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## **V. BODY OF THE PROJECT REPORT (15 Pages)**

### **A. Summary of Phase I Results**

The awarded start date for the Phase I study was October 1, 2015. However, due to reasons beyond our project team's control, we could not initiate the actual project related tasks until December 2015. This report will summarize our achievements of the first four months of this project. Although started late, we will be able to complete all four project tasks promised in the Phase I proposal, well in time.

### **1. Background and Problem Definition**

**People:** The burgeoning demand for high-technology applications, including high strength permanent magnets, electronic displays, and applications in a variety of renewable energy technologies, like wind turbine and solar panels have significantly increased the need for rare earth elements (REE) in recent years. Unfortunately, US is not rich with the REE mineral deposits; the USGS Report (2016) estimates the REO (rare earth oxides) equivalent of natural REE mineral resources in the US to be 1.8 million tons in comparison to the world reserve of 130 million tons. Nearly 75% of the REE need in the US is being met by imports, mostly from China. Knowing the strategic importance of REEs in future, China has, in recent years, instituted export quota, which means US can no longer rely on REE imports. We will have to find indigenous sources for REEs or REE substitutes to continue to provide even common consumer items like cell phones, televisions, computers etc. to the general population. Fortuitously, US is rich with coal and coal ash that contain REE minerals in low concentration. A recently published study (Bryan et al., 2015) estimates that as much as 5.4 million tons of REOs may be present in coal resources of four eastern States and nearly 6.6 million tons in the western States. Clearly, the estimated amount of REEs present in US coal is much larger than in the natural REE deposits. However, the challenge is the low concentration of REE in coal that makes it difficult to extract REE from coal. Only during the last few years, the scientific community in the US has started serious examination into the REE extraction from coal and coal ash.

Coal mining and utilization activities are generally blamed for causing numerous safety and environmental problems. One of the environmental problems is associated with the huge amount of coal ash that is produced during electricity generation. Therefore, coal-fired power plant operators/owners would definitely like to get involved in such a study that can help them to find valuable REEs dumped in their ash ponds. Considering the large amount of coal ash being generated annually, producing a high-value commodity with the usage of an environmentally sustainable approach will definitely draw people's attention.

**Prosperity:** The successful completion of this study will not only be beneficial to the society and earth and environment but also be economically beneficial to the abovementioned end users. There are some industries (high tech applications) that are totally dependent on the REEs. So finding a sustainable way for the extraction of REEs from a waste material (like coal ash), which is abundantly available in the US would help find an indigenous source for REEs, which will undoubtedly help US's economy. The coal companies can create a new revenue stream out of their coal ash using the proposed approach: instead of disposing of their coal ash as a waste (that might be considered as a hazardous waste in the future) they can extract high-value material, like REEs out of it. There is a high cost associated with the disposal of coal ash generated at the coal-fired power plants. The SIU coal power plant is such an example. The university's power plant can only be operated to provide 15% of the university power and in the meanwhile has to pay thousands of

dollar per year to haul away around 13,000 tons of coal ash. Our proposed project can help such coal power plants make use of their coal ash that is considered as waste.

**Planet:** Coal power in the United States accounted for 39% of the country's electricity production in 2014. Although coal's contribution to the entire energy mix is gradually decreasing, coal's use will continue for many decades to come all over the world, including the US. As a result, millions of tons of coal ash are being stored in ponds, landfills, and abandoned mines. Many of these sites lack adequate safeguards, leaving nearby communities at risk from potential large scale disasters. Many investigations have shown that coal ash contains a verity of toxic metals (arsenic, mercury, lead) these are blowing, spilling and leaching from storage units into air, land and drinking water. The proposed approach will definitely consider different technologies to recover (or eliminate) the hazardous metals from coal ash while recovering the desired REEs. The management of the waste stream(s) resulting from the REE extraction flowsheet will be a necessary component of a successful REE resource development. In this project, for each process in both Physical and Chemical separation the produced solid residue and the aqueous solution will be managed in a sustainable manner and all of the possible impacts will be considered in the comprehensive flow-sheet for a sustainable planet.

**Educational Tool:** Rare earth element extraction from coal ash is a new field. Therefore, the Phase I award of this P3 project prompted our faculty adviser (PI) to start teaching a graduate level course (ENGR 593) this semester on the general topic of rare earth mineral processing, with special emphasis on coal ash processing for REE extraction. Many of the graduate students involved in the on-going P3 project are already learning the theory in the class and through literature review as a requirement for the class in the form of oral presentations and term papers. That is helping us to plan and design the experiments needed for this study. We are going to video record the experiments and upload to our project website ([www.usepap3.siu.edu](http://www.usepap3.siu.edu)) in due course.

