Recovery of High Purity Rare Earth Elements (REE) from Coal Ash via a Novel Electrowinning Process: Final Report

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Recovery of High Purity Rare Earth Elements (REE) from Coal Ash via a Novel Electrowinning Process:

Final Report

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Executive Summary

The goal of this project is to produce a high purity, separated (>90%) rare earth oxide (REO) product from coal-based sources. This product will be generated using the following three steps:

1. Battelle's Acid Digestion Process (ADP): The ADP leaches milled and pretreated coal fly ash with nitric acid, roasts the loaded acid solution containing rare earth elements (REE) and produces a pregnant REE solution.

2. Solvent Extraction (SX) Upgrading: The solvent extraction removes REE from the pregnant solution using an organic extractant, then strips REE from the organic phase, yielding a mixed loaded REE solution/material.

3. Rare Earth Salts' (RES) Electrochemical Separation and Purification Process: The staged electrochemical process separates REE from the mixed loaded REE solution/material, producing a separate REO product.

This report covers laboratory testing, production of a high purity coal-based REO, process design of the overall REE recovery and purification process, technoeconomic assessment (TEA), and a commercialization plan discussing the overall REE recovery and purification process.

The laboratory testing was performed in three stages – preliminary testing to inform the optimization of Battelle's Upgrading SX and RES' separation and purification processes (Step 2 and Step 3 above), followed by solution SX upgrading laboratory testing, and separation and purification processes laboratory testing. All testing in this report was performed starting from a pulverized coal combustion (PCC) power plant ash, which had an average REE+Y+Sc concentration of 513 parts per million (ppm).

The first stage of the laboratory testing is described in Section 2.0 (Preliminary Testing and Feedstock Discussion), which consists of an analysis of the feedstock used during this project. It also provides data from roasting and SX studies, which were used to inform the testing associated with SX upgrading. Furthermore, this section describes how zinc was a challenge in RES' separation and purification processes. This was discovered by testing RES' separation and purification processes using a surrogate solution provided by Battelle. The surrogate solution contained the expected concentration of REE and contaminants, which were predicted using data from preliminary roasting and SX studies. The overall concentration of the solution was 50 g/L with respect to metals, and it was approximately 60% REE. The balance of material was primarily zinc (major contaminant), iron, and aluminum, and with approximately 50 mg/L of organic extractant material.

The report continues describing testing of Battelle's SX upgrading (Section 3.0). This section outlines the necessary steps to achieve a targeted REE purity (60% of the measured solutes) out of the SX step. The best result empirically achieved was 55% and the best projected result from the models was 58%. The models described in this section can be used to estimate optimal operational points for the extraction and stripping processes, where high selectivity for REE is accomplished. The primary contaminants are zinc and aluminum; this section also explains Battelle's solution for the selective separation of zinc from REE using a commercially available cationic extractant. Based on the information from Section 2.0, the selective separation of zinc from REE is of high importance due to the tendency of zinc to follow the REE in SX and other separation processes, impacting the ability to achieve a separated, saleable REO product.

The third stage of the laboratory testing is described in Section 4.0 (Rare Earth Salts Separation Process - Laboratory Testing). This section covers laboratory testing to determine ideal operating parameters for the successful separation of REE (Step 3 above) from the REE mixture produced through Battelle's SX upgrading process (Step 2 above). Testing was performed on either surrogate solution provided by Battelle, surrogates produced in-house, or mineral concentrates that RES procured for its commercial demonstration plant (CDP). Some of the most important testing in this section pertains to RES' research to reduce the amount of zinc in the impregnated REE solution by using chemical approach (pH and complexing agents) and using RES's proprietary technology. The approach that yielded the best result was a precipitation process using tartaric acid under pH control. It was found that at a pH of 2.1, the precipitate material was composed of 92% REE and 2% zinc. This test utilized the surrogate solution provided by Battelle. Also, during this stage of the project, the flow rate of the electrowinning process was examined to determine the approximate operating conditions and expected separation flow rates for the system without zinc contamination. The initial conditions were set within the operating parameters as outlined within the patented process. However, modifications were required to obtain the expected splits within the separation process. Additionally, fractions from different initial sources were combined at a specific point in the separation process to ensure the coal-sourced material could be mixed in with other materials at various points in the process flow with no loss of efficiency in the process, enabling a more efficient and flexible purification train.

Following the laboratory testing, the production of a high purity coal-based REO product is described in Section 5.0 of this report. The production starts with Battelle's ADP, yielding a pregnant REE solution, which is then fed to the SX upgrading process (commercially available cationic extractant is used for removal of zinc). The loaded REE stripped solution (nitric acid solution), containing the REE and other metals with a low concentration of zinc, is roasted at a high temperature to convert REE nitrates into oxides. At this temperature, most of the alkali and alkali earth metal nitrate salts, such as, barium, calcium, potassium, and sodium nitrates are not converted to oxides, facilitating the separation of these impurities from REE oxides by performing a water wash step follow by a filtration step. The product is a high aluminum/REE oxide material with a lower zinc concentration than the earlier surrogate solution mentioned. This high aluminum/REE oxide material is then fed to RES' conversion process. During this process, the high aluminum concentration is not an issue since aluminum remains an insoluble oxide during the conversion of REE to soluble salts and can be recovered as a potential high purity byproduct (>99% purity, potentially). During the roasting step of Battelle's ADP, an iron/scandium material is also produced. This material is treated by RES' conversion process to recover scandium and make an iron byproduct. As a result of further testing, RES found that the conversion process could allow for the production of a pure scandium chloride or oxide product (>99% purity) along with a substantial amount of an iron chloride or oxide byproduct (also >99% purity).

The REE salt obtained from the conversion process is dissolved in hydrochloric acid yielding a loaded REE solution. The remaining zinc in the loaded REE solution is removed by precipitating the REE using tartaric acid under pH control. The zinc remained in the solution and the REE precipitate is calcined at a high temperature and re-dissolved in hydrochloric acid, yielding a concentrated REE solution. This solution is then fed to their electrowinning process to obtain the final coal-based REO product. The products obtained during this project are the following:

- Approximately 1.1 grams of oxide material, having a TREO (Total Rare Earth Oxide) concentration of >90% with an 89% +/- 2% lanthanum content (oxide basis).

- Approximately 0.2 grams of oxide material having a TREO concentration of >95% with a 90% +/- 2% lanthanum content (oxide basis).

At the end of this project, a TEA was performed on the overall Battelle and RES processes to recover high purity REO from coal fly ash. The assessment was informed by a chemical process model based upon laboratory testing results, preliminary sizing estimates for the equipment and a factored capital cost estimation. This TEA suggested for a 20-year project, the rate of return is 27.6% on a capital investment of $76.4 million, with a simple payback period (FCI/annual cash flow) of 3.8 years. However, the process is dependent upon a ferric chloride byproduct for profitability, and scandium being the bulk of the rare earth revenue stream. The availability of byproducts from coal-based sources may actually be a benefit compared to other marginal sources, such as monazite sands, which have minimal other mineral values to subsidize the REE recovery.

Looking toward commercialization, the process needs to be scaled to an integrated bench-scale size, capable of producing sample quantities to engage potential offtake partners for REO and byproducts. A shift should be made toward the development of byproducts that subsidize REE recovery from coal sources, and the validation of the marketability of the key products. In particular, high purity scandium oxide product needs to be generated from coal sources so that end users can validate whether it is usable in their processes and their financial tolerance. Additionally, key byproducts from the process such as ferric chloride and aluminum oxide need to be generated in quantities that can be tested by commercial end users. As feedback from end users is received regarding the samples, the integrated bench-scale unit can be adjusted to meet end user requirements.

Once the rare earth products and byproducts have been validated by end users at the integrated bench-scale, the process will be scaled through two stages of piloting, first at 0.5 tonnes per hour, then 15 tonnes per hour of coal ash before a commercial plant is built. Rare Earth Salts has an existing 18 ton per day of REO plant operating and has made significant progress in placing the rare earth products from this system into the market. It is expected that the coal-based REE from the pilot plants can be processed in their existing system with minimal adjustments, and even blended with current feed streams so that customer validation of the coal-based REE can be accomplished quickly with minimal process interruptions.

1.0 Introduction

As directed by Congress, the United States (U.S.) Department of Energy (DOE) is investigating the economic feasibility of the recovery of REE from domestic U.S. coal and coal byproducts. The Department of Energy's National Energy Technology Laboratory (NETL) has characterized a number of REE-bearing samples of coal and coal-related materials. Rare earth elements have been found in varying concentrations ranging up to 1,000 ppm by weight in the following materials in the United States: coal mine roof and floor materials, run-of-mine coal, prepared coal, partings, pit cleanings, coal preparation refuse, and tailings. REE can be found in coal byproducts, including ash, coal-related sludge, and mine drainage. Certain coals can contain a higher ratio of heavy (generally more valuable) REE than found in other sources of REE such as natural ores. DOE is particularly interested in sources that have higher than 300 ppm REE. Since most coal materials start at REE concentrations well below 1,000 ppm, the yield of REE from any separation process is likely to be low, and minimizing costs associated with recovery is a key challenge. Therefore, DOE has funded groups with novel processes, able to recover REE from coal sources, while minimizing the processing costs.

The REE are the 14 naturally occurring elements between lanthanum and lutetium on the periodic table, along with yttrium and scandium which have similar chemical properties. Their symbols and atomic numbers are listed in Table 1 for reference. They have become critical in renewable energy and defense applications, where they are used to make magnets for motors and generators, metal alloys, and in various sensor components. Occasionally, yttrium and scandium are considered separately, and so the group of rare earth elements is sometimes referred to as REE+Y+Sc for clarity in this report. Element 61, promethium, is not naturally occurring and not included in the analyses for this report.

Table 1: List of rare earth elements, their symbols, and their atomic numbers.

Rare Earth Elements, Symbols, and Atomic Numbers											
Sc	Scandium	21	Pr	Praseodymium	59	Gd	Gadolinium	64	Er	Erbium	68
Y	Yttrium	39	Nd	Neodymium	60	Tb	Terbium	65	Tm	Thulium	69
La	Lanthanum	57	Sm	Samarium	62	Dy	Dysprosium	66	Yb	Ytterbium	70
Ce	Cerium	58	Eu	Europium	63	Ho	Holmium	67	Lu	Lutetium	71

Battelle has been validating the economic viability of recovering REE from coal ash using its patented (US6011193) closed-loop Acid Digestion Process (ADP). Based on results from the sampling and characterization work, a PCC plant fly ash was selected as the target feedstock for the process. The plant selected for this study operates in Ohio on primarily Appalachian Basin coals and had a high total REE+Y+Sc concentration at 513 ppm +/- 13 ppm. A TEA done on Battelle's ADP process suggested that it could be economically applied to between 5% and 47% of U.S. coal sources.

The goal of this project is to produce a high purity, separated (>90%) rare earth oxide (REO) product from coal-based sources. This product will be achieved using the following three steps:

1. Battelle's ADP: The ADP process involves pretreatment of ash (milling and caustic leaching), leaching of pretreated ash with nitric acid, roasting of loaded acid solution

       containing REE, and water leaching of residual from roasting step, resulting in a REE pregnant solution.

2.   Solvent Extraction (SX) Upgrading: The SX involves the extraction of REE from a pregnant REE solution using an organic extractant (note after extraction, the aqueous phase will be a residual solution and the organic phase will contain REE), and stripping of REE from the organic phase product obtained from the extraction using an acid solution (the stripped solution will be the final purified product containing REE, organic traces, and traces of other metals for further separation in the electrowinning process).

3.   Rare Earth Salts' (RES) Electrochemical Separation and Purification Process: The staged electrochemical process will separate REO products from the mixed REE solution. Testing by RES will also include investigation of options to minimize the solvent extraction steps.

This report covers laboratory testing, production of the high purity coal-based REO, process design of the overall REE recovery and purification process, TEA, and commercialization plan discussion of the overall REE recovery and purification process.

The laboratory testing was done in three stages – preliminary testing to inform the optimization of Battelle's SX upgrading and RES' separation and purification processes (Step 2 and Step 3 above), followed by SX upgrading laboratory testing, and separation and purification processes laboratory testing. All testing in this report was performed starting from a PCC power plant ash, which had an average REE+Y+Sc concentration of 513 ppm.

Sections 2.0 through 5.0 of this report discuss the laboratory testing and production of high purity coal-based REO. Following the laboratory optimization testing and production of REO, a process design (Section 6.0) and technoeconomic assessment (Section 7.0) of Battelle's and RES' processes to recover high purity REO from coal fly ash was conducted. The intent of this economic study was to identify key economic hurdles to commercialization so that a rational development plan can be constructed (Section 8.0).

2.0 Preliminary Testing and Feedstock Discussion

2.1 Coal-based Feedstock

This project focused on coal fly ash from PCC power plants. PCC ash is readily available, as many of the largest coal power plants operate PCC furnaces. In fact, as of 2013, over 90% of the global coal power generation capacity was from PCC plants (IEA Clean Coal Centre, 2013). Additionally, fly ash is already a small particle size source, reducing the amount of comminution required, and is a coal-based REE source that does not require permitting, bonding, maintaining, or closing of a coal mine. The American Coal Ash Association estimates over 40 million short tons of fly ash was produced in the United States in 2015, while only about 55% of this coal byproduct was reused in other applications, with the balance going to landfills or ash ponds (American Coal Ash Association, 2015).

The feedstock utilized during this project comes from a specific operating PCC electricity generating unit (EGU) in Ohio. This EGU is at a plant with two additional units, but uses a separate source of feed coal which has contained consistently high (500+ ppm) REE concentrations. The EGU has the option to divert fly ash to separate it from the other units, making it an attractive target for a co-located REE recovery plant. Currently, fly ash is landfilled, and occasionally mixed with flue gas desulfurization wastes.

Table 2: Summary of the REE content in PCC ash used during this project.

Elements	Concentration, ppm
Lanthanum	73.8
Cerium	151
Praseodymium	17.3
Neodymium	68.1
Samarium	15
Europium	3.24
Gadolinium	14.6
Terbium	2.4
Dysprosium	15.1
Holmium	3.2
Erbium	9.1
Thulium	1.33
Ytterbium	8.4
Lutetium	1.27
Yttrium	92
Scandium	37
REE+Y+Sc	512.84

Battelle has already conducted a characterization study of PCC power plant ash as feedstocks in its ADP development project (Battelle, 2017). Four samples were analyzed in 2016, from two separate stacks of fly ash in the landfill. Then, prior to the 2017 laboratory testing for Battelle's ADP, four fly ash samples from the same EGU were analyzed. In 2016, the samples averaged 545 ppm total REE, and in 2017 the samples averaged 478 ppm total REE, and they had consistently high concentrations of scandium and yttrium. Although REE concentrations

dropped from the first samples in 2016, these samples suggest that the fly ash maintains high concentrations over extended periods of time. The PCC power plant ash during this project had a total REE concentration of about 513 ppm (see Table 2).The PCC power plant ash was milled to reduce particle size prior to the ADP step of the proposed technology.

2.2   Preliminary Roasting Studies

In Battelle's ADP, a thermal process is implemented to separate base metals (e.g. Al, Fe) from the REE. This step takes place after milled and pretreated PCC power plant ash has been leached with nitric acid. The leached acid, containing REE and other metals, is roasted at an optimal temperature where the base metals are converted to oxides, allowing the REE to be leached away from them with a water wash, resulting in a REE pregnant solution. Therefore, at the beginning of this project, preliminary roasting experiments were performed with the purpose of finding this optimal temperature. Roasting tests were conducted at four temperatures between 140°C and 190°C (140, 157, 173, and 190°C). These temperatures were chosen based on the results obtained from past studies (see the final report for DE-FE0027012: "Recovery of Rare Earths Elements from Coal and Coal Byproducts via a Closed Loop Leaching Process", Battelle, June 7, 2017). To obtain a loaded solution for the roasting experiments, PCC power plant ash was leached using 35% nitric acid for 30 minutes at a high temperature. The leached acid solution was then filtered and used for the roasting experiments explained above. The procedure for these experiments is available in Appendix A. The results from these experiments also helped with predicting concentrations of REE and other metals in a surrogate solution, which was prepared by Battelle. This surrogate solution was sent to RES, allowing preliminary testing of their purification process with expected levels of REE, contaminants, and organic material (Section 2.4.2).
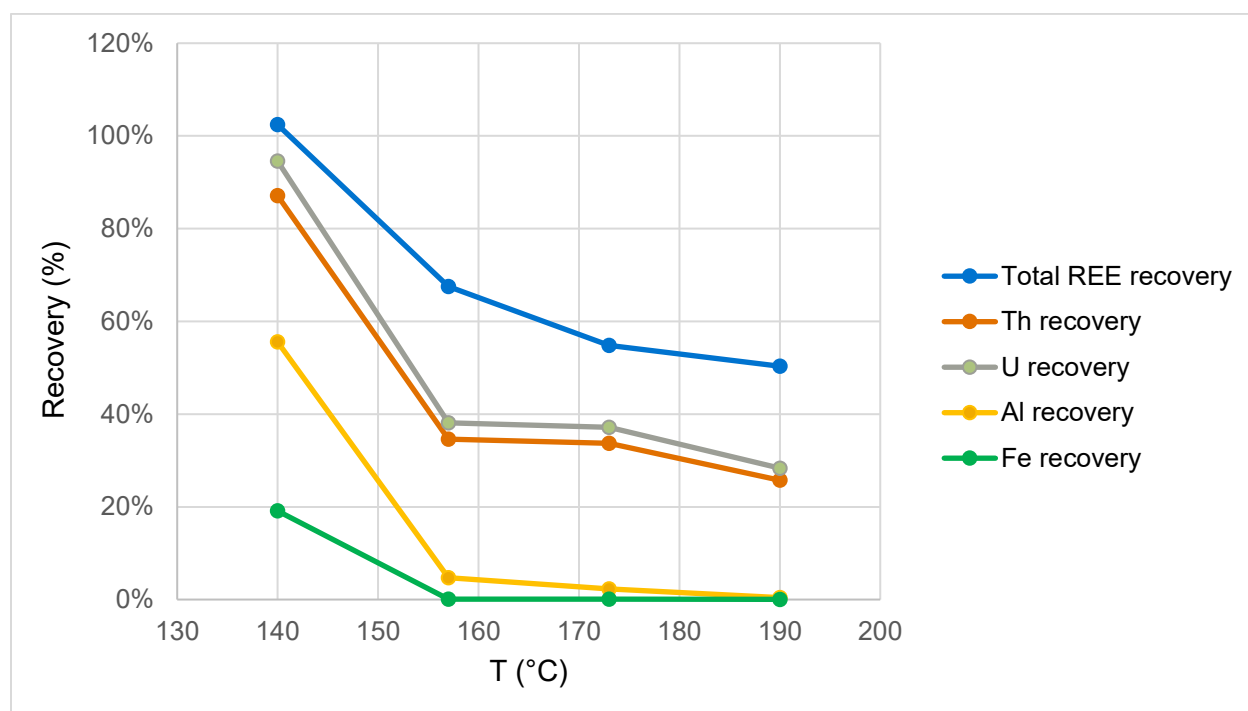
Figure 1: Roasting temperature vs. recovery of REE and different contaminants in loaded water (feed to SX process).

Figure 1 shows the result of preliminary roasting experiments. At temperatures below 157°C, an increase in REE recovery is observed along with an increase in the recovery of major contaminants (e.g. Fe, Al) and other contaminants of concern (e.g. Th, U). At temperatures above 157°C, a decrease in REE recovery is observed as well as a decrease in the recovery of major contaminants. Based on these results, ~157°C is a near optimal roasting temperature at which most of the iron (0.07% of the iron is recovered) and aluminum (4.7% of the aluminum is recovered) are oxidized and rare earths remain as nitrates (68% of the REE are recovered, with much of the loss as low value cerium oxide).

2.3   Preliminary Solvent Extraction (SX) Studies

The main objectives of the REE preliminary SX tests were to tailor the pH ranges and acid combinations used in the SX experimental design (further information about experimental design in Section 3.0), and to understand the effect of adding reducing agents to the SX process. The results from these experiments also helped to predict the REE and contaminants concentrations in the surrogate solution prepared by Battelle.

A reducing agent study was first performed during this preliminary SX studies. The reducing agent was added before the extraction step, attempting to reduce the iron remaining in the solution (Pregnant REE solution after roasting process) from ferric to ferrous iron, making the reduced iron less likely to be extracted. The results obtained show that the addition of sodium metabisulfite, sodium thiosulfate, and iron powder didn't impact the high percent of iron extracted (see Table 3). However, it was also discovered that iron would not strip in the REE stripping step at a pH of 0.75 as originally expected (see Table 4). Therefore, REE can be recovered in the stripped solution, and iron will remain in the extractant, which will be stripped during an extractant regeneration step.

Table 3: Percent of iron extracted after addition of different reducing agents.

