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RESEARCH PERFORMANCE PROGRESS REPORT

1. COVER PAGE

- a. Federal Agency and Organization Element to Which Report is Submitted: NETL/DOE
- b. Federal Grant or Other Identifying Number Assigned by Agency: DE-FE00027069
- c. **Project Title:** A Pollution Prevention and Economically Viable Technology for Separation of Rare Earth Elements from Powder River Basin Coal Ashes
- d. PD/PI Name, Title and Contact Information (e-mail address and phone number):

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- f. Submission Date: 11/29/2017
- g. **DUNS Number:** 0696909560000
- h. Recipient Organization: 1000 E. University Ave., Laramie, WY 82071
- i. **Project/Grant Period:** 3/1/2016-8/31/2017
- j. Reporting Period End Date: 11/29/2017
- k. Report Term or Frequency: Final
- 1. Signature of Submitting Official:

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2. ACCOMPLISHMENTS

a. Major Goals of the Project

The overall objective of the proposed project is to develop a novel, environmentally innocuous, and cost-effective technology with enhanced performance and scalability for recovering high-value REEs from coal fly ash. The goal is to enrich the REEs from at least 300 ppm in coal fly ash (eventually coal and other coal utilization byproducts) to 2 wt% (on an elemental basis) as targeted by DOE in DOE-FOA-0001202. The new technology generates near-zero pollution, can achieve at least 90% REE recovery from coal fly ash, and has 50% energy and 30% cost reductions compared to conventional REE recovery technologies. By the end of the Phase 1 of the project, the innovative REE separation technology will be successfully developed based on the analysis of bench-scale test results in technical and economic perspectives. By the end of the Phase 2 of the project, the proposed technology will be ready for pilot-scale bench demonstration. The specific objectives include:

- Successfully identify and sample the PRB coal fly ashes that have at least 300 ppm REEs and establish a database regarding their sources, locations, supply amounts, logistics, sampling time, and methods used for characterizing the coal fly ashes physical/chemical properties such as REE concentrations and bulk/surface composition.
- Successfully develop robust processes to produce FeOOH containing at least 2.0 weight % total REE content on an elemental basis. This recovery will be measured on a dry basis from PRB coal fly ashes with high overall recovery efficiency of RREs and low pollutant emissions.
- Reduce REE recovery energy consumption compared to currently commercialized REE recovery technologies.
- Decrease the overall coal fly ash based REE recovery cost compared to currently commercialized REE recovery technologies.
- Develop the new proposed bench-scale coal fly ash based REE recovery technology through optimization of operation parameters and detailed process and equipment designs.

During the period of the project, the Milestone Status representing actual performance in comparison with the Milestone Log will be submitted quarterly. According to DOE's requirements, the Milestone Status will include:

- (1) The actual status and progress of the project.
- (2) Specific progress made toward achieving the project's milestones.
- (3) Any proposed changes in the project's schedule required to complete milestones.

ASTM Number	Standard Description	Analytical Instruments
D5759 - 12	Ash sampling and Testing	
D3178	С, Н	Combustion tube, TGA
D2795,D3682	CaO,MgO, SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , TiO ₂ , P ₂ O ₅ ,Na ₂ O, K ₂ O, P ₂ O ₅	Spectrophotometric/chelatometric/flame photometry/Atomic absorption
WK44003	REEs, and CaO,MgO, SiO ₂ ,	
D4326-13	Al ₂ O ₃ , Fe ₂ O ₃ , TiO ₂ , P ₂ O ₅ ,Na ₂ O, K ₂ O, P ₂ O ₅ , MnO ₂ , SrO ₂ , BaO	XFS/XRF
D3989	REEs	EDTA-titration
US DOE Topical Report DOE/NETL- 2016/1794	REEs	ICP-MS

 Table 1- Analytic procedures and standards for sampling and analytical characterization

Task List

Task 1 – Project Management and Planning

Task 2 – Sampling and Characterization of Proposed Feedstock

Subtask 2.1 – Preparation for feedstock sampling and characterization plan

Subtask 2.2 - Sampling and characterization experiments.

Subtask 2.3 - Sampling and characterization report preparation.

Task 3 – REE Process Feasibility Study

Subtask 3.1 - Set up the Aspen process simulation model.

Subtask 3.2 - Select waste management strategy for the process model.

Subtask 3.3 - Compare the proposed technology with other advanced REE extraction and recovery technologies.

Subtask 3.4 - Perform ASPEN process model simulations.

Subtask 3.5 - Calculate capital, operating and maintenance costs.

Subtask 3.6 - Analyze market demand and pricing for REEs and other recovered value-added elements.

Subtask 3.7 - Set up financial analysis model and perform financial analyses.

Subtask 3.8 - Summarize results of subtasks 3.1 through 3.7 and develop recommendations for technology optimization.

Task 4 – Laboratory Scale Leaching, Separation, and De-Watering Tests

Subtask 4.1 - REEs and other valuable materials leaching from coal ashes. Subtask 4.2 - Separating REEs+other-valuable materials loaded FeOOH from leaching mixture.

Subtask 4.3 - De-watering FeOOH for obtaining at least 2 wt-% REEs containing solid.

Task 5 – Life Cycle Analysis (LCA).

Task 6 – Preparation of Phase I Design Package and Phase II Renewal Application Documents.

Subtask 6.1 - Phase 1 design package preparation. Subtask 6.2 - Phase 1 summary report preparation. Subtask 6.3 - Phase 2 application package.

b. What was accomplished under these goals?

The project management plan (Task 1), the coal fly ash sampling and characterization plan (Subtask 2.1), the *Sampling and characterization experiments (Subtask 2.2)*, and part of the laboratory scale leaching, separation, and de-watering tests (Task 4) have been completed as discussed below.

Task 1 - Project Management and Planning

This task has been completed. We have developed a project management plan to foster team interaction, track deliverables, maintain and implement a project risk management plan, interface with the Department of Energy (DOE), and report progress and financials in accordance with the requirements set forth in the award document.

Task 2 - Sampling and Characterization of Proposed REE Feedstock

While significant progress has been made in identifying field site locations and compositional assessment of potential coal ashes containing rare earth elements (REEs), continued effort is essential to identify the "best" source to support future commercial REE production. The investigation into chemical and physical characterizations, REE concentrations, and phase compositions of the coal ashes are essential in the development of viable REE separation processes.

Subtask 2.1 - Preparation for Feedstock Sampling and Characterization Plan

The sampling, analytical, and procedural techniques based on ASTM standards (D5759-12 to obtain coal ashes from power plants, ASTM D346 for sampling coal ashes from lots of less than 100 tons, and ASTM D346 & D2013 for crushing dividing and meshing procedure of collected coal as samples) and DOE reports as listed in aforementioned Table 1 and stated in SOPO (Task 2) have been used to characterize all the fly ashes collected to date. The methods include ICP-MS (NexION 300S, Perkin Elmer) for REE composition/concentration analysis, a SEM-EDX (Model #51-XMX0005, Oxford Instruments America) [Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Detection (EDX)] for sample morphology and bulk concentration, an in-situ XRD (X-ray Diffraction, Smartlab Rigaku) for bulk phase analysis, an in-situ XPS (X-ray photoelectron spectroscopy) for surface composition/oxidation state analysis, a TEM (Transmission Electron Microscope, Tecnai G2 F20 S-Twin, FEI) for particle size distribution, a TGA (Thermogravimetric Analyzer, SDT Q600 apparatus, TA Instruments) for sample thermal stability, and an absorption column for sorption/desorption kinetic data.

Subtask 2.2 - Sampling and Characterization Experiments

Coal fly ashes (tested at UW) had been collected from six different power plants (for bench scale REEs extraction experiments), including Cherokee (CH), Dave Johnston (DJ), Dry Fork Station (FS), Jea (JE), Laramie River Station (LR), and Wyodak (WD). The coal used by these power plants was from Power River Basin (PRB). Prior to the following tests, all the coal fly ash samples were passed through a No. 200 sieve. Samples were dried to constant mass in a vacuum

oven at 105 °C. A vario MACRO cube elemental analyzer (vario MACRO cube, Elementar) was used for elemental analysis under vario MACRO cube CHNS mode. The coal 50 method was adopted to measure the elements in the coal fly ash samples, including C, H, N and S. The details of the coal 50 method can be seen in Table 2.2.1.

O ₂ dosing time 1	30 s
O ₂ dosing time 2	200 s
O ₂ dosing flow 1	50 mL/min
O ₂ dosing flow 2	100 mL/min
O ₂ cut off threshold	30%
Autozero delay N	15 s
Autozero delay S	15 s
Peak anticipation N	70 s
Peak anticipation C	150 s
Peak anticipation H	75 s
Peak anticipation S	80 s
Desorpt. CO ₂	240 °C
Desorpt. H ₂ O	150 °C
Desorpt. $SO_2(1)$	100 °C
Desorpt. $SO_2(1)$ time	60 s
Desorpt. $SO_2(2)$	230 °C

Table 2.2.1- Details of the coal 50 method for elemental analysis

A Quadrasorb Gas Sorption Surface Area and Pore Size Analyzer (Quadrasorb-evo, Quantachrome instruments) was used for surface area analysis. Samples were degassed at 150 °C for 8 hours under vacuum. The surface area was obtained by the Brunauer-Emmett-Teller (BET) method.

A Perkin Elmer NexION 300S ICP-MS was used for the total contents of rare earth elements in the samples. The instrument was operated under standard mode and all analyses were completed using external standards and RE as the internal standard. In the digestion procedure, solid samples were prepared by mixing coal fly ashes with calcined LiBO₂ (lithium metaborate) at

a ratio of 1:8. Prior to fusion, samples were mixed by stirring with a platinum rod in a 99.95% platinum crucible. The open crucible was heated to 1,100 °C for five minutes in a muffle furnace. After fusion, the melt was removed from the oven and allowed to cool down to a homogeneous glass. The glass was digested in 5% HNO₃ trace metal solution on low heat with continuous stirring. The platinum crucibles were rinsed three times with 5% HNO₃ to ensure that the sample glass was completely digested. Once digestion was complete, the sample was diluted to a final volume of 100 ml with DI water. Blank samples containing only lithium metaborate were prepared and processed in the same way as that used for fly ash samples. The accuracy of the fusion method was assessed by using the standard reference materials (SRM 1633c) from National Institute of Standards and Technology (NIST) for coal fly ash.

Subtask 2.3 - Sampling and Characterization Report Preparation

Elemental analysis

Coal fly ashes were collected from six different power plants including Cherokee (CH), Dave Johnston (DJ), Dry Fork Station (FS), Jea (JE), Laramie River Station (LR), and Wyodak (WD). The coals used by these power plants were all from the Power River Basin (PRB). Prior to the tests, all the coal fly ash samples were passed through a No. 200 sieve. Samples were dried to constant mass in a vacuum oven at 105 ^oC. A vario MACRO cube was used for elemental analysis under vario MACRO cube CHNS mode (Figure 2.3.1). Coal 50 method was used to measure the CHNS in the coal fly ash samples, as indicated in Table 2.2.1. The results were summarized in Table 2.3.1.

Sample ID	C (%)	H (%)	N (%)	S (%)
СН	0.88	0.21	0.03	4.19
DJ	0.89	0.82	0.06	5.58
FS	1.8	0.31	0.03	3.41
JE	0.52	0.01	0.02	1.28
LR	0.26	0.25	0.02	0.91
WD	0.56	0.24	0.04	3.5

Table 2.3.1 Elemental analysis for coal fly ash samples.



Figure 2.3.1 Vario MACRO cube elemental analyzer at UW for measuring CHNS in coal fly ashes.

Brunauer-Emmett-Teller (BET) surface area

Brunauer-Emmett-Teller (BET) surface area of coal fly ashes was evaluated by using nitrogen adsorption isotherms obtained at -196 °C with a Quantachrome Autosorb-iQ instrument (Figure 2.3.2). Samples were degassed at 150 °C for 8 hours under vacuum. The surface areas of samples are shown in Table 2.3.2. The coal fly ash samples have a wide range of BET surface areas, from 0.076 to 19.32 m²/g-ash, although all the fly ashes resulted from combustion of the coal from the same region - PRB. This suggests that the characteristics of coal fly ashes are significantly impacted by the ways of coal preparation and combustion.

Sample ID	Surface area/m ² ·g ⁻¹
СН	1.734
DJ	13.743
FS	5.99
JE	0.076
LR	0.905
WD	19.32

Table 2.3.2 BET surface areas of the coal fly ash samples.



Figure 2.3.2 Quantachrome Autosorb-evo for Brunauer-Emmett-Teller (BET) surface area measurement instrument at UW.

Lanthanide analysis

A Perkin Elmer Nexion 300 ICP-MS (Figure 2.3.3) was used for the total contents of rare earth elements in the samples. The instrument was operated under standard mode and all analyses were completed using external standards and Re as the internal standard. In the digestion procedure,

solid samples were prepared by mixing coal fly ashes with calcined LiBO₂ (lithium metaborate) at a ratio of 1:8. Prior to fusion, samples were mixed by stirring with a platinum rod in a 99.95% platinum crucible. The open crucible was heated to 1,100 °C for five minutes in a muffle furnace. After fusion, the melt was removed from the oven and allowed to cool to a homogeneous glass. The glass was digested in 5% HNO₃ (trace metal) on low heat with continuous stirring. The platinum crucibles were rinsed three times with



Figure 2.3.3 Perkin Elmer NexION 300S ICP-MS system at UW.

5% HNO₃ to ensure that the sample glass was completely digested and the sample was diluted to the scale of 100 ml. Blank samples containing only lithium metaborate were prepared and processed in the same way as that used with fly ashes. Part of the sample piles are photoed and shown in Figure 2.3.4. The accuracy of the fusion method was assessed using the National Institute of Standards and Technology (NIST) standard reference material (SRM) for coal fly ash, SRM 1633c. The moisture and organic carbon concentrations are shown in Table 2.3.3 for dry mass basis (DMB) and dry ash basis (DAB) calculations, while the total REEs in each sample are summarized in Table 2.3.4. DJ ash not only has the highest organic carbon or unburned carbon (4.26%) but also contains the highest moisture (6.54%). This is due to the fact that porous carbon is hydrophilic and has adsorbed moisture. Cerium (Ce), neodymium (Nd), lanthanum (La) and yttrium (Y) are among the most dominant REE elements in all tested coal fly ashes. Please note that the JE coal fly ash was no longer used for further experimentation as the sample was from one of the previous projects and some information about the sample was not accurately recorded.



Figure 2.3.4 Piles of REEs containing samples from leaching and separation processes for ICP-MS analysis.