## **2. Purpose, Objectives, Scope**

The overall goal of this Phase I study was to examine the feasibility of extracting rare earth and other strategic minerals (REM) from coal ash containing REEs in very low concentrations. The specific project objectives outlined to achieve the abovementioned goal are as follows:

1. To characterize coal ash samples collected from multiple regions of the country and investigate the feasibility of extracting rare earth minerals and elements using combined physical and chemical separation techniques.
2. To envision a process flowsheet(s) for the rare earth element (REE) recovery from coal ash, which could vary based on the characteristics of REMs present in coal fly ash and bottom ash generating in different regions of the US.

## **3. Data, Findings, Outputs/Outcomes**

The project tasks and their timeline proposed to accomplish the abovementioned project objectives for the Phase-I study with a presumed project start date of August 15, 2015, were as follows:

Task 1: Sample Collection (August 15-October 14, 2015)

Task 2: Characterization of REMs in coal ash (October 15-December 14, 2015)

Task 3: REO Extraction using Physical Separation Methods (Dec 15, 2015 - April 14, 2016)

#### Task 4: REM extraction using Chemical Separation Methods (April 15 - August 14, 2016)

However, due to a number of reasons beyond our control, we could not start working on the project until December 2015. We are now four months into the project. So far we have fully completed Task 1; Tasks 2 and 4 are partly complete; Task 3 has not yet started. The results obtained are described separately for each task in the following section.

### 3.1 Tasks 1 & 2: Sample Collection & Characterization:

We obtained a total of fourteen coal samples of all different ranks, from anthracite to lignite, originally collected from different regions of the US and preserved at the Department of Energy's Penn State coal sample bank ([www.energy.psu.edu/copl/doesb.html](http://www.energy.psu.edu/copl/doesb.html)). We burned the coal in a furnace in our laboratory to produce ash samples for each coal type. We got each ash sample analyzed for nearly seventy different elements (including REE and other strategic and precious metals) by the BV Minerals ([www.bureauveritas.com/um](http://www.bureauveritas.com/um)) in Canada using the ICP-MS (Inductively Coupled Plasma Mass Spectroscopy). Nine REEs, such as La, Sc, Ce, Pr, Nd, Sm, Eu, Gd and Pm, are generally referred as the light REE (LREE), whereas the remaining eight (Y, Tb, Dy, Ho, Er, Tm, Y6, Lu) are considered in the more valuable heavy REE (HREE) category. The basic properties of all coal samples, those were predetermined by the Penn State Coal Bank, are compared with our REE data generated from this study in Table 1. Although no specific correlation was obvious, a careful analysis would indicate that the total REE content in coal samples was more related the volatile matter content than any other parameters, including vitrinite reflectance (V.Ro). The individual REE content of these samples are listed in Table 2.

Table 1: The basic characterization data of all fourteen coal samples collected for this study.

Sample Id	Coal Rank	LREE (ppm) (dry)	HREE (ppm) (dry)	TREE (dry)	Ash % (dry)	S % (dry)	C % (dmmf)	H % (dmmf)	VM % (dmmf)	Vitrinite %	V.Ro %
DECS-21	Anthracite	606	98	704	11.2	0.5	91.5	4.1	3.9	87	5.19
DECS-19	Low Volatile	455	168	623	4.6	0.74	90.6	4.9	18.7	89	1.71
DECS-30	Medium Volatile	426	81	507	3.9	0.79	88.5	5.4	30.9	77	1.16
DECS-13	Medium Volatile	642	108	750	4.2	0.62	88.8	5	25.7	77	1.35
DECS 3	Medium Volatile	197	49	247	5.4	0.65	88.1	5.9	28.2	94	1.28
DECS-23	High Vol. A	258	59	317	9.4	3.87	84.6	5.8	42.3	79	0.73
DECS-18	High Vol. B	138	31	169	12.3	4.21	82.2	6	45.6	86	0.56
DECS-2	High Vol. C	150	29	178	16.2	4.52	81.8	5.7	43.8	87	0.52
DECS-27	Sub Bit. A	131	23	154	13.9	0.72	79.2	5.4	40.6	74	0.46
DECS-26	Sub Bit. B	259	59	318	7.6	0.43	76.2	6.2	48.1	86	0.29
DECS-11	Lignite A	166	65	231	9.6	0.74	74.1	4.5	61.6	74	0.35
DECS-8	Sub Bit. C	359	79	438	13.8	0.73	75.8	5.3	51.8	79	0.37
DECS 1	Sub Bit. C	200	36	236	15.8	0.99	75.9	5.8	55.5	78	0.36

Table 2: REE concentration in the ash of each sample determined using ICP-MS.

