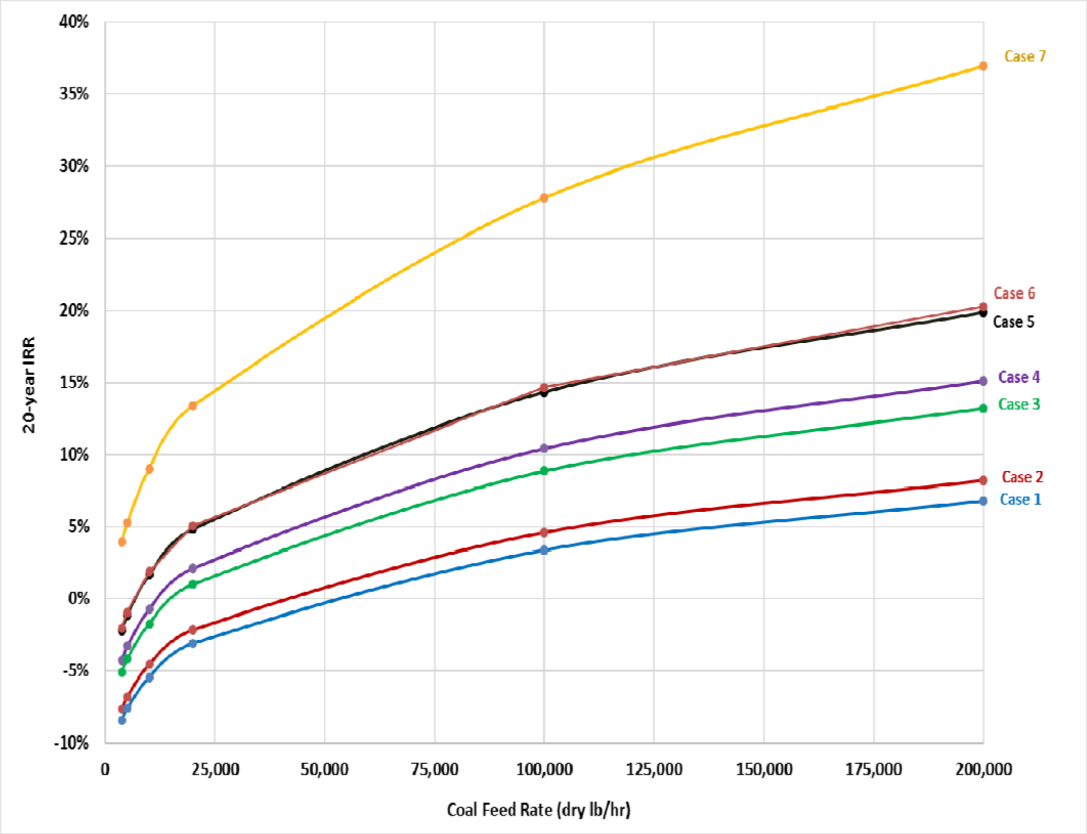
- 2wt% REE using Feedstock A is achievable using the 3-stage concentration approach
- Feedstock B results in lower REE concentration with the same methods
- The proposed plant concept is highly profitable
  - Integration within existing coal conversion facility allows increased efficiency through synergy as well as multiple product streams besides REE to augment economics
  - IRR ranging from 23 to 69% depending on sensitivity case
  - Base case at 35% IRR and simple payback of 3 years

TEA Results – Scale Projections



TEA Results –
'Stand-Alone' Economics of REE Process

- Case 1, 2015 prices for REE
- Case 2 Decrease CAPEX by 10%
- Case 3. Target only Co, Dy, Er, Eu, Ga, Ge, Lu, Nd, Pr, Tb, Tm Sc, Y
- Case 4. Target only Co, Dy, Er, Eu, Ga, Ge, Lu, Nd, Pr, Tb, Tm Sc, Y and decrease CAPEX by 10%
- Case 5. Increase Revenue by 10%
- Case 6. Co-location with conversion to individual oxides
- Case 7. represents 2015 REE prices Increase revenue by 25%



Project Schedule – Remaining Items

- Task 4 – Laboratory tests for bench-scale design parameters (March/April)
- Task 5 – Bench-scale system design (April)

Acknowledgements

Project Team Members

- Dan Laudal, UND
- Dan Palo, Barr Engineering
- Shane Addleman, PNNL
- Ned Kruger, NDGS

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- Dennis James, NA Coal
- Charlie Bullinger and Sandra Broekema, GRE

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Questions?