Ashes	Moisture (%)	Organic carbon (%)
СН	0.41	1.91
DJ	6.54	4.26
FS	0.84	2.91
LR-1	0.37	0.61
LR-2	0.08	0.43
WD	1.23	3.08

Table 2.3.3 Moisture and organic carbon content of coal fly ashes

	СН	DJ	FS	LR-1	LR-2	WD
As received fly ashes	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Ce	166.2	133.2	147.8	158.1	170.3	160.3
Dy	10.7	11.5	13.7	11.8	14.8	15.0
Er	6.8	6.6	8.0	7.3	8.9	8.6
Eu	3.5	4.2	5.1	3.8	5.8	5.2
Gd	14.1	14.8	21.5	15.0	22.3	22.6
Но	2.1	2.2	2.7	2.4	2.9	2.9
La	88.6	71.1	74.7	86.0	88.6	83.3
Lu	1.1	1.0	1.2	1.2	1.3	1.2

Nd	99.6	85.9	98.7	97.6	108.7	106.3
Pr	22.9	16.2	22.8	22.3	24.7	24.4
Sm	14.8	15.1	22.2	15.2	23.7	23.0
Tb	1.8	2.0	2.4	2.0	2.5	2.6
Tm	1.0	1.0	1.1	1.1	1.3	1.2
Y	60.4	58.6	69.5	68.0	76.4	73.2
Yb	6.7	6.1	7.1	7.0	8.2	7.5
Total REEs (ppm)	500.5	429.7	498.5	498.7	560.2	537.0
	CII		TC			
	СН	DJ	FS		LR-2	WD
DMB (dry mass basis)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Ce	166.9	142.6	149.0	158.7	170.4	162.3
Dy	10.8	12.3	13.8	11.9	14.8	15.2
Er	6.9	7.1	8.1	7.3	8.9	8.7
Eu	3.5	4.5	5.1	3.8	5.8	5.2
Gd	14.1	15.8	21.7	15.1	22.3	22.9
Но	2.2	2.4	2.7	2.4	2.9	2.9
La	89.0	76.1	75.4	86.3	88.6	84.3
Lu	1.1	1.1	1.2	1.2	1.3	1.2
Nd	100.0	91.9	99.6	97.9	108.8	107.6
Pr	23.0	17.4	23.0	22.4	24.7	24.7
Sm	14.8	16.2	22.4	15.3	23.7	23.3
Tb	1.8	2.1	2.4	2.0	2.5	2.6
Tm	1.0	1.1	1.1	1.1	1.3	1.2
Y	60.6	62.7	70.1	68.2	76.4	74.1
Yb	6.7	6.5	7.2	7.0	8.2	7.5
Total REEs (ppm)	502.6	459.7	502.7	500.5	560.7	543.7
	1	ı	1			1
	СН	DJ	FS	LR-1	LR-2	WD
DAB (dry ash basis)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)

Ce	170.1	148.9	153.5	159.7	171.1	167.5
Dy	11.0	12.8	14.2	11.9	14.9	15.6
Er	7.0	7.4	8.3	7.4	9.0	8.9
Eu	3.6	4.7	5.3	3.8	5.8	5.4
Gd	14.4	16.5	22.4	15.2	22.4	23.6
Но	2.2	2.5	2.8	2.4	2.9	3.0
La	90.7	79.5	77.6	86.9	89.0	87.0
Lu	1.2	1.1	1.2	1.2	1.3	1.2
Nd	101.9	96.0	102.6	98.5	109.3	111.1
Pr	23.5	18.1	23.7	22.6	24.8	25.4
Sm	15.1	16.9	23.1	15.4	23.8	24.0
Tb	1.9	2.2	2.5	2.0	2.5	2.7
Tm	1.1	1.1	1.2	1.1	1.3	1.2
Y	61.8	65.5	72.2	68.6	76.8	76.4
Yb	6.9	6.8	7.4	7.1	8.2	7.8
Total REEs (ppm)	512.4	480.2	517.8	503.6	563.1	561.0

XRD analysis of coal fly ashes

Both raw or as-received coal fly ashes and ashes treated with supercritical CO₂-H₂O were analyzed with XRD manufactured by Rigaku with Cu K α radiation. The working voltage and current of the X-ray tube were fixed at 40 kV and 40 mA, respectively. All X-ray diffraction patterns were analyzed using Jade 7.5 of Material Data, Inc. (MDI), and peak profiles of individual reflections were determined by a nonlinear least-squares fit of the Cu K α corrected data. A thin layer of the sample was mounted evenly onto a zero background quartz plate, followed by running with a scan range of 2 θ between 10 - 90 ° and at a scan rate of 4 °/min with a chopper increment of 0.02.

X-ray diffraction patterns of the original and treated samples mentioned in last paragraph are almost completely identical except that there is an additional peak at ~29° (pointed with an arrow in the Figure 2.3.5) in the treated sample. This peak likely represents (Ca, Mg) CO₃ phase. Ca and Mg are two major inorganic species in coal fly ash. During the extraction process, pH of

reaction system was lowered by the supercritical CO₂-H₂O fluid. These two elements can be dissolved in the liquid phase. However, (Ca, Mg) CO₃ precipitate is formed when CO₂ is released after the extraction. The precipitate is then deposited onto the surface of coal fly ash particles. Thus, CO₂ could be used to assist in rare earth elements extraction from coal fly ashes. Doing so could not only help the improvement of rare earth elements extraction efficiency but also reduce the usage of acids or other chemicals, rare earth elements extraction agents, and thus the cost and negative environmental impact of the rare earth elements extraction.



Figure 2.3.5 X-ray diffraction patterns of coal fly ash from Laramie River [Red line: original coal fly ash; black line: coal fly ash treated by supercritical CO₂-H₂O fluid at initial pressure of 5,000 psi, 50 °C for 2 hours]

Identification of coal fly ash resources

To find at least 10 million tons of coal fly ashes with their REEs concentrations being higher than 300 ppm, a number of energy companies in eight states (WY, UT, SD, ND, CO, NE, WI, and MT) have been contacted. Non-disclosure agreements (NDAs) have been signed between University of Wyoming and energy companies such as PacifiCorp, which was designed to protect both UW and the fly ash supplying companies. As an example, the landfill sites and ponds in Huntington (UT) site owned by PacifiCorp, alone hold ~9.9 million cubic yards of coal fly ashes.

Laramie River Station Basin (WY) has ~9.2 million cubic yards of fly ashes. These are equivalent to 10.9 and 10.2 million metric tons (The estimates are based on a loose bulk density of 90 lbs. /ft³) of coal fly ashes, respectively. WEC Energy Group has 20 million tons in its landfill sites and an annual production of 650,000 - 750,000 tons. Basin Electric Power has 19 million tons of ash in Wyoming and North Dakota while Alliant Energy Corp holds 100 million tons of ash in Iowa and Wisconsin. A total of 158 million tons of ash are identified in five states (Iowa, North Dakota, Utah, Wyoming, and Wisconsin). As until the due date of the final report of this project, a total number of 36 coal ashes were received from these companies and analyzed. The REEs concentration is found to range from 156.0 to 590.3 ppm on DMB. Five out of the 36 samples are below the target REEs concentration set by DOE. A summary of the collected ash samples and the information associated to each ash is presented in Table 2.3.5. The tonnage of fly ash that does not meet the 300 ppm target is estimated to be 8 million tons. Therefore, approximately 150 million tons of fly ash with REEs content over 300 ppm is identified by the UW-RIT-UWV team. The amount of REEs in the identified fly ash is between 61,567 to 88, 373 tons on an elemental basis. Figure 2.3.6 and 2.3.7 show the distribution of coal fly ash resources and the pile of samples received.

Ash Codes	State	City	Name of	Company	Quanti	DMB	DAB
			Plant		ty		
					(millio		
					n tons)		
I-AEC-L5	Iowa	Lansing	Lansing	Alliant Energy	100	491.4	491.8
				Corp			
I-AEC-O6	Iowa	Ottumwa	Ottumwa	Alliant Energy		590.3	590.5
				Corp			
I-AEC-PC4	Iowa	Cedar	Prairie Creek	Alliant Energy		402.7	403.5
		Rapids		Corp			
ND-BEP-	North	Beulah		Basin Electric	19	156.0	157.9
BH-1	Dakota			Power			
ND-BEP-	North	Beulah		Basin Electric		160.1	161.1
BH-2	Dakota			Power			
ND-BEP-	North	Stanton	Leland Olds	Basin Electric	1	268.9	269.2
LO1	Dakota			Power			

Table 2.3	8.5 Summa	ary of the	fly ash	collection	and analyses
		•	~		-

ND-BEP-	North	Stanton	Leland Olds	Basin Electric		327.4	327.6
LO2	Dakota			Power			
WY-BEP-	Wyoming	Gillette	Dry Fork	Basin Electric		492.1	495.7
DFS1			Station	Power			
WY-BEP-	Wyoming	Gillette	Dry Fork	Basin Electric		440.6	447.5
DFS2			Station	Power			
WY-BEP-	Wyoming	Wheatland	Laramie River	Basin Electric	-	444.5	449.0
LRS1			Station	Power			
WY-BEP-	Wyoming	Wheatland	Laramie River	Basin Electric		420.1	421.2
LRS2			Station	Power			
UT-PC-H-1	Utah	Huntington	Huntington	Pacificorp	19	374.0	374.2
UT-PC-H-2	Utah	Huntington	Huntington	Pacificorp		331.3	375.6
UT-PC-	Utah	Castle Dale	Hunter	Pacificorp		349.9	350.1
HCD-1							
UT-PC-	Utah	Castle Dale	Hunter	Pacificorp		358.0	401.2
HCD-2							
Wy-PC-DJ-	Wyoming	Glen Rock	Dave Johnston	Pacificorp		353.6	411.1
1							
Wy-PC-DJ-	Wyoming	Glen Rock	Dave Johnston	Pacificorp		340.8	341.0
2							
Wy-PC-JB-	Wyoming	Point of	Jim Bridger	Pacificorp		166.6	166.7
1		Rocks					
Wy-PC-JB-	Wyoming	Point of	Jim Bridger	Pacificorp		300.5	300.9
2		Rocks					
Wy-PC-N-	Wyoming	Kemmerer	Naughton	Pacificorp		342.7	475.8
1							
Wy-PC-N-	Wyoming	Kemmerer	Naughton	Pacificorp		252.0	252.4
2							
Wy-PC-N-	Wyoming	Kemmerer	Naughton	Pacificorp		480.6	480.7
3							
Wy-PC-N-	Wyoming	Kemmerer	Naughton	Pacificorp		508.2	707.8
4							
Wy-PC-W-	Wyoming	Gillette	Wyodak	Pacificorp		419.2	422.6
1							
Wy-PC-W-	Wyoming	Gillette	Wyodak	Pacificorp	1	373.4	376.2
2							

WI-ER-	Wisconsin	Elm Road	WEC Energies	20	452.6	452.9
W10						
WI-ER-W7	Wisconsin	Elm Road	WEC Energies		455.0	456.4
WI-OC-W5	Wisconsin	Oak Creek	WEC Energies		427.6	427.9
WI-OC-W6	Wisconsin	Oak Creek	WEC Energies		423.3	423.5
WI-P1-W8	Wisconsin	Presque Isle	WEC Energies		382.0	394.7
WI-P1-W9	Wisconsin	Presque Isle	WEC Energies		331.7	331.8
WI-PP-	Wisconsin	Elm Road	WEC Energies		516.9	520.4
W11						
WI-PP-	Wisconsin	Pleasant	WEC Energies		502.5	503.1
W12-1		Prairie				
WI-PP-	Wisconsin	Pleasant	WEC Energies		428.2	428.7
W12-2		Prairie				
WI-WPS-	Wisconsin	Weston	WEC Energies		314.8	315.0
W3		Plant				
WI-WPS-	Wisconsin	Weston	WEC Energies	1	328.7	334.0
W4		Plant				



Figure 2.3.6 A map showing the distribution of coal fly ash resources identified by UW-RIT-UWV team. An estimate of 150 million tons of coal fly ash contain REEs over 300 ppm.



Figure 2.3.7 the pile of coal fly ash collected from five states for REEs content analysis.

Task 3 – REE Process Feasibility Study and Life Cycle Analysis (LCA)

Subtask 3.1: Set up the Aspen Process Simulation Model

An accounting framework model was set up to simulate the energy and material flows of the supercritical extraction process when scaled up. Super critical extraction with proprietary solution (PS) is modeled. The model and data structure is discussed in this section.

The proposed new technology, lab scale tests have determined the operating parameters required to produce an FeOOH based concentrate containing at least 2% REEs by weight on a dry solids basis. The REE leaching and separation technology uses PS enhanced with CO₂ and aqueous PS solution for post treatment. This study performs techno-economic analysis of the proposed new technology for REEs recovery from Powder River basin (PRB) coal ashes. The set of processes starting from coal ash at a generation plant and ending with usuable REEs can be summarized as in figure 3.1.1



Figure 3.1.1: Process flow diagram for conversion of coal ash to REEs through PS enhanced with CO₂. The box indicates boundary of analysis. The Enrichment process is outside of scope of analysis. A similar structure has been used for all reagents.

The analysis models the REEs extraction phase in the production process. The enrichment process takes the output of the proposed supercritical process and results in separated REEs with

purities suitable for sale. This enrichment process is outside of the scope of the DOE solitication and this analysis.

The annual production of 75% pure REEs oxides is assumed to be 1000 tons. Based on the ash used (500 ppm REEs) and recovery rates of 75% (PS enhanced with CO₂) and 69% (PS without enhancement), approximately 5,000 and 4,500 tons of ash need to be processed daily, respectively. The batch size is 15-ton of coal ash and a total of 40 batch reactors are to be constructed in the scenarios.

The model integrates data from experiments performed by the University of Wyoming along with data on PS enhanced with/without CO₂. The amount of reactant complex per ton of coal ash was calculated by extrapolation, maintain solvent mass to feed ratio (S/F) as constant, a method that is often used to study the scale up of bench technologies (Prado, et al., 2011; Prado & Meireles, 2010; Prado, et al., 2012).

The yields of REEs is taken from experimental results from the University of Wyoming, shown in Table 3.1.1.

DMB	Enhanced PS	PS
Ce	87.0	100.3
Dy	11.9	12.4
Er	6.8	7.1
Eu	3.1	3.1
Gd	15.8	16.8
Но	2.3	2.4
La	44.9	51.4
Lu	0.9	0.9
Nd	68.9	76.8
Pr	12.1	13.6
Sm	13.6	14.4
Tb	2.1	2.2
Tm	0.9	0.9
Y	70.4	71.4
Yb	5.9	6.1
Sc	20.2	21.7

Table 3.1.1: Yields of REE from PS enhanced with/without CO₂ on DMB basis.

The input requirements to process one-ton of coal ash with the PS process thus obtained are listed below:

- Ehanced with CO₂
 - Coal ash = 1 ton
 - $CO_2 = 3 \text{ tons}$
 - With 99% recapture per cycle, each cycle requires refill of 0.03 tons
 - PS = 3 tons, 5% concentration

Acid leaching of ash post extraction

- Coal ash = 1 ton
- PS = 6 tons, 5% concentration
- Temperature = 70 degree centigrade
- Without enhancement
 - Coal ash = 1 ton
 - PS = 9 ton, 5% concentration
 - Temperature = 70 degree centigrade

Given the temperature and pressure, the density of CO_2 was assumed to be 0.662 gm per cm³ (Zorca, et al., 2007). It has been assumed that the transpotation of ash is neglegible as the designe of the extraction units is to be movable so that the extraction process can be done *in situ* in the vicinity of the ash sources and coal-fired power plants. In addition, the waste heat from power plants can supply for the heating for reactors.

Assumptions for REE content of coal ash

In addition to 6 samples from Powder River basin available for this project, data on the concentration of REE in 153 samples reported in the literature were collected. The samples varied globally, 84 from U.S, 46 from Europe and 23 from Asia. Of the 153 samples, only those samples that reported all the 14 REEs were included for the analysis. In the case of the sample available at Wyoming, the concentration of the highest valued REE (Scandium) was not measured, therefore the U.S. minimum and maximum concentration of Scandium in coal ash were assumed only for

those 6 samples. Table 3.1.2 shows the elemental concentration of coal ash with minimum and maximum value. Average REE prices between years 2010 and 2014 were used.

PRB coal is sub-bituminous. The contents of sub-bituminous coal was obtained from Tharaniyil 2013 (Table 3.1.3). Heavy metal contents of Wyoming PRB coal was obtained from Stricker & Ellis 1999 (Table 3.1.4).

Table 3.1.2: Bounds for concentrations and value content of REEs in coal ash. Bounds were obtained by calculating total REE value for all complete data sets and identifying maximum and minimum economic value. (Całus Moszko, et al., 2016; Hower, et al., 2013; Mayfield & Lewis, 2013; Smolka-Danielowska, 2010; Zhang, et al., 2001). Note: In the case of the sample available at Wyoming, the concentration of the highest valued REE (Scandium) was not measured therefore U.S. minimum and maximum concentration of scandium in coal ash were assumed for those 6 samples.