Sample ID	Rank of Coal	La	Sc	Ce	Pr	Nd	Sm	Eu	Gd	LREE	HREE	TREE
DECS-21	Anthracite	149.0	17.0	255.7	31.0	110.3	22.7	4.3	16.2	606	98	704
		Y	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		68.1	2.2	13.0	2.3	6.4	0.8	4.6	0.6			
DECS-19	Low Volatile Bituminous	La	Sc	Ce	Pr	Nd	Sm	Eu	Gd	455	168	623
		95.0	19.2	177.8	24.0	92.8	21.3	4.8	20.1			
		Y	Tb	Dy	Ho	Er	Tm	Yb	Lu			
DECS-30	Medium Volatile Bituminous	117.6	2.9	19.6	4.2	12.0	1.5	9.2	1.3	426	81	507
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
		105.9	22.6	166.8	20.5	78.3	15.8	3.7	12.2			
DECS-13	Medium Volatile Bituminous	Y	Tb	Dy	Ho	Er	Tm	Yb	Lu	642	108	750
		55.6	1.8	10.5	2.1	5.7	0.8	4.4	0.6			
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
DECS-3	Medium Volatile Bituminous	122.4	25.7	257.0	35.2	141.9	30.2	7.0	22.6	197	49	247
		Y	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		38.1	23.7	76.7	8.4	35.8	6.6	1.5	6.4			
DECS-6	High Volatile-A Bituminous	34.7	0.9	5.6	1.1	3.3	0.5	3.0	0.4	200	45	245
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
		55.4	10.2	78.0	9.4	32.2	7.1	1.6	6.1			
DECS-23	High Volatile-A Bituminous	Y	Tb	Dy	Ho	Er	Tm	Yb	Lu	258	59	317
		31.4	0.8	5.2	1.1	3.2	0.4	2.8	0.4			
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
DECS-18	High Volatile-B Bituminous	57.5	13.6	103.6	13.4	48.1	10.2	2.4	9.1	138	31	169
		Y	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		40.1	1.2	7.6	1.6	4.5	0.5	3.5	0.5			
DECS-2	High Volatile-C Bituminous	La	Sc	Ce	Pr	Nd	Sm	Eu	Gd	150	29	178
		31.5	8.5	55.3	6.7	24.4	5.7	1.3	4.5			
		Y	Tb	Dy	Ho	Er	Tm	Yb	Lu			
DECS-27	Sub Bituminous-A	21.1	0.6	4.0	0.8	2.4	0.3	1.9	0.3	131	23	154
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
		33.2	8.9	62.1	7.4	27.0	5.6	1.3	4.3			
DECS-26	Sub Bituminous-B	Y	Tb	Dy	Ho	Er	Tm	Yb	Lu	259	59	318
		19.0	0.6	3.9	0.7	2.1	0.2	1.6	0.2			
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
DECS-8	Sub Bituminous-C	34.8	5.6	52.8	6.6	21.7	4.4	1.0	3.7	359	79	438
		Y	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		76.2	22.6	138.6	18.8	71.2	15.0	3.8	12.4			
DECS-1	Sub Bituminous-C	51.7	2.0	11.4	2.1	6.1	0.8	4.6	0.7	200	36	236
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
		42.2	9.2	85.8	9.6	39.5	6.8	1.6	5.5			
DECS-11	Lignite-A	Y	Tb	Dy	Ho	Er	Tm	Yb	Lu	166	65	231
		24.5	0.8	4.9	0.8	2.4	0.3	2.0	0.3			
		La	Sc	Ce	Pr	Nd	Sm	Eu	Gd			
		40.2	11.6	63.8	8.0	27.4	6.9	1.5	6.7			
		Y	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		45.6	1.0	6.9	1.5	4.9	0.6	3.8	0.6			

Based on the REE concentration data listed in Table 1, it can be inferred that the REE contents of the higher rank coals, such as Anthracite and low volatile Bituminous coal are generally higher than the lower rank coals, such as Lignite and high volatile-C Bituminous coal. The bar chart in Figure 1 also reveals similar trend with a few anomalies. However, by examining the data listed in Table 1 for the same rank coals obtained from different origin, it can also be inferred that there are other unknown factors that significantly affect the REE concentration of coal. For example, for the medium volatile coal rank, three samples, DECS 3, 13 and 30, originating respectively from Colorado, West Virginia and Virginia were analyzed to show 247, 507 and 750 ppm of REE in their ash. Clearly, this much of variance cannot be just attributed to chance.