Reducing agent	Conditions	% of Iron Extracted
Sodium Metabisulfite	Starting pH 3.34 (Equilibrium pH 2.38)	96.9%
Sodium Thiosulfate	Starting pH 3.34 (Equilibrium pH 2.39)	97.3%
Iron Powder	Starting pH 3.35 (Equilibrium pH 2.41)	99.5%

Table 4: Percent of REE and iron stripped during REE stripping step at starting pH 0.74 (equilibrium pH 0.84).

Species	% Stripped
Fe	0.61%
REE+Y+Sc out of total available	87.60%
REE+Y+Sc out of total measured	15.68%

One complication encountered during the above preliminary tests was the slow disengagement of the aqueous and organic phases in the extraction step. The addition of a modifier to the extractant (15% Cyanex 572 in Solvent 467) provided improvement in phase disengagement. The modifiers studied were isodecanol (Exxal 10) and tributyl phosphate (TBP). The amount of modifier added to the extractant was based on the fact that if the amount of modifier exceeded the amount of current active ingredient (Cyanex 572), disengagement between the active ingredient and modifier may occur, causing operational challenges during the extraction process.
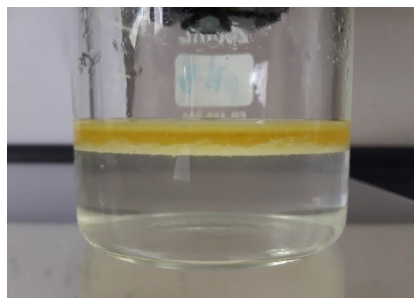
Figure 2. After extraction with 13.2%:12% Cyanex 572:TBP extractant

Figure 3. After extraction with 13.2%:12% Cyanex 572:Exxal10 extractant
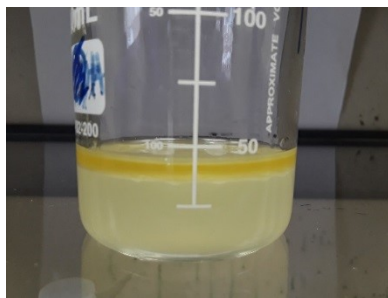
Figure 4. After extraction with 15% Cyanex 572 extractant

Figure 2, Figure 3, and Figure 4 show the disengagement between the organic and aqueous phases after extraction using the current extractant (15% Cyanex 572) and the two modifiers studied (Exxal 10 and TBP). In each case, the extraction was performed at starting pH 2.5, with a mixing time of 10 minutes and mixing speed of 600 to 800 rpm. The most favorable phase disengagement between the organic and aqueous phase occurred after extraction with 13.2%:12% Cyanex 572:TBP extractant (see Figure 2). Following this testing, two more extraction tests were performed to investigate the difference between the performance of the current extractant (15% Cyanex 572) and the new modified extractant (13.2%:12% Cyanex 572:TBP). The extraction tests were performed at starting pH 3.3, with a mixing time of 20 minutes and mixing speed of 600 to 800 rpm. The results obtained are shown in Table 5. The results show that the performance of Cyanex:TBP extractant is superior to the Cyanex 572 extractant alone. Therefore, TBP was incorporated into the extraction portion of the design of experiments to further investigate the performance of Battelle's modified extractant. The design of experiment for SX is discussed in Section 3.0.

Table 5: Extraction results for 15% Cyanex 572 and 13.2%:12% Cyanex 572:TBP.

Elements	% Extracted	
	15% Cyanex 572 (equilibrium pH 2.43)	13.2%:12% Cyanex 572:TBP (equilibrium pH 2.29)
Sc	93.2%	93.2%
Y	84.2%	99.1%
La	10.2%	12.8%
Ce	24.1%	43.3%
Pr	24.8%	53.7%
Nd	24.6%	61.3%
Sm	50.5%	93.8%
Eu	58.8%	96.9%
Gd	54.3%	96.5%
Tb	76.7%	98.7%
Dy	85.6%	99.4%
Ho	86.6%	99.4%
Er	90.4%	99.2%
Tm	95.8%	99.4%
Yb	97.9%	99.4%
Lu	97.7%	99.3%
REE+Y+Sc out of total available	43.89%	63.9%

2.4 Preliminary Separation Studies

2.4.1 Battelle Surrogate Solution

Battelle synthesized a surrogate solution and sent it to RES for preliminary testing on their separation technology. The surrogate solution was designed based on the results of preliminary roasting and SX testing as explained in Section 2.2 and Section 2.3, respectively. This solution allowed RES to test their purification process with expected levels of contaminants and organic material. The overall concentration of the solution was 50 g/L (approximately 3.7-liters of solution) with respect to metals, and was approximately 60% REE. The balance of material was primarily zinc (major contaminant), iron and aluminum, with approximately 50 mg/L of organic extractant material remaining after the SX, which was included in the surrogate.

2.4.2 Rare Earth Salts Initial Testing

Rare Earth Salts performed the initial step in the separations process on the as-received surrogate solution obtained from Battelle. The separation was performed in a newly constructed experimental apparatus within the range of what a normal separation would be run (proprietary). Separations performed using a newly constructed apparatus typically take a number of cycles (3-5) before solid material is obtained from the experiment. The surrogate solution indicated little to no solid development after 10 cycles, indicated there was an issue in the system. The experiment was repeated, yielding the same results.

Further analysis of the system indicated that the only two factors RES had not addressed in previous systems was the presence of the organic component (residual from the SX process) and the presence of a significantly high concentration of zinc. An experiment using a surrogate without zinc, but with the presence of the organic component, yielded separation as expected, narrowing the problematic variable to zinc. The experimental conditions were then changed such that much higher potentials than typically used were applied to the system yielding a small amount of material which was high in zinc but did not afford a reasonable separation of either the rare earths or the zinc from the rare earths.

Based on this result, alternate routes were investigated by Battelle to produce the REE concentrate (feedstock to RES separation technology). Section 3.3 describes Battelle's effort to selectively separate zinc from REE using a commercially available extractant. Concurrently, RES examined ways to reduce the amount of zinc in the REE impregnated solution by using a chemical approach (pH and complexing agents) and using RES's proprietary technology (see Section 4.2). For further information on RES' initial testing see Appendix D.

3.0 Solvent Extraction (SX) Upgrading Laboratory Testing

3.1 Introduction

This section discusses the laboratory testing performed to determine proper operational parameters in the SX circuit. The laboratory testing was completed in two stages – extraction tests and stripping tests. Data obtained from preliminary testing was used to determine pH ranges and acid combinations for these experiments. All testing was performed starting from a PCC power plant ash, which had an average REE+Y+Sc concentration of 513 ppm. The ash was first milled in water, then leached with nitric acid to extract the REE, roasted to omit iron, aluminum, and most heavy transition metals, then leached back into water before SX testing (see Appendix B).

Surface response models were generated for the extraction and stripping of REE from leach solutions derived from PCC power plant ash. These models could be used to estimate optimal operational points for the extraction and stripping processes, where high selectivity for REE is accomplished. Recovery in single stage operations are generally low for the stripping sections, on the order of 30-40%, but it is expected that this could be overcome by running in multiple stages with careful control of pH.

At the outset of the project, the target for REE purity out of the SX step was 60% of the measured solutes. The best result empirically achieved was 55% and the best projected result from the model is 58%. The primary contaminants were zinc and aluminum. Based on work done by RES, the zinc was a known challenge in the separation and purification process, whereas the aluminum could be easily handled. With this information, Battelle selected a new extractant composition which was demonstrated in this work to be selective for zinc over the REE and could be implemented prior to the traditional SX steps as a pretreatment to remove zinc. With zinc removed beforehand, we have confidence that the REE purity out of the stripping step can exceed 60% of the measured solutes. Details can be also found in Appendix C.

3.2 Rare Earth Extraction

For the REE extraction testing, mixing time, starting pH, and modifier concentration were the factors selected for investigation, since they were the most impactful factors in the REE extraction operation based on the preliminary testing discussed in Section 2.3 and Appendix C of this report. The experimental design selected for this testing was a Box Behnken design, incorporating the three factors mentioned and three different levels for each factor. Three center points were included in the design to capture experimental error and no blocking factors were identified (Box & Behnken, 1960). The REE stripping tests were treated independently, using the optimized factors from the REE extraction tests as the feedstock for the experiments. This experimental design collected the necessary data to develop surface response models featuring all linear, quadratic, and cross-terms for use in optimizing the REE extraction process.

The design of experiment for REE extraction consisted of 15 tests. The results obtained are shown in Table 6, with the favorable results highlighted in blue. The data obtained from this experimental design were used to develop surface response models for REE recovery and REE purity (Table 7 and Table 8 show a summary of the models for REE recovery and REE purity, respectively). These two response models allowed for the prediction of the maximum REE recovery and purity that can be obtained in the extraction process within the conditions investigated in this experimental design. Based on the two models, approximately 97% recovery of REE and a maximum REE purity of ~25% can be achieved (see Table 9).

For the validation of the response models for REE recovery and REE purity, fitted line plots of the models were graphed (Figure 5 and Figure 6 are the fitted line plots for the REE recovery and REE purity model, respectively). It can be observed that the response model for REE recovery is a good fit to the data gathered in the experimental design, validating the second order model obtained. The response model for REE purity shows potential non-random scattering of the empirical versus model data, which could be improved with further testing. However, the second order model for REE purity was also the model yielding the best linear fit.

Table 6: Results obtained from the extraction design of experiments (single stage) Favorable results are highlighted in blue.

Test Number	Starting pH	Equilibrium pH	Mixing time (min)	Addition of TBP (Cyanex 572:TBP)	REE Recovery	REE Purity
1	3.28	2.51	20	13.2%:12%	69.7%	12.1%
2	2.52	2.34	20	14.1%:6%	69.2%	19.5%
3	2.52	2.48	1	14.1%:6%	24.1%	26.6%
4	3.28	2.86	1	15%:0%	37.3%	7.5%
5	4.03	3.06	1	14.1%:6%	75.2%	9.4%
6	4.03	2.73	10	13.2%:12%	78.0%	14.3%
7	3.26	2.65	10	14.1%:6%	79.6%	17.7%
8	3.26	2.65	10	14.1%:6%	79.2%	22.6%
9	2.51	2.43	10	13.2%:12%	65.6%	17.4%
10	4.02	2.74	20	14.1%:6%	84.3%	13.4%
11	3.27	2.64	10	14.1%:6%	77.8%	24.8%
12	2.49	2.37	10	15%:0%	35.7%	12.7%
13	3.26	2.74	1	13.2%:12%	65.7%	13.0%
14	4	2.79	10	15%:0%	71.2%	7.4%
15	3.26	2.56	20	15%:0%	58.9%	15.3%

Table 7: Summary of the REE recovery response model (second order model) for REE extraction showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-6.565
pH	3.892
t	0.172
TBP	1.663
pH:t	-0.040
pH:TBP	-0.289
t :TBP	-0.019
pH^2	-0.519
t^2	-0.002
TBP^2	-0.524
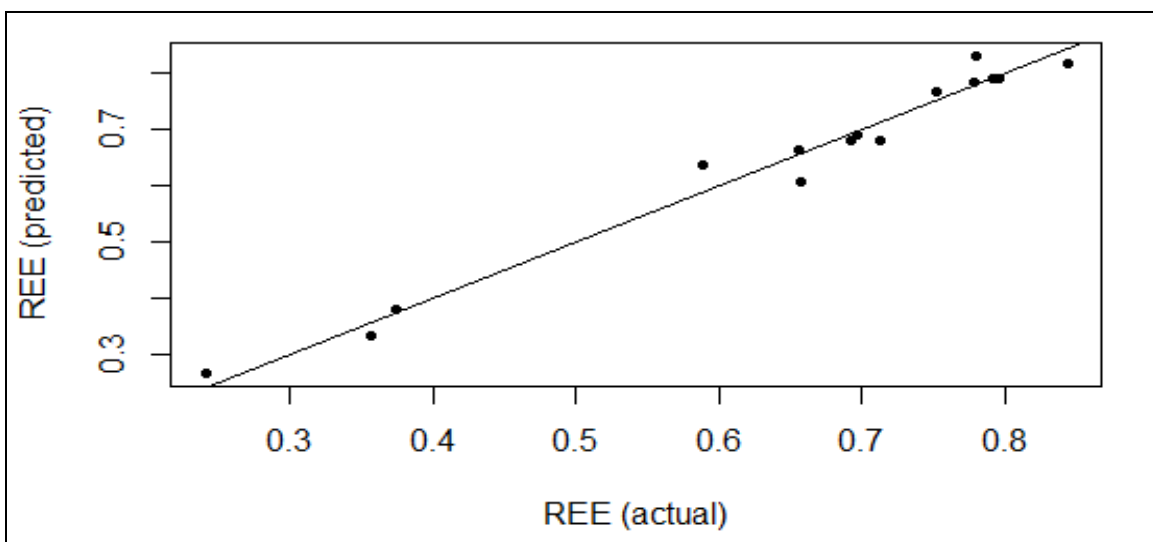
Figure 5: Fitted line plot of the REE recovery response model (second order model) for REE extraction.

Table 8: Summary of the REE purity response model (second order model) for REE extraction showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-2.842e+00
pH	2.386e+00
t	1.0099e-02
TBP	5.6446e-01
pH:t	-3.628e-03
pH:TBP	-5.600e-02
t :TBP	-3.900e-03
pH²	-4.775e-01
t²	-7.761e-05
TBP²	-3.926e-01
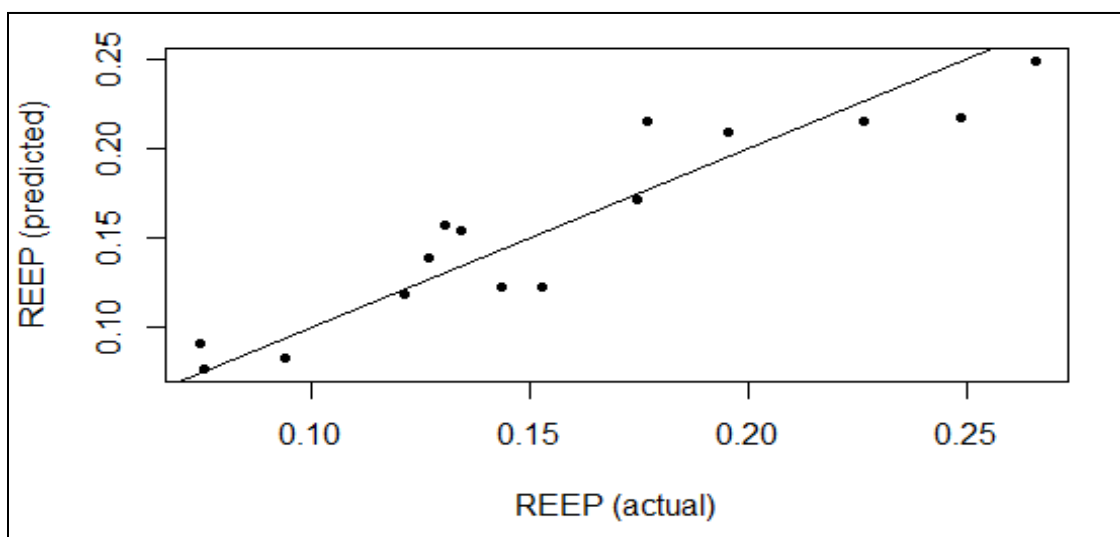
Figure 6: Fitted line plot of the REE purity response model (second order model) for REE extraction.

Table 9: Optimized factors for one stage REE extraction, equilibrium pH (pH), mixing time (t), and Cyanex 572:TBP concentration (TBP).

Results	Estimates
Maximum REE recovery	~97% at equilibrium pH 3.06, mixing time 10.4 mins, and TBP of 0.55 (Cyanex 572:TBP = 13.9%:7.6%)
Maximum REE purity	~25% at equilibrium pH 2.46, mixing time 1 min, and TBP of 0.54 (Cyanex 572:TBP = 13.9%:7.5%)

3.3 Zinc Extraction

Most coal sources contain zinc which needs to be removed, as it tends to follow the REE in SX and other separation processes and will impact the ability to achieve a separated, saleable product. A review of the COALQUAL database showed that the median zinc concentration on an ash basis for all samples is 113 ppm, with an average of 317 ppm. Further, the ratio of zinc to REE has a median of 0.35. The coal ash used in Battelle's process has a zinc concentration of 160 ppm with a ratio of zinc to REE of 0.31. Although the zinc concentration is higher than the median, it is still in the range of many coal sources, and the ratio of zinc to REE is near the median, but slightly lower. This suggests that our experience with zinc is likely to be representative of other REE sources, and the development of a simple scrubbing step to remove zinc from REE pregnant leach solutions will enable commercial development of coal-based REE sources. Therefore, during this study, a commercially available cationic extractant compound was investigated to selectively extract zinc from REE.

Table 10: Results of a selectively extraction of zinc from REE using a commercially available cationic extractant compound.

Element	%Extracted
Sc	91.8%
Y	0%
La	3.6%
Ce	4.1%
Pr	0%
Nd	0%
Sm	5.9%
Eu	11.8%
Gd	8.9%
Tb	7.1%
Dy	4.5%
Ho	7.3%
Er	5.7%
Tm	8.4%
Yb	12.3%
Lu	9.1%
REE excluding Sc	2.6%
Zn	25.1%

First, range finding tests were performed at different pH and concentration ranges. The most promising results were obtained at the following conditions: starting pH 4.01, 15 minutes of mixing time, 15% active ingredient in diluent and an organic to aqueous (O:A) ratio of 1:4 (see Table 10). Roughly 25% of zinc was extracted while only extracting ~2.6% of REE (excluding Sc). Therefore, this approach is a promising discovery for the selective separation of zinc from REE. Even though ~92% of scandium was extracted, Battelle believes that scandium could be selectively stripped using high molarity stripping solutions and different acid combinations.

Based on these results, further investigation on the new commercially available extractant was performed. Three tests were carried out at different pH and a different O:A (1:6) than the preliminary test performed. Mixing time and extractant concentration where constant for all tests. The results obtained from these tests are shown in Table 11. These tests are a single stage extraction. Therefore, recovery could be improved using multiple stage extraction.

Table 11: Results for the selective extraction of Zn using a commercially available cationic extractant compound (single stage).

Element	% Extracted					
	Test 1		Test 2		Test 3	
	Actual starting pH 3.15	Equilibrium pH 2.73	Actual starting pH 4.00	Equilibrium pH 3.81	Actual starting pH 5.64	Equilibrium pH 5.35
Sc	95.6%		90.6%		33.4%	
Y	0%		1.9%		29.0%	
La	0%		0.9%		10.2%	
Ce	0%		0%		10.4%	
Pr	0%		0%		12.7%	
Nd	0%		0%		11.5%	
Sm	0%		0%		18.2%	
Eu	0%		0%		20.4%	
Gd	0%		0%		21.2%	
Tb	0%		3.0%		27.1%	
Dy	0%		4.5%		28.1%	
Ho	0%		5.4%		28.4%	
Er	0%		6.5%		30.3%	
Tm	0%		9.9%		30.0%	
Yb	0%		13.0%		30.5%	
Lu	0%		11.1%		30.7%	
REE excluding Sc	0%		1.31%		17.8%	
Zn	0%		8.3%		71.7%	

At equilibrium pH of 3.81 the extraction of zinc is significantly higher than the REE (excluding Sc). Most importantly, there is no extraction of some of the most valuable REE (e.g. Nd, Pr), and the separation factor for zinc over the combined REE is high. Therefore, if this extraction was to be performed in multiples stages, a successful separation of zinc from REE (excluding Sc) would be achievable. Also, at an equilibrium pH of 3.81, the extraction of Zn is ~8.3% compared to just ~1.3% of the REE (excluding Sc) showing the high selectivity of the cationic extractant used for Zn over the REE (excluding Sc). This high selectivity is also observed in Figure 7. High selectivity is observed at higher pH values. However, during this test, REE, Zn, and other elements precipitated when pH was adjusted to 5.35, leading to reduced recovery in the extractant. In practice, the zinc extraction will likely be limited to the pH of the leachate solution (typically above 4) to avoid loss of materials in precipitates but will be done in multiple stages to increase zinc recovery. Furthermore, even though a high percent of scandium was extracted during the selective separation of zinc from REE, Battelle believes that scandium could be selectively stripped using high molarity stripping solutions and different acid combinations.