Element	PRB		U	S	WORLD		
Concentration	Min	Max	Min	Max	Min	Max	
Cerium	170	171	170	216	11.2	345	
Dysprosium	11.0	14.9	11.0	18.5	0.5	2.3	
Erbium	7.0	9.0	7.0	17.0	0.3	6.8	
Europium	3.6	5.8	3.6	7.5	0.4	1.7	
Gadolinium	14.4	22.4	14.4	121.5	0.9	13.8	
Holmium	2.2	2.9	2.2	7.5	0.1	3.5	
Lanthanum	90.7	89.0	90.7	117	6.8	174.8	
Lutetium	1.2	1.3	1.2	9.0	0.1	1.8	
Neodymium	102	109	102	104.5	4.1	135.1	
Praseodymium	23.5	24.8	23.5	74.5	1.1	39.0	
Scandium	4.2	45.9	4.2	45.9	3.8	70.9	
Samarium	15.1	23.8	15.1	21.0	0.9	13.9	
Terbium	1.9	2.5	1.9	30.5	0.4	0.9	
Thulium	1.1	1.3	1.1	8.5	0.0	1.2	

Yttrium	61.8	76.8	61.8	113.5	8.6	120.8
Ytterbium	6.9	8.2	6.9	11.0	0.3	2.4
Total REE value	98.7	395	98.7	525	30.6	557
(Value \$/ton)						

Table 3.1.3: Contents of sub-bituminous coal, Source: (Tharaniyil, 2013)

	Bituminous		Sub-bituminous			
	Coal (%	by	Coal (% by			
	weight)		weight)			
SiO ₂	61.0		46.7			
Al ₂ O ₃	25.4		18.8			
Fe ₂ O ₃	6.6		5.9			
CaO	1.5		17.8			
MgO	1.0		4.0			
Na ₂ O	0.9		1.3			
K ₂ O	0.2		0.3			

Table 3.1.4: Other metal content of coal (ppm), Source: (Stricker & Ellis, 1999)

	low	High	Mean
Other metals	(ppm)	(ppm)	(ppm)
Antimony	0.0	17.0	0.5
Arsenic	0.2	19.0	2.6
Beryllium	0.1	3.3	0.5
Cadmium	0.0	3.0	0.2
Chromium	0.6	50.0	6.1
Cobalt	0.4	27.0	1.9
Lead	0.5	17.0	3.0
Manganese	0.2	210	26.0
Mercury	0.0	27.0	0.1
Nickel	0.7	35.0	4.6
Selenium	0.1	16.0	1.1
Uranium	0.1	12.0	1.3

PRB coal has an ash content of 6.44% (Stricker & Ellis, 1999). Assuming all of the heavy metals remain in the ash the amount of heavy metals in PRB ash was calculated using the mean values.

Subtask 3.2: Select Waste Management Strategy for the Process Model

Disposal of coal ash and coal combustion products is quite costly (up to \$30/Mg(Sell, McIntosh et al. 1989)) and can have severe environmental impacts due mainly to the potential for leaching of heavy metals (Adriano, Page et al. 1980, Carlson and Adriano 1993, Rowe, Hopkins et al. 2002). A process that can remove heavy metals would have the potential to greatly reduce these disposal costs as well as mitigate harmful leaching in landfill environments as studies have found leaching to occur at rates greater than regulation allows (Table 3.2.1). Assuming the removal rates of heavy metals followed those of the rare earth metals, it would be conceivable to reduce restricted heavy metal concentrations to below the total threshold limit concentration for most problematic metals, opening the door for other less expensive disposal pathways (Table 3.2.2). The last column of Table 3.5 shows the required removal rates of heavy metals from coal ash to ensure the remaining coal ash would pass the leaching test. Note the required removal rates are less than the 97% metal removal rate for the supercritical extraction process for all metals except lead and chromium. If the content of all metals of concern could be sufficiently reduced, the processed coal ash could be classified as non-hazardous waste.

Table 3.2.1. Leaching results and toxicity characteristics for heavy metals found in coal ash, many including cadmium, chromium, lead, and selenium are above the maximum concentration limits allowed by regulation (EPA 2009).

	Mercury		Antii	nony	Ars	enic	Bar	ium	Во	ron	Cadn	nium
	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
Total in Material (mg/kg)	0.01	1.5	3	14	17	510	590	7000	NA	NA	0.3	1.8
Leach Results (ug/L)	0.01	0.5	0.3	11000	0.32	18000	50	670000	210	270000	0.1	320
Toxicity Characteristics (ug/L)	L) 200		- 5000		100	0000		-	10	00		
Max Conc Limit (ug/L)		2		5	1	.0	20	000	7000	DWEL	۵,	5
	Chromium		Cobalt		Le	ad	Molyb	denum	Sele	nium	Titar	nium
	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
Total in Material (mg/kg)	66	210	16	66	24	120	6.9	77	1.1	210	0.72	13
Leach Results (ug/L)	0.3	7300	0.3	500	0.2	35	0.5	130000	5.7	29000	0.3	790
Toxicity Characteristics (ug/L)	50	000		-	50	000		-	10	000	-	
Max Conc Limit (ug/L)	1	00		-	1	.5	200 [DWeL	5	50	2	2

Table 3.2.2. Concentrations in fly ash, Total Characteristic Leaching Protocol (TCLP), Total and Soluble Threshold Limit Concentrations (TTLC/STLC), and Required Removal Rate to pass leaching test.

	Fly Ash	Bottom Ash	TCLP	STLC	TTLC	Req Re	moval Rate
	mg/kg	mg/kg	mg/l	mg/l	mg/kg	Fly Ash	Bottom Ash
antimony	16	BDL		15	500	6%	
arsenic	260	21	5	5	500	98%	76%
barium	5100	3600	100	100	10,000	98%	97%
beryllium	2.6	14		0.75	75	71%	95%
cadmium	3.7	BDL	1	1	100	73%	
chromium	300	1100	5	5	2500	98%	100%
cobalt	502	92		80	8000	84%	13%
copper	220	120		25	2500	89%	79%
lead	230	53	5	5	1000	98%	91%
mercury	0.51	0.07	0.2	0.2	20	61%	
molybdenum	60	27		350	3500		
nickel	230	440		20	2000	91%	95%
selenium	18	4.2	1	1	100	94%	76%
silver	17	15	5	5	500	71%	67%
thallium	45	BDL		7	700	84%	
vanadium	329	289		24	2400	93%	92%
zinc	680	370		250	5000	63%	32%

Using output values supplied by the University of Wyoming based on their process, the RIT team conducted a life-cycle assessment using the inventory analysis and use these results to inform a robust waste management plan. These results can be compared to environmental impact results of REE mining and production that have inventories available for examining a variety of endpoints (Hurst 2010, Paul and Campbell 2011, Tharumarajah and Koltun 2011, Morf, Gloor et al. 2013). The functional unit of kg REE produced will be used for comparison, see Section 5.

Radioactive Elements in Coal Ash

Potential concerns with the radioactivity of process products were scoped. There are radioactive elements present in coal and further concentrated in coal ash (Lauer, Hower, Hsu-Kim, Taggart, & Vengosh, 2015). Among these, uranium-238 (U-238) and thorium-232 (Th-232) are stable isotopes of naturally occurring uranium and thorium in the Earth's crust and present in enriched levels in coal ash (Table 3.2.2) (Peterson et al., 2007). These materials are radioactive and their radioactivity levels (specific activity) can be measured in both coal and coal combustion residuals (CCRs). The average activity of Th-232 and U-238 in the Earth's crust is presented below (Table 3.2.3). Additionally, for the Appalachian, Illinois, and Powder River coal regions, the mean and range value of radionuclide activity for U-238 and Th-232 are calculated by Lauer et al. (Table

3.2.4). These measurements are then used to calculate how much larger the radioactivity levels are in the ash versus the average levels throughout the Earth.

	²³² Th	²³⁸ U
Half-life (billion years)	14.05	4.468
Upper continental crust		
Activity (Bq/kg)	43	35

Table 3.2.3 Half-lives and Specific Activity of natural radionuclides (Aubrecht, 2003)

Table 3.2.4 Mean and Range Value of Radionuclide Activity in Coal and Coal Combustion Residuals (CCRs) (Bq/kg) (Lauer et al., 2015)

	Sample #	Th-232			U-238		
		Mean	Rai	nge	Mean	Rar	nge
Appalachian	n		Low	High		Low	High
coal	3				20	18	21
CCRs	14	112	79	131	171	131	248
Illinois							
coal	5				30	23	43
CCRs	28	67	49	81	228	135	341
Powder River							
coal	3				12	6	21
CCRs	12	86	80	96	114	85	142

When compared to the occurrence of U-238 and Th-232 in the Earth's crust, both U-238 and Th-232 have larger concentrations in coal ash. As ratios (Table 3.2.5), the concentration of U-238 and Th-232 for all three regions where these elements were measured are larger than one, indicating that the concentrations of U-238 and Th-232 in coal ash are larger than they are in the Earth's crust. If a spill occurs or if humans are subjected to these radioactive materials that are left over in the waste ash, they will experience higher doses of radiation than compared to what they can expect in their daily lives based on the natural occurrence of these materials alone.

Table 3.2.5 Ratio of Radioactive Elements in CCRs to Crustal Occurrence

	Appalachian	Illinois	Powder River
Th-232	2.60	1.14	2.23
U-238	4.89	3.86	4.06

While the potential for radioactivity is present, large scale regulations targeting coal ash are not currently in place and organizations in the United States including the Environmental Protection Agency (EPA) consider the amount of radioactive materials in coal ash to be small enough such that no regulations need to be enacted (EPA, 2016). On a broader term, the EPA has established regulations for the accidental release of Uranium to the environment and considers waste releases that contain .1 curie (Ci) of radioactivity be reported and cleaned up. For Thorium, the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) established that should a release of Thorium (designated a hazardous substance) occur that was greater than 3.7E+7 becquerel (Bq), the people in charge should report the incident to the National Response Center. These two reportable thresholds for U-238 and Th-232 are used to identify whether the thorium and uranium present in the waste ash after extraction of the REE from 1 ton of coal ash are large enough in quantity such that their radioactivity poses a concern for environmental and human health. The mean radioactivity levels of CCRs for the three regions stated above are tested. Both the thorium and uranium that are present in the waste of the ash are well below the reportable limits and should pose limited concern among interested stakeholders (Table 3.2.6) (Table 3.2.7).

	Table 3.2.6	CERCLA	Reportable	Radioactivity	Levels for	1 ton of Ash
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	Thorium in Ash (kg)	Radioactivity (Bq)	CERCLA Reportable Level (Bq)	Region
Th-232	0.00054	0.06	3.70E+07	Appalachian
		0.04	3.70E+07	Illinois
		0.05	3.70E+07	Powder River

	Uranium in Ash (kg)	Radioactivity (Bq)	Radioactivity (Ci)	EPA Reportable Level (Ci)	Region
U-238	0.00018	0.03078	8.32E-13	0.1	Appalachian
		0.04104	1.11E-12	0.1	Illinois
		0.02052	5.55E-13	0.1	Powder River

Subtask 3.3: Compare the Proposed Technology with other Advanced REE Extraction and Recovery Technologies

Two sets of work assessing alternative technologies were done in this subtask. In the first, two technologies were selected for detailed process modeling: Super critical extraction with tributylphosphate (TBP) and acid leaching. The technologies are summarized below and preliminary results on material flows and economic estimations appear in subtasks 3.4, 3.5, and 3.7.

In the second set of work, analysis was begun on an alternative source of REEs in addition to coal ash: recycling of waste electronics. REE content in electronics waste and recycling technologies are summarized in this section.

Super critical extraction with tributylphosphate (TBP):

Kermer, et al., 2016 conducted an extensive study comparing different methods of extracting metals from lignite ash in Germany. In order to enrich, separate and mobilize valuable substances from the lignite ashes, mechanical and thermal pre-treatment methods as well as chemical and biological leaching approaches were applied. Mechanical ash pre-treatment provided enriched fractions but still suffered from low yields. Thermal ash processing showed multiple significant phase changes compared to original ash. Extraction with SC-CO₂ and chemical leaching (using aqueous HCl) of untreated and thermally treated ash provided high extraction for the metals like Al, Ca, Fe, Mg, etc. Highest values were obtained with thermally treated ash.

One of the early examples of extraction of rare earth elements using super critical materials can be seen in the works of Kayo Sawada. He experimented with the use of tributylphosphate (TBP) Complex with HNO₃ and H₂O in Supercritical CO₂ for the extraction of Uranium from UO₂ powder (Sawada, et al., 2005). The TBP complex was mixed with UO₂ powder in SF- CO₂ at 25 MPa, 323 K. It was found that UO₂ reacted with HNO₃ contained in the TBP complex at a HNO₃/U ratio of approximately 4:1. The TBP complex seems to form a reversed micelle structure in SF-CO₂, and that the chemical stoichiometry of UO₂ dissolution depends on the concentration of HNO₃ in the water cores in the complex. In designing a SFE process, the dissolution stoichiometry of one mole of uranium reacting with four moles of HNO₃ can be used to describe the overall dissolution of UO₂ using the TBP complex in SF-CO₂.

For super critical extraction with TBP, two scenarios were designed. The chemical to REE oxide ratio was obtained based on data from Shimizu et al, 2005 for one and Samsonov, et al., 2007 for the other. These two studies were referred to in particular as the sample they used to extract REEs from had the most number of REEs in comparison to other studies.

Shimizu, et al., 2005 experimented with extraction of REEs from wastes from luminescent materials, i.e. in fluorescent bulbs. Y, Eu, La, Ce and Tb were the major elements identified in the sample, and the contents were 29.6, 2.3, 10.6, 5.0 and 2.6 wt%, respectively. REEs amounted to 50% of the luminescent material by weight. Y and Eu were present as oxides, whereas La and Ce were present as phosphates. The reactant was a combination of TBP-HNO₃-H₂O. The study experimented with two molecular ratios of TBP:HNO₃:H₂O in the reactant complex. The ratio in complex A was 1.0:1.8:0.6 while that in complex B it was 1.0:1.3:0.4. Since complex B provided higher yields, the industrial scale model assumes inputs as per complex B. Other experimental parameters have been summarized in table 3.3.1.

Reactant (Complex B)	2	cm ³
Luminescent material	20	mg
Temperature	333	Κ
Pressure	15	Мра
Extraction time	120	Mins
CO ₂ flow	2	cm ³ /min

Table 3.3.1: Experimental parameters, Shimizu, et al., 2005

The dissolution yields of Y, Eu, were >99, >99 respectively, while that for La, Ce and Tb were <7% each.

Samsonov, et al., 2007 experimented with the extraction of actinides from the mixture of their oxides. The sample consisted of UO₂, PuO₂, Eu₂O₃ and AmO₂ in the ratios 6.14:2.2:0.4:0.004. The extraction efficiency for the four metals were 89.6, 93.1, 91.0 and 88 percent respectively. This study also used TBP-HNO₃ as a reactant and tried three complexes with molar ratios of TBP:HNO₃ being (1) 1:3, (2) 1:8 and (3) 1:12. The best results were obtained when using complex with TBP:HNO₃ molar ratio of 1:12 and that is what was used in the techno-economic model. The actinide to complex molar ratio was approximately 1:20. Other parameters have been listed in table 3.3.2

Reactant (Complex 3)	828	mg*
REE oxides	8.7	mg
Temperature	333	Κ
Pressure	25	Mpa
Extraction time	90	Mins
CO ₂ flow	0.5	cm ³ /min
* 0 1 1 1 1 1 1	a 0 1	

Table 3.3.2: Experimental parameters, Samsonov, et al., 2007

*Calculated based on 1:20 molar ratio

Given the temperature and pressure, the density of CO_2 was assumed to be 0.662 gm per cm³ (Zorca, et al., 2007).