Another important observation from all sample data is that majority of the REEs present in coal ash are of the light REE (LREE) category. Only a maximum of 27% of REE was found to be of the more valuable heavy REE (HREE) category in the low volatile Bituminous coal sample (DECS-19), as listed in Table 1.

We also analyzed each coal sample for other strategic and precious metals. As listed in Table 3, all the elements (Ga, Ge, Au, Sb, W, Nb, Pd, Pt) were present in extremely low concentrations; therefore, our investigation for the subsequent tasks focused on REEs only.

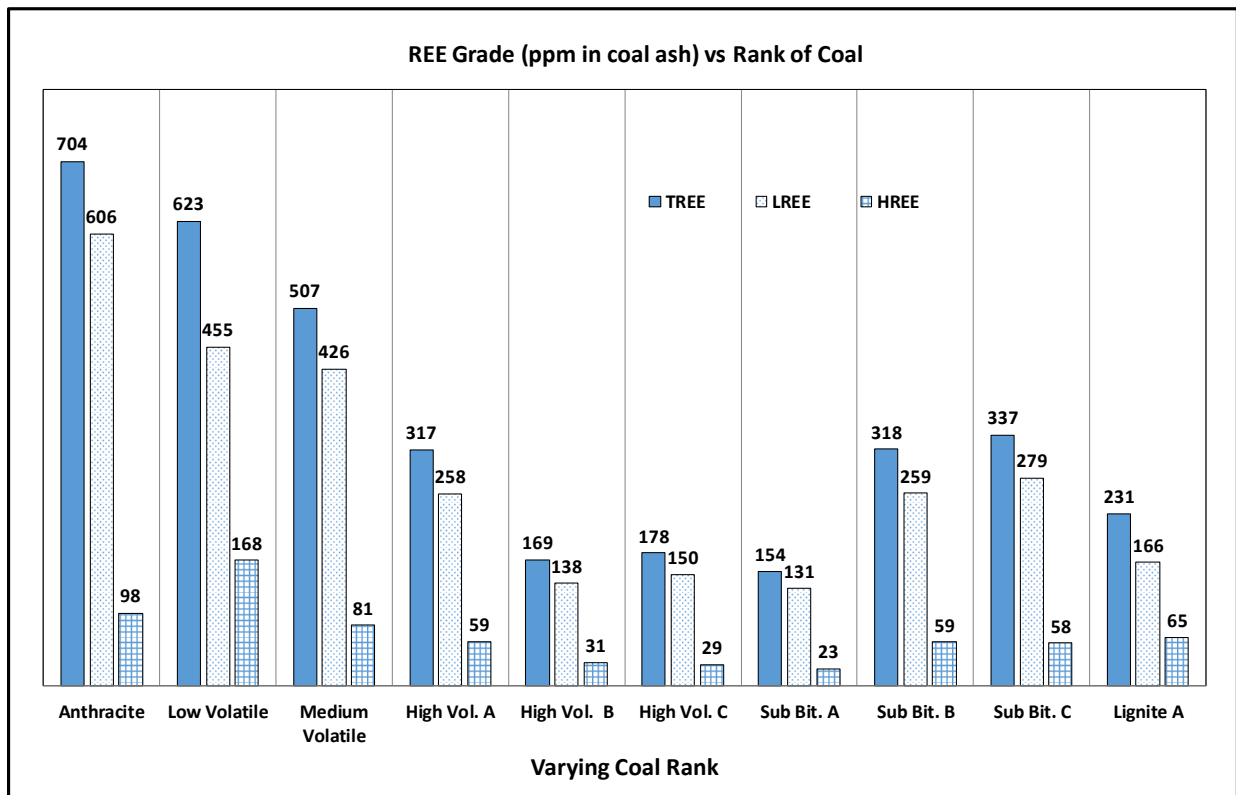


Fig. 1- REE Grade Vs coal rank from coals originating from different regions of the US.

Table 3: Concentration of non-REE strategic and precious elements in coal ash.