Section 5.2.2 discusses further the removal of zinc using the cationic extractant mentioned above. The section presents the extraction of the REE, while leaving most of the zinc in solution, when the REE concentration on the SX feed solution is higher. At this point, the REE can be easily stripped from the extractant with a high molarity nitric acid solution. This was the SX approach use to generate a mixed REE material with low concentration of zinc, which was then purified and separated into REO products (see Section 5.0 for more information).
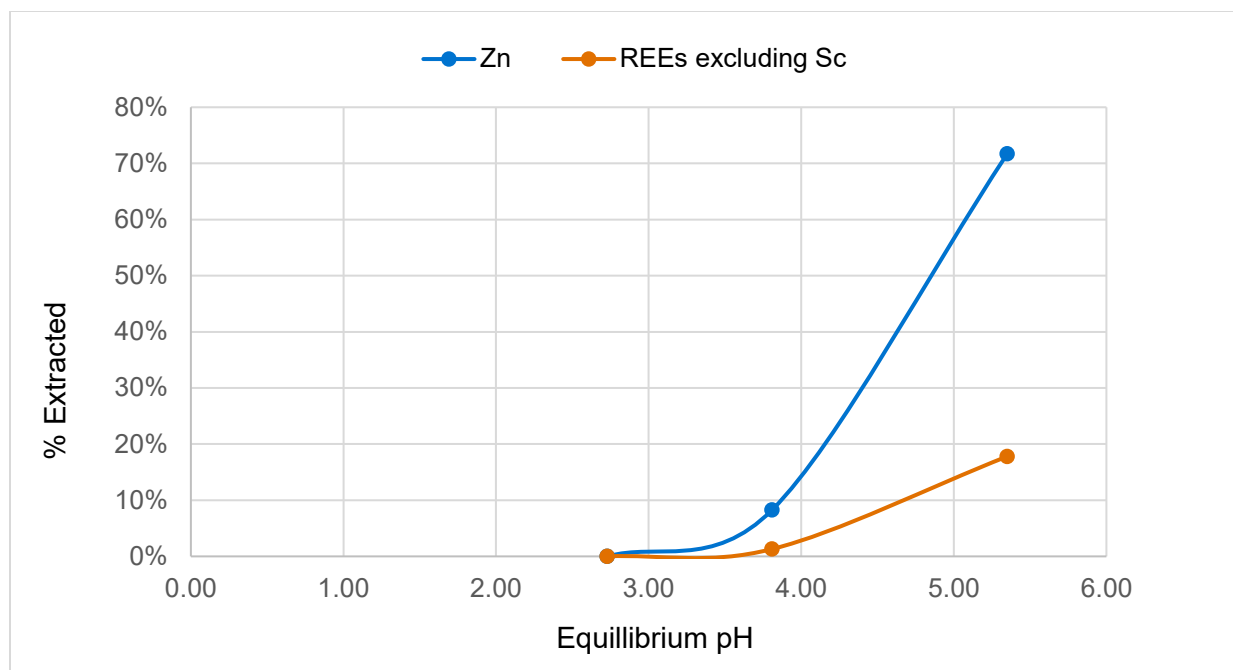
Figure 7: Relationship between equilibrium pH and percent extracted of Zn and REE excluding scandium.

3.4   Rare Earth Stripping

For the REE stripping tests, mixing time and starting pH were selected for investigation since they were the most impactful factors in the stripping operation based on the preliminary testing discussed in Section 2.3 and Appendix C of this report. The experimental design selected was a Box Behnken design, similar to the extraction tests. However, the stripping tests include only two factors at 3 levels; therefore, a full factorial 3^2 experimental design, with limited replicates, was chosen (Box & Behnken, 1960).

Rare earth stripping is an important step in the SX process, since it performs much of the purification of the REE. Therefore, two different experimental designs were performed. One experimental design investigated the stripping of REE from the loaded extractant at low a pH (0.5-1.0), and the other one at a high pH (1.4 – 2.4). The results are shown in Table 12 and Table 14 (low pH stripping and high pH stripping, respectively). The highest results obtained for low and high pH stripping were approximately 49% and 55% REE purity, respectively.

Similar to the REE extraction design, the data obtained from these two experimental designs were used to develop surface response models for REE purity (Table 13 and Table 15 show a summary of the REE purity response models for the low pH REE stripping and high pH REE stripping, respectively). These two response models allowed for the prediction of the maximum REE purity that can be obtained in the stripping process within the conditions investigated in the two experimental designs. The model for high pH REE stripping predicted the highest purity of approximately 58% at an equilibrium pH 1.61 and mixing time of six minutes.

For the validation of the response models, fitted line plots were also graphed (Figure 8 and Figure 9 are the fitted line plots of the REE purity response models for the low pH REE stripping and high pH REE stripping, respectively). It can be observed that both response models are strong fits to the data gathered in the experimental designs, validating the second order models obtained.

3.4.1   Low pH REE Stripping

Table 12: Results obtained from the low pH REE stripping design of experiments (single stage).

Test Number	Starting pH	Equilibrium pH	Mixing time (min)	REE Purity
1	0.74	0.76	10	30.5%
2	1.03	1.12	10	45.3%
3	0.52	0.57	20	19.0%
4	0.76	0.75	20	29.2%
5	0.52	0.59	10	22.4%
6	0.52	0.52	20	17.9%
7	0.50	0.60	1	35.4%
8	0.72	0.77	10	35.4%
9	0.72	0.76	10	35.5%
10	1.00	1.06	1	48.5%
11	0.52	0.59	20	19.6%
12	1.00	0.99	20	37.7%
13	0.74	0.78	1	41.0%

Table 13: Summary of the REE purity response model (second order model) for low pH REE stripping showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-0.0109
pH	0.7713
T	-0.0155
pH:t	0.0055
pH^2	-0.2715
t^2	0.0002
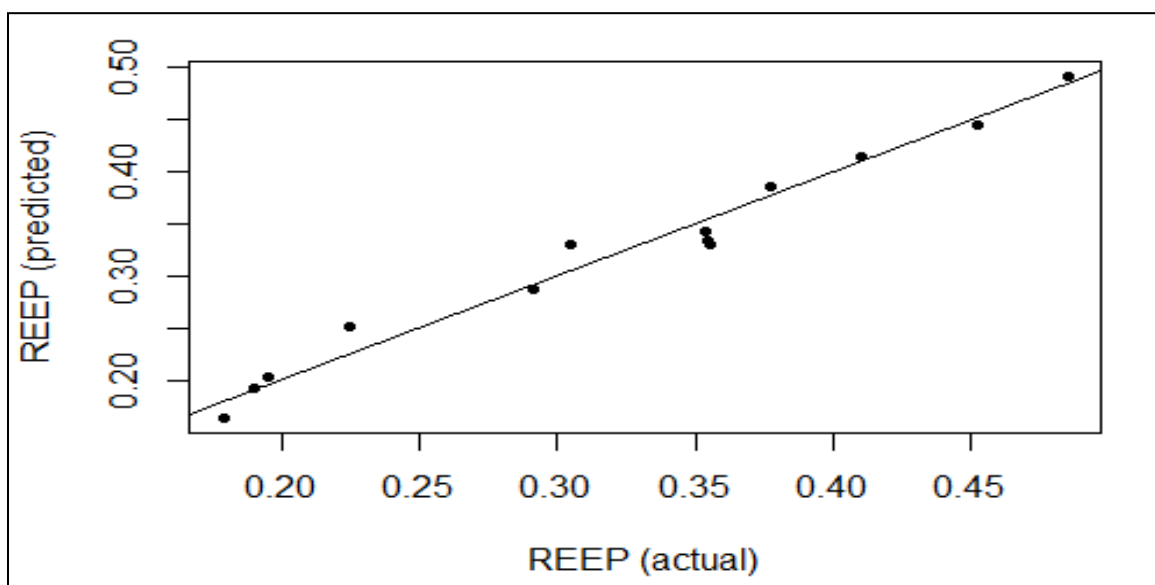
Figure 8: Fitted line plot of the REE purity response model (second order model) for low pH REE stripping.

3.4.2 High pH REE Stripping Results

Table 14: Results obtained from the high pH REE stripping design of experiments (single stage).

Test Number	Starting pH	Equilibrium pH	Mixing time (min)	REE Purity
1	1.80	1.86	1	53.7%
2	1.80	1.87	10	53.7%
3	1.80	1.86	10	55.1%
4	1.31	1.37	10	52.6%
5	1.79	1.84	10	53.0%
6	1.31	1.35	1	53.2%
7	1.29	1.28	20	34.6%
8	1.29	1.21	20	37.4%
9	2.32	2.35	20	21.8%
10	2.31	2.41	10	24.7%
11	1.78	1.70	20	46.2%
12	2.31	2.40	1	20.5%
13	1.28	1.25	20	38.9%

Table 15: Summary of the REE purity response model (second order model) for high pH REE stripping showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-0.7738
pH	1.6824
T	-0.0008
pH:t	0.0046
pH²	-0.5311
t²	-0.0006
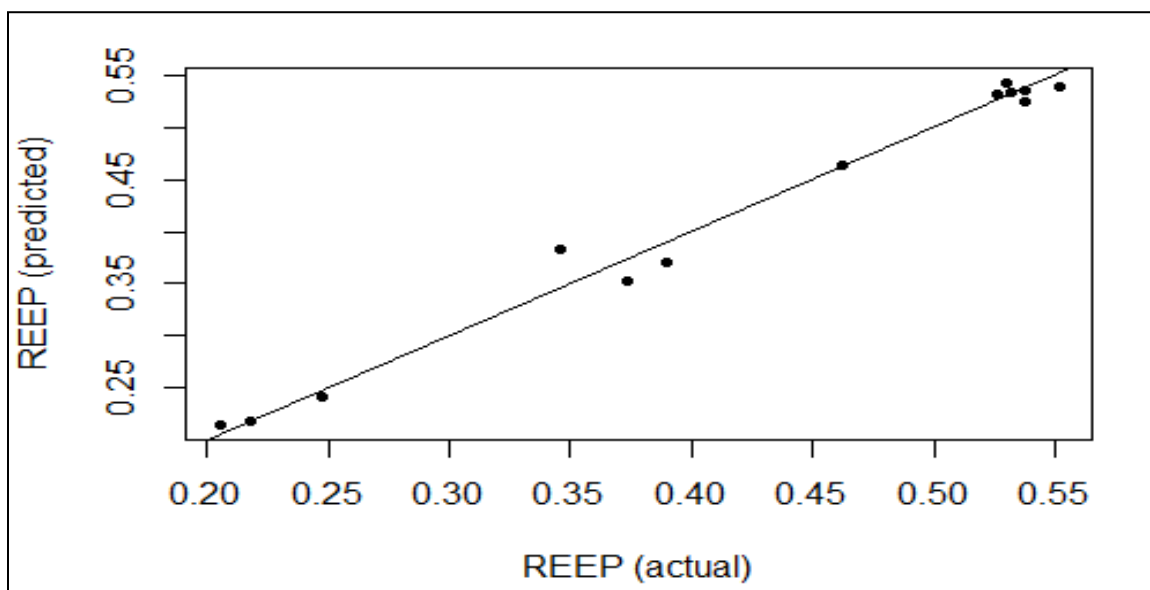
Figure 9: Fitted line plot of the REE purity response model (second order model) for high pH REE stripping.

4.0 Rare Earth Salts Separation Process - Laboratory Testing

4.1 Introduction

The goal of this testing was to determine ideal operating parameters for the successful separation of REE from the REE mixture produced through Battelle's SX upgrading process. Testing was performed on either surrogate solution provided by Battelle, surrogates produced at RES using commercially available chemicals, or mineral concentrates that RES has procured for its commercial demonstration plant (CDP).

Initial experiments with the Battelle's surrogate solution indicated an issue that RES had not previously experienced, which was determined to be the high concentration of zinc present in the solution. Therefore, alternate routes were investigated by Battelle to produce the REE concentrate (feedstock to RES separation technology). Section 3.3 describes Battelle's effort to selectively separate zinc from REE using a commercially available extractant. Concurrently, RES examined ways to reduce the amount of zinc in the impregnated REE solution by using a chemical approach (pH and complexing agents) and using RES's proprietary technology.

During this testing, the electrowinning process flow was also examined, determining the approximate operating conditions and expected separation flow for the system without zinc contamination. The initial conditions were set within the operating parameters as outlined within the patented process and a few modifications were required to obtain the expected splits within the separations process. Additionally, fractions from different initial sources were combined at a specific point in the separations process to ensure that the coal-sourced material could be mixed in with other materials at various points in the process flow with, no loss of efficiency in the process. Appendix D describes additional information about RES process.

4.2 Zinc Removal Testing

Following initial attempts to separate the REE and zinc through RES' proprietary electrowinning process more traditional wet chemical techniques were employed. The initial surrogate solution obtained from Battelle was at a substantially lower pH than typical for the starting solutions through the RES separations process. Due to the low pH, sodium hydroxide (either ~5M or ~10M) was used to increase the pH of the system to facilitate precipitate formation as either a hydroxide or tartrate (complexing agent used). The sodium hydroxide concentrations were chosen to minimize the change in volume and thus the concentration of the original surrogate solution. The pH increase was either done by slow additions of sodium hydroxide ('titration') or through larger additions (typically one addition, but in some cases a second or third addition was required to reach the desired pH).

The initial experiment utilized sodium hydroxide (~5M) as the only precipitating agent. A small amount of precipitate was formed at the three pHs examined in the experiment: 5.84, 6.06 and 6.11. The amount of precipitate collected at all three pHs was minimal and due to the fact that; a) very little solid was collected to this point, and b) there was little preferential precipitation at the highest pH, which is at the lower edge of where the rare earth hydroxides are known to begin precipitating, the experiment was stopped and the use of complexing agents was examined.

In order to further understand the tartaric acid/zinc/rare earth system, a systematic study was undertaken examining the solution and precipitate behavior as a function of pH. The surrogate solution was mixed with tartaric acid and allowed to equilibrate, yielding a solution at pH < 0.5. Sodium hydroxide was then added in small increments with the solution allowed to equilibrate

overnight before samples were taken (the precipitate was only collected at a few points in the experiment). Figure 10 shows a summary of the results.

The experiment resulted in a solid that was 99.2% REE and 0.8% zinc at pH = 1.8 with 85% of the REE removed from the solution (weighted percentages). The effective removal was increased to > 91% at a pH of 2.1 composed of 92% REE and 2% zinc. The remaining experiments yielded results that were less satisfactory than the previous two, with the 3rd experiment yielding a solid that was 5% zinc with ~65% of REE removed. The remaining experiments showed no improvements over the previous experiments.
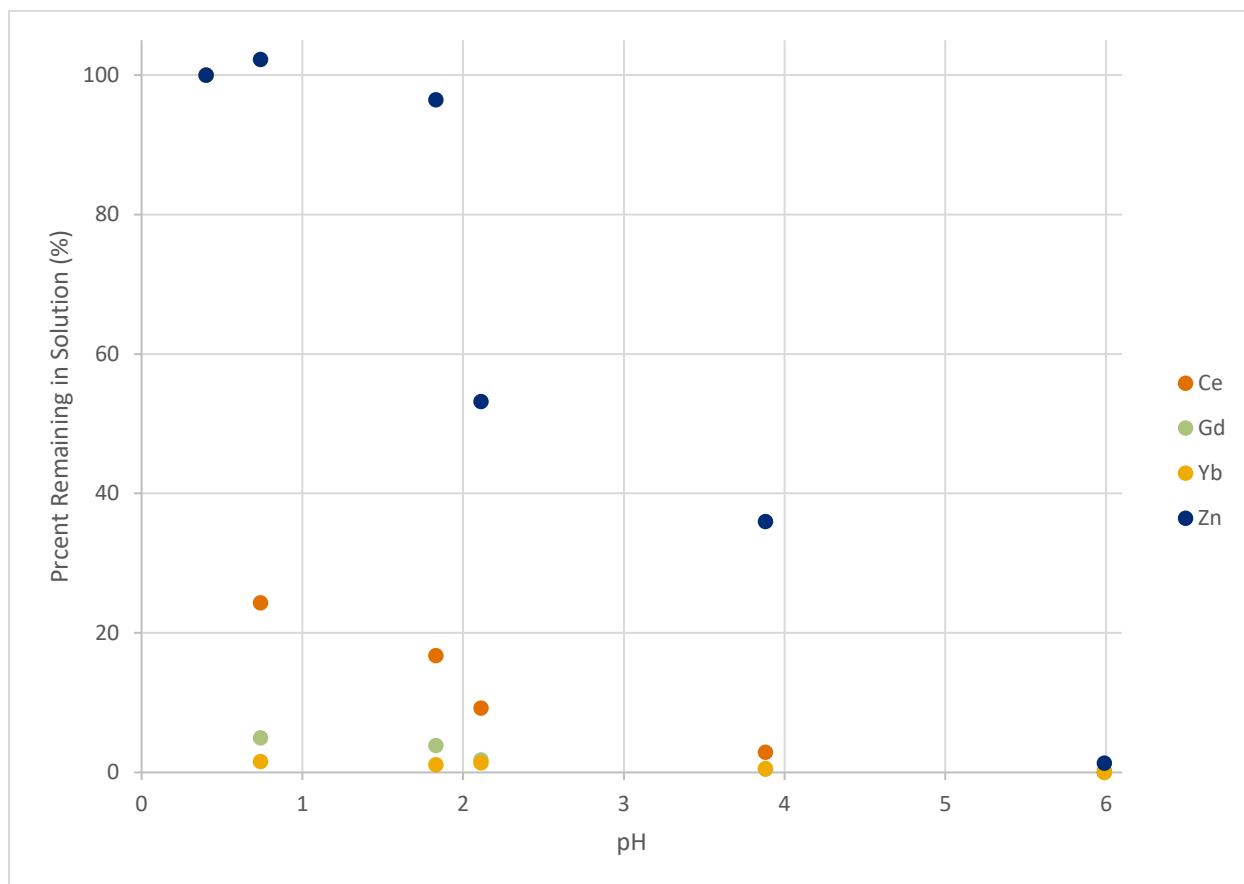
Figure 10: Plot of the percentage remaining in solution for cerium (Ce, representative of the light rare earths), gadolinium (Gd, representative of the mid rare earths), ytterbium (Yb, representative of the heavy rare earths) and zinc (Zn) as a function of pH in the system.