Acid leaching to recover REEs from coal ash

Acid leaching is often used in the extraction of REEs from their ores. In China, extraction processes use a vessel or heap leaching and are often accomplished in situ (Chi, Xu, Yu, & He, Resources and exploitation of rare earth ore in China, 2013). The REEs in the leach solution can then be precipitated through the addition of oxalic acid or ammonium bicarbonate. Digesting the ores in sulfuric and/or hydrochloric acid destroys the fluorocarbonate matrix and REEs are converted to their sulfates or chlorides. If REEs are in sulfate form, they are converted to hydroxides by digestion in a strong caustic solution. Hydroxides are subsequently dissolved in hydrochloric acid. Once REEs are in chloride form, they are separated by solvent extraction. The Molycorp process and the Goldschmidt Process are examples of acid leaching. The acid leaching process is usually used for extraction from bastnasite, monazite, and xenotime where the ores are in the form of flurocarbonates (Peiro & Mendez, 2013).

Peiro and Mendez has published an extensive literature review of various leaching processes and their yields. The REEs contained in bastnäsite, are extracted by roasting with 98% sulfuric acid at 500°C in a rotary kiln. Monazite concentrate is alkali treated. Roasting, mostly used for sulfidic sources of metals, is one of the most important and the most complex of all the pyrometallurgical unit operations. This process is carried out by heating the sulfides in air or in oxygen. A sulfide ore or concentrate is roasted to: (I) oxidize partially the sulfur content; (II) oxidize to sulfates, also regarded as sulfation roasting; and (III) remove completely sulfur by converting all sulfur to oxides. The energy requirement of this process is estimated to be 0.20–0.27 GJ/ton of bastnäsite (Peiro & Mendez, 2013).

REE from waste electronics

Rare earth elements (REE) can be recycled from end of life products and research in the techniques and potential to do so has been increasing in recent years. According to Binnemans et al.(Binnemans, Jones et al. 2013), permanent magnets, nickel-metal hydride batteries, and lamp phosphors are applications with major sources of REE's given their use in electric vehicles, hard disc drives, and fluorescent lamps. Additionally, CRT phosphors, catalysts, polishing powders, and glasses are briefly discussed as sources of REE's. From Buchert et al. (Buchert, Manhart et al. 2012), electronic waste materials including LCD television screens and computer monitors, LED's, smartphones, as well as notebooks have the potential to be sources of REE recycling. Among notebooks in Germany, a myriad of REE are present including 15,159 kilograms of neodymium in all German notebooks sold in 2010. Additional REE also include praseodymium and dysprosium at 1,945 and 426 kilograms respectively for notebooks sold in Germany in 2010. Smartphones also have a significant amount of neodymium and praseodymium at 385 kilograms and 77 kilograms in all smartphones sold in Germany in 2010. With efficient collection and recovery methods these sources of REE could be substantially important to overall REE supply.

Technologies and techniques of rare earth element recycling are varied. When recycling REEs from end of life fluorescent lamps, lamp phosphors can be directly reused and repurposed or to acquire purer rare earth oxides, hydrometallurgical techniques can extract REE from the phosphors(Binnemans and Jones 2014). In rare earth magnets, REE that come from hard disk drives can be selectively grounded, concentrated, and collected. Further magnetic and electrostatic techniques may be applied to separate different metallic elements. A hydrometallurgical process is then used to further separate the REE(Tanaka, Oki et al. 2008, Binnemans and Jones 2014). A further technique includes the usage of hydrogen at atmosphere pressures to separate the magnets in hard disk drives and produce a powder of NdFeB which can then be used in other products(Binnemans and Jones 2014). Pyro metallurgical techniques are also available for the extraction of REE. Some of these techniques include melting and extraction of REE that are in a metallic state(Binnemans and Jones 2014). An electroslag procedure is also used when high amounts of clean scrap(Binnemans and Jones 2014). REE can also be extracted through liquid metal extraction in a process which dissolves rare earth alloys in liquid alloy system(Binnemans and Jones 2014). Lastly, the glass slag method brings REE in contact with a molten flux that can dissolve REE from alloys which then supercool to glass(Binnemans and Jones 2014). While these

techniques and methods are not exhaustive, they do contain a broad summary of REE recycling techniques from end of life products.

Subtask 3.4: Perform ASPEN Process Model Simulations

The work in this subtask for the period is simulation of process energy and material flows for extraction of REEs from coal ash using Supercritical Extraction with PS. REE input and output assumes using coal ash with maximum value among global samples...

Mass Balance for PS enhanced with CO2:

Material and energy inputs for processing one ton of coal ash is shown in table 3.4.1. Although heavy metals can also be extracted using super-critical CO_2 , they require a different ligand and not PS used in this case (Halili, et al., 2015; Kermer, et al., 2016). It is therefore assumed that heavy metals do not get picked up in this process.

Process materials	Input	Extraction efficiency	Process materials	Output	Emission/Waste	
REE laden ash (tons)	1.0		Soluble REEs	0.0001	Leftover Ash	~0.5
CO_2 (tons)	3	99%	CO ₂	2.97	CO ₂	0.03
5% PS (tons)	15	0	PS	-	PS	-
Oxides (tons)	0.95	~10%	Oxides	0.1	Oxides	0.85
REE (grams)	924	24% to 100%	REE	660	REE	264
Heavy Metals (grams)	46.7	0%	Heavy Metals	0	Heavy Metals	46.7

Table 3.4.1: Inputs and outputs for processing one ton of coal ash with PS

In table 3.4.1, inputs are all the materials going into the process, outputs are all usable materials obtained and emission/waste are all the material that are not used. Every ton of coal requires 3 tons of CO₂ (99% of which is recycled) and 15 tons of 5% PS. The REEs react with the PS to form soluble REEs. REEs are to be collected and CO₂ is to be captured and recycled for the next batch. It is assumed that there is a leakage of 1% in every cycle. Heavy metals and other oxides remain with the coal ash which may then be discarded but is more often used for other value added applications such as filler for cement and concrete. The overall extraction efficiency of REEs is 75%.
Mass balances of Super-critical Extraction with TBP

The detailed inputs and outputs for processing one ton of coal ash as per Shimizu et al, 2005 is shown in table 1.4.2. Although heavy metals can also be extracted using super-critical CO_2 , they require a different ligand and not TBP-HNO₃ complex used in this case (Halili, et al., 2015; Kermer, et al., 2016). It is therefore assumed that heavy metals do not get picked up in this process.

Table 3.4.2: Inputs and outputs for processing one ton of coal ash using TBP, as per Shimizu etal, 2005

Process	Input	Extraction	Process	Output	Emission/Waste	
materials	mput	efficiency	materials	Supur		
REE laden ash			REE(NO ₃)			
(tone)	1.0		with TBP	0.42	Leftover Ash	~1
(tons)			Complex			
SC-CO ₂ (tons)	23.7	99%	CO_2	23.5	CO ₂	0.24
TBP (tons)	0.3	0	TBP	-	TBP	-
HNO ₃ (tons)	0.1	0	HNO ₃	-	HNO ₃	-
H ₂ O (Tons)	0.0	0	H ₂ O	-	H ₂ O	-
Oxides (tons)	0.95	0	Oxides	0	Oxides	0.95
REE (grams)	934	7% to 99%	REE	465	REE	469
Heavy Metals	467	0%	Heavy Metals	0	Heavy Metals	467
(grams)	+0.7	070	neuvy wietuis	0	ficut y filetais	10.7

In Table 3.4.2, inputs are all the materials going into the process, outputs are all usable materials obtained and emission/waste are all the material that are not used. Every ton of coal requires 23.7 tons of CO₂ (99% of which is recycled) and 400 kg of TBP-HNO₃-H₂O complex. The REEs react with the Nitric acid to form REE(NO₃).TBP. REE (NO₃).TBP along with SC-CO₂ is sent to the collection chamber. Once the pressure is released, the CO₂ vaporizes and it is captured and recycled for the next batch. It is assumed that there is a leakage of 1% in every cycle. The REE(NO₃) and TBP is collected for further processing (listed under output). Heavy metals and other oxides remain with the coal ash which may then be discarded. The extraction efficiency of different REEs varies between 7% and 99%. Cerium is the most abundant REE contributing to around 33% by weight. Cerium oxide however has poor solubility in the TBP complex and only 7% is captured.

Findings from analyzing the process according to Samsonov et al. 2007, been summarized in table 3.4.3, were similar.

Process	Input	Extraction	Process	Outpu	Emission/Waste	
materials		efficiency	materials	t		
REE laden ash (tons)	1		REE(NO ₃) with TBP Complex	0.05	Leftover Ash	~1
SC-CO ₂ (tons)	5.09	99%	CO ₂	5.04	CO ₂	0.05
TBP (tons)	0.03	0	TBP	-	TBP	-
HNO ₃ (tons)	0.01	0	HNO ₃	I	HNO ₃	-
H ₂ O (Tons)	0.00	0	H ₂ O	-	H ₂ O	-
Oxides (tons)	0.95	0	Oxides	0	Oxides	0.95
REE (grams)	934	7% to 91%	REE	580	REE	353
Heavy Metals (grams)	46.7	0%	Heavy Metals	0	Heavy Metals	46.7

Table 3.4.3: Inputs and outputs for processing one ton of coal ash using TBP, as per Samsonov et

al, i	2007
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Scaling up of this process revealed that it used less reagents per ton of coal ash in relation to Shimizu et al, 2005. This process therefore incurs a lower reagent bill. Processing time is also lower at 1.5 hours compared to 2 hours for Shimizu et al, 2005 thereby increasing the ash processed per year.

Mass balances of acid leaching

In this study, six scenarios for leaching processes were taken from Peiro and Mendez, 2013. The study is a literature review and compiles data from several sources. The quantities of chemical reagents and the yield for each process to treat a ton of bastnasite was obtained and the same amount was applied per ton of coal ash to ascertain the reagent usage for processing a ton of coal ash (S/F constant).

The input-output tables for each process are summarized in Tables 3.4.4- 3.4.9 (Peiro & Mendez, 2013).

Table 3.4.4: Mass balance for acid leading of one ton of REE from Bayan-Obo China (yield =

Chemical	Formula	Input	Output
Bastnasite	RECO ₃ F	5.97	1.31
Sulfuric acid	H_2SO_4	4.41	0.97
Sodium chloride	NaCl	12.32	11.52
Sodium hydroxide	NaOH	1.64	0.36
Hydrochloric acid	HCl	1.17	0.26
Water	H ₂ O	1.9	3.47
Hydrofluoric acid	HF		0.47
Sodium sulfate	Na ₂ SO ₄		3.03
RE sulfate	$RE(SO_4)_3$		1.36
RE disulfate	RE2(SO4)3.Na2SO4.12H2O		1.34
RE hydroxide	RE(OH) ₃		0.4
RE chlorides	RECl ₃		2.92
Total		27.41	27.41

80%) (Peiro & Mendez, 2013)

Table3.4.5: Mass balance for acid leading of one ton of REE from Molycorp Process (yield =

Chemical	Formula	Input	Output
Bastnasite	RECO ₃ F	1.95	0.16
Hydrochloric acid	HCl	1.35	0.44
Sodium hydroxide	NaOH	0.33	0.03
RE fluorides	REF ₃		0.08
RE hydroxides	RE(OH) ₃		0.03
Water	H ₂ O		0.29
Sodium fluoride	NaF		0.32
Carbon dioxide	CO ₂		0.4
RE chlorides	RECl ₃		1.89
Total		3.63	3.63

92%) (Peiro & Mendez, 2013)

Table 3.4.6: Mass balance for acid leading of one ton of REE from Goldschmidt Process (yield =

Chemical	Formula	Input	Output
Bastnasite	RECO ₃ F	2.56	0.08
Chlorine	Cl ₂	2.44	1.55
RE fluorides	REF ₃		0.74
RE chlorides	RECl ₃		1.89
Oxygen	O ₂		0.2
Carbon dioxide	CO ₂		0.55

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Table 3.4.7: Mass balance for acid leading of one ton of REE from direct chlorination (yield =

Chemical	Formula	Input	Output
Bastnasite	RECO ₃ F	2.73	0.25
Chlorine	Cl ₂	1.58	0.7
RE fluorides	REF ₃		0.74
RE chlorides	RECl ₃		1.89
Oxygen	O ₂		0.2
Carbon dioxide	CO_2		0.55
Total		4.32	4.32

91%) (Peiro & Mendez, 2013)

Table 3.4.8: Mass balance	for acid leading	of one ton of REE	from direct alka	li treatment

Chemical	Formula	Input	Output
RE phosphate	REPO ₄	2.21	0.22
Sodium hydroxide	NaOH	1.23	0.12
Nitric acid	HNO ₃	1.94	0.37
RE hydroxides	RE(OH) ₃		0.16
Trisodium phosphate	Na ₃ PO ₄		1.52
RE nitrate	$RE(NO_3)_3$		2.55
Water	H ₂ O		0.45
Total		5.39	5.39
Total		5.39	5.39

developed by Rhone-Poulenc (yield = 85%) (Peiro & Mendez, 2013)

Table 3.4.9: Mass balance of the extraction of 1 ton of REE using acid treatment (Peiro &

	-		
Chemical	Formula	Input	Output
RE phosphate	REPO ₄	2.92	0.44
Sulfuric acid	H_2SO_4	7.58	7.33
Oxalic acid	$H_2C_2O_4$	1.83	0.51
Phosphoric acid	H ₃ PO ₄		1.13
RE sulfate	$RE_2(SO_4)_3$		0.46
RE oxalate	$RE_2(C_2O_4)_3$		0.37
RE oxides	RE ₂ O ₃		1.2
Carbon dioxide	CO ₂		0.55
Carbon monoxide	СО		0.35
Total		12.33	12.33

Mendez, 2013)

Subtask 3.5: Calculate Capital, Operating and Maintenance Costs

Costs

The calculation of cost in this part is based on annual production of 1000 tons REE oxides with 75% purity. Cost consists of capital cost, operational cost of extraction and impurity removal, operational cost of separation and other costs. The cost of a movable extractor for PS enhanced with CO₂ process is assumed to be \$500,000 while the reactor for PS without CO₂ process is \$100,000 per unit. The capital cost for extraction reactors are \$25,000,000 and \$5,000,000, respectively for the two extraction methods (with/without CO₂). The operational cost of extraction and impurity removal is \$322,048,044 for the enhanced process and \$327,526,423 for the PS only extraction. The cost of separation is \$1,918,000 for both methods. Other cost including power, calcination, labor, packaging, wage, depreciation, transportation is estimated at \$1,242,000 for both process. For detailed calculation and assumptions, please see Table 3.5.1-3.5.4.

3.5.1 Capital cost for PS leaching enhanced with/without CO₂. Depreciation is assumed to be 20 years.

PS+CO ₂	Unit #	\$/unit	Total \$
Extraction Tanks (8,000 Gallon)	50	500,000	25,000,000
Separation stages (9 circuits)	835	5,800	4,843,000
Grand total \$			29,843,000
Depreciation \$/yr./ton REEOs, based on 20 years			1,492
PS	Unit #	\$/unit	Total \$
Extraction Tanks (8,000 gallon)	50	100,000	5,000,000
Separation stages (9 circuits)	835	5,800	4,843,000
Grand total \$			9,843,000
Depreciation \$/yr./ton REEOs,			492
based on 20 years			

3.5.2 Operational cost of extraction and impurity removal for PS leaching enhanced with/without CO₂.

PS+CO ₂	Annual Consumption (ton)	\$/ton	\$/annum	\$/ton
5% PS	14,810,911	20	296,218,216	296,218
CO ₂	49,370	460	22,710,063	22,710
OA	8,333	140	1,166,667	1,167
NH ₄ Cl	12,931	100	1,293,098	1,293
Water	500,000	1.32	660,000	660

Grand total \$			322,048,044	322,048
PS	Annual Consumption (ton)	\$/ton	\$/annum	\$/ton
5% PS	16,220,333	20	324,406,659	324,407
CO ₂	-	-	-	-
OA	8,333	140	1,166,667	1,167
NH4Cl	12,931	100	1,293,098	1,293
Water	500,000	1.32	660,000	660
Grand total \$			327,526,423	327,526

3.5.3 Operational cost of separation for both PS leaching enhanced with/without CO₂.

	Annual Consumption (ton)	\$/ton	\$/annum	\$/ton
HCl (31%)	8,000	70	560,000	560
MP507K	20	2,400	48,000	48
NaOH	2,700	200	540,000	540
OA	1,100	700	770,000	770
Grand total \$			1,918,000	1,918

3.5.4 Other costs for both PS leaching enhanced with/without CO₂.

	\$/annum	\$/ton
Power	52,000	52
Calcination	42,000	42
Labor	200,000	200
Packaging	15,000	15
wage	200,000	200
Depreciation	33,000	33
Transportation	700,000	700
Grand total \$	1,242,000	1,242

Input costs – materials and energy

The assumed cost of various inputs and reagents has been summarized in table 1. The model assumes that PS may be bought from the market or acquired from secondary sources at a reduced price. It is assumed that the processes would take place in a state dominated by coal power. The fuel price in Wyoming is therefore chosen for this example.