PSU Sample ID	Coal Rank	Other Strategic Mineral Concentrations (ppm)							
		Ga	Ge	Au	Sb	W	Nb	Pd	Pt
DECS-21	Anthracite	10.55	<0.1	2.70	1.54	0.80	<0.02	<10	2.50
DECS-19	Low Volatile Bituminous	15.00	0.40	2.40	6.40	3.70	0.14	<10	13.00
DECS-30	Medium Volatile Bituminous	26.9	0.2	2.5	2.47	72.5	<10	<10	21
DECS-13	Medium Volatile Bituminous	25.90	1.15	1.70	5.33	10.55	0.03	<10	9.50
DECS 3	Medium Volatile Bituminous	14.20	<0.1	0.70	1.05	0.60	1.65	<10	4.00
DECS-6	High Volatile-A Bituminous	14.2	0.5	2.1	1.08	3.4	0.43	<10	6
DECS-23	High Volatile-A Bituminous	16.80	0.40	0.70	0.94	2.40	0.08	<10	7.00
DECS-18	High Volatile-B Bituminous	8.60	0.90	<0.2	2.97	13.70	0.13	<10	4.00
DECS-2	High Volatile-C Bituminous	9.10	0.40	0.50	0.61	0.20	0.04	<10	3.00
DECS-27	Sub Bituminous-A	13.00	0.40	5.30	0.34	24.90	0.04	<10	4.00
DECS-26	Sub Bituminous-B	26.80	0.50	7.10	1.57	10.20	1.10	<10	12.00
DECS-8	Sub Bituminous-C	27.70	0.20	8.00	0.99	9.20	0.15	<10	7.00
DECS 1	Sub Bituminous-C	26.10	1.05	2.35	1.91	1.15	0.54	<10	4.50
DECS-11	Lignite-A	14.90	2.10	2.20	1.03	29.60	0.92	<10	10.00

REEs have their distinct properties; for example, most REEs have high specific gravity. But their concentration in the coal ash is so small that density separation cannot be utilized to preconcentrate REEs unless we find the major mineral in coal ash-bearing REE; for example kaolinite. Then kaolinite could be targeted during the physical separation steps to preconcentrate the REEs. Therefore, to prepare for the Physical Preconcentration step to be examined in Task 3, more mineralogical characterization will be performed in Task 2 using X-ray diffraction (XRD) and scanning electron microscopy (SEM) on the above two samples to find the major mineral bearing REE present in coal ash.

**3.2 Task 4: REE Extraction using Chemical Separation Methods:** Based on the results obtained from Tasks 1 & 2, two samples, i.e., DECS-21 and DECS-19 have been selected to be examined in Tasks 3 and 4 for their REE extraction potentials. The DECS-21, an anthracite coal channel sample, originally collected from the Lykens Valley #2 seam in Columbia, Pa, was found to have among the highest total REE (TREE) content above 700 ppm and light REE (LREE) content above 600 ppm. The other coal sample DECS-19 is a low volatile bituminous coal channel sample that originated from the Pocahontas #3 seam in Buchanan, Va. It has the highest percentage of heavy REE (HREE), having much higher demand than its lighter counterpart.

Ideally, we would have completed the physical separation work of Task 3 before initiating our chemical separation task of on Task 4. However, to make ourselves ready for this Phase-I report and Phase-II proposal deadline, we took a conscious decision, in consultation with our faculty advisers to skip Task 3 and complete it in due course. The physical separation methods would have helped us preconcentrating the REEs in coal ash; however the real enrichment will be obtained through the chemical/hydrometallurgical processing. That's why we pursued Task 4 and have completed four (a total of 60 tests ) out of five process steps on one sample, i.e., the anthracite coal sample, DECS-21. The tests were conducted in four steps:

- Leaching tests, to dissolve the REEs present in ash into an acid solution;
- Solvent extraction tests, to extract the REEs from the leachate solution using an organic extractant;
- Scrubbing tests, to remove the impurities from the organic phase;
- Precipitation tests to allow the rare earth oxides to precipitate;
- Calcination of the precipitated REO product to produce a dry REO powder

**3.2.1 Ash Leaching Experiments:** About 5 kg of coal sample was obtained from the US DOE's Coal Sample Bank maintained at Penn State University. The coal sample was burned in several phases in a laboratory muffle furnace at 750° C to generate the fine ash material to serve as the feedstock for the leaching experiments. initiate our experiments.

Based on our literature survey, nitric acid (70% HNO<sub>3</sub>) was the acid we selected to use for the leaching tests. An experimental program was designed to vary three process parameters, such as acid concentration (at four levels), solid content (at two levels) and leaching time (two levels); temperature was kept constant for all experiments. Thus, with two replicates for each test, a total of 32 experiments were conducted using a 4x2x2 factorial design. The specific operating condition and REE recovery to leachate solution for each test are listed in Table 4. Exactly 100 ml of nitric acid (at varying molar concentration) was used for each test. A high-temperature water bath was placed on a shaker with a speed of 100 rpm to provide a good mixing and contacting environment inside the Erlenmeyer flask to facilitate REE minerals to dissolve in the acid solution. The temperature of the water bath was set at 85 degrees Centigrade. Filtration of the leached fly ash was performed right after the leaching tests to prevent any unwanted leaching time. Whatman filter paper with a pore size of 8 μm was used for the whole tests. All liquid test samples were shipped to the spectroscopy lab of the University of Nevada at Lincoln (UNL).