4.3   General Separation Flow Study

Based on the difficulties in using the surrogate solution with a high zinc concentration, a suitable alternate surrogate was produced. The solution was then subjected to typical experimental conditions for the electrowinning separation of REE. The solid material collected had higher concentrations of some elements (relative to the starting solution) and lower concentrations of others. The solid material could further be separated into 'lots' of various concentrations as it was collected over time. The initial separation steps grouped the REE into pairs or triads for separation as shown in Figure 11 to Figure 13. Figure 11 shows the initial groupings for the light REE, while Figure 12 and Figure 13 show the mid and heavy REE, respectively. These figures show the amount of each element remaining in solution as a function of time, a direct correlation

to the composition of the solid as a function of time. The lowest member of the group above is included in each figure as a point of reference.
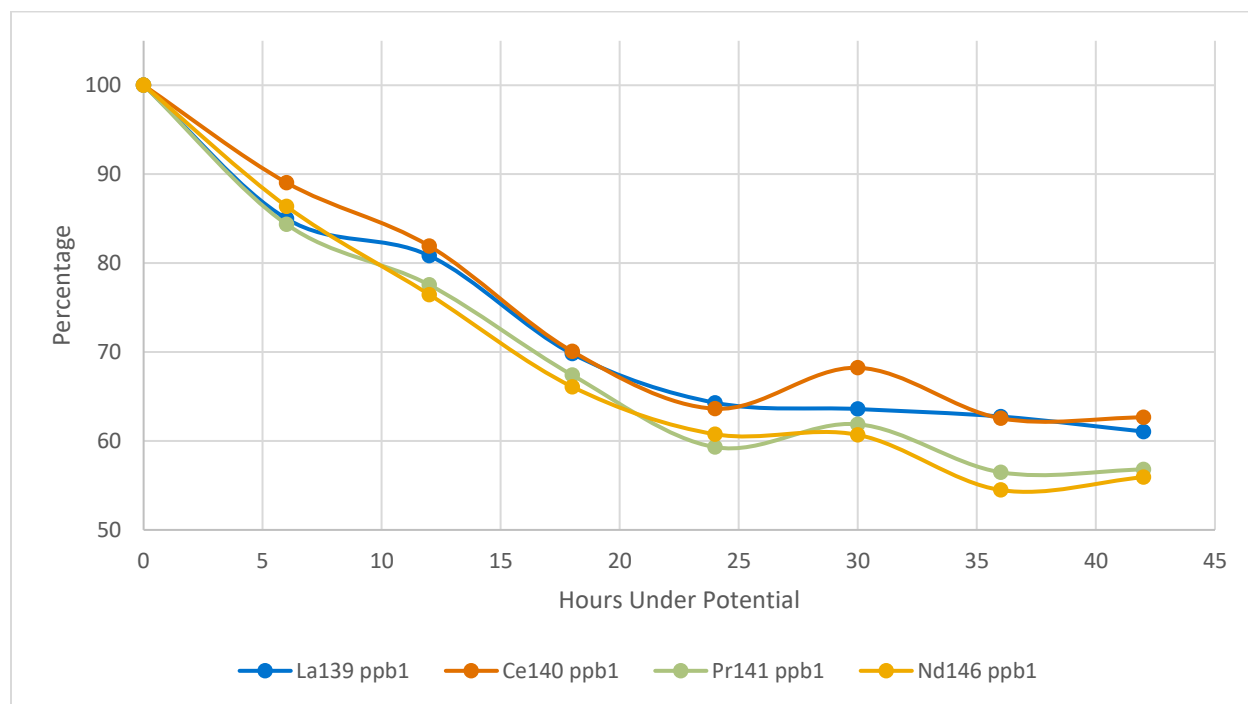
Figure 11: Percentage of original material (light REE) remaining in solution as a function of time spent under potential during the electrowinning process.
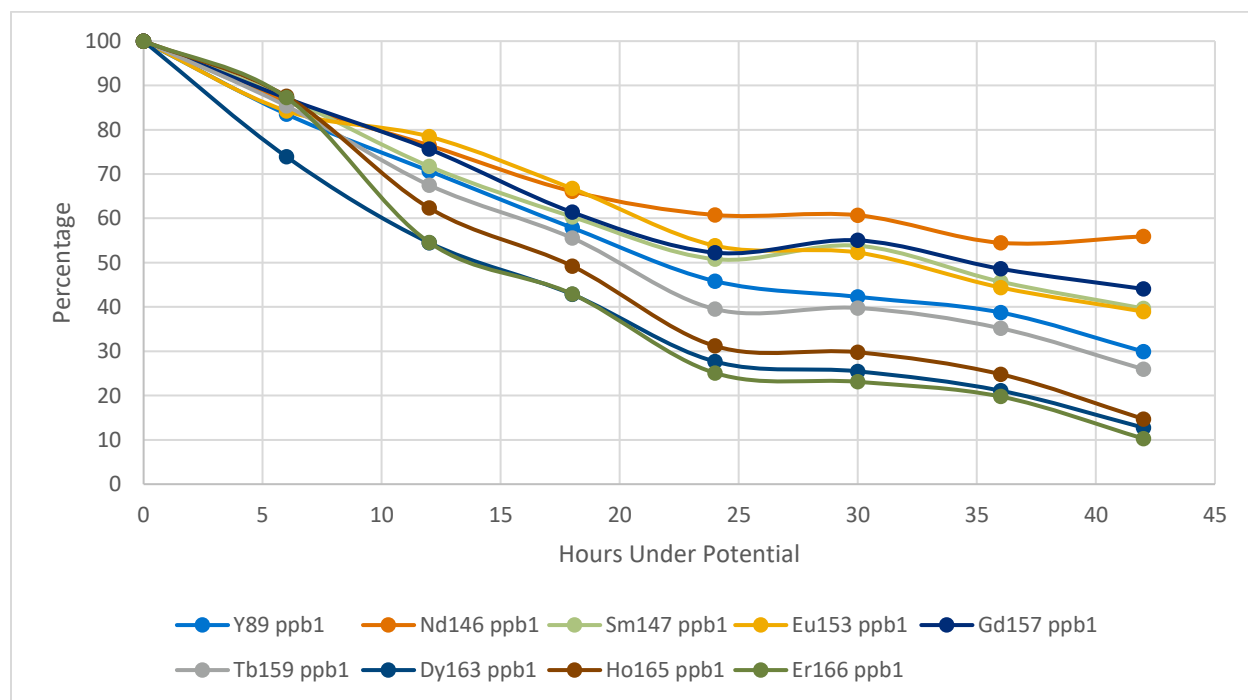
Figure 12: Percentage of original material (mid REE) remaining in solution as a function of time spent under potential during the electrowinning process.
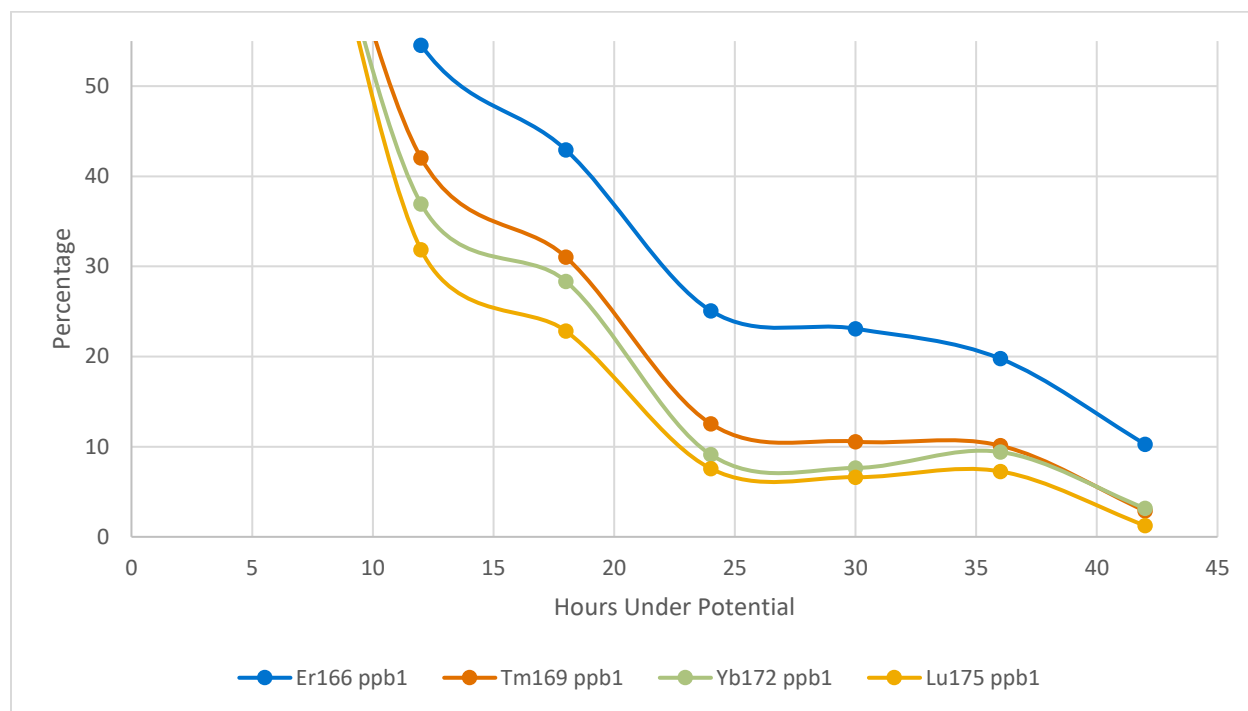
Figure 13: Percentage of original material (heavy REE) remaining in solution as a function of time spent under potential during the electrowinning process.

The progress of the separation can also be measured in a function defined as 'upconversion'. Upconversion or percent upconversion can be defined mathematically in Equation 1 where the percentage in solution is defined as the solution at the beginning of the iteration from which the solid is obtained.

$$upconversion = 100 * \frac{percentage\ in\ solid}{percentage\ in\ solution}$$

(Equation 1)

Upconversion values greater than 100 indicate the material is preferentially moving into the solid phase and values less than 100 indicate that the material is preferentially remaining in solution. Figure 14 and Figure 15 represent the upconversion values for the light and heavy REE, respectively.

Further experiments examining the process flow in the separations scheme focused on the light REE (La, Ce, Nd, and Pr) as they generally comprise anywhere from 60% (the final material received from Battelle and brought into solution at RES) to 95% (a typical concentrate from a bastnaesite ore). Both surrogate and mineral concentrate samples were examined in this stage and intermediate products were combined to ensure that materials from multiple sources would continue to process without changes to the separation scheme. Notable outputs from these experiments were a > 98.5% pure didymium product with a ratio of ~82% Nd to ~18% Pr and a >98.5% La product. The didymium product was one isolated for production due to the interest from a number of rare earth magnet producers.
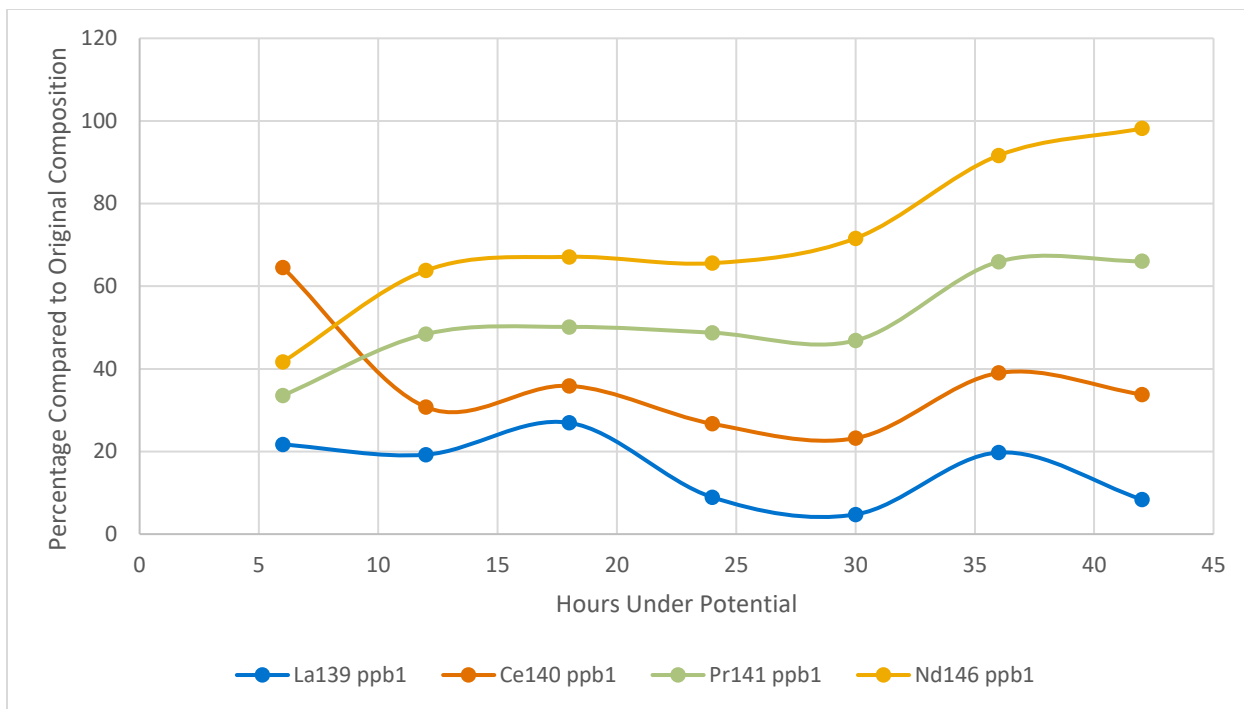
Figure 14: Percent upconversion values for the light rare earth elements as a function of time spent under potential.
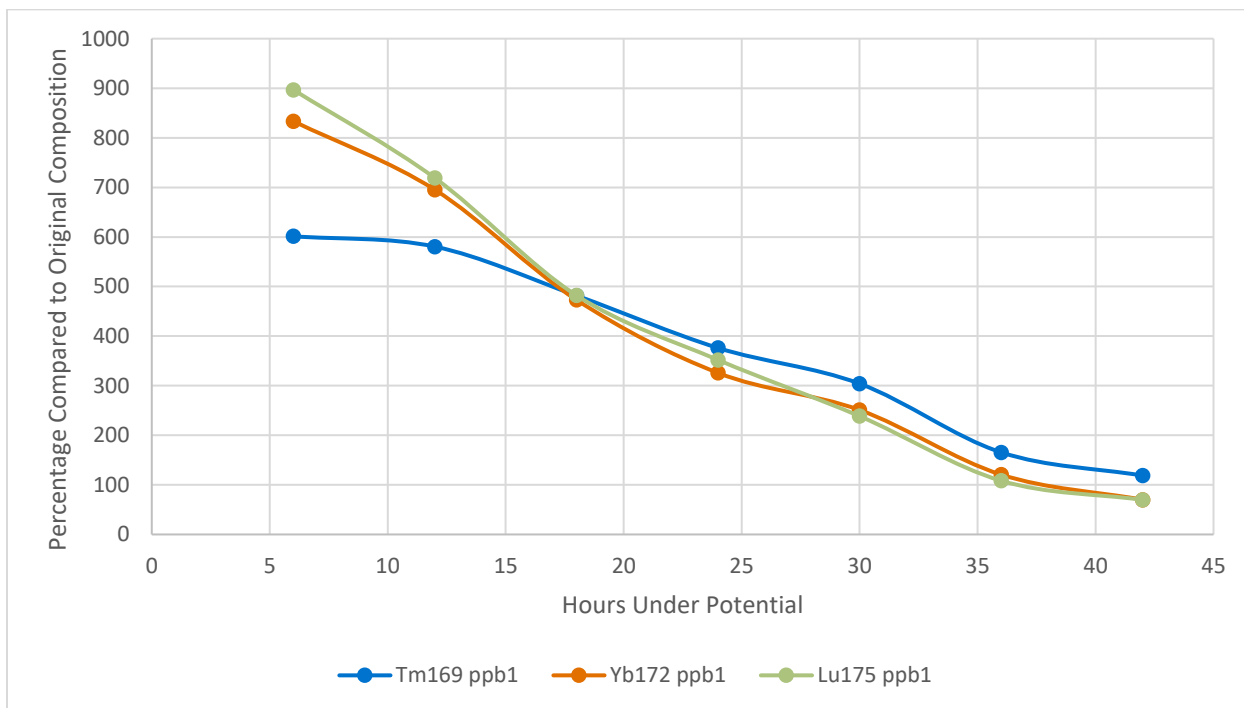
Figure 15: Percent upconversion values for the mid rare earth elements as a function of time spent under potential.

5.0 Coal-Based Rare Earth Oxide (REO) Product

5.1   Introduction

Battelle has shown that a purity of 50-60% combined REE can be obtained using ADP and SX upgrading process without the removal of zinc. However, the selective separation of zinc from REE is of high importance due to the tendency of zinc to follow the REE in SX and other separation processes, impacting the ability to achieve a separated, saleable product. Therefore, a slightly different approach was implemented for the production of a purified REO product after analyzing the test results explained above (Section 2.0 through Section 4.0).

First, Battelle created a REE pregnant solution by processing PCC fly ash via ADP. The products from ADP were an iron/scandium material and a REE pregnant solution. The REE pregnant solution was fed to the new SX upgrading process to remove zinc using a commercially available cationic extractant, and nitric acid as stripping solution. The stripped solution, containing the REE and other metals with a low concentration of zinc, was then roasted at approximately 250°C to convert the REE nitrates into oxides. At this temperature, the majority of alkali and alkaline earth metal nitrate salts, such as, barium, calcium, potassium and sodium nitrates are not converted to oxides, facilitating the separation of these impurities from REE oxides by performing a water washing step follow by a filtration step. This step provided a combined REE oxide material suitable for RES' conversion process followed by the electrowinning process for the final separation of REO product (see Figure 17).

The product obtained from Battelle's ADP and SX upgrading was a high aluminum/REE oxide material with a lower zinc concentration than earlier surrogate solutions studied. This high aluminum/REE oxide material was then fed to RES' conversion process. During this process, the high aluminum concentration was not an issue since aluminum remains an insoluble oxide during the conversion of REE to soluble salts and can be recovered as a potential high purity byproduct (>99% purity). The iron/scandium material obtained from ADP was also treated by RES' conversion process. It was found that this process could allow for the production of a pure scandium chloride or oxide product (>99% purity) along with a substantial amount of an iron chloride or oxide byproduct (also >99% purity).

The REE salt obtained from the conversion process was dissolved in hydrochloric acid yielding a loaded REE solution. The remaining zinc in the loaded REE solution was removed by precipitating the REE using tartaric acid under pH control. The zinc stayed in solution, and the REE precipitate was calcined at a high temperature and re-dissolved in hydrochloric acid making a concentrated REE solution. This solution was fed to RES' electrowinning process to obtain the final coal-based rare earth oxide (REO) product. The first product obtained was an approximately 1.1 grams oxide material having a TREO concentration of >90% with an 89% +/- 2% lanthanum content (oxide basis). The second product was an approximately 0.2 grams oxide material having a TREO concentration of >95% with a 90% +/- 2% lanthanum content (oxide basis). See Figure 16 shows one of the products obtained in this project.
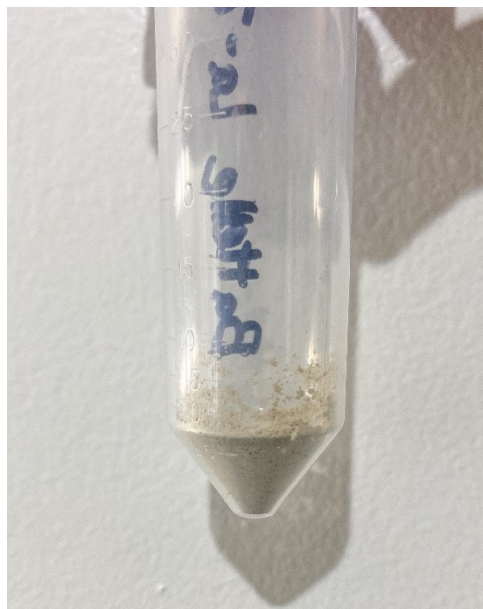
Figure 16: REO material obtained (1.1 grams with TREO concentration of >90% with an 89% +/- 2% lanthanum oxide.
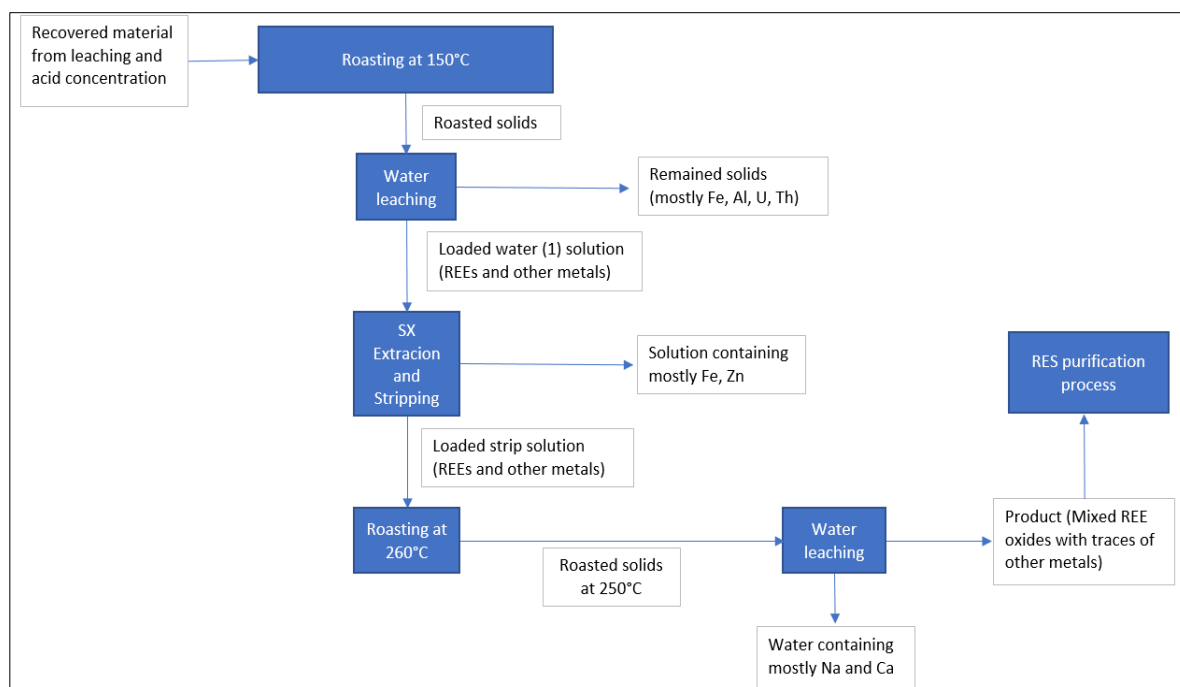
Figure 17: Approach for the production REO product at laboratory scale.

5.2   High Coal-Based Aluminum/REE Oxide Material

5.2.1   Battelle's ADP (12 kg of PCC fly ash per batch)

For the production of the high aluminum/REE oxide material, which was then fed to RES' conversion and purification processes, Battelle assembled a larger laboratory scale ADP capable of processing 12 kg of PCC fly ash per batch (see Figure 18). First, milled PCC fly ash was leached with approximately 34% nitric acid at a temperature of 90°C. The loaded acid was then concentrated follow by a roasting step, which was performed at 150°C based on preliminary roasting studies (Section 2.2). At this temperature, iron and aluminum are converted to insoluble oxide materials and can be separated from REE nitrates using a water leaching step follow by filtration. The product from this step was a pregnant REE solution, which was then fed to an SX upgrading process for zinc removal. In the roasting step, the majority of the scandium was also converted to oxide staying with iron and other impurities in the solid product. However, this product was treated later using RES' conversion process to potentially recover scandium and produce an iron chloride byproduct. Section 5.3.1 will describe this step in more detail.