The cost of materials is obtained by combining the required quantities of materials and energy inputs from table 3.5.5

Item	Price	Unit	Source
Water	\$5.00	/1000	https://www.chovonposity.org/Indox.conv2NID-044
water	\$3.00	gallon	https://www.cheyennecity.org/index.aspx?INID=944
Electricity	\$77.6	/MWh	https://www.eia.gov/electricity/state/wyoming/
Liquid CO ₂	\$460	/ton	(del Valle, et al., 2005)
DC	\$20	/ton	If obtained from secondary sources. Quote from
гэ	\$20	/1011	University of Wyoming

Table 3.5.5 Material and energy prices

Based on the data, an excel based model was developed to evaluate the economic viability, material flow and emissions should the process be expanded to an industrial scale. The results are shown in Subtask 3.7.

Subtask 3.6: Analyze Market Demand and Pricing for REEs and other Recovered Value Added Elements

Rare earth elements (REEs) are widely demanded due to varying applications in clean energy technologies, electronics, healthcare, and defense (Romans 2008, Bauer, Diamond et al. 2010, E.C. 2010, Moss, Tzimas et al. 2011). Consumption of rare earth oxides (REOs) in the United States has varied greatly over the last decade, due in part to significant manufacturing recessions during this period (Figure 3.6.1).



Figure 3.6.1 Estimated rare earth oxide (REO) consumption in the United States, estimated as some data is withheld due to low number of producers (USGS 2016)

Estimates of global REE demand show an increase in consumption, however, worldwide demand was approximately 105,000 metrics tons in 2011 with a prediction for about 160,000 metric tons by 2016 (Hatch 2012). The major sectors driving this demand are permanent magnets, metal alloys, catalyst, and polishing powders. A majority of global demand comes from China (68%) followed by Japan and Southeast Asia (16%) shown in Table 3.6.1.

End Use	China	USA	Japan & SE Asia	Others	Total
Permanent Magnets	16500	500	3500	500	21000
Metal Alloys	15000	1000	4000	1000	21000
Catalysts	11000	5000	2000	2000	20000
Polishing Powders	10500	750	2000	750	14000
Phosphors	5000	500	2000	500	8000
Glass Additives	5500	750	1000	750	8000
Cermaics	3000	1500	2000	500	7000
Other	3500	500	1500	500	6000
Total Demand	70000	10500	18000	6500	105000
Market Share	68%	10%	16%	6%	100%

Table 3.6.1. Global estimates of demand for REOs in 2011(Hatch 2012)

World production in the last decade has become quite concentrated in China as shown in Figure 3.6.2 Some estimates of REE production suggest that China produces as much as 97% of the rare earth elements that are available through new production. Export quotas imposed by China in 2009/2010 reduced exports by as much as 40% and cause concern about future supply disruptions (Massari and Ruberti 2013). Demand projections will need to consider the functional needs of the competing application sectors as detailed in Tables 3.6.2 and 3.6.3 for these materials.



Figure 3.6.2 Global REO production showing a concentration in China(Bleiwas and Gambogi 2013, Gambogi 2013, Gambogi 2014, Van Gosen, Verplanck et al. 2014).

Table 3.6.2. REE common applications or products(Du and Graedel 2011, Du and Graedel 2013, Peiró, Méndez et al. 2013, Hubler 2016, Voncken 2016)

Element	Symbol	Applications
Yttrium	Y	Alloys; red phosphors for flat screens and lighting (liquid crystal
		display (LCD), light-emitting diodes (LEDs); camera lenses (as a glass
		additive for heat and shock resistance); microwaves; and radar
Lanthanum	La	Alloys; battery alloys (nickel-metal-hydride (NiMH) as LaNiH); auto
		catalysts (catalytic converters for internal combustion vehicles); fluid
		cracking catalyst (FCC); glass additive (improves optical properties);
		ceramic superconductors; polishing powder
Cerium	Ce	Polishing powder; fluid cracking catalyst (FCC); automotive catalytic
		converters; glass additive (reduces rate of discoloration); alloy
		(primarily misch metal used as flint in lighters and torches); ceramic
		coatings; cathodes for solid-oxide fuel cells; capacitors; semi-
		conductors; and more
Praseodymiu	Pr	Alloy (misch metal, magnesium for aircraft industry); glass additive
m		(pigmenting, blocks infrared radiation); auto catalyst (catalytic
		converter); batteries; magnets; ceramics; polishing powder
Neodymium	Nd	Permanent magnets (neodymium-iron-boron magnets (NdFeB), see
-		magnet applications below); lasers; auto catalysts (catalytic
		converters)
Samarium	Sm	Magnets (samarium-cobalt (SmCo)); calibration material for
		spectrophotometer wavelengths; reducing reagent; defense
		applications (neutron absorber for nuclear reactors, lasers, capacitors)
Europium	Eu	Primarily used as a phosphor (for blue coloring in flat screen monitors,
		televisions, lighting, etc.); defense applications (nuclear control rods,
		lasers)
Gadolinium	Gd	Magnets and magnet alloys (magnetic cooling, magnetic resonance
		imaging (MRI machines)); red phosphors; nuclear reactor shielding;
		defense applications (computer storage devices, semiconductors and
		electron tubes, magnetic and optical recording devices)
Terbium	Tb	Solid-oxide fuel cells; green phosphors; luminescent materials; lasers
		(defense application)
Dysprosium	Dy	Magnets (neodymium-iron-boron (NdFeB) magnet additive); defense
		applications (nuclear control rods, ceramics for electronics)
Others:	Sc	Alloys (aluminum); metal halide light bulbs; petrochemical (oil
(Scandium,		refining); aircraft parts and equipment (defense application)
Promethium,	Pm	Used almost exclusively in research, not found in nature, used for
Holmium,		producing X-rays
Erbium,	Но	Nuclear reactors; magnetic flux concentrator; lasers (medical and
Thulium,		dental applications (safe to the human eye)); semiconductors and
Ytterbium,		electron tubes (defense application)
and Lutetium)	Er	

	Glass additives (photographic filter, safety glasses (for welders and
	glass blowers)); medical and dental lasers, production of nuclear fuel
Tm	rods; alloys; energy wires and cables (defense application)
	Lasers; radar systems; remote sensing; semiconductors and electron
Yb	tubes (defense application)
	Strengthening of steel; electronic devices; very few commercial
Lu	applications; energy wires and cables (defense application)
	Petrochemical (oil refining); energy wires and cables (defense
	application)

Table 3.6.3. End product categories for REE demand(Yoldjian 1985, Hubler 2016, Voncken

2016)

Products	End-Products
Magnets	Electrical and electronic devices (speakers, computer hard disk drives), electric vehicles, wind turbines, magnetic resonance imaging (MRI machines) magnetic cooling
Battery Alloys	Electrical and electronic devices, electric vehicles
Metallurgy (except batteries)	Alloys, steel
Auto Catalysts	Internal combustion engines vehicles
FluidCrackingCatalysts (FCC)	Petrochemical production, catalysts for breaking up long hydrocarbon chains
Polishing Powders (abrasives)	Various glass products and industries
Glass Additives	Various glass products (e.g. camera lenses)
Phosphors	Liquid crystal displays (LCD), plasma panels, lighting
Ceramics	Ceramic products (ceramic tiles, electronic ceramics)
Others	Likely to include lasers and superconductors

Table 3.6.4 shows historical pricing for REE metals not adjusted for inflation. REE prices show high year-to-year volatility, another factor impacting their designation as critical. Sensitivity analysis to price should be conducted for all economic feasibility assessments as large deviations are to be expected, particularly in cases where a supply chain disruption occurs, as is common with low dispersion production as shown previously. The REE prices were calculated as a product of REO prices provided by USGS and stoichiometric multiplier to convert from oxide to the metal.

Metal Prices	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Cerium	38.7	38.7	38.7	38.7	55.3	79.9	79.9	36.9	36.9	122.9	28.3	9.8	6.1
Dysprosium	137.7	137.7	137.7	137.7	172.2	183.6	183.6	195.1	355.8	1836.3	1159.2	619.8	453.3
Erbium	177.5	177.5	177.5	177.5	183.3	189.0	189.0	114.5	189.0	257.7	NA	NA	NA
Europium	1146.3	1146.3	1146.3	1146.3	1157.9	1389.5	1389.5	1852.7	1621.1	3821.2	2825.3	1308.5	951.8
Gadolinium	149.8	149.8	149.8	149.8	161.4	172.9	172.9	172.9	190.2	275.5	106.0	54.2	54.2
Holmium	504.1	504.1	504.1	504.1	744.7	859.3	859.3	859.3	859.3	NA	NA	NA	NA
Lanthanum	27.0	27.0	27.0	27.0	35.2	46.9	46.9	35.2	44.6	117.3	27.0	9.4	5.9
Lutitium	3980.2	3980.2	3980.2	3980.2	3980.2	3980.2	3980.2	2047.0	2501.8	4548.8	NA	NA	NA
Neodymium	33.2	33.2	33.2	33.2	52.5	70.0	70.0	49.0	73.5	314.9	136.5	81.6	73.5
Praseodymium	43.1	43.1	43.1	43.1	58.5	87.8	87.8	44.5	70.2	263.3	134.6	110.0	141.6
Samarium	505.6	505.6	505.6	505.6	465.0	406.8	406.8	151.1	203.4	137.2	72.1	16.3	8.1
Scandium	9204.2	9204.2	9204.2	9204.2	NA	NA	NA	3835.1	5369.1	5675.9	7210.0	7670.2	7670.2
Terbium	629.3	629.3	629.3	629.3	941.1	999.9	999.9	1058.7	1646.9	3235.0	2293.9	1116.4	838.7
Thulium	2627.2	2627.2	2627.2	2627.2	2855.7	2855.7	2855.7	1713.4	1713.4	NA	NA	NA	NA
Ytterbium	387.2	387.2	387.2	387.2	455.5	512.4	512.4	370.1	427.0	512.4	NA	NA	NA
Yttrium	111.8	111.8	111.8	111.8	63.5	63.5	63.5	55.9	63.5	209.6	111.8	31.8	20.3

Table 3.6.4. Historical REE pricing (\$/kg), not adjusted for inflation(USGS 2016). NA = Not available.

Economic feasibility calculations also considered the prices of value added products as detailed in that section. Any comparison of these value-added products will also require comparison to other value added products produced from fly ash however (Figure 3.6.3).



Figure 3.6.3. Quantities of Value added uses of coal ash in the U.S. in 2012

In the following paragraphs, variability in REEs prices and coal ash content are analyzed

to determine the recovery yields needed to meet NETL target and the economic value of recovered REEs.

Figure 3.6.4 compares the total REEs that can be extracted from coal ash between different extraction techniques and the NETL target REEs recovery rate. Low, median, and high represents the range of total REE concentration among 153 samples of coal ash around the world (Moszko et al. 2016, Smolka-Danielowska 2010, Hower et al. 2013, Zhang 2001, and NETL 2016). Physicochemical methods, hydrometallurgical methods, and supercritical CO₂ methods of REE extraction are compared to understand how much REE are necessary to extract to at least fulfill the NETL requirements. The average (Med) REEs recovery rate passes the NETL threshold at 80% and above yields, therefore hydrometallurgical, and supercritical CO₂ methods can extract enough REEs to pass the NETL target, while physiochemical process fails. When looking at the maximum level of REEs extraction, the NETL target is passed at about a 20% yield and all three of the techniques represented in Figure 3.6.4 would be able to extract enough resources.



Figure 3.6.4. Total REE extraction as a function of yield efficiencies for three grades of coal ash (Low = lowest REE content, Med = Median REE content, High= Highest REE content. The dashed lined shows the NETL program target (ppm).

We also group REE coal ash according to economic value contained, obtained by multiplying the content of each REE in one ton by the price of that REE, the average historical

price between 2010 to 2014. Note that this is distinct from characterization by total REE mash, as in the NETL target. The economic value of contained REE was estimated for 153 coal ash samples was calculated, and the lowest and highest value ashes selected for three geographic aggregations: PRB, the U.S. and globally. Note that due lack of availability of data for scandium content in PRB ash, this is approximated with two cases, one with maximum scandium content found in the U.S. data sample (45.9 ppm for Fly ash from Central Appalachian coal) and a second with the minimum (4.2 ppm from a bottom ash sample) (NETL 2016).

The results for ranges of REE value for the three geographic regions are shown in Figure 3.6.5. Globally, the variability in REE value can vary between \$30 and \$556 per ton. Japan has the lowest and Poland has the highest REE values. The variability decreases substantially for the Powder River basin coal ash between \$100 and \$394 per ton. The variability in the value is dictated by the elemental prices. Note that the results are sensitive to the content of Scandium, Lutetium and Europium, which have average prices of \$6,720, 3,525 and 2,105 per kg respectively, 1 to 2 orders higher than the other REEs.



Figure 3.6.5. Left. Ranges in total REE value in coal ash by geographic region (\$/ton of coal ash). Right. Value as a function of recovery yield for Powder River basin coal ash

Subtask 3.7: Set up Financial Analysis Model and Perform Financial Analyses

The work in this subtask is estimation of capital and running costs of scaled up extraction of REEs from coal ash using PS enhanced with CO₂. The estimation is based on finding analogous data for other process in industrial situations. These are thus scoping results intended to identify important issues in developing an economically feasible scaled-up process.

As will be seen, using this approach leads to a direct scale-up the laboratory process inputs having costs exceeding the value of REEs contained in coal ash. It is thus important to explore pathways to realize an economically feasible scale-up process. In the models, Sc and other by-products such FeOOH and AlOOH are accounted for revenue. We consider different sets of assumptions for the process parameters, materials prices and process yields. The volume of the extraction tank is 8,000-gallon with daily processing capacity of 10 tons fly ash. A total number of 50 such extraction tanks could reach the output of 1000 tons REE oxides per year (75% purity). Please refer to Section 3.5 for the detailed assumptions. The results of the financial analyses are presented in Table 3.7.1 and 3.7.2 for the two processes. The data are based on the lab scale experiments performed at the University of Wyoming.

PS+CO ₂	tons/annum	\$/ton	\$/annum	\$/ton RREOs
REEOs	1,000	13,950	13,950,000	13,950
Alooh	145,701	2,000	291,402,000	291,402
FeOOH	57,237	2,000	114,474,000	114,474
Sc	36	4,200	150,140	150
Total			419,976,140	419,976

3.7.1 Revenue of REEOs and by-products from PS enhanced with CO₂ process.

3.7.2 Revenue of REEOs and by-products from PS process.

PS	tons/annum	\$/ton	\$/annum	\$/ton RREOs
REEOs	1,000	13,950	13,950,000	13,950
Alooh	137,914	2,000	275,828,000	275,828
FeOOH	62,684	2,000	125,368,000	125,368
Sc	36	4,200	153,191	153
Total			415,299,191	415,299

Based on these assumptions, the percent profit over cost are 28.7% for the enhanced process and 26.9% for the PS only extraction. Table 3.7.3 summarizes the revenue, cost, depreciation, net profit and percent profit over cost for the two approaches.