Table 4– Operating conditions and the results of the leaching tests

Test #	COAL ASH LEACHING TEST VARIABLES				LEACHATE CONCENTRATION			LEACHING RECOVERY %		
	Acid Concentration (mol/l)	Solid Concentration (g/l)	Time (min)	Temperature (°C)	LREE (ppm)	HREE (ppm)	TREE (ppm)	LREE	HREE	TREE
1	0.30	30	20	85	8.1	1.5	9.6	45.9	54.7	47.0
2	0.30	100	20	85	25.7	4.7	30.4	41.9	50.8	43.0
3	1.00	30	20	85	10.5	1.7	12.2	59.7	64.4	60.3
4	1.00	100	20	85	30.8	5.3	36.1	49.6	55.8	50.4
5	3.00	30	20	85	12.2	2.0	14.2	70.0	75.6	70.7
6	3.00	100	20	85	35.0	5.6	40.6	56.2	59.1	56.6
7	6.00	30	20	85	12.3	1.8	14.1	68.9	66.8	68.6
8	6.00	100	20	85	39.6	6.0	45.6	65.5	65.2	65.5
9	0.30	30	60	85	10.9	1.9	12.8	59.8	68.2	60.9
10	0.30	100	60	85	28.0	5.2	33.2	42.0	51.0	43.2
11	1.00	30	60	85	12.7	2.2	14.9	71.0	81.7	72.4
12	1.00	100	60	85	36.7	6.0	42.7	59.9	64.0	60.4
13	3.00	30	60	85	13.8	2.1	16.0	77.1	77.7	77.2
14	3.00	100	60	85	40.4	6.4	46.9	65.0	67.8	65.3
15	6.00	30	60	85	16.0	2.4	18.4	90.9	88.2	90.5
16	6.00	100	60	85	44.4	6.6	51.1	71.0	69.8	70.9
17	0.30	30	20	85	7.9	1.6	9.4	44.2	57.2	46.0
18	0.30	100	20	85	19.7	4.1	23.9	31.1	42.7	32.7
19	1.00	30	20	85	10.7	1.9	12.6	60.9	71.9	62.4
20	1.00	100	20	85	31.6	5.6	37.2	50.1	58.3	51.2
21	3.00	30	20	85	12.5	2.1	14.6	69.1	76.4	70.1
22	3.00	100	20	85	34.8	5.7	40.4	56.1	60.2	56.7
23	6.00	30	20	85	13.0	2.0	15.0	72.9	73.7	73.0
24	6.00	100	20	85	37.4	5.7	43.1	59.8	60.0	59.8
25	0.30	30	60	85	10.3	2.0	12.3	55.8	69.3	57.6
26	0.30	100	60	85	29.4	5.3	34.7	48.6	57.5	49.8
27	1.00	30	60	85	11.5	2.0	13.5	64.9	73.0	65.9
28	1.00	100	60	85	29.7	5.1	34.8	47.7	53.9	48.5
29	3.00	30	60	85	16.0	2.6	18.6	88.7	94.2	89.4
30	3.00	100	60	85	34.3	5.3	39.7	59.9	60.8	60.0
31	6.00	30	60	85	15.2	2.3	17.4	84.7	83.9	84.6
32	6.00	100	60	85	43.3	6.4	49.7	73.2	70.6	72.9

As indicated in Table 4, the highest recovery of 90.5% for TREE and 90.9% for LREE was obtained from Test 15 that was conducted using 6 M acid solution, 30 g of ash/liter of acid solution and 60 minutes of leaching time. Clearly, higher molarity, longer retention time and lower solid content, which means less amount of REE to dissolve, resulted in the higher recovery of LREEs. But as indicated in Test 29, the highest molarity did not produce the highest recovery for the HREEs; the intermediate level of molarity, i.e., 3 M resulted in 94.2% HREE recovery. Additional results not shown in the table, indicate that the pregnant leachate solution also contained many impurities, notably, Mg, Al, S, K, and Ca etc.