Figure 18: Laboratory scale ADP (12 kg of PCC fly ash per batch).

5.2.2   Small Batch SX Tests – Zinc Removal

Small batch tests were performed using the REE pregnant solution, obtained from Battelle's ADP above, and commercially available extractant before advancing to the larger batch SX upgrading process. Table 16 and Table 17 summarize the results of this testing, which found 72.9% of REE extracted, with just 6.78% of zinc extracted, making this a successful separation. Stripping of the REE was also successful when using 10% nitric acid strip solution. Using the information found during this testing, the larger batch SX upgrading process was performed (see Section 5.2.3).

Table 16: Extraction results using loaded water recovered from Battelle's ADP and cationic extractant.

Species	% Extracted (single pass)
Sc	23.08%
Y	39.62%
La	93.02%
Ce	93.11%
Pr	92.04%
Nd	91.00%
Sm	86.52%
Eu	83.17%
Gd	72.52%
Tb	70.99%
Dy	69.39%
Ho	62.37%
Er	55.49%

Species	% Extracted (single pass)
Tm	40.67%
Yb	32.46%
Lu	21.32%
Total REE+Sc+Y	72.90%
Zn	6.78%
Fe	0%

Table 17: Stripping results using loaded organic recovered from extraction test and 10% nitric acid strip solution.

Species	% Stripped (single pass)
Sc	100.00%
Y	92.82%
La	73.38%
Ce	79.06%
Pr	79.67%
Nd	77.90%
Sm	83.49%
Eu	87.07%
Gd	90.48%
Tb	99.06%
Dy	92.24%
Ho	100.00%
Er	93.81%
Tm	98.81%
Yb	90.74%
Lu	100.00%
Total REE+Sc+Y	82.15%

5.2.3   SX Upgrading – Zinc Removal

The REE pregnant solution obtained from Battelle's ADP (larger laboratory scale) was fed to the large batch SX upgrading process. In the extraction step, the commercially available cationic extractant was contacted three times with the pregnant REE solution. Then, the loaded organic, carrying the REE, was stripped in a three-stage stripping step using 10% nitric acid solution. The stripped REE solution was then roasted at approximately 250°C to convert the REE nitrates into REE oxides. At this temperature, the majority of alkali and alkaline earth metal nitrate salts, such as, barium, calcium, potassium and sodium nitrates are not converted to oxides, facilitating the separation of these impurities from REE oxides by performing a water washing step follow by a filtration step (see Figure 19). This step provided a combined REE oxide material suitable for RES' conversion process followed by the electrowinning process for the final separation of salable REE oxide products. The product contained a high aluminum/REE oxide material (~200 g of total material/~9.8 g of total REE) with a lower zinc concentration than earlier surrogate solutions studied (see Table 18).

Table 18: Aluminum/REE oxide material (product of Battelle's ADP and SX upgrading) and REE/zinc solution (product of RES' conversion process) concentrations.

Species	Concentration (Aluminum/REE oxide)	Concentration (concentrated REE solution)[1]
Total REE	4.9%	53.3%
Aluminum	90.8%	0%
Zinc	1.2%	13.0%
Other metals	3.1%	33.7%

[1]Concentration after RES conversion process. Aluminum stayed as insoluble oxide. REE salt is dissolved in hydrochloric acid yielding a concentrated REE solution with the shown concentration.

The high aluminum concentration of the material produced by Battelle's ADP and SX upgrading was not an issue for RES' conversion and separation processes, since aluminum stayed as an insoluble oxide during the conversion of REE to soluble salts. In other words, aluminum acts as an inert in RES' overall purification process. Furthermore, the insoluble aluminum oxide could be recovered as potential byproduct with purity ranging from 99% to >99.9% purity (see Section 5.3.2).
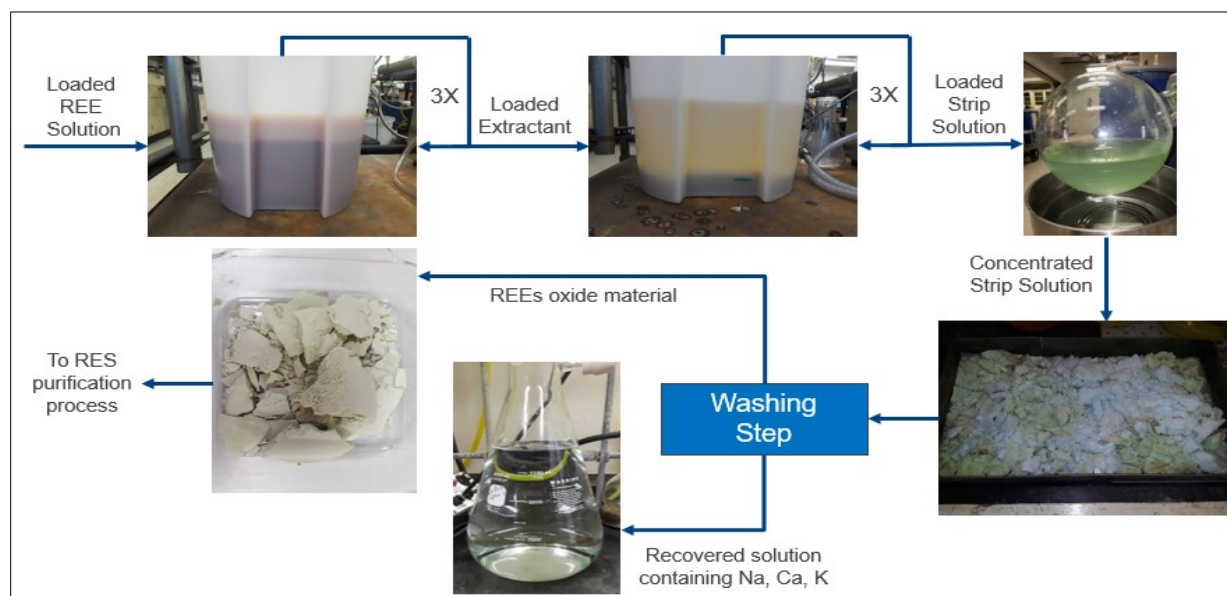
Figure 19: SX upgrading steps.

Battelle delivered two different materials to produce the final purified REO product at RES. The first material was a surrogate with the same concentration of REE and other metals as the material obtained after the SX upgrading process. The second material was the actual coal-based material obtained through Battelle's ADP and SX upgrading process. This material was spiked with metal oxides, with the same distribution of metals as the original material, to achieve the allowable mass rate for RES' conversion and purification processes.

5.3   Coal-Based High Purity REO Product

5.3.1   Scandium Recovery

Scandium was removed earlier than the remaining REE during Battelle's ADP and SX upgrading processes. It was removed along with the bulk of the iron (iron/scandium material) during the roasting step as explained in Section 5.2.1. Rare Earth Salts received a sample of the scandium and iron mixture, and it was subjected to RES' proprietary conversion process.

The experiment confirmed that the scandium was concentrated in the solid product, while the bulk of the iron was removed from the sample. The amount of scandium present in the sample (<100 mg) was too small to allow for a quantitative assessment of the process, including determining the efficiency of the process. Additionally, due to the minimal amount of material, the larger laboratory furnace could not be used for the process, which didn't allow for the collection of the iron product for testing. However, it is estimated that this process could allowed for the production of a pure scandium chloride or oxide product (>99% purity) along with a substantial amount of an iron chloride or oxide byproduct (also >99% purity).

5.3.2   Conversion and Separation Processes

Rare Earth Salts received material from Battelle in the form of a high aluminum/REE oxide material. The REE were extracted from the aluminum matrix using RES' proprietary conversion process, which left the majority of the aluminum matrix but did extract the majority of the transition elements (including zinc) from the matrix along with the REE. One potential byproduct of this first step in the process would be an alumina material. Depending on the type of impurity content from a more fully optimized SX extraction process, this alumina byproduct could have a purity ranging from 99% to >99.9% purity.

The material obtained during the first conversion process (REE salt) was dissolved using hydrochloric acid yielding a concentrated REE solution (see Table 18). The REE were then precipitated using tartaric acid under pH control. Later, the precipitated REE were calcined at a high temperature and re-dissolved using hydrochloric acid under conditions such that the final pH was approximately 4. This precipitation process to remove the remaining of zinc is best described in Section 4.2.

The loaded REE solution obtained from the step explained above was fed to the electrowinning process. The REE were separated following the scheme discussed in Section 4.3 until the four light REE, lanthanum, cerium, praseodymium and neodymium, were remaining. The separation parameters were then adjusted for finer control of the separation to produce two fractions; one high in lanthanum, and one high in the other three remaining elements. Once the lanthanum was near the 90% target, an experimental technique for precipitating cerium from solution at a high purity was used on the system. The results were as expected, producing a 90%+ purity cerium oxide product. However, during the procedure an accident occurred and contaminated the solution with a material high in cerium, praseodymium and neodymium (with lesser amounts of lanthanum). Further iterations of the experimental technique were performed to remove the remaining cerium from the system (given the ICP results, it is estimated that the resulting cerium material was approximately 60% coal material and 40% contaminate). Given the much larger amount of lanthanum in the system and the lower lanthanum content in the contaminate, it is estimated to be over 70% coal-based material.

The method produced a cerium product that each fraction was over 91% cerium and a lanthanum fraction that was approximately 90% lanthanum. The resulting material was precipitated from solution as an oxalate and then fired at 1100℃ for between one and two hours. The cerium product was again subject to contamination as the crucible cracked during the firing, causing it to be contaminated beyond recovery. The lanthanum was fired as two different products as a second precipitation was able to recover more of the material. The first product obtained was an approximately 1.1 grams oxide material having a TREO concentration of >90% with an 89% +/- 2% lanthanum content (oxide basis). The second product was an approximately 0.2 grams oxide material having a TREO concentration of >95% with a 90% +/- 2% lanthanum content (oxide basis).

6.0 Process Design

6.1 Introduction

Section 6.0 describes the overall REE recovery process through purified REO products (see Figure 20). It includes the design basis, mass and energy balances and process flow diagrams for an integrated process. Stream tables upon which the economics are based are provided in Appendix E and are referenced in this section.
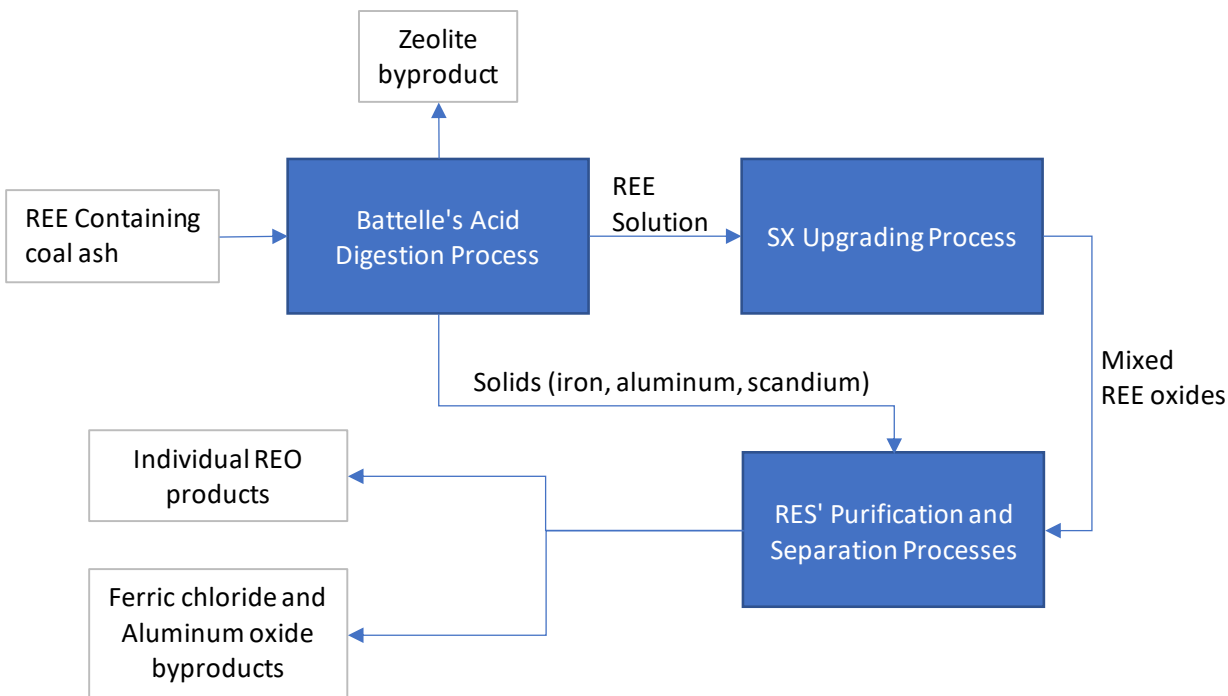
Figure 20: Overall REE recovery process schematic.

6.2 Process Description

6.2.1 Battelle's Acid Digestion Process (ADP) Description

The continuous rare earth recovery process (see Figure 21) starts with four distinct steps: pretreatment and aluminosilicate byproduct generation (caustic blowdown 1-06 stream in Figure 21 feeds the byproduct generation process), acid leaching, acid recovery and preliminary product generation. Acid leaching to access REE content of the ash is operated in a closed loop process, allowing for the recovery and reuse of the bulk of the nitric acid used in the process. Primary process feeds include the REE containing fly ash material sourced from a PCC EGU, a caustic hydroxide feed (nominally sodium hydroxide), makeup nitric acid and process water. The primary process outputs are fly ash stripped of REE, an aluminosilicate (zeolite) byproduct generated during the pretreatment process (caustic blowdown 1-06 stream), wastewater blowdown and the REE concentrate stream. The proposed design production scale plant will process 30,000 kg (30 tonnes) of ash per hour.

The pretreatment begins with a milling step, which reduces the median ash particulate size from 55 µm to 4.5 µm. This size reduction provides better access to the particle for leaching and may be performed in a jet mill or stirred media mill. Once the ash has been milled, it is treated with a sodium hydroxide solution to remove some of the silica and alumina present in the ash. This allows improved access to REE in the acid leaching step. A caustic leaching residence time of

one hour in 10% sodium hydroxide solution at 90°C is sufficient to liberate REE in the acid step based on preliminary laboratory data. The ash is filtered out of the caustic solution and rinsed with water to remove entrained caustic before proceeding to the acid leaching operation. After the leach step, the caustic solution is loaded with silicate and aluminate, which can be precipitated into zeolite material. Separation of the ash from the pretreated caustic solution is accomplished using a rotary drum filter with a water rinse. After the pretreatment, the ash is fed to the ADP and mixed with a nitric acid stream (approximately 34 wt.%) before being pumped through a heater to an elevated, sub-boiling temperature, and into the leaching reactor. The leaching temperature is expected to be 80-90°C. Total flow rate, temperature and stream composition for the caustic pretreatment and acid leaching process are shown in Table 16 and Table 17 of Appendix E. PFD stream numbers are also shown in the tables.

After the leach process, the ash is filtered out in a vacuum drum filter and transferred to an ash drying operation. The leachate, containing unreacted nitric acid, is recycled to the reactor to ensure complete utilization of the acid fed to the process. The ash dryer is important for economic recovery of REE since the high temperatures will boil off and convert any entrained nitrates, allowing them to be recovered in the closed loop process. Additionally, this drying step ensures removal of any nitrates from the ash, preventing the discharge of nitrates from the ash allowing for safe storage of the ash, or for use as a pozzolan. The ash dryer is a rotary-type drum dryer, indirectly heated to a temperature of up to 155°C (see Table 18 and Table 19 of Appendix E).

Off gases from the acid leach process, consisting of nitric acid and other NOx species, are swept with an air stream and fed along with the REE-loaded leachate into a roasting operation. The roaster will operate in two stages, the first to concentrate the liquid feed into a slurry, and the second to crystallize the REE salts. The concentration step will use a conventional evaporation unit heated to 120°C, while the crystallization step will be done in a spray dryer, reaching temperatures high enough (between 120°C and 155°C) to convert some of the metal nitrates to oxides. By roasting the metal nitrate salts to dryness and then to a temperature of approximately 155°C, many non-rare earth metal salts (such as iron and aluminum) are converted to metal oxides, releasing NOx gases, which are swept along with other process off-gases to the absorption column. Based on laboratory testing, rare earth nitrates, however, are not converted to oxides at temperatures less than approximately 250°C and will therefore remain in their nitrate salt form. This step provides a water-soluble rare earth concentrate, enriched in rare earth materials, suitable for feed to Battelle's SX upgrading and RES' purification processes. Table 20 and Table 21 from Appendix E are the stream tables for the roasting process.

As discussed, all off-gases of the process, consisting of nitric acid vapor and NOx gases, will ultimately be swept to an absorption column system for recovery. Optionally, these vapors may be compressed and fed through a heat exchanger to preheat the acid feed to the roaster, then to a condenser to recover nitric acid for recycle, prior to being fed to the column. Any NOx gas generated in the roaster, leaching, and ash drying processes needs to be oxidized to NO_2 prior to being absorbed back into the acid stream. This oxidation rate is improved at higher temperatures and can occur in the drying and roasting processes with the presence of air. As the gas passes through the condenser, it is then cooled, which is preferable for the absorption of the NO_2 back into the liquid phase. Gas will flow through the absorption column in a single pass, where it is contacted with recycled nitric acid as an absorbent. The liquid recirculated in the column consists of acid recovered from the roaster. Nitric acid recovered in the column will be recycled back to the leach reactor to complete the acid recycle process. A small fraction of this stream will be sent to a distillation column, which will distill and separate the water-nitric acid mixture, allowing for the proper concentration of nitric acid to be maintained in the reactor.

The concentrated nitric acid recovered in the distillation column will be recycled to the acid leaching process, while the water recovered in the distillate will be treated to a neutral pH and purged from the system, ensuring that a buildup of water does not occur in the process (see Table 22 of Appendix E for acid recovery steps).

6.2.2   Overall ADP Energy Balance

Table 19 and Table 20 show the overall energy balance; heating and cooling requirements for the Battelle ADP. The lower heating value of natural gas was used for the calculations and assuming 30% energy efficiency. Inlet temperature and outlet temperature of the cooling water was assumed to be 25°C (at 30 psig) and 40°C, respectively.

Table 19: Preliminary Heat Duty for ADP 30,000 kg/hr Full-scale Process.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
Acid Leach Reactor Preheater (HX-201)	63.62	Natural gas	16.21
Rotary Kiln Roaster Ash Dryer (K-1)	12019.92	Natural gas	3062.40
Roasting Process Evaporator (EVAP-1)	35917.50	Natural gas	9150.96
Roasting Process Roaster (K-2)	2797.44	Natural gas	712.72

Table 20: Preliminary Cooling Duty for ADP 30,000 kg/hr Full-scale Process.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
ESP Condenser (COND-1)	10691.67	Cooling water	613880.00
Evaporator Condenser (COND-2)	35682.50	Cooling water	2048651.00
Roasting Process Condenser (COND-3)	5540.83	Cooling water	318200.00
Absorption Column HTXR (HX-501)	79.23	Cooling water	4549.30
Caustic Scrubber HTXR (HX-502)	61.85	Cooling water	3551.46
Distillation Column Water Product HTXR	6970.89	Cooling water	400298.00
Distillation Column Acid Product HTXR	2491.29	Cooling water	143064.00

6.2.3   Solvent Extraction Upgrading and Purification Processes

Solvent extraction followed by a high temperature roasting step was used to further concentrate REE and produce a mixed REE concentrate of 50-60% REE oxides, which is able to be further separated into individual rare earth oxides for sale in the market using RES' electrowinning process. It is expected that SX and the high temperature roasting step will remove monovalent and divalent cations, as well as select transition metals, especially zinc (an undesired species for the electrowinning process), from the REE feed stream. This combined REE oxide stream will be the feedstock to the electrowinning process, which consists of a conversion (potential iron chloride and aluminum oxide byproducts are made during this process) step followed by the final separation of salable REO products.

The combined REE oxide stream obtained from the upgrading SX process may contain aluminum as contaminant. However, this is not an issue for RES' conversion and separation processes since aluminum remained as an insoluble oxide during the conversion of REE to soluble salts. Furthermore, the insoluble aluminum oxide could be recovered as a potential byproduct with purity ranging from 99% to >99.9% purity.

Primary process feeds for upgrading SX and purification processes include the REE product collected from ADP, extractant and stripping solutions for the SX steps, conversion reagent for RES' conversion process, and process water. The primary process outputs are potential byproducts (iron chloride and aluminum oxide) generated during the conversion process, wastewater and strip solutions blowdown, and the final sealable REE oxide products (see Figure 22).