	PS+CO ₂	PS
Revenue	419,976,044	419,976,044
Cost	325,208,044	330,686,423
Depreciation	1,492,150	492,150
Net profit	93,275,850	88,797,471
Profit/ton REEOs (\$)	93,276	88,798
Profit/ton ash (\$)	56.7	49.3
% profit over cost	28.7	26.9

3.7.3 Profitability of PS enhanced with/without CO2

Subtask 3.8: Summarize Results of Subtasks 3.1 through 3.7 and Develop Recommendations for Technology Optimization

There are many opportunities to reduce process cost and/or increase income in the scalingup development of the PS process. To describe more completely, economic competitiveness depends on an appropriate combination of the following:

- High concentration of REEs in coal ash, preferably close to 1000 ppm with high concentration of the more valuable rare earths like Lutetium, Scandium, Samarium, Terbium and Thulium.
- 2. Development of larger extraction equipment to lower \$/ton capital costs.
- 3. Shortening batch time.
- 4. Lowering energy costs by:
 - Co-locating the facility with a coal electricity plant and using waste heat.
 Heating with natural gas accounts for \$15 per ton of coal ash processed.
 Using waste heat could help eliminating this expense.
- 5. Reducing reagent costs through some combination of:
 - Lower consumption per batch,

- Increased recycling.
- 6. High yield, particularly of high value REEs such as Scandium.
- 7. Higher REE commodity prices.
- 8. Further development of value-added byproducts. Post-processing coal ash can still be used for concrete, cement, structural fills, etc. and byproducts of the extraction process (e.g. FeOOH, AlOOH) are also high value.

Task 4 – Laboratory Scale Leaching, Separation, and De-Watering Tests Experiment setup

A lab-scale supercritical CO₂ extraction set-up has been established at the University of Wyoming and another at the West Virginal University as shown in Figure 4.0.1 (a) and 4.0.2, respectively. The REEs extraction system at UW consists of a liquid CO₂ cylinder (99.99%, with a dip tube inside), a cylinder heating jacket (with maximum heating temperature at 238 °F), a SFT-10 CO₂ pump (with a pressure delivery range of 0 to 10,000 psi and a flow rate range of 0.01 to 24.00 ml/min), a high pressure reactor (including a heating furnace, a 100 mL vessel, a SFT-mag drive mixer, a pressure gauge with a maximum pressure of 10,000 psi, inlet/outlet valves, a back pressure regulator, and a rupture disc), and a RxTrol B Controller (including a vessel heater, two temperature sensors for reactor wall/interior mounting, an open loop agitator, and a speed controller). The set-up at WVU consists of a liquid CO₂ cylinder (99.99%, with a dip tube inside), high pressure generator (Model 87-6-5, with a pressure delivery range of 0 to 5,000 psi and a flow rate range of 0.01 to 60.00 mL/min), a high pressure reactor (including a heating plate, a 100 mL Teflon vessel, a pressure gauge with a maximum pressure of 5,000 psi, a vessel heater with a maximum temperature of 350 °C, inlet/outlet valves, and a rupture disc).

A high temperature (up to 3,000 °C) furnace manufactured by Materials Research Furnace Inc. can be used for de-watering and thermal decomposition (Figure 4.0.1 b). The concentrations of REEs and other inorganic elements in original coal fly ashes, extraction solutions and REEs containing solids have been determined by Perkin Elmer NexION 300S ICP-MS (Figure 2.3.3).



Figure 4.0.1- The equipment used for REEs extraction at UW [a) The lab-scale supercritical CO₂ REE extraction set-up; b) high temperature furnace (Materials Research Furnace) for processing REEs-containing solids]

Initially, the team found that $FeCl_3$ along with supercritical CO_2 -H₂O could be used to obtain the 2% REEs-containing solids. However, realizing that fly ashes contain high concentrations of Fe, thus the team decided to use the Fe resources in fly ashes themselves for assisting REEs extraction. Fe in fly ashes can react with HCl to form FeCl₃. Therefore, HCl along with supercritical CO_2 -H₂O was used for REEs extraction, and the method was successfully used to achieve solid containing 2% REEs.

With the progress of the project, the team has found that PS solutions along with supercritical CO_2 -H₂O show much better performance on overall REE extraction than PS alone although PS solutions do better works than HCl solutions along with supercritical CO_2 -H₂O as reported below or in the following sections. The advantages of using PS for REEs extraction include

- Green
- They are the byproducts of various biomass or biomaterial processing so dependence on environmentally undesired strong inorganic acid in the first step of the overall REEs extraction process can be completely

avoided or the low-value or wasted renewable resources can be used to fully replace the mineral methods vital to state-of-the-art REEs extraction technologies.

- They can be produced from increasingly concerned CO₂ with a number of processes including photocatalysis – with the fact considered, we could eventually fully depend on CO₂ in the first step of the overall REEs extraction process
- PS is biodegradable so the environmental impact of waste containing very low concentration of PS should be minimal.
- Unprecedented desired selectivity
 - PS is the strongest acid found so far to reject the dissolving of the unwanted elements largely contained in fly ashes such as Ca, Si, Al and others in the first step of the overall REEs extraction process, or the dissolving selectivity of the undesired impurities in the first step of the overall PS based REEs extraction process is the lowest.
 - PS is the best candidate to lead to easy precipitation of REEs in the solutions resulting from the first step of the overall REEs extraction process, or the precipitation selectivity of REEs in the solutions resulting from the first step of the overall PS based REEs extraction process is the highest.
- Perfectly unique in its acidity
 - The pHs of the solutions resulting from the first step of the overall PS based REEs extraction process are in the best range in which REEs can be maximally precipitated, or no pH adjustments are needed for the second step of the overall REEs extraction process. This results in
 - Reducing chemical consumption
 - Simplifying the subsequent REEs separation and purification
 - Contributing the reduction of the overall REEs extraction cost.
- Inexpensive
 - o Low-concentration PS solutions are widely available, thus inexpensive

 REEs precipitations from PS based REEs containing solutions do not need citric acid, while REEs precipitations from HCl based REEs containing solutions needs citric acid.

Subtask 4.1 - Determine REE Leaching Rates and Efficiency from Coal Ash

Supercritical CO₂ extraction

Coal fly ashes sampled from five (5) coal-fired electric generation power plants were tested. These five power plants include one at Cherokee in Colorado and four at Dave Johnston, Dry Fork Station, Laramie River Station, and Wyodak in Wyoming. All of them use PRB coal. All the coal fly ashes were characterized for their concentrations of moisture and organic carbon as well as total REEs according to the methods described in file "Copy of REE Research Database Template_08_22_2016 (version 1)". All the aqueous samples were analyzed by ICP-MS (Perkin Elmer NexION 300S ICP-MS) following the guideline of "USGS Open File Report 02-223-K". The results are presented in Table 4.1.1.

Table 4.1.1 Total REEs of coal fly ashes from 5 power plants [CH: Cherokee; DJ: Dave Johnston; FS: Dry Fork Station; LR: Laramie River Station; LR-1 and LR-2 designate samples received from different times; WD: Wyodak; DMB: dry mass basis; DAB: dry ash basis].

	Lanthanides + Y			Lanthanides only			
	As received	DMB	DAB	As received	DMB	DAB	
Ashes	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	
СН	500.5	502.6	512.4	440.1	442.0	450.6	
DJ	429.7	459.7	480.2	371.0	397.0	414.7	
FS	498.5	502.7	517.8	429.0	432.6	445.6	
LR-1	498.7	500.5	503.6	430.7	432.3	435.0	
LR-2	560.2	560.7	563.1	483.9	484.2	486.3	
WD	537.0	543.7	561.0	463.8	469.6	484.6	

Extraction procedure using HCl solution

A loading ratio of three (3) g ash per thirty (30) ml of Nano-pure water was used throughout the tests. The ash-water mixture/liquor was placed in the chemical reactor (Figure 4.1). The liquid CO_2 was pumped into the reactor at a rate of 2.5 ml/min after it was sealed to a pressure of 1,000/3,000 psi at ambient temperature (~25 °C). The extraction temperature of the reactor was set to 50/100/175 °C and extracted for either two (2) or six (6) hours. The first time when the temperature reached the set point, the pressure was higher. As CO_2 dissolved, the pressure dropped gradually and stabilized when the extraction solution system is saturated with CO_2 . The samples were subsequently filtered and leached with 2% HCl. The leachate was filtered for further measurement or experiments. The results are reported as "as received", "dry mass basis" and "dry ash basis", as shown in Table 4.1.2.

Table 4.1.2 Examples of recovered REEs from the ash of various power plants [CH: Cherokee; DJ: Dave Johnston; FS: Dry Fork Station; LR: Laramie River Station; LR-1 and LR-2 designate samples received from different times; WD: Wyodak; DMB: dry mass basis; DAB: dry ash basis].

	Lanthanides + Y			Lanthanides only		
	As received	DMB	DAB	As received	DMB	DAB
Ashes	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
СН	219.8	220.8	225.0	191.4	192.2	195.9
DJ	324.8	347.6	363.1	276.0	295.3	308.5
FS	368.2	371.3	382.4	311.1	313.8	323.2
LR-1	334.1	335.3	337.4	287.0	288.0	289.8
LR-2	376.4	376.7	378.3	323.1	323.3	324.7
WD	404.4	409.5	422.5	340.0	344.2	355.2

The extraction conditions including temperature (50, 100, 175 °C), initial pressure (1,000, 3,000 psi) and duration (2, 6 hours) were tested. The results are presented in Figure 4.1.1. Each coal ash was undertaken 5 steps extraction by 2% HCl solution after supercritical treatment. The

second step extraction is the most effective one and generates the most concentrated REEs, followed by the third. The first, fourth and five steps extraction are not as effective. The results suggested that the extraction conditions, temperature, initial pressure, and duration have minimal impact on the REEs extraction. The results also have an implication that the acid can be recycled for REEs extraction, as depicted in Figure 4.1.2. The coal fly ash-water mix liquor after supercritical extraction is typically neutral or alkaline and holds great buffer capacity. It requires addition of acids to lower the pH of the ash-water mix liquor before REEs can be solubilized. The first Step acid extraction is basically a process of neutralization, i.e., most of the protons are consumed by the base in the ash. Once the base in the ash is significant reduced, acid extraction is naturally more effective and has higher yields (second step extraction). For the third step or four step extraction, the amount of extracted REEs diminished. But the REEs containing solution has most of the acid unconsumed. The REEs containing acid can be recycled for the next cycle of acid extraction, i.e., the third step or fourth step extraction aliquot is reused as a first step acid to neutralize the newly generated ashes by supercritical CO_2 . The benefits include a) the amount of acid used for REEs extraction can be significantly reduced, by 25% or 33%, depending on which extraction aliquot is reused; b) the concentration of REEs in the first step extraction is increased because the solution contains REEs from the last step extraction of the first ash and the first step extraction of the second ash.



Figure 4.1.1 REEs extraction over temperature, initial CO₂ pressure, and duration. Following the supercritical extraction, each coal ash was treated by 2% HCl solution for five steps. The numbers

for each sample represents the tested condition. For example, 1-50-2 represents the tested condition of 1,000 psi initial pressure, 50 degrees Celsius and 2 hours' extraction time.



Figure 4.1.2 Schematic diagram of near-zero-emission REEs extraction following SC-CO₂/acid treatment. CO_2 can be collected as waste and the acid can be generated from bio-waste if PS is used. The solution from the very last step extraction of the first ash was reused for the first step extraction of the second ash (newly generated sample).

REEs leaching efficiency

The reactor was allowed to cool down to ambient temperature once the extraction was done. The valve of the chemical reactor was opened to remove CO_2 . The ash-water mixture was collected. The pH of the mixture ranges from 7.5 to 10, a condition that renders REEs insoluble as confirmed by ICP-MS analyses. The mixture was filtered through 0.45 μ m paper filters. The

filtrate was discarded. The collected ash was extracted with 30 ml 2% HCl acid for five (5) times. The leachate was filtered and collected separately for further concentration or diluted for REEs measurement by ICP-MS. The recovery efficiency was indicated in Table 4.1.3.

Table 4.1.3 Recovery efficiency in percent (%) [CH: Cherokee; DJ: Dave Johnston; FS: Dry Fork Station; LR: Laramie River Station; LR-1 and LR-2 designate samples received from different times; WD: Wyodak; DMB: dry mass basis; DAB: dry ash basis].

	Lanthanides + Y			Lanthanides only		
		Total			Total	
	Recovered	REEs		Recovered	REEs	
Ashes	(ppm)	(ppm)	Recovery (%)	(ppm)	(ppm)	Recovery (%)
СН	219.8	500.5	43.9	191.4	440.1	43.5
DJ	324.8	429.7	75.6	276.0	371.0	74.4
FS	368.2	498.5	73.9	311.1	429.0	72.5
LR-1	334.1	498.7	67.0	287.0	430.7	66.6
LR-2	376.4	560.2	67.2	323.1	483.9	66.8
WD	404.4	537.0	75.3	340.0	463.8	73.3

The breakthrough of our technology is simultaneous leaching and extraction of REEs elements by $FeCl_3$ solution in $SC_{CO2-H2O}$ biphases, as well as surface neutralization. Moderate acidity of $SC_{CO2-H2O}$ biphase: the acidity of CO_2 -water system has been well documents as follows:

 $CO_2+H_2O=H_2CO_3$ $H_2CO_3+H_2O=HCO_3^-+H_3O^+$ (pH>4.5) $HCO_3^-+H_2O=CO_3^{2-}+H_3O^+$ (pH>8.3)

By the Henry's law, high CO₂ pressure could push the dissociation reaction of carbonic acid, and results into stronger acidity. Experimental and theoretical prediction concluded that the pH of

water in equilibrium with CO₂ is about 2.80-2.93 at 25-70 °C and the pressure range of 70-200 atm (British Geological survey, 1999, Gopalan, A.S., 2009).

The acidity at 2.8-2.93 is exactly the point to break silica matrix, which greatly promote the releasing of REE from encapsulated structure (Balkose, D., 1990, Titulael, M., 1994, Hannrahan, J.P., 2003). Moreover, supercritical water is beneficial for REEs releasing because hydrogen ions are helpful to liberate ions from solid matrices by ion exchange mechanisms.

The pH dependency for REEs leaching efficiency from coal ashes has not clearly illustrated in theory. Current practice to break "glass" matrix of coal ash by HNO₃, HCl or H₂SO₄ adopted strong acidity (pH <1) approach of REE recovery from ores. Unfortunately, the low leaching efficiency of USGS survey indicated that strong acidity may not be economically-viable for REE leaching. Recent study suggested the effect of acidity varies considerably dependent on the ash characteristics. Moreover, numerous studies concluded the neutral form of metal at pH=3 can be most efficiently extracted by supercritical CO₂ (Li, J., 1998, Wai, C., 2000). Overall, metal ions at pH=3 should provide necessary acidity to break SiO₂ structure, and stable neutral complex for S_{CO2} extraction with reasonable solubility.