**3.2.2 Solvent Extraction (SX) Experiments:** Although high REE recovery is very much desirable, we wanted to focus on the REE grade in this first series of tests. As shown in Table 4, test 16 resulted in the maximum REE concentration (51.1 ppm) in the leachate solution. We utilized those test conditions to produce more than 1 liter of leachate solution to serve as the feed for the SX test series. We used a 2<sup>3</sup> experimental program varying three important factors, such as pH, organic(O)/aqueous(A) and solvent concentration in kerosene, each at two levels, as listed in Table 5. Using two replicates for each test condition, we conducted a total of sixteen SX tests (test 33-48 in Table 5). Based on our literature survey, we used a 1:1 mixture of tributyl phosphate (TBP) and Cyanex 572 as the organic extractant and Kerosene as the diluent for all SX test. A

mixing time of 10 minutes was also kept constant for the organic solvent and leachate solution mixture of 100 ml for all tests. Very clear organic phase above the aqueous phase was observed. For operating condition listed for the test no. 40, three stages of solvent extraction was performed to examine the level of improvement in the REE grade achievable by pursuing multiple stages of SX. The test samples are still being analyzed at the UNL's lab.

Table 5 - Solvent Extraction test conditions

Test #	Solvent Extraction Test Conditions								SX Product Volume (ml)	
	Solvent Concentration (%)	pH	O/A	Time (min)	Kerosene (ml)	TBP (ml)	Cyanex (ml)	pH	Aqueous	Organic
33	30	0.5	1:4	10	14	3	3	0.5	90	19
34	30	0.5	4:1	10	56	12	12	0.5	27	78
35	30	1.0	1:4	10	14	3	3	1.2	105	19
36	30	1.0	4:1	10	56	12	12	1.2	28	78
37	50	0.5	1:4	10	10	5	5	0.5	100	20
38	50	0.5	4:1	10	40	20	20	0.5	25	79
39	50	1.0	1:4	10	10	5	5	1.2	101	21
40	50	1.0	4:1	10	40	20	20	1.2	28	77
41	30	0.5	1:4	10	14	3	3	0.5	113	18
42	30	0.5	4:1	10	56	12	12	0.5	28	77
43	30	1.0	1:4	10	14	3	3	1.2	117	15
44	30	1.0	4:1	10	56	12	12	1.2	28	78
45	50	0.5	1:4	10	10	5	5	0.5	102	20
46	50	0.5	4:1	10	40	20	20	0.5	33	80
47	50	1.0	1:4	10	10	5	5	1.2	115	15
48	50	1.0	4:1	10	40	20	20	1.2	27	78

**3.2.3 Scrubbing Tests:** During the solvent extraction process, many of the undesired impurity elements such as, K, Fe, Ca, K, S, Al also get extracted from the leachate solution. To remove the impurities from the REEs, multiple stages of scrubbing of the organic phase are usually required. Hot water at 70 (°C) was used in the scrubbing stage. Hot water with two different A/O ratio (2:1 and 4:1), and two different number of stages (2 and 4) were used to remove the impurities. With two replicates, for each test condition, a total of 8 scrubbing tests, as listed in Table 6, were conducted. The aqueous (raffinate) and organic phases were separated using separating funnels and shipped for ICP-MS analysis.

Table 6: The operating conditions used for Scrubbing and Precipitation Stripping tests.

Test #	Scrubbing Test conditions				Test #	Precipitation-Stripping			
	A/O	No. of Stages	Orgnic phase (ml)	Hot water (ml)		Oxalic Acid Concntration (w/w %)	Time (min)	pH	O/A
49	2	2	35	70	57	10	30	2.3	1:1
50	2	2	35	70	58	10	30	2.3	1:1
51	2	4	35	70	59	10	30	3.3	1:1
52	2	4	35	70	60	10	30	3.3	1:1
53	4	2	35	140					
54	4	2	35	140					
55	4	4	35	140					
56	4	4	35	140					

**3.2.4 Precipitation Stripping Tests:** After scrubbing the loaded organic and removing some of the impurities, precipitation with oxalic acid was directly performed on the enriched organic phase without stripping stage, which can decrease the consumption of acid which is used as stripping reagent. Different Parameters such as Oxalic Acid (%), time (min), pH and O/A ratio are effective in the precipitation stage. For each test, exactly 45 ml of the organic phase was used, with 10% oxalic acid, with an O/A of 1:1. At this time, pH was the only variable used and a total of four tests were conducted with two replicates for each test condition, as indicated in Table 6. Initially lower pH close to 1 and below were tested; since no precipitation resulted at that pH range, pH above 2, were tried. Good precipitation was observed at pH 2.3 and 3.3. after allowing sufficient amount of residence time (30 min). All three different phases, precipitated solid, aqueous and organic are shown in Figure 2. The aqueous phase is the precipitating solution, and the organic solution is the stripped organic extractant. The solid phase (precipitate) is solid rare earth oxalate as well as many remaining impurities. The REE oxalates was calcined at high temperature to obtain the rare earth oxide powders. The test samples are still being analyzed for REE contents.