6.2.4   Solvent Extraction Upgrading

The REE product collected from the ADP process is mixed with water and then filtered using a drum filter to remove major impurities converted into oxides during the roasting process, such as aluminum, iron, uranium, and thorium. In the roasting step, most of the scandium will also be converted to oxide staying with iron and other impurities in the solid product. However, this product is treated later, recovering scandium and making iron chloride as a byproduct during RES' conversion process. After this wash step, the leach solution will go into the SX upgrading process (see Table 23 of Appendix E for streams composition of the washing process).

The leach solution from water wash step will be extracted at pH 2-3 using a commercially available extractant, which will selectively extract REE from other metals, especially zinc. The laboratory test results suggest a ~73% extraction of total REE with just ~7% of zinc extracted in one stage (see Section 5.2.2). At this larger scale, multiple stages are used resulting in >95% of REE and <20% of zinc extracted. The selective separation of zinc from REE is of high importance due to the tendency of zinc to follow the REE in SX and other separation processes impacting the ability to achieve a separated, saleable product. After extraction, REE will be stripped using 10% nitric acid solution yielding a concentrated REE solution that then will be roasted at a high temperature. Most of the striping solution will be recovered in the condenser of the high temperature roasting process. After REE have been stripped, the extractant will be regenerated using a combined acid solution to clean the extractant before being recycle back to the extraction step. Based on preliminary laboratory testing, the extractant loss during the SX process is less than 200 ppm of the active ingredient (see Table 24 and Table 25 of Appendix E for streams composition).

After the SX process, the loaded strip solution will be roasted at approximately 250°C to convert REE nitrates into oxides. At this temperature, the majority of the alkali and alkaline earth metal nitrate salts, such as, barium, calcium, potassium and sodium nitrates are not converted to oxides facilitating the separation of impurities from REE oxides by performing a water washing step. This step is followed by a filtration step using a drum filter providing a high purity combined REE oxide material. This material is suitable for RES' conversion process followed by electrowinning process for the final separation of salable REE oxide products. Additionally, the loaded stripped solution is recovered using a condenser which recovers ~93% of the solution. The non-condensable from this step will be directed to the absorption column in the ADP (see Table 26 of Appendix E for streams composition).

6.2.5   Purification Process

The purification process consists of two steps. First, REE oxides from the SX upgrading and solids from the roasting step will be directed into the RES conversion process. In this process, REE, including scandium left behind in the roasting step, are converted to water soluble salts leaving other impurities as insoluble oxides (mostly aluminum oxide). A water wash step is performed follow by a filtration step using a drum filter to remove the oxides from REE salts. The resulting product is a high purity REE solution suitable for RES' electrowinning process. Also, the insoluble aluminum oxide could be recovered as potential byproduct with purity ranging from 99% to >99.9% purity. Additionally, a potential iron chloride byproduct is produced during the conversion process helping to offset the cost of the overall REE recovery process (see Table 27 and Table 28 of Appendix E for streams composition). The final step will be the RES electrowinning process where the concentrated REE solution will be separated into individual saleable REO products in several stages (see Table 29 of Appendix E for streams composition).

6.2.6   Overall Energy Balance for SX and purification process

Table 21 and Table 22 show the overall energy balance (heating and cooling requirements for Battelle's SX and RES' purification process). The lower heating value of natural gas was used

for the calculations and assuming 30% energy efficiency. Inlet temperature and outlet temperature of the cooling water was assumed to be 25°C (at 30 psig) and 40°C, respectively.

Table 21: Preliminary Heat Duty for SX upgrading and Purification Processes.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
Oxide Conversion Spray Dryer (SD-1)	824.50	Natural gas	210.06
Pre-Conversion Spray Dryer (SD-2)	8379.63	Natural gas	2134.94
Salt Conversion Furnace (FUR-1)	12661.17	Electricity	N/A
Separation Process Heat Required	5903.72	Electricity	N/A

Table 22: Preliminary Heat Duty for SX upgrading and Purification Processes.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
Stripping Solution Condenser (COND-4)	685.41	Cooling water	39354.82
Water Product Cooling (9-11) Duty	6719.72	Cooling water	385836.00
Water Product Cooling (10-07) Duty	397.38	Cooling water	22816.78
Iron Chloride Cooling (10-08) Duty	2109.31	Cooling water	121112.70
Conversion Reagent Recycle Cooling (10-09) Duty	701.46	Cooling water	40275.25
Water Product Cooling (11-03) Duty	6779.39	Cooling water	383004.00

6.2 Process Flow Diagrams

Figure 21 and Figure 22 are the process flow diagrams for Battelle's ADP and the overall SX upgrading and purification process, respectively.
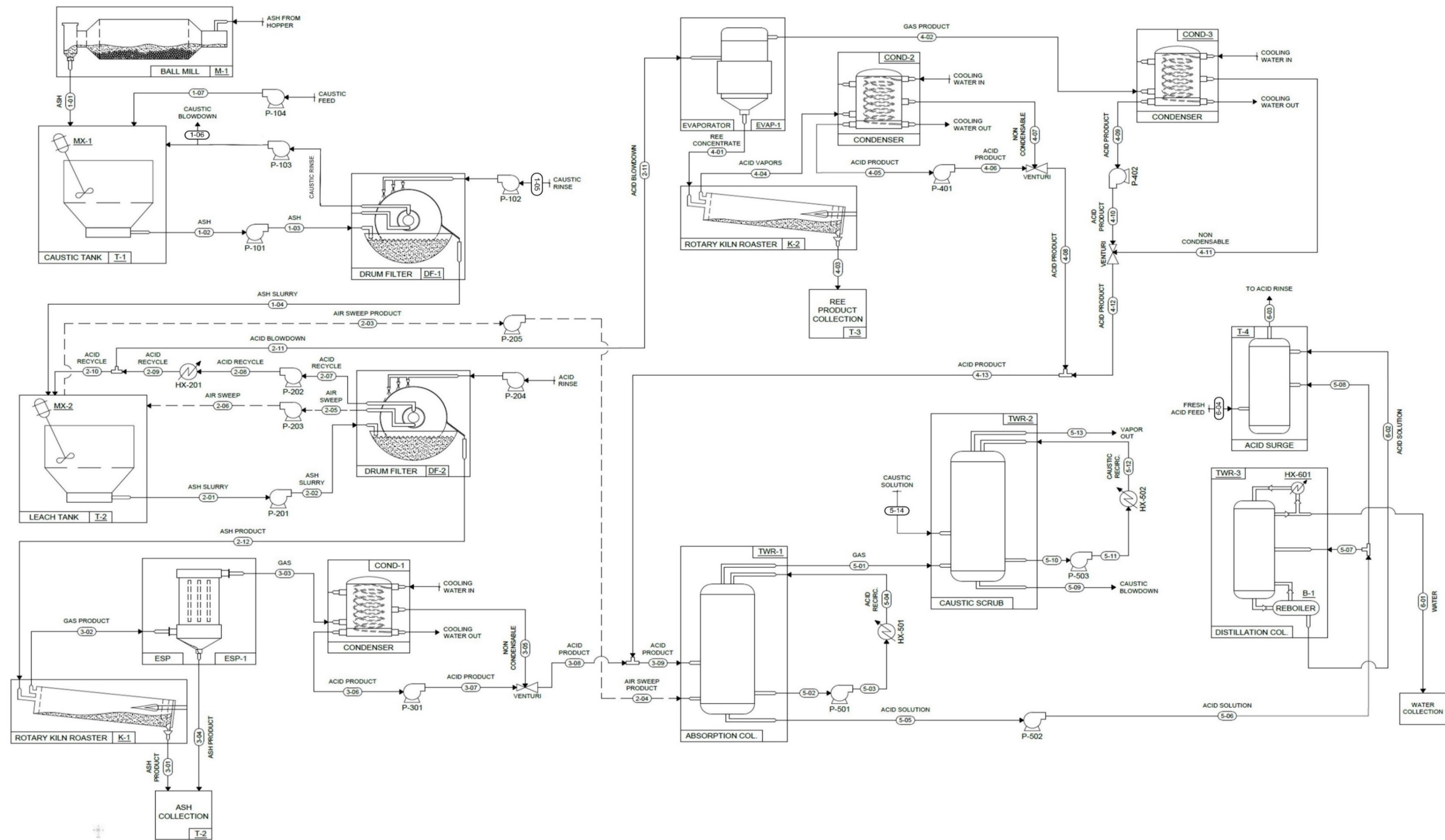
Figure 21: Preliminary PFD for Battelle's ADP Full-scale Process.

Figure 22: Preliminary PFD for Battelle's SX upgrading and RES Purification Full-scale Processes.

7.0 Technoeconomic Assessment (TEA)

7.1   Introduction

Final economics were run for the process to inform the technology transfer and commercialization plan. The intent of this economic study was to identify key economic hurdles to commercialization so that a rational development plan can be constructed. Accordingly, contingencies are lower than would be expected for a process design at this phase, and the ultimate costs reflect what one would expect for a mature, commercial plant operation assumed to operate well under the currently understood process parameters. Stream tables upon which the economics are based are provided in Appendix E, and process diagrams are shown in Figure 21 and Figure 22.

7.2   Summary of TEA Method

The procedure used in this work follows the Electric Power Research Institute's (EPRI) Technical Assessment Guide (TAG™) guidelines for cost estimation of emerging technologies. The total capital requirement (TCR) of a rare earth recovery system takes into account the direct costs of purchasing and installing all processing equipment (denoted as the Process Facilities Capital, PFC), in addition to a number of indirect costs such as the general facilities cost, engineering and home office fees, contingency costs, and several categories of owner's costs. These costs are used to determine the overall cost of Battelle's ADP and SX upgrading process, and RES' purification process for recovery and purification of REE. Figure 23 outlines the TAG method developed by EPRI.
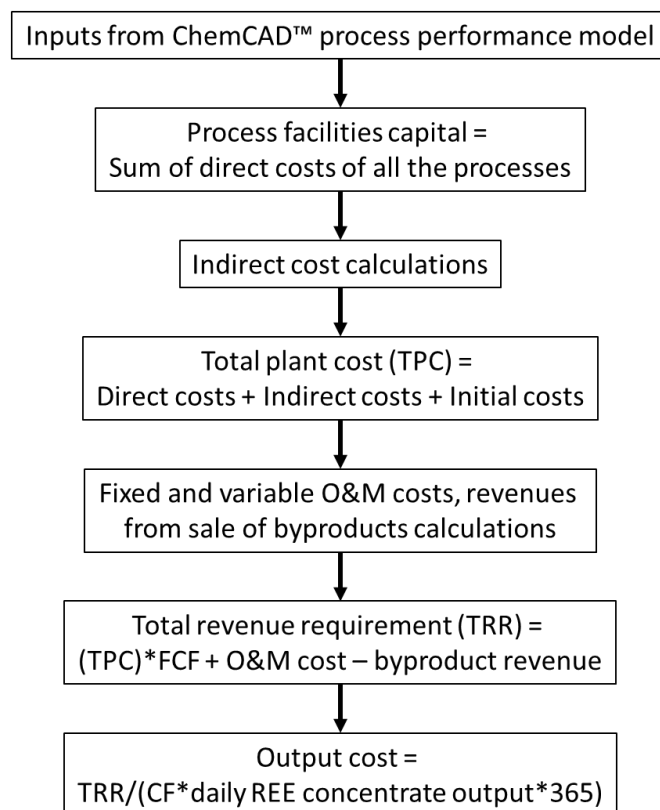
Figure 23: Method of cost assessment (Electric Power Research Institute (EPRI), 1986)

7.3   Capital Cost Analysis

The process facilities capital (PFC) of a component refers to the capital required to purchase and install a major process at the facility. Ideally, these costs are known and come from prices quoted from an equipment manufacturer. When manufacturer data is not available, installed cost data is derived from references describing costs for installing similar processes. Equipment costs are then scaled using well-documented cost correlations (Tribe & Alpine, 1986). Table 23 lists the nominal cost values for a rare earth recovery system using the process in this project.

The total direct capital cost of the rare earth recovery system is approximately $55 million. The most capital-intensive process area is the evaporator-condenser associated with the acid recovery system, which accounts for approximately one quarter of the total direct capital costs of the system. The evaporator-condenser is used to recover nitric acid from the leached stream and reduces the annual operating expenses associated with reagent cost.

Table 23: Installed costs for major process areas of the rare earth recovery plant.

Direct Costs for All Major Process Areas ($1000, 2015)

Coal Ash Handling	$361	Reactor Recirc. Pump	$20
Caustic Pretreat CSTR	$60	Column Sump Pump	$16
Pretreat Rotary Filter	$3,401	Filter Pump	$25
Pretreat CSTR Acid	$60	Evaporator Feed Pump	$8
Pretreat Zeolite Filtration	$60	Acid Recycle Pump	$8
Pretreat water wash	$224	Acid Makeup Pump	$8
Leach Reactor	$271	Column Blower	$104
Knockout Vessel	$187	Distillation Column	$3,911
Filter	$4,040	Oxide/Nitrate Separation	$970
Rotary Dryer	$2,277	Solvent Extraction	$747
Crystallizer/Custom Rotary Dryer	$3,402	Pre-Stripper	$1,196
Column	$263	Stripper	$2,391
ESP	$1,329	Scrubber	$2,391
Reactor Heat Exchanger	$215	Scandium Scrub	$297

Direct Costs for All Major Process Areas ($1000, 2015)

Column Heat Exchanger	$218	Post SX Leach	$970
Evap. Condenser	$13,234	Spray Dryers	$2,348
Roaster Condenser	$766	Furnace Items	$3,427
Reactor Feed pump	$25	REO Purification	$6,322
Process Facilities Capital			**~$55,552**

In addition to the Process Facilities Capital costs, there are a number of other capital cost items (often referred to as indirect costs) that are applied. Traditionally, these are estimated as percentages of the total PFC. These additional costs are divided into the following categories:

- Engineering and home office fees (EHO)
- General facilities capital (GFC)
- Process contingency
- Project contingency
- Royalty charges

The sum of these costs, called the total plant cost (TPC), is developed on the basis of overnight construction. Overnight cost is the cost of a construction project if no interest was incurred during construction, as if the project was completed "overnight." (Stoft, 2002) These costs are summarized in Table 24.

Table 24: Summary of estimated direct and indirect capital costs for the rare earth recovery process. These costs are the basis for estimating the total plant cost—a major component of the total capital requirement of the plant.

Capital cost elements	Nominal Value	Component Cost ($Million, 2015)
Process Facilities Capital (PFC)		$55.5
Engineering and Home Office Fees	7% PFC	$3.9
General Facilities	10% PFC	$5.6
Project Contingency	10% PFC	$5.6
Process Contingency	10% PFC	$5.6
Total Plant Cost (TPC) = Sum of the above		**$76.2**

General facilities capital (GFC) is the capital required for the construction of general facilities such as buildings, roads, shops, etc. This cost is usually estimated to be between 5 and 20% of the PFC. Engineering and home office overhead is included if the cost estimates for the general facilities capital do not include these fees as part of the equipment costs. For these fees, 7 and 15% of the PFC is typical. Royalty charges are included as indirect capital costs and typically range from 1 to 10% of PFC.

The EPRI TAG method uses two types of contingencies: the process contingency and the project contingency. The process contingency is a capital cost contingency factor applied to a new technology in an effort to quantify the uncertainty in the technical performance and cost of commercial scale equipment (Electric Power Research Institute (EPRI), 1986). Therefore, a higher process contingency factor is used for more basic cost estimates. Table 25 shows how the maturity of the technical design influences the process contingency.

Table 25: Process contingency cost guidelines ((EPRI), 1993).

Technology status	Process contingency cost (%PFC)
New concept with limited data	40+
Concept with bench-scale data	30-70
Small pilot plant data	20-35
Full-sized modules have been operated	5-20
Process is used commercially	0-10

EPRI recommends that separate process contingencies be given for each major process systems. For the REE recovery and purification processes, this work uses a default process contingency of 10% for a commercial process, as this commercialization plan aims to identify future-looking economic hurdles, rather than considering costs if built today.

The project contingency is a capital cost contingency factor that is intended to cover the cost of additional equipment or other costs that would result from a more detailed design of a definitive project specific to the actual site. Specifically, the project contingency addresses the need for site preparation, building construction, ancillary process equipment, structural support, and miscellaneous equipment required when the actual plant is built. Table 26 lists the project contingency cost guidelines as suggested by EPRI. This work uses a simplified design intended to be applicable for a range of equipment options.

Table 26: Project contingency costs. The contingency costs are compared to the American Association of Cost Engineers (ACEE) technology Class ranking system.

EPRI cost calculation	Design effort	Project contingency
Class I (~AACE Class 5/4)	Simplified	30-50
Class II (~AACE Class 3)	Preliminary	15-30

EPRI cost calculation	Design effort	Project contingency
Class III (~AACE Class 3/2)	Detailed	10-20
Class IV (~AACE Class 1)	Finalized	5-10

Like the process contingency, EPRI recommends that project contingencies be applied for each plant selection and this work uses finalized design effort values for each supply chain step outside of the recovery process. Regarding Battelle's recovery process, a project contingency factor of 10% is used as the default value. As with the process contingency, this is a low value, but intended to allow for forward looking identification of economic hurdles rather than the anticipated cost of building a plant today.

The total capital requirement (TCR) includes all the capital necessary to complete the entire project. These items include:

- Total plant cost (TPC)
- Allowance for funds used during construction (AFUCC)
- Prepaid royalties
- Inventory capital
- Pre-production costs

Table 27 summarizes the steps required to calculate the total capital requirement. The total capital requirement for the rare earth recovery process is approximately $80 million. This includes all direct and indirect capital costs associated with the project.

Table 27: Indirect capital costs for a rare earth element recovery plant.

Capital cost elements	Nominal Value	Component Cost ($1000, 2015)
Total Plant Cost (TPC)		$76,109
AFUDC (interest during construction)	0.5% TPC	$381
Royalty Fees	0.5% PFC	$278
Pre-Production (fixed)	1 month fixed O&M	$729
Pre-production (variable)	1 month variable O&M	$2,433
Inventory Capital	0.5% TPC	$381
Total Capital Requirement (TCR)		$80,311

7.4   Operating Cost Analysis

The operating and maintenance (O&M) costs are usually estimated for one year of operation. These can be divided into fixed O&M and variable O&M costs. These costs are discussed in this section. The fixed O&M (FOM) costs include the costs of plant maintenance (materials and labor) and labor (operating labor, administrative, and support labor). Table 28 is a summary of fixed O&M costs. Operating labor costs are estimated based on correlations between labor hour requirements and the plant's daily capacity (Peters, Timmerhaus, & West, 2003).

Table 28: Fixed operating and maintenance cost parameters and their deterministic values.

Fixed O&M Costs	Units	Nominal Value
Major processing steps	#	19
Cor'l'n for Op. Labor	Hrs./day-step	14
Operating Labor Rate	$/hr	$46.43
Total Maintenance Cost	%TPC	2.5%
Maint. Cost allocated to labor	% FOM maint.	40%
Admin. & Support labor cost	% total labor	30%

The variable O&M (VOM) costs include the cost of materials consumed (make-up acid, process water, etc.), utilities, and services used (waste transport and disposal). These quantities are determined in the CHEMCAD performance model. The unit cost of each item (e.g. dollars per tonne of coal ash) is a parameter specified as a cost input to the model. The total annual cost of each item is then calculated by multiplying the unit cost by the total annual quantity used or consumed. Total annual quantities are dependent upon the facility's annual operating capacity factor. The individual components of variable O&M costs are explained in more detail below (see Table 29). Note that the unit costs for all of the consumables are based on publicly available sources.

Table 29: Variable operating and maintenance cost components and their deterministic values.

Variable O&M Costs	Units	Nominal Value
Coal Ash	$/tonne	$-
Makeup Nitric Acid	$/tonne	$600
Dilution Water	$/tonne	$0.3
Leached Ash Disposal	$/tonne	$10.3
Natural Gas	$/GJ	$1.26
Electricity	$/MWh	$6.73
SMBS Price	$/tonne	$280
HCl Price	$/tonne	$115
NaOH Price	$/tonne	$320
Extractant Price	$/kg	$8.30
Wastewater Disposal	$/kliter	$0.30
Hazardous Wastewater Disposal	$/kliter	$18.79
Avg. Price for Salable Ash	$/tonne	$(30.00)
Selling Price for Ferric Chloride	$/tonne	$(400.00)
Conversion Reagent Price	$/tonne	$200.00

The nominal (default) values of all major operating and maintenance (O&M) costs in the REE recovery process model are summarized in Table 30. Note that the cost of coal ash is zero for the deterministic case.

Table 30: Variable and fixed operating cost component results for a rare earth recovery plant.