There are several environmental benefits to apply $SC_{CO2-H2O}$ system for pH adjustment during leaching and extracting: CO₂ emission is widely regarded as the major contribution to global climate change and USDOE-NETL has multiple on-going programs/strategies to stabilize atmospheric CO₂ levels by carbon capture and sequestration (CCS). However, due to high energy needs associated with CO₂ and air separations, Most CCS approaches, such as pre-, post- and oxycombustion will incur significant energy and cost penalties. The proposed concept of $SC_{CO2-H2O}$ extraction of PRB ash is exploring a novel technology for CO₂ utilization, which potentially provides economic benefit for successful deployment of CCS system to meet USDOE and NETL's mission on energy diversity of fossil fuel energy. Secondly, Cl⁻ ion presented in FeCl₃ system, could simultaneously integrate with acidity of $SC_{CO2-H2O}$, functioning as hydrochloric acid (HCl). HCl is documented as the best leaching agents for PRB ash in USGS survey because of its high efficiency to solve REE-enriched phosphate (monazite), carbonate through stable chelating structure with Cl⁻ ion. Therefore, the operation and handling of strong mineral hydrochloric acid in conventional hydrometallurgical process is totally avoided, which is of significantly importance for economic, environmental and safety benefits.

PS extraction

Extraction procedure using PS solution

A loading ratio of three (3) g ash per thirty (30) ml of PS of various concentrations was used (5%, 10%, 20%, 30%, and 40%). The same ash was extracted for multiple steps (4). No heating or mixing was used. In addition, experiment with a combination of SC-CO₂ and 20% PS in one step was performed to investigate the impact of super-critical CO₂ on the REEs leaching effectiveness.

REEs leaching efficiency

Coal fly ash from Dry Fork Station (FS) was leached by a variety of concentrations of PS in ambient temperature and pressure. Each sample was leached with four aliquots of PS. The results are summarized in Table 4.1.4. The extraction efficiencies range from 31.4% to 65.5%. Coal fly ash treated with 20% PS has the greatest yield (0.327 mg REEs/g ash). The yield of SC-CO₂ with PS in one leaching step is 0.377 mg/g, which is about 10% higher than plain PS.

Table 4.1.4 Recovery efficiency in percent (%) [Concentration of PS: 5%, 10%, 20%, 30%, 40%; FS coal fly ash].

Ash	REEs/ash (mg/g)	Total REEs/ash (mg/g)	Extraction efficiency (%)
PS-5%	0.157	0.499	31.4
PS-10%	0.169	0.499	33.9
PS-20%	0.327	0.499	65.5
PS-30%	0.161	0.499	32.2
PS-40%	0.245	0.499	49.0
SC-CO ₂ -			
PS-20%	0.377	0.499	75.5

Effects of supercritical CO₂ treatment

This experiment was designed to study the impact of supercritical fluid (SC-CO₂) for REEs extraction when compared to non-SC-CO₂ extraction. The ashes treated with SC-CO₂ was extracted by 2% HCl solution for 4 steps. The 4 aliquots of extracted solution were combined and REEs concentrations were determined by ICP-MS. The results are presented in Figure 4.1.3. The results demonstrate that supercritical treatment has enhanced the extraction efficiency for the subsequent REEs extraction by 2% HCl solution. The impact ranges from minuscule (0.6%) to significant (28.7%). The combination of SC-CO₂ and PS could also increase the extraction efficiency by as much as 10% in one leaching step (The recovery of REEs was 75.5% for SC-CO₂ plus 20% PS treatment, Table 4.1.4). Thus SC-CO₂ could be used as a green method to improve REEs extraction.



Figure 4.1.3 Effect of supercritical treatment on the subsequent REEs extraction by acid (2% HCl).

Impurity elements

Ca, Al, Mg, Si, and Fe are the major components of impure elements for HCl extraction while Ca, Al, Mg, and Fe are major impure elements for PS treatment (Figure 4.1.4). Ca comprises of around 70% of the impurities. Even though the treatment concentration of PS (40%) is significantly higher than HCl (2%), the amounts of major inorganic impurities are generally lower

as shown in Figure 4.1.4. Particularly, the amount of Ca extracted by HCl is about 45% higher than that of PS treatment. Silicon is hardly found in PS treated sample. When 5% PS is used, the inorganic impurities in the resultant extraction solution will be much lower. This suggests that the cost for post-processing of removing impurities could be significantly reduced due to the use of PS, which is a very important discovery in the proposed project. A lot of biowaste streams from biomass processing contain PS. Thus, use of PS along with SC-CO₂ for REEs extraction will not only fundamentally change people's impression that REEs extraction pollutes the environment but also significantly reduce the overall cost of REEs extraction. Using two wastes, CO₂ typically from fossil utilization and by-product PS frequently from biomass processing, for REEs extraction creates a win-win situation for both critical material production and environmental protection.



Figure 4.1.4 the high abilities of PS in rejecting undesired inorganic impurities during the 1st step of the overall REEs extraction technology proposed by the team [Please note that 40% PS instead of 5% PS is used. The inorganic impurities in the extraction solution resulting from even **40%** PS are lower than that obtained with 2%. Assuming that 2% PS is used, then the concentrations of inorganic impurities in the resulting extraction solution should be much lower.

Subtask 4.2 - Perform Separation Tests of Leached REEs from Coal Ash

Supercritical CO2 and HCl method

An aliquot of 20 g filtered leachate was placed in a 50 ml vial. Citric acid (0.8 mmol) and oxalic acid (1 mmol) were sequentially added to the leachate with an interval of 15 min. A tumbler was used for mixing. Then, the pH of the leachate was adjusted to 1.2 using a 4 M NaOH solution. The Cherokee (CH) and Dry Fork Station (FS) leachate showed visible precipitates, while the leachates from other fly ashes remained clear. However, when the pHs of the four clear leachates were adjusted to 2.0, they started to show precipitates. Then all six samples were attached to a tumbler and shaken for 48 hours for better mixing and precipitation. The precipitates were collected by filtration with a 0.45 μ m paper filter, followed by combusting the precipitates which mainly are lanthanide oxalate [Ln₂(C₂O₄)₃] at 900 °C for 6 hours to remove their organic carbons and form lanthanide oxide (Ln₂O₃). The concentrations of REEs in the final product – the REEs containing solids were obtained in two ways. The first one is based on the mass difference between the measured REEs in as-received fly ashes and the measured REEs in the precipitated and filtered solutions. The second method is to dissolve the REEs containing solids and then measure the REEs in the obtained solutions. The team has found that the results from two methods were consistent.

<u>PS</u>

REEs separation from the solution resulting from PS based REEs extraction is simpler than from HCl based REEs extraction. Firstly, there was no need for adjusting the pH of the solution resulting from PS based REEs extraction prior to precipitating REEs with oxalic acid. In addition, citric acid was not needed for PS based REEs extraction, while it is needed for HCl based REEs extraction. Therefore, the REEs separation process based on PS is much more environmentfriendly. The amount of REEs in the final product – the REEs containing solids resulting from PS based were obtained in the same ways as that with HCl based.

The tests showed that REEs can be precipitated by oxalic acid in a wide range of pH (1.2-3.5). The separation efficiency is shown in Table 4.2.1, 79.5% to 93.3% of the soluble REEs were precipitated by oxalic acid for PS treatment and 0 to 96.7% for HCl treatment. The separation by oxalic acid precipitation is more consistent with PS treatment than HCl. Precipitate was formed for all PS treatments. Extraction solutions had no precipitate when oxalic acid was applied for the DJ and WD samples and minimal precipitate was formed for the LR sample. That is because the pH of REEs containing solution produced by HCl treatment tends to be lower than PS treatment and thus more complicated water chemistry. This complex water chemistry might have hindered the REEs-oxalate precipitation. The mechanism is unclear and further investigation will be needed. However, the results suggest that the selectivity of oxalic acid to REEs is generally better for PS extraction than that of HCl.

PS solutions	Separation efficiency (%)	HCl solutions	Separation efficiency (%)
PS-5%	79.5	CH-HCl-2%	96.7
PS-10%	91.1	DJ-HC1-2%	0
PS-20%	90.6	FS-HC1-2%	46.9
PS-30%	93.3	LR-1-HCl-2%	10.6
PS-40%	90.3	LR-2-HCl-2%	3.4
		WD-HCl-2%	0

Table 4.2.1 Separation efficiency by oxalic acid.

Subtask 4.3 - Perform De-Watering Tests on Concentrated REEs

Direct precipitation

Supercritical CO₂

REEs-oxalate precipitates were separated by filtering the solution through a 0.45 μ m membrane filter paper. The precipitates were calcined at 900 °C for 6 hours to remove their organic carbons. The solutions prior to and after precipitations were measured by ICP-MS and the amounts of REEs in precipitates were calculated according to the difference of measured masses. The precipitates are in form of lanthanide oxalate [Ln₂(C₂O₄)₃]. When heated at 900 °C, they decomposed, while lanthanide oxide (Ln₂O₃) were formed. Table 4.3.1 shows the percentages of REEs (element based) in the REEs containing solids. Solids containing 2-wt% REEs were produced from FS coal fly ash.

Table 4.3.1 Percent of REEs in precipitate using oxalic acid [CH: Cherokee; DJ: Dave Johnston; FS: Dry Fork Station; LR: Laramie River Station; LR-1 and LR-2 designate samples received from different times; WD: Wyodak; DMB: dry mass basis; DAB: dry ash basis].

Ashes	mg REEs in precipitate from filtration	mg REEs in resultant extraction solution	% REEs in	Precipitate	% REEs in
	0.020			(iiig)	1.10
СН	0.238	0.246	96.7	20.2	1.18
DJ	0.000	0.399	0.0	0.9	0.00
FS	0.206	0.438	46.9	9.9	2.08
LR-1	0.041	0.390	10.6	4.3	0.96
LR-2	0.010	0.291	3.4	5.9	0.17
WD	0.000	0.464	0.0	11.4	0.00

PS

Each coal fly ash was extracted by using prepared PS solutions with four consequently steps. The resulting leachates from the four leaching steps were mixed and then filtered with a 0.45 μ m membrane filter paper. The detailed procedure was described in the report section for **Subtask 4.2**. The resulting precipitates were then calcined in a muffle furnace to remove their organic compounds. The calcined precipitates were treated with 3 M NH₄Cl solution overnight to remove calcium (Ca). The products contain REEs ranging from 2.07% to **10.8%** on an elemental basis (Table 4.3.2) after Ca removal (See Table 4.3.3). The original data are presented in Appendices section (Table A1). Figure 4.3.1 (b) shows the REEs containing solid (10.8% on an elemental basis) produced by oxalic acid precipitation. PS-5% solid was further treated with 4 M NaOH solution at ambient temperature for 72 hours for silicon (Si) and aluminum (Al) removal. Approximate 20% of impurity was removed and the percent REE oxide was increased 26%.

Table 4.3.2 Percent of	of REEs in p	recipitate us	ing oxalic	acid (Dry	Fork Station	and C	Cherokee	coal
fly ash).								

		% REEs in
	mg REEs in	product (REEs-
Fly ashes	precipitate	containing solids)
FS-PS-5%	0.261	2.07

FS-PS-10%	0.354	3.51
FS-PS-20%	0.851	2.69
FS-PS-30%	0.444	3.67
FS-PS-40%	0.548	<u>6.02</u>
CH-PS-10%	13.3	<u>10.81</u>

Coagulation method with PS extraction

REEs-containing solution was coagulated with NH₄OH solution cyclically to removed Ca and Mg (Figure 4.3.2). The Fe dissolved from the original ash was acting as the coagulant. After the removal of Ca and Mg, oxalic acid was added to precipitate REEs from the solution. The precipitates are in form of lanthanide oxalate $[Ln_2(C_2O_4)_3]$. When heated at 900 °C, they decomposed, while lanthanide oxide (Ln_2O_3) were formed. The REEs product is dissolved in nitric acid solution and the concentration of REEs was measured by ICP-MS. The products contain 35.6% REEs on an elemental basis (Figure 4.3.1 (c) and Table 4.3.3). A 99.4% REEs on the oxide basis was achieved beyond the funded period (October, 2017), equivalent to 82.7% on an elemental basis. The composition of the product can be found in Table A1 in the Appendices Section.



Figure 4.3.1 Coal fly ash (a), REEs containing solids (b) 10.8% and (c) 35.6% produced by the team's new green REEs extraction method.

Table 4.3.3 Percentage of individual REEs and impurities in the final product (35.6% on an elemental basis).

Ce	Dy	Er	Eu	Gd	Но	La	Lu
1.3%	2.1%	1.3%	0.6%	2.4%	0.4%	4.4%	0.2%

Nd	Pr	Sm	Tb	Tm	Y	Yb	
8.1%	1.7%	2.5%	0.4%	0.2%	9.0%	1.1%	
Al	Fe	Ca	Κ	Mg	Na	Si	
3.9%	15.5%	34.5%	0.2%	0.8%	2.2%	7.6%	

Impurities removal

Silicon (Si), calcium (Ca), aluminum (Al), Iron (Fe) and magnesium (Mg) are the major elements in coal fly ashes. For example, 1 g Dry Fork Station coal fly ash contains 236.1, 181.8, 70.1, 23.4 and 10.4 mg of Ca, Si, Al, Mg and Fe, respectively. Considerable amounts of these undesired inorganic elements simultaneously dissolves along with REEs during extraction processes when conventional leaching agents (such as HCl) are used. Fortunately, the research team has found that PS shows much better performance on limiting the leaching of these inorganic elements. However, the effect of the leached inorganic ions on the REEs concentration of REEs containing solid still cannot be neglected because the inorganic impurity in REEs precipitate. It typically accounts for more than 90% of total inorganic impurity in term of mass. One of the important characteristics of REEs is that they are insoluble under alkaline and weak acidic condition. The NH4Cl solution is able to solubilize calcium, whereas REEs remain their solid forms. Over 90% of calcium can be removed. Also, Mg, Si and Fe were also partially removed by this Ca removal method.

Table 4.3.4	Impurity	removal	from	the	REEs-containing	precipitate	[These	impurities	were
dissolved by	v NH4Cl so	olution and	d remo	oved	by filtration].				

10 ⁻³ mg/3-g ash	Al	Fe	Ca	Mg	Si
PS-40% Aqueous-Ca	19	181	30437	222	121
PS-40% Solid-Ca	552	1011	1831	98	260
Total	571	1192	32268	321	381
Removal %	3.3	15.2	94.3	69.4	31.7

The team has developed impurities removing methods to remove major inorganic impurities. Repetitive coagulation is found to effectively remove impurities including Ca, Mg, K,

and Na up to 99% in three coagulation cycles. Over 90% of Fe was also removed by this method. Al and Si served as coagulant. 87.2% of the total impurities was removed.



Figure 4.3.2 Inorganic impurities species removed by repetitive coagulation. Al and Si serve as coagulant while Ca, Mg, K, Na and Fe are removed by coagulation process.

Wet chemistry of FeOOH floc: FeOOH floc is standard operation in removal fluoride, phosphate, Cr, Mn in water treatment facility. (Hua, M., 2012; Burian, S. J., 2000). As the precursor of FeOOH, FeCl₃ are commercially available with low cost. In the range of pH=2-8, multiple Fe(OH)x species are presented in aqueous condition, and generally named as iron hydroxide or marked as FeOOH. Those stable species include Fe^{3+} , Fe^{2+} , $FeOH^{2+}$, $Fe(OH)_2^{2+}$, FeOH⁺, and Fe(OH)₃. It should be specially noted that various oxidation state (+3 or +2), high surface area (~200 m²/g), surface OH group and ionic charge of FeOOH species illustrate a whole maps of precipitation, redox reaction, surface coordination and surface adsorption/desorption kinetics to capture REEs (USDI, 1959, USDI, 1962, Ping, Z., 1999). Moreover, with the extra OH enriched on the center of Fe ion, the negative charged Fe(OH)x nano-gel will also presented in FeOOH flocs (discussed below). The bulk diffusion of REEs into bulk phase of FeOOH cluster is also reported through ionic exchange kinetic due to its high vacancy of solid phase (Wu, D., 2010). Therefore, it is no doubt that the FeOOH possess high efficiency to capture various metal ions, including REEs as cheating agent, coagulant and flocculent.