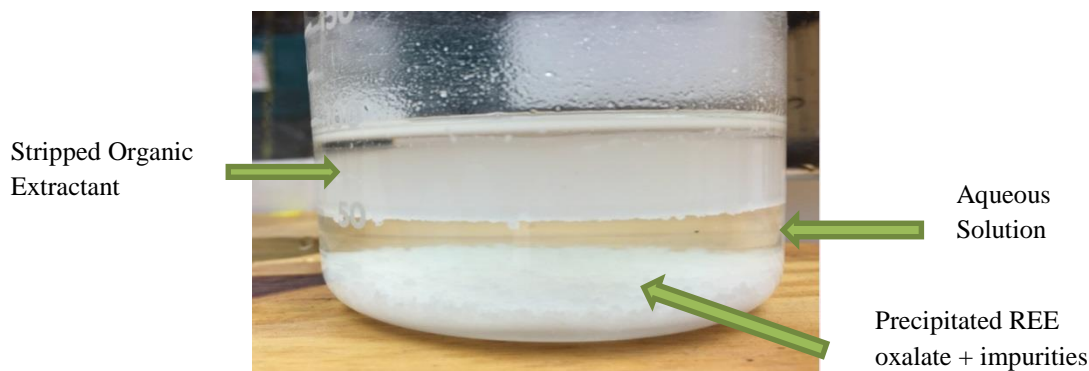


Figure. 2 – Three distinct phases after precipitation stripping

#### 4. Discussion, Conclusions, Recommendations

We have completed nearly half of the project work so far. Based on the results we have obtained, we are very hopeful about the technical feasibility of the concept. If the concept is economically viable, it will increase REE reserve of the US by nearly six-fold (from 1.8 million ton to 11.8 million ton) and make us less dependent on REE imports. REEs are at the heart of many high-tech applications, such as consumer electronics, wind turbine, solar panels etc. So qualitative benefits to people, prosperity, and the planet are understandable. Based on the results obtained from this on-going Phase I study, following conclusions/recommendations may be made.

- The characterization work completed on fourteen coal samples of different coal ranks, from lignite to anthracite, originating from all over the country indicated a maximum coal ash REE content of more than 700 ppm. Majority of the REEs were of the LREE category. A maximum of 27% of HREE was found in a low volatile bituminous coal sample. The concentration of other strategic minerals, with the exception of lithium, were extremely low, below 10 ppm in most cases. That's why it was decided to restrict our attention to REEs only.

- It can be inferred that the REE contents of the higher rank coals, such as anthracite and low volatile bituminous coal are generally higher than the lower rank coals, such as lignite and high volatile-C bituminous coal. However, no specific correlations could be established.
- More characterization study using XRD and SEM will be needed to identify the specific major minerals associated with the REEs in coal ash. The resulting information will be useful for the Physical Preconcentration study to be conducted later in this project.
- The acid leaching tests conducted using a 4x2x2 factorial design indicate that the highest level of LREE recovery is achieved at the highest molarity of the acid solution, lowest solid content and longest retention time. However, the highest recovery of HREEs needed only an intermediate level of acid molarity.
- In addition, a total of sixteen solvent extraction tests, eight scrubbing tests, and four precipitation-stripping tests have been completed and ICP-MS analysis of the tests samples is being done in a commercial laboratory at this time. The results from those samples will lead us to next round of experiments. Our goal is to produce approach a grade of 2% REE in the product starting from an REE concentration of ~700 ppm in the feed coal ash.
- We will study one other coal sample to have a better understanding of the optimum operating conditions and their relation to coal ranks and other specific characteristics of coal.
- Cost analysis will be conducted in the Phase II study.

It may be noted that all ICP-MS analysis for solid samples were done at the commercial lab of BV Minerals ([www.bureauveritas.com/um](http://www.bureauveritas.com/um)) in Canada and liquid samples in the spectroscopy lab at the University Nebraska-Lincoln (<http://redoxbiologycenter.unl.edu>). We have an ICP-MS set up in our university; but that is the only one for the entire university; so its turn-around time is much longer; that's why we had to look for a reliable lab outside.

##### **5. Assurance that research misconduct has not occurred during the reporting period**

*Yes, we assure that there was no misconduct.*

**C. References (In addition to the 15-page limit for the *Body of the Project Report*)**

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