Variable Cost Component	Variable O&M Cost ($1000/yr)	Fixed Cost Component	Fixed O&M Cost ($1000/yr)
Coal Ash	$0	Operating Labor	$4,508
Makeup Nitric Acid	$10,678	Maintenance Material	$1,903
Makeup Water	$95	Maintenance Labor	$761
Solid waste disposal	$787	Admin. & Support Labor	$1,581
Natural Gas	$894	**REE Process Total Fixed Costs ($1000/yr)**	**$8,753**

Variable Cost Component	Variable O&M Cost ($1000/yr)	Fixed Cost Component	Fixed O&M Cost ($1000/yr)
Electricity	$2,628		
Solvent Extraction Reagent	$24		
Caustic	$197		
Hydrochloric Acid	$2		
Conversion Reagent	$13,797		
Hazardous Disposal	$14		
Purification	$209		
REE Process Total Variable Costs ($/yr)	**~$29,325**	**Total O&M Costs ($/yr)**	**~$38,078**

A discounted cash flow model was constructed using the capital and manufacturing costs presented. This model used the rare earth oxide selling prices listed in Table 31, which has some prices redacted as they are values proprietary to the marketing consultant source.

Table 31: Rare earth oxide prices used in the economic assessment

Element	Value US$/kg, Oxide Basis
Lu	XXX.x (proprietary price)
Sc	4200.0
Ce	2.0
Dy	230.0
Er	34.0
Eu	150.0
Gd	32.0
Ho	XX.x (proprietary price)
La	2.0
Nd	42.0
Pr	52.0
Sm	2.0
Tb	400.0
Tm	XX.x (proprietary price)
Y	6.0
Yb	XX.x (proprietary price)

The discounted cash flow model used assumptions as shown in Table 32. For a 20-year project, the net present value equates to approximately $54 million, with a simple payback period (FCI/annual cash flow) of 3.8 years. The rate of return is 27.6%. The discounted payback period is just over 12 years.

Table 32: Financial assumptions used in the discounted cash flow model

Capital Cost Escalation (nominal annual rate)	3.6%
Equity	50%
Loan Interest	6%
Loan Term, years	10
Working Capital (% of FCI)	0.00%
Type of Depreciation	DDB
General Plant	150
Depreciation Period (Years)	20
Construction Period (Years)	3
% Spent in Year -3	10.00%
% Spent in Year -2	60.00%
% Spent in Year -1	30.00%
Internal Rate of Return	15.00%
Income Tax Rate	38.00%
Cost Year Increment	annual average

A key takeaway from the economic analysis is that rare earth oxide sales alone are not sufficient to cover costs for the process. Revenues from REO sales are roughly $34 million against O&M costs of $38 million, so profits are entirely dependent upon the sale of byproducts; primarily the ferric chloride byproduct. Lesser revenue is also realized from sales of upgraded fly ash after leaching (assuming 50% of the fly ash is placeable), and sales of zeolite which are assumed only to cover the cost of pretreatment of the fly ash with caustic. Another item of note is the high value of scandium, which represents over 90% of the value of REO in this feedstock. Scandium is a very small market with niche applications, and the placement of large volumes of scandium at the estimated price needs to be validated.

8.0 Marketing/Commercialization Discussion

8.1 Rare Earth Uses and Production

Rare earth elements are widely used in catalysts, glass manufacture, sensors, and magnets. The magnetic rare earth elements are particularly valuable as their high magnetism reduces the size of motors and generators used in electric vehicles and wind turbines. They additionally find use in defense applications for armoring alloys, weapons guidance systems, night vision goggles, and communication systems (King, 2016). As shown in Figure 24, lanthanum and cerium find the most use by volume, as they are the most common rare earth elements and commonly used in petroleum upgrading catalyst and glass manufacture. By value, however, the magnetic rare earths, such as neodymium, praseodymium, and dysprosium far outweigh most others.
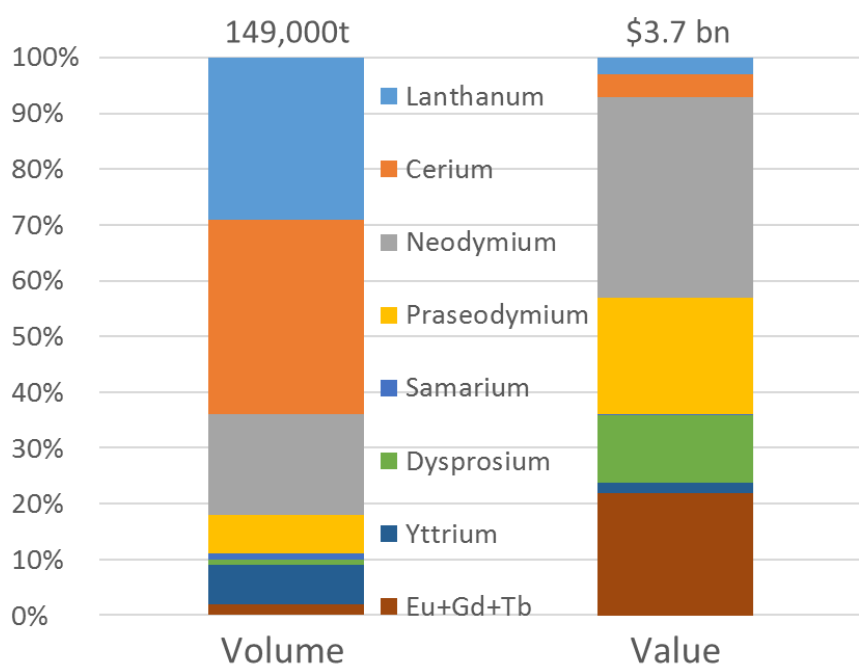
Figure 24: Global rare earth consumption by volume and value in 2015 (Argus, 2016).
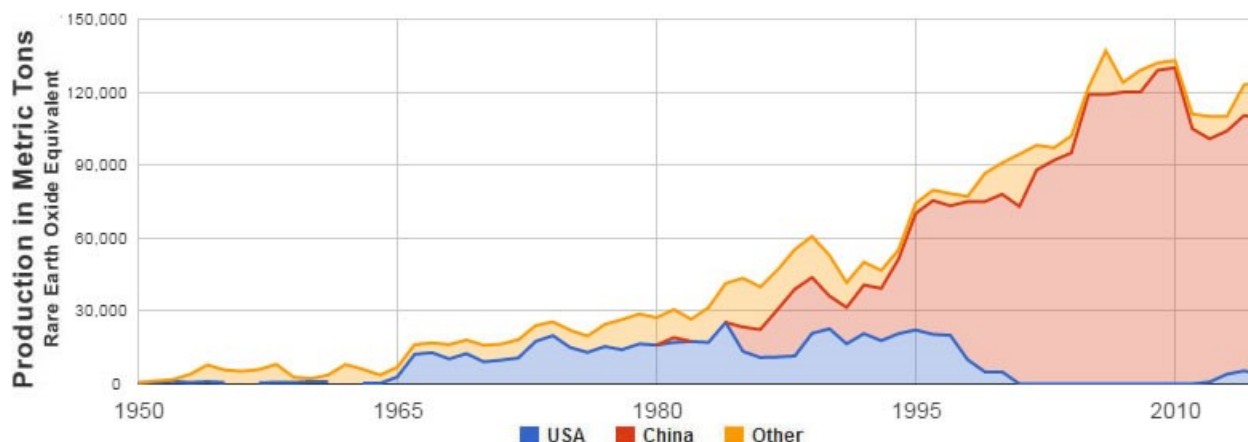
Figure 25: History of rare earth production, in metric tons of rare earth oxide equivalent, between 1950 and 2015. The United States' market share increased in the mid-1960s when color television increased demand. When China began selling REE at very low prices in the late-1980s and early-1990s, mines in the United States were forced to close because they could no longer make a profit. When China cut exports in 2010, rare earth prices skyrocketed. That motivated new production in many areas (King, 2016).

Application of rare earth elements began in earnest with the advent of color television, which relied heavily on europium. The US controlled most of the REE supply for a few decades before China began to dominate production in the 1990s, as illustrated in Figure 25. US production came back online from the Mountain Pass mine in California briefly, around 2013, after Chinese export restrictions caused a spike in REE prices. China has since relaxed these restrictions, lowering prices and causing the shutdown of the Mountain Pass mine.

China has enjoyed decades as the low-cost supplier of REE, due to a combination of subsidies to state-owned businesses and competitive deposits in the Bayan Obo region, Sichuan region and South China adsorption clays. There is also production of REE from an Australian deposit. Furthermore, there are known deposits around the world that have not yet or are not currently being exploited due to economic constraints, including the idled Mountain Pass mine in California.

The first step in a typical REE value chain consists of the mining of the ore. This step is usually followed by physical beneficiation, which consists of milling and usually flotation or occasionally magnetic separation steps. The upgraded mineral concentrate is then 'cracked' to leach the rare earths into an acidic solution, which may be cleaned by selective precipitation and then fed to a solvent extraction circuit. Solvent extraction separates and purifies the individual REE, and due to the chemical similarity between sequential REE, this process can take hundreds of mixer settler stages. It is common for the concentrated strip solutions from solvent extraction to be precipitated with oxalate addition, then calcined to oxides for sale in the market.

The South China Clays are notable as a deposit since they are similar in both concentration of REE and distribution of heavy REE to many coal deposits. However, they are ion exchangeable deposits, which are simpler to exploit than phosphate minerals more common to coal deposits, which require chemical cracking. The South China clays are leached with ammonium sulfate solution, precipitated with oxalic acid, then calcined and sent for separation and purification, with little need for mineral beneficiation and none for chemical cracking.

8.2   Technology Development and Commercialization Plan

The economic analysis performed in this project suggests that byproducts are critical to the economic sustainability of REE from coal sources. In fact, when considering marginal REE sources, the potential byproducts available from coal sources may make it more attractive than higher grade sources such as monazite sands. Beyond scale up of the coal REE recovery technology, there needs to be a transition to development and validation of co-products that are easily placed in the market to subsidize REE recovery. Obvious targets from coal sources include aluminum and iron products due to their prevalence in the mineral composition of coal. Battelle's and Rare Earth Salts' processes are capable of generating high purity ferric chloride and aluminum oxide products. Future work should place equal emphasis on these subsidizing co-products as the rare earth products.

8.2.1   Product Validation

As with any new technology, validation of the generated products with potential offtake groups is critical to commercialization because it resolves purity or product issues early in the development process and begins to form relationships with key commercialization partners. The most important products in this process, from a revenue standpoint, are scandium oxide and ferric chloride. Scandium is critical due to its high value, and ferric chloride is critical due to its high volume. We expect to be able to generate a high purity aluminum oxide product at high volumes, which could be another important product. Other rare earth oxides, aluminum oxide some base metals such as copper, zeolite products, and high-quality fly ash are lesser byproducts that can contribute to the process profitability.

On this project, it was demonstrated that products can be produced at a commercially relevant purity, and outreach to potential offtake groups can begin. Offtake groups will generally ask for independent analysis along with samples, which are easily handled under non-disclosure and material transfer agreements that the project team is familiar with implementing. Feedback from these groups on the purity and quality is a critical part of the sample process and will be used to improve and tailor the process for production of salable products.

8.2.2   Technology Readiness Level

RES' electrowinning technology for the purification of REE recovered from recycled fluorescent light bulbs to a standard purity of 99.9% is currently classified as a TRL 7, with a fully integrated prototype validated for recycling of REE from lightbulbs. RES' process is among the first low-cost, REE separation units recycling REE from feedstock materials, and is expected to operate at a production rate of 18 metric tons per month. However, the process concept for using the electrowinning purification technology, capable of separating and purifying REE and critical materials (CM) recovered from coal-based feedstocks to concentrations exceeding 90% purity, is currently being implemented by Battelle and RES. Therefore, the TRL is classified as 3.

Battelle's ADP and SX process are currently classified as a TRL 3, with preliminary design in place to build a high-fidelity, bench-scale integrated system for advancement to TRL 5. The full, combined processes of ADP, SX, chloride conversion and electrowinning will be advanced to TRL 5 after bench-scale integrated work. It will be the first time that they are integrated in a continuous bench-scale unit, with ADP feeding SX, and SX feeding RES' chloride conversion and electrowinning processes to generate 90% purity or higher separated REO and CM products. The technology maturation plan presented is outlined in Table 33.

The ultimate goal for this integrated technology is advancement from TRL 3 to TRL 9, which is a commercially operated plant capable of producing salable REO (including scandium oxide) and CM products at a concentration of 90 to 99.9% in an economical and environmentally benign manner. Battelle anticipates commercialization will be in REE and CM recovery from coal

sources, enabling domestic REE/CM sources and new outlets for coal products. Furthermore, the recycling acid leach of the ADP process, coupled with SX upgrading and RES' purification steps, can be applied to many other resource recovery or recycling operations.

Table 33: Expected technology maturation plan.

Year	Milestones	Performance Targets	TRL Achieved at Milestone
2019	Complete laboratory bench testing and bench-scale process design	Determine process parameter influence on bench-scale performance	3
2021	Complete continuous bench process demonstration (~12.5 lb/hr ash feed)	Integrated system performance on coal ash feedstocks at bench-scale and demonstrate REE/CM product of 90-99.9% purity	5
2023	Execute pilot demonstration (~0.5 ton/hr, ~80x scale up)	Validate system performance, including REE/CM purity greater than 99.9%	6
2026	~30x (~15 ton/hr) scale-up pilot plant demonstration	Technology scale-up issues addressed	7
2027	Commercial unit demonstration (~30-80 ton/hr)	Technology commercial start-up	8
2027+	Long-term commercial operating system	Long-term, cost-efficient, and environmentally benign REE/CM supply technology	9

8.2.3   Future Technical and Commercial Development Work

The first step in the development of the integrated technology is to further develop Battelle's SX process for REE concentration. In this research, coal fly ash has been fed to Battelle's ADP, reaching a combined REE product of 2% purity and a Fe/Al+Sc oxide material. The combined REE product contains some aluminum, which will be selectively removed from REE during the extraction step of the SX process, producing two streams, a loaded organic extractant stream containing the REE and an aluminum nitrate stream at >50% purity. Next, the loaded organic extractant stream is stripped with acid to yield a purified REE solution. This solution is then roasted at 250°C to calcine REE, separating them from calcium and sodium (undesired species in the purification process). The result will be a purified mixed REO product at 40 to 50% purity. To achieve these purity results or higher, Battelle would optimize the extractant formulation and process variables, such as residence time and stripping conditions, to develop a set of operating conditions for bench-scale testing. Optimization will allow advancement of the SX technology to a TRL of 4. Continuous bench-scale testing using these process parameters could be conducted to further advance the TRL to 5.

To advance RES' chloride conversion and electrowinning technologies for coal-ash applications from a TRL 3 to a TRL 5, RES will work first with a surrogate material with similar chemical composition that is representative of the effluent of Battelle's ADP and SX process. While some of work was performed during this project, more research needs to be conducted to optimize the chloride conversion and electrowinning process parameters specifically for the SX process effluent, removing contaminants commonly associated with coal-ash REE/CM feedstocks, while maintaining salable REO (including scandium oxide) and aluminum oxide products of 90 to 99.9% purity, and producing ferric chloride as a key byproduct. After optimization of the chloride conversion and electrowinning processes using a surrogate material, Battelle would provide a derived material from a coal ash source processed using Battelle's ADP and SX technologies.

In future efforts, RES maintains the ability to operate continuous small-scale electrowinning cells, capable of demonstrating the optimized technology at a TRL of 5. Throughout this step, it will be important to monitor the enrichment of radionuclides, like uranium and thorium, as avoiding enrichment to actionable levels will be a key step in maintaining an environmentally benign process. The ferric chloride byproduct is a key revenue source to support REE recovery from coal sources, and its development will contribute heavily to future commercialization.

It is expected that funding for the advancement to TRL 5 will come primarily from government sources, with some commercial investment supporting the project. At TRL 5, interaction will begin with mining/commodity groups who could be potential licensees/operators of the technology at the commercial scale. These interactions will include sharing of economic projections and models, samples, and demonstrations of the technology operating on coal feedstocks. Rare Earth Salts has already made significant progress in placing their REO products in the market, and as the owners of the purification process, it is expected that they will be able to add coal-based sources into their product stream for sale with minimal modifications. This will be validated with outputs from the integrated bench-scale system.

After bench-scale integration, the integrated technology will have advanced from TRL 3 to TRL 5. Advancement from a TRL of 5 to a TRL of 7 can be executed in two pilot demonstrations, each building upon the scale and complexity of the previous. Anticipated pilot scales are shown in Table 33.

The primary parameters to be evaluated in the two pilot-scale plants are stream scaling factors and process control conditions. The scales of the pilot plants to advance the integrated technology from TRL 5 to TRL 6, and subsequently from TRL 6 to TRL 7, will be chosen to allow for common process equipment design calculations to be used to size and specify the required unit operations, allowing for scale-up data to be confidently collected, without requiring a capital-intensive plant to be built. At this point in the technology development process, industrial partners interested in operating the technology will be identified and required funding for these pilots will gradually transition from primarily government sources to commercial partners. It is anticipated that the industrial groups most interested in the technology will be REE commodity producers, mining companies, and potentially large REE and CM product end users. Throughout the pilot demonstration, maintaining a salable REE and CM product of high purity (90 to 99.9%) will be a key pilot parameter to monitor, along with reagent feed rates and waste production rates.

Demonstrating that this integrated technology will be a cost-efficient and environmentally benign REE and CM supply technology will be key to identifying and securing investors in the technology. It is anticipated that a TRL of 7 would be reached by 2026, which is a time when REE are anticipated to increase greatly in demand. This demand is expected to accelerate exponentially between 2020 and 2025, and China, which is the current primary supplier of REE, will not be able to keep up with this demand, in turn allowing for alternative sourcing technologies to enter the market.

9.0   Conclusions and Next Steps

Surface response models have been generated for extraction and stripping of REE from leach solutions derived from PCC fly ash. These models can be used to estimate optimal operational points for the extraction and stripping processes where high selectivity for REE is accomplished. The initial target for REE purity out of the solvent extraction step was 60% of the measured solutes. The best result empirically achieved was 55% and the best projected result from the model is 58%, which compare well against the target. The primary contaminants are zinc and aluminum. Based on work done by RES, the zinc was a known challenge in the separation and purification process, whereas the aluminum can be easily handled. With this information, Battelle selected a new extractant composition that was demonstrated in this project to be selective for zinc over the REE and can be implemented prior to the traditional solvent extraction steps as a pretreatment to remove zinc. Rare Earth Salts also demonstrated a wet chemical process to selectively separate zinc from REE. This process was able to separate the majority of the zinc from a REE/zinc solution. Additional research is required to determine which of these methods is most economical for zinc removal.

Another important output of this project was the high purity (>90%), separated REO product from coal-based sources. Battelle created this product by leaching large volumes of PCC fly ash using Battelle's ADP and concentrating the leach solution prior to the SX upgrading process. The upgraded REE solution was roasted again, obtaining an aluminum/REE oxide material. This material was then fed to RES' conversion process making a REE salt product and an insoluble aluminum oxide byproduct. The REE salt product was then dissolved in hydrochloric acid , and the REE was precipitated using tartaric acid under pH control. The REE precipitate, now free of zinc, was calcined at high temperature and re-dissolved in hydrochloric acid, making a concentrated REE solution. This solution was then fed to RES' electrowinning process for the final separation and purification. Finally, two products were obtained meeting the objectives of this study:

- Approximately 1.1 grams oxide material having a TREO concentration of >90% with an 89% +/- 2% lanthanum content (oxide basis).

- Approximately 0.2 grams oxide material having a TREO concentration of >95% with a 90% +/- 2% lanthanum content (oxide basis).

Having developed a process design capable of producing high purity REO, a TEA was performed on the combined processes to recover high purity REO from coal fly ash. The assessment was informed by a chemical process model based on laboratory testing results, preliminary sizing estimates for the equipment and a factored capital cost estimation. This TEA suggested that for a 20-year project, the rate of return is 27.6% on a capital investment of $76.4 million, with a simple payback period (FCI/annual cash flow) of 3.8 years. However, the process is dependent upon a ferric chloride co-product for profitability and scandium as the bulk of the rare earth revenue stream. The availability of co-products from coal-based sources may actually be a benefit compared to other marginal sources, such as monazite sands, which have minimal other mineral values to subsidize the rare earth recovery.

One of the next steps from this study is commercialization. The reported process for the production of high purity REO/CM products needs to be scaled to an integrated bench-scale that is able to produce sample quantities to engage potential offtake partners for REO and byproducts. A shift needs to be made toward the development of co-products that subsidize REE recovery from coal sources, and validation of the marketability of the key products. In particular, high purity scandium oxide product needs to be generated from coal sources so that end users can validate whether it is usable in their processes and their financial tolerance.

Additionally, key byproducts from the process such as ferric chloride and aluminum oxide need to be generated in quantities that can be tested by commercial end users. As feedback from end users is received on the samples, the integrated bench-scale unit can be adjusted to meet end user requirements.