The detailed knowledge on the kinetic of RRE-doped FeOOH is limited because of complicated reaction networks. It was widely accepted that sorption efficiency was affected by multiple parameters: pH value, sorbent doze, ionic strength, reaction temperature etc. Recent study on pH dependence of La(III) uptakes indicated that the sorption capacity increase from 1.9 (mg/g of sorbent) to 98.7 as pH increase from 2.2 to 3.5. Above pH 3.5, pH effect on uptake capacity became less significant, which suggested that adsorption of La is mainly consequence of complexation with surface OH group. However, other literature indicated that hydroxylation of La could happen at higher pH, and optimum values should be 5.0, even 5.0-5.9. More detailed research on dissolved REE from mine water demonstrated that the sorption of La should start at pH of ~6, and Yb adsorbed at lower pH (6.7). Moreover, valuable HREEs (Heavy-REEs) are preferentially sorbed at lower pH than LREEs (Light-REEs) (Wu, D., 2010, Verplank, P.L., 2004). 50% of Yb was removed from solution at pH~6.7 and 50% of La was removed at pH~7.7. A special case is Ce, which indicate less pH dependency than other REEs elements because it could be reduced by FeOOH flocs from Ce(III) to insoluble Ce(II). But the reduction of Eu is not observed even it is expectable from potential calculation. There is report that laser excitation could be helpful to purify Eu from recycled REE materials (Wu, D., 2010, Ping, Z., 1997).

The effect of ionic strength is investigated with La as the representative of REEs. At lower ionic strength, ionic strength has little influence on REE uptakes. However, if the concentration of Na⁺ and Cl⁻ is more than 0.03mol/L, the uptakes of REEs greatly decrease with the increasing of ionic strength. A reasonable explanation is there is a competitive reaction between REEs with Na⁺. At high ionic strength, the competition of REE and Na⁺ become significant, resulting lower REE uptakes. Generally, lower reaction temperature could improve uptake capacity because the adsorption reaction is exothermic, and higher sorbent doze improve REE sorption because of greater sorption site.

In another aspect, the effective capture/adsorption of REE by FeOOH can be justified by natural phenomena. Geological study of REE distribution in seawater of nearshore sediments (Buzzards bay, MA, Sydney Basin, Nova Scotia, Nanling, China) demonstrated strong positive correlation between REE and Fe concentration: Ce and heavy (more valuable) REEs could be 10-30 times of enrichment over interface of Fe-containing ores, which has been contribute to the
formation of insoluble Ce(OH)₂₋₃ complex by reduction and coordination chemistry (Elderfild, H., 1987, Birk, D., 1991, Xiao, Y., 2015).

Electric neutralization of REE cations: Electric neutralization of RRE³⁺ by negative FeOOH play the key role to improve the solubility of RRE into $S_{CO2-H2O}$ extraction. With surface absorption of hydroxyl group or other anions, such as Cl⁻, SO₄⁻ or CO₂²⁻, surface FeOOH could be negative charged. The charge on iron gel has long been attributed to two indistinguishable mechanisms: 1) amphoteric dissociation of surface OH group, and b) hydrolysis of amphoteric M(OH)x complex. The surface charge of FeOOH is mostly pH dependency, and the zero point of charge (ZPC) is influenced by preparation method, precursor, morphology and impurities (Park. G., 1965) The ZPC of some FeOOH are summarized in following Table 4.5:

Type of FeOOH	Preparation method	ZPC
Alpha, Gorthite	Aging of NaOH+FeCl ₃	5
	Fe(NO ₃) ₃ +NaOH	8
	Fe(NO ₃) ₃ +KCl+NaCl	7.4
	FeCl ₂ +H ₂ O ₂	6.7
Beta, Lepidocrocite	Natural ore with H ₂ O2/H ₂ O leaching	7.4
	FeSO ₄	5.4-7.3
Amphous hydroxide	Fe(NO ₃) ₃ with NaCl	4.3

 Table 4.5:
 Surface charges of FeOOH system

It is very clear that the negative charged FeOOH flocs can be dominated in the range of pH=4.3-8 of neutral or very weak basic condition, which can be easily achieved by depressurizing of system pressure. Solid conclusion has established in literature that the presence of RREs impurity could increase 1.2 of ZPC of FeOOH system, which verified the neutralization of RREs by FeOOH hydrous oxide. In addition, the presence of large amount of negative SiOOH (ZPC of

2.3-4.3) can also helpful to neutralize the positive RREs cation and improve the extraction efficiency (Cvjeticanin, D., 1984).

TEM analysis of REEs containing solids

Dispersion of REEs particles was analyzed by a transmission electron microscopy (TEM, FEI, Tecnai G2 F20 S-Twin 200 kV). Samples for TEM observations were prepared by dispersing the catalysts in ethanol and drying one drop of the solution on copper grids.

The TEM images shown in Figure 4.3.3 are the intermediates or final products of REEs bearing solids. The solids were produced by using PS solutions with different concentrations of (5%, 10%, 20%, 30%), followed by adding oxalic acid for precipitation. The precipitated solids were processed for removal of their impurities including Ca and Mg and/or Al and Si. All the images (a, b, c, d) of the REEs containing solids show similar lattice space patterns, indicating that the solids contain REEs. However, the solid resulting from the treatment with 5% PS solution shows more pronounced lattice space pattern than others do due to the removal of its Al and Si, while the fact does not appear with other samples because their Al and Si have not be removed yet.



Figure 4.3.3 TEM analysis results of REEs containing solids resulting from PS solutions with different concentrations [a) 5% PS treatment containing 2.07% REEs; b) 10% PS treatment containing 3.51% REEs; c) 20% PS treatment containing 2.69% REEs; d) 30% PS treatment containing 3.67% REEs; e) original coal fly ash]

SEM analysis of REEs containing solids

Morphology and dispersion of REE oxide particles were studied using a scanning electron microscope in HV mode with an accelerating voltage of 20 kV (SEM-EDS, FEI, Quanta FEG MK2; Oxford Instruments America, Model #51-XMX0005).

SEM results of original coal fly ash and REEs containing solids produced from PS with various treatment concentrations are shown in Figure 4.3.4 through 4.3.8. Ce, La, Nd, and Y are dominant REE species in the solids. The images show that these REE elements were evenly distributed. The EDS spectra demonstrated that Ca, Fe, Mg, Al, Si are the dominant inorganic impurities in the solids. This agrees well with the ICP-MS analyses. Although most Ca has been removed by addition of NH₄Cl solution, residual Ca still comprises a great portion of impurities. In original coal fly ash sample, Si is predominant morphologically.





Figure 4.3.4 SEM analysis of REEs containing solid generated from PS-5% [a) Morphology of REEs containing solid; b) REEs dispersion, Ce, La, Nd and Y; c) EDS spectrum of minerals].



Figure 4.3.5 SEM analysis of REEs containing solids generated from PS-10% [a) Morphology of REEs containing solid; b) REEs dispersion, Ce, La, Nd and Y; c) EDS spectrum of minerals].



Figure 4.3.6 SEM analysis of REEs containing solid generated from PS-20% [a) Morphology of REEs containing solid; b) REEs dispersion, Ce, La, Nd and Y; c) EDS spectrum of minerals].





Figure 4.3.7 SEM analysis of REEs containing solid resulting from PS-30% [a) Morphology of REEs containing solid; b) REEs dispersion, Ce, La, Nd and Y; c) EDS spectrum of minerals].



Figure 4.3.8 SEM analysis of original coal fly ash (the spherical particles are Si).

c. What opportunities for training and professional development has the project provided?

Two students, Mr. Andrew Thomas Jacobson and Mr. Kaiying Wang as well as Mrs. So Tie Tjeng and one research scientist Dr. Zaixing Huang at UW at UW, have been hired to work on the project.

One postdoc Dr. Yan Luo at WVU has been hired to work on the project, one graduate student Mr. Lei Bai has involved in instrumental setup under the WVU's startup cost.

d. How have the results been disseminated to communities of interest?

At this point in the project, the methods of disseminating the technology in the project includes hosting lab tours for visitors such as UW faculty, Wyoming K-12 students and staff, and various companies to allow different members of the community (education, business, and academia) understand the research being conducted and enhance public understanding of science, technology, and the humanities.

- e. What do you plan to do during the next reporting period to accomplish these goals?
- Determine REE Leaching Rates and Efficiency from Coal Ash
- Perform Separation Tests of Leached REEs from Coal Ash
- Perform De-Watering Tests on Concentrated REEs

Table 8- Milestone goals and dates of realization

Associated milestones	Milestone title	Realization Dates	Quantitative or qualitative goals	
Milestone 1	Updated project management plan (UPMP)	Completed	M1-The UPMP is completed and submitted according to NETL's requirements.	
Milestone 2	Updated sampling and characterization plan (USCP)	Completed	M2- USCP is completed and submitted according to NETL's requirements.	
М3	Sampling and characterization of coal ash	Completed	M2.1- Discover at least 10 million tons of coal ash that have at least 300 ppm REEs. M2.2- Complete sampling and characterization of identified PRB coal ashes that have at least 300 ppm REEs. M2.3 Sampling and characterization report is finished and submitted.	

	Feasibility study	Completed	M3.1- Environmental, technical and economic feasibility of recovering REEs from the proposed feedstock by geographic location are determined.	
M4			M3.2- 50% less energy consumption of the new REEs recovery technology compared to state-of-art process is achievable based on the feasibility study. M3.3- Feasibility report will be	
			submitted to NEL.	
M5	2 wt% REE material production	Exceeded the goal	M4. FeOOH containing at least2.0 weight % total REE contenton an elemental basis andmeasured on a dry basis isproduced.	
M6	Life cycle analysis	Completed (Incorporated in Task 3)	M5- Life cycle analysis is completed.	
M7	Preparation for phase I report and phase II application	Completed	M6- Phase I design package and summary report, and Phase II application package are submitted for NETL.	

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3. **PRODUCTS**

The project has just begun. No information has been released to the public to date except for presentation of the technologies main ideas to lab visitors.

- a. Publications, conference papers, and presentations.
- i. Journal publications

No journal publications have been released to date.

- ii. Books or other non-periodical, one-time publicationsNo books or other non-periodical, one-time publications have been released to date.
- iii. Other publication, conference papers and presentationsNo other publication, conference papers and presentations have been released to date.
- *Website(s) or other Internet site(s)*No websites have been released to date.
- *c.* Technologies or techniquesNo technologies have been released to date.
- *Inventions, patent applications, and/or licenses* No inventions, patent applications, and/or licenses have been released to date.
- *e.* Other productsNo other products have resulted from the research to date.

4. PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

a. Individuals involved in the project

UW

- 1. Name: Maohong Fan
- 2. Project Role: Co-Principal Investigator and the Current Principal Investigator

- 3. Nearest person month worked: 0.25
- 4. Contribution to Project: Dr. Fan has co-managed and then managed the project. He is in charge of performing all the tasks of the project.
- 5. Funding Support: 0.25 month from the funded project
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

Party 2

- 1. Name: Dr. Hertanto Adidharma
- 2. Project Role: Principal Investigator and current Co-Principal Investigator
- 3. Nearest person month worked: 0.25
- 4. Contribution to Project: Dr. Adidharma has managed, co-managed and performed on the tasks of the project.
- 5. Funding Support: 0.25 month from the funded project
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

- 1. Name: Dr. Maciej Radosz
- 2. Project Role: Co-Principal Investigator
- 3. Nearest person month worked: 0.25
- Contribution to Project: Dr. Radosz has co-managed and performed on the tasks of the project.
- 5. Funding Support: 0.25 month from the funded project
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None

9. If traveled to foreign country, duration of stay: None

Party 4

- 1. Name: Kaiying Wang
- 2. Project Role: Researcher
- 3. Nearest person month worked: 2
- 4. Contribution to Project: Mr. Wang has prepared the current supercritical CO₂ extraction set-up for performing REEs extraction experiments.
- 5. Funding Support: State of Wyoming
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

Party 5

- 1. Name: Andrew Thomas Jacobson
- 2. Project Role: Researcher
- 3. Nearest person month worked: 0.3
- 4. Contribution to Project: Mr. Jacobson has helped the team characterize the fly ash samples.
- 5. Funding Support: State of Wyoming
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

- 1. Name: So Tie Tjeng
- 2. Project Role: Researcher
- 3. Nearest person month worked: 1
- 4. Contribution to Project: Mrs Tjeng has helped the team characterize the fly ash samples.

- 5. Funding Support: State of Wyoming
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None

b. What other organizations have been involved as partners?

WVU

Party 1

- 1. Name: Hanjing Tian
- 2. Project Role: Co-Principal Investigator
- 3. Nearest person month worked: 0.5
- 4. Contribution to Project: Dr. Radosz has co-managed and performed on the tasks of the project.
- 5. Funding Support: From the funded project
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

- 1. Name: Yan Luo
- 2. Project Role: Researcher
- 3. Nearest person month worked: 2
- 4. Contribution to Project: Dr. Luo's works are focused on experimental set-up construction and RREs characterization.
- 5. Funding Support: From the funded project

- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

Party 3

- 1. Name: Lei Bai
- 2. Project Role: Researcher
- 3. Nearest person month worked: 1
- 4. Contribution to Project: Mr. Bai works are focused on assisting in Dr. Luo in experimental set-up construction and RREs characterization.
- 5. Funding Support: From the funded project
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

RIT

- 1. Name: Eric Williams
- 2. Project Role: Co-Principal Investigator
- 3. Nearest person month worked: 0.1
- 4. Contribution to Project: Dr. Williams has co-managed and performed on the tasks of the project.
- 5. Funding Support: From the funded project
- 6. Collaborated with individual in foreign country: None
- 7. Country of foreign collaborator: None
- 8. Travelled to foreign country: None
- 9. If traveled to foreign country, duration of stay: None

Party 2

- 10. Name: Gabrielle Gaustad
- 11. Project Role: Co-Principal Investigator
- 12. Nearest person month worked: 0.1
- 13. Contribution to Project: Dr. Gaustad has co-managed and performed on the tasks of the project.
- 14. Funding Support: From the funded project
- 15. Collaborated with individual in foreign country: None
- 16. Country of foreign collaborator: None
- 17. Travelled to foreign country: None
- 18. If traveled to foreign country, duration of stay: None
- c. Have other collaborators or contacts been involved?

To date, no other collaborators or contacts have been involved.

6. CHANGES/PROBLEMS

- *a.* Changes in approach and reasons for changeNo change in approach has occurred during the reporting period.
- b. Actual or anticipated problems or delays and actions or plans to resolve them There have been no problems or delays in the project to date.
- *c.* Changes that have a significant impact on expenditures.There is no such change.
- *d.* Significant changes in use or care of human subjects, vertebrate animals, and/or biohazards

There has been no change sin use or care of human subjects, vertebrate animals, and/or biohazards.

e. Change of primary performance site location from that originally proposed
 There has been no change of primary performance site location from that originally proposed.

7. SPECIAL REPORTING REQUIREMENTS

There is no special reporting requirement for the project.

8. BUDGETARY INFORMATION

\$599,987 from DOE has been spent on this project.

Appendices

	6.02%	8.22%	10.81%	35.64%	82.73%
mg/kg	product	product	product	product	*product
Ce	14698	28577	37591	12746	9964
Dy	2170	2015	2650	21402	43386
Er	1335	1437	1891	12661	25567
Eu	549	606	798	5593	11162
Gd	2780	2665	3505	24068	52501
Но	418	509	670	4237	8533
La	6440	8142	10710	44278	96586
Lu	176	171	225	1582	3153
Nd	11440	19541	25706	80995	166344
Pr	2522	3333	4384	17238	43653
Sm	2505	2565	3375	24613	47620
Tb	374	405	532	3707	7003
Tm	181	187	246	1764	3354
Y	13385	10699	14074	90440	286256
Yb	1231	1305	1716	11055	22265

Table A1 Composition of REEs products on an elemental basis

*The product was produced in October, 2017 beyond the funded period. The value of 82.73% is on an elemental basis, equivalent to 99.41% on an oxide basis.