Once the rare earth products and byproducts have been validated by end users at the integrated bench-scale, the process will be scaled through two stages of piloting, first at 0.5 tonnes per hour, then 15 tonnes per hour of coal ash before a commercial plant is built. Rare Earth Salts has an existing 18 ton per day of REO plant in operation and has made significant headway in placing the rare earth products from this system into the market. It is expected that the coal-based REE from the pilot plants can be processed in their existing system with minimal adjustments, even blended with current feed streams, so that customer validation of the coal-based rare earth elements can be accomplished quickly with minimal process interruptions.

From a technical standpoint, there are additional steps beyond the scope of this project. Review of the USGS COALQUAL database suggests that zinc concentrations are likely to be high in all coal sources that contain REE. Therefore, further work on zinc removal and selectivity could benefit multiple methods for REE recovery. The current work focused on nitrate solutions with high iron and aluminum contents, but the extraction may vary in chloride or sulfate solutions that could be used in other processes. Additionally, zinc removal may enable better recovery of scandium. Rare Earth Salts' proprietary process would be able to selectively recover scandium in the roasted solids, provided the zinc is removed. An improved process could feasibly leach all of the zinc from the first roasted solids, extract the zinc while leaving the REE in solution and allow all of the REE and scandium to be recovered from a single solid concentrate.

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Appendices

Appendix A: DOE Preliminary Experimental Test Plan for Recovery of High Purity REE from Coal Ash

Battelle Project 100111989

Preliminary Experimental Test Plan for Recovery of High Purity Rare Earth Elements (REEs) from Coal Ash via a Novel Electrowinning Process

BATTELLE

Goal

The goal of this testing is to provide an estimation of organic and other metals traces in the stripped solution containing rare earth elements (REEs) after implementing Battelle's acid digestion process (ADP) and solvent extraction. The tests are needed to enable the design of a novel electrowinning process for the recovery of high purity REEs from coal ash.

Objectives

The final product of this testing will be a solution containing high concentration of REEs, organic traces, and other metal traces. This product will be achieved using the following two steps. Figure 1 shows a schematic representation of these two steps:

1. Battelle's ADP: The ADP process involves pretreatment of ash (milling and caustic leaching), leaching of pretreated ash with nitric acid, roasting of loaded acid solution containing REEs, and water leaching of residual from roasting step, resulting in a loaded water solution will contain REEs.
2. Solvent Extraction: The solvent extraction involves the extraction of REEs from loaded water solution using an organic extractant (the aqueous phase will be a residual solution and the organic phase will contain REEs), and stripping of REEs from organic phase product obtained from extraction using hydrochloric acid solution (the stripped solution will be the final purified product containing REEs, organic traces, and traces of other metals for use in the electrowinning process).
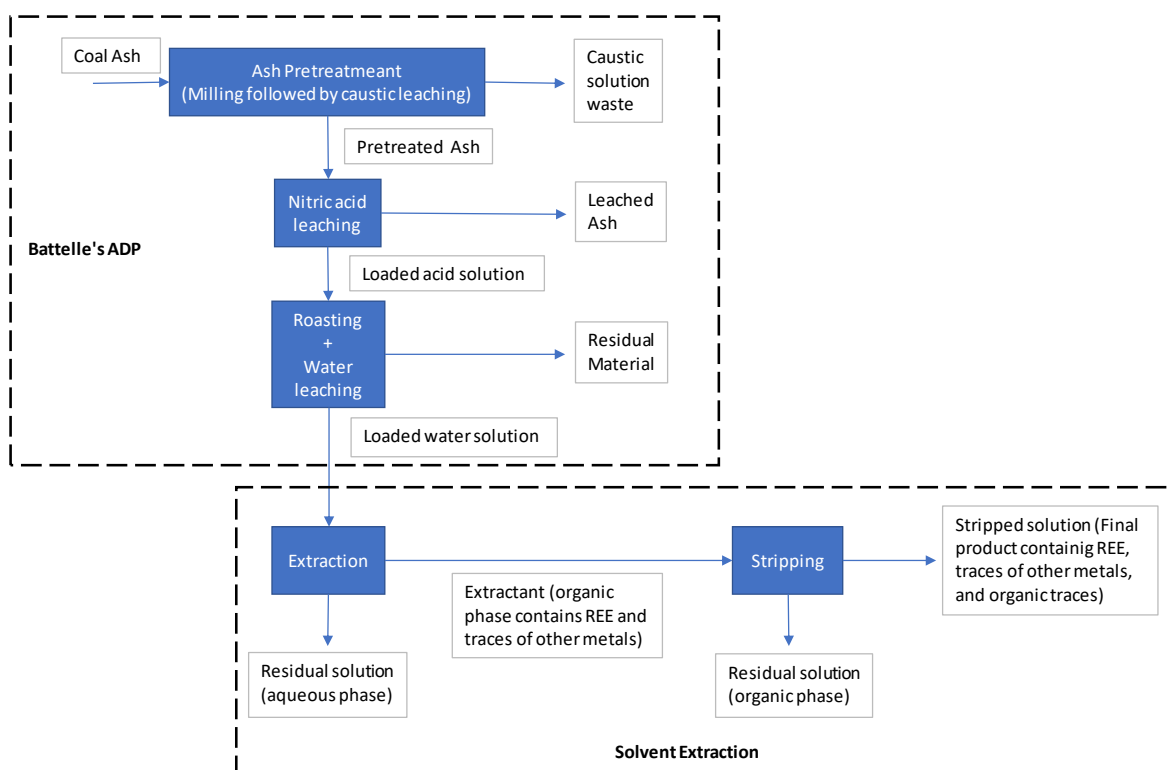
Figure 1: Schematic representation of Battelle's ADP and Solvent Extraction processes.

Test Approach

Ash Pretreatment

Milling of Ash

Coal fly ash will be milled to reduce the particle size, using the following steps: Experiment will be carried out using a ball mill, 1000 ml ceramic vessel, and zirconium oxide particles as grinding media.

- Add 120 g of ash, 300 ml of deionized water (DI) water, and 300 g of Zirconium Oxide particles to the ceramic vessel.
- Mill of ash for 24 hours at ambient temperature.
- After 24 hours, filter water using EMD Millipore 142 mm Hazardous Waste Pressure Filter System.
- Dry remaining ash at approximately 100°C, until ash is completely dried. Milled ash will be used for next step (caustic leaching).

Caustic Leaching

Milled ash will be leach with caustic solution (10% Sodium Hydroxide) to leach silica and alumina from ash particles to give better access to the REEs in the acid leaching step:

- Prepare 1 liter of 10% sodium hydroxide (See Table 2 for preparation details) solution and add it to a 2 liter round-bottom flask.
- Heat solution to 90°C and add 120 g of milled ash.
- Mix for 1 hour at about 700 rpm, using an overhead mixer,
- After reaction period, filter caustic solution using a pressure filter system with a 0.45 μm polyvinylidene fluoride (PVDF) filter.
- Wash ash remaining with DI for 5 minutes. Repeat this step until filtered water pH is equal or less than 10.
- Recover and dry ash and take a 3 gram sample. This sample is the final pretreated ash that will be used in the nitric acid leaching step.

Nitric Acid Leaching and Roasting

Nitric acid (34%) will be used for leaching (See Table 2 for preparation details), and reaction temperature will be 90°C. In this set of experiments the starting acid solution will be reused in order to fully load the solution with REEs. However, there will be other mixed salts in this solution like sodium nitrate, calcium nitrate, aluminum nitrate and iron nitrate, with aluminum nitrate and iron nitrate being major contaminates. The next step is roasting.

Roasting is an important step to recover REE because iron and aluminum can be oxidized at temperatures between 100°C and 200°C, generating an insoluble oxide material. For this roasting experiment, the temperature will be set at 130°C.

Nitric Acid Leaching

Four nitric acid leaching experiments will be performed (See Table 1). The same set up and test apparatus will used for all the leaching tests (See Figure 2). Reactions will be performed in a round-bottom flask in a heating mantle with forced air in the headspace that exhausts through a caustic bath. The caustic bath neutralizes any noxious fumes that may be generated in the reaction. The tests will be also run inside a fume hood.
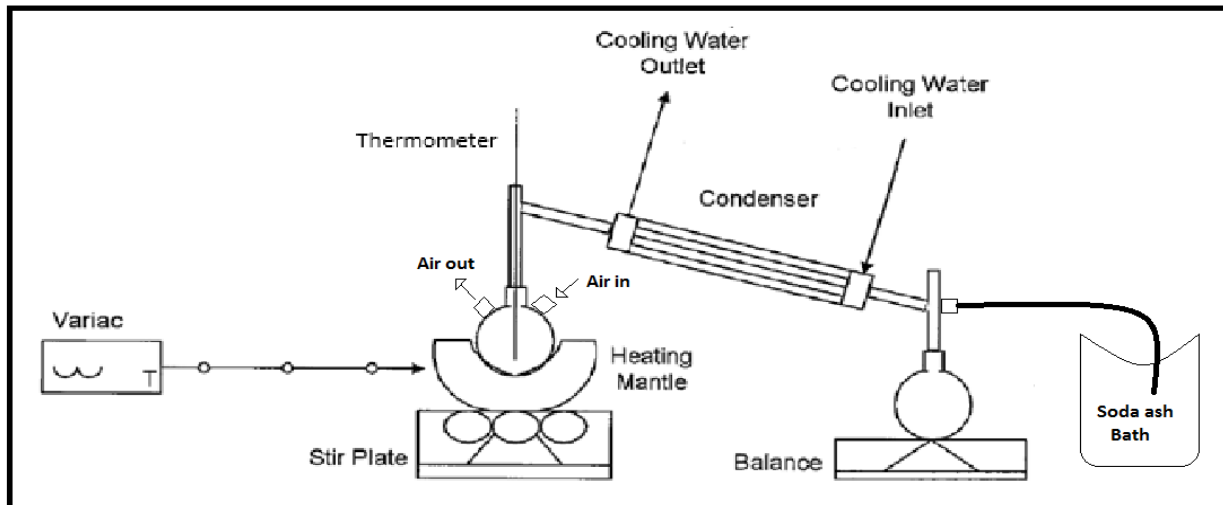
Figure 2 - Test apparatus and set up that will be used for every leaching experiment.

All leaching experiments with nitric acid will follow the procedure listed below:

- In a fume hood, add 500 mL of 34% nitric acid solution to a round-bottom flask with a running air purge to a caustic bath, and a thermometer in the top stem. Add a stir bar and begin mixing the solution.
- Set the temperature controller to the desired temperature (90°C). Wait for the acid to reach this temperature.
- Add desired amount of ash (pretreated) to the solution and begin a timer.
- End the experiment after 30 minutes reaction time by turning off the heater. Wait for the solution to cool down, and filter acid (loaded acid solution) using a pressure filter system with a 0.45 µm PVDF filter.
- Recover loaded acid solution (take a 12 mL sample) and discard the remaining ash in a waste container appropriate for low pH oxidizing waste.

Table 1: Experiments list for Nitric Acid Leaching

Experiment	Nitric Acid	Pretreated Ash
1	500 mL (34% HNO$_3$)	25 g
2	Re-use acid from Experiment 1	25 g
3	Re-use acid from Experiment 2	25 g
4	Re-use acid from Experiment 3	25 g

Roasting
In this experiment, the loaded acid solution will be roasted using a temperature controlled oven in a fume hood. Any fumes out from the oven will be directed into a condenser followed by an acid scrubber, prior to being discharged into the hood. The roasting temperature for this experiment will be between 100°C and 150°C, using the following steps:

- Take loaded acid solution obtained from nitric acid leaching step and put it in the control oven for 2 hours.

- Put the residual material into a 500-mL beaker and add 300 mL of DI water.
- Stir the mix for 5 minutes and filter water using a pressure filter system with a 0.45 μm PVDF filter.
- The loaded water solution should contain REE (take a 12 mL sample), and most of the residual insoluble material will be iron oxide (save residual material). This loaded water solution will be used for solvent extraction step.

Solvent extraction

Solvent extraction will be used for removal of monovalent and divalent cations along with select transition metals. The solvent extraction process is divided into two steps (extraction and stripping).

Extraction

Before starting the extraction test, the pH of loaded water solution recovered from roasting step is adjusted to a desired pH (3 – 4) using 10% nitric acid or 10% sodium carbonate solutions (See Table 2 for preparation details). Here are the steps to follow for extraction process:

- After adjusting the loaded water solution to pH 3-4, add 150 mL of loaded water solution and 75 mL of 15% CYANEX 572 in Solvent 467 diluent (See Table 2 for preparation details) into a 500-mL beaker. Two phases will be observed (organic and aqueous)
- Mix the two phases for 30 minutes at 2400 rpm with an overhead mixer.
- Using a 500-mL separatory funnel, separate the aqueous phase from the organic phase.
- Take a 12 mL sample of aqueous solution, and save organic phase for the stripping step.
- Repeat this experiment one more time. At the end, combine the organic phase remained from each experiment of the two experiments.

Stripping

A 10% hydrochloric acid (HCl) (See Table 2 for preparation details) will be used as stripping solution. The following are the steps for the stripping process.

- Make 200 mL of 10% hydrochloric acid solution and added to a 500-mL beaker.
- Add 100 mL of loaded organic phase collected from extraction step into the 500-mL beaker with HCl solution.
- Mix the two phases for 30 minutes at 2400 rpm with an overhead mixer.
- Using a 500-mL separatory funnel, separate the aqueous phase from the organic phase.
- Save organic phase, and take a 12-mL sample of the stripped solution (aqueous phase) in a glass sample container.
- Send 12-mL sample of the stripped solution. for Total Organic Carbon (TOC) measurements.

Preparation of Solutions

In each step of the Battelle's ADP and Solvent Extraction process, solutions need to be preparade to perform each experiment. Table 2 shows the solutions preparation and the steps in which the solution will be prepared. Each of these solutions will be prepare at the respective experimental step.

Table 2 – Solution preparation for each experiment

Solution	Preparation	Experiment
10% Sodium Hydroxide	1000 g of DI water + 112 g of SODIUM HYDROXIDE REAGENT (ACS)	Caustic pretreatment
34% Nitric Acid	400 g of DI water + 400 g	Nitric Acid Leaching

Solution	Preparation	Experiment
	NITRIC ACID, REAGENT ACS (68-70%) *Always add acid to water.*	
10% Nitric Acid	200 g of DI water + 34.5 g NITRIC ACID, REAGENT ACS (68-70%) *Always add acid to water.*	Extraction (pH adjustment)
10% Sodium Carbonate	200 g of DI water + 22.3 g SODA ASH, LIGHT, TECH, (SODIUM CARBONATE)	Extraction (pH adjustment)
15% CYANEX 572	200 g of Solvent 467 + 35.3 g CYANEX 572	Extraction
10% Hydrochloric Acid	200 g of DI water + 75 g HYDROCHLORIC ACID, CERTIFIED ACS 37% IN WATER	Stripping

Appendix B: DOE Experimental Test Plan for Recovery of High Purity REE from Coal Ash

Experimental Test Plan for Recovery of High Purity Rare Earth Elements (REEs) from Coal Ash

BATTELLE

Goal

The goal of this testing is to provide a high purity stream of rare earth elements (REEs) from coal ash after implementing Battelle's acid digestion process (ADP), upgrading solvent extraction, and Rare Earth Salts (RES) purification and separation process. The tests are needed to enable the design of a novel electrowinning process for further purification of the high purity stream of REEs into mixed or individual metal oxides. This test plan document is specific to the ADP and solvent extraction portions that will be performed by Battelle, while the RES test plan is a separate standalone document.

Objectives

The final product of this testing will be a high purity (>90%) rare earth oxide product. This product will be achieved using the following three steps:

1. Battelle's ADP: The ADP process involves pretreatment of ash (milling and caustic leaching), leaching of pretreated ash with nitric acid, roasting of loaded acid solution containing REEs, and water leaching of residual from roasting step, resulting in a loaded water solution which contains REEs. Figure 1 shows a schematic representation of the first two steps.
2. Solvent Extraction (SX): The solvent extraction involves the extraction of REEs from loaded water solution using an organic extractant (the aqueous phase will be a residual solution and the organic phase will contain REEs), and stripping of REEs from organic phase product obtained from extraction using hydrochloric acid solution (the stripped solution will be the final purified product containing REEs, organic traces, and traces of other metals for use in the electrowinning process).
3. RES Electrochemical Separation and Purification Process: The staged electrochemical process will separate rare earth oxide products from the mixed rare earth solution. RES testing will also include investigation of options to forego the solvent extraction steps.
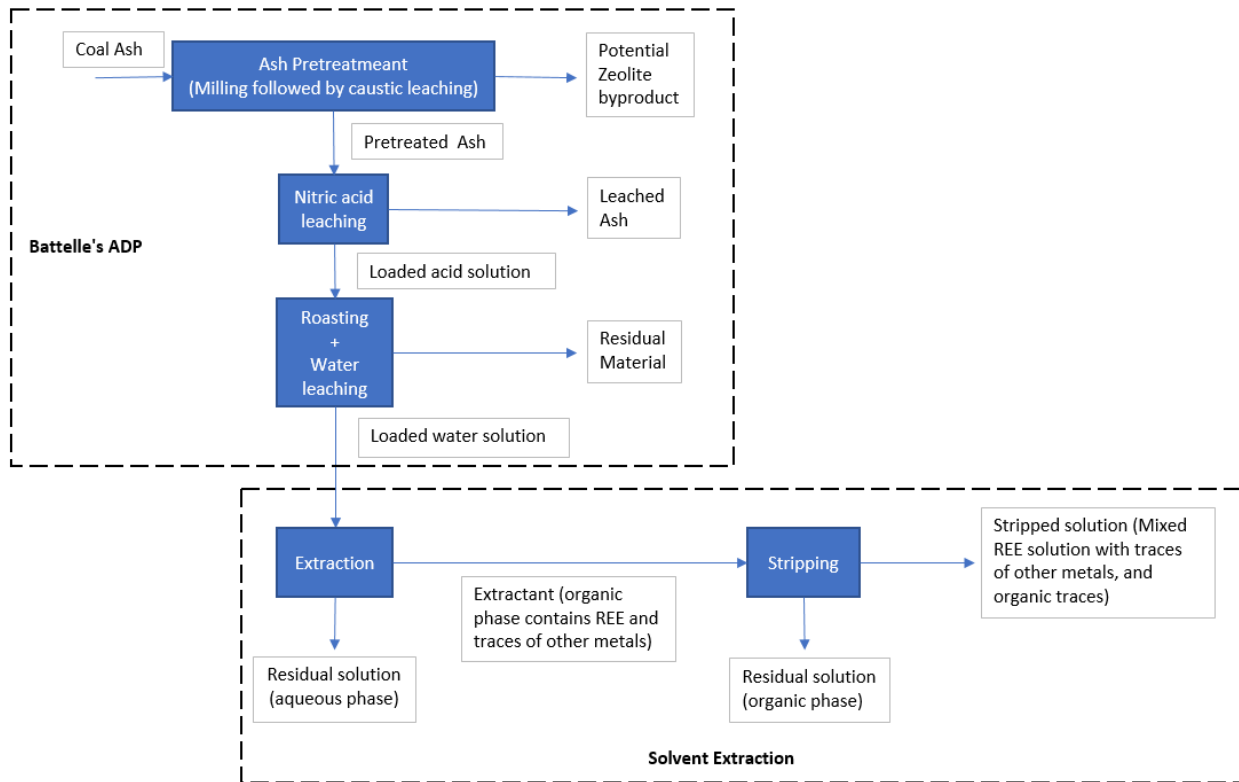
Figure 1: Schematic representation of Battelle's ADP and Solvent Extraction.

Test Approach

For testing, batches of 3.75 kg will be processed at a time. This amount was selected based on leaching reactor volume and mixing constraints. With the exception of milling the ash, Battelle's ADP will be performed under a fume hood with the following equipment (See Figure 2):

Figure 2: Equipment that will be used for caustic leaching, acid leaching, and roasting processes.

- 50-liter round bottom flask in a control thermocouple heating mantle with forced air in the headspace for exhaust of fumes
- Controlled overhead mixer with stainless steel impeller
- Stainless steel condenser with cooling jacket
- Condensate recovery vessel
- Vacuum pump to force circulation of gases through the condenser
- Temperature controlled oven for roasting
- Heavy duty peristaltic pumps for liquid transfers
- Heavy duty vacuum pump for ash disposal

Ash Pretreatment

Milling of Ash

Coal fly ash will be milled to reduce the particle size, in batches of 6 kg. This will be carried out using a canister roller, three 6.5-liter ceramic vessels, and ceramic particles as grinding media, using the following steps:

1. Add 2 kg of ash, 2.5 liters of deionized water (DI) water, and 4.6 kg of ceramic particles to each of the three 6.5-liter ceramic vessels.
2. Mill the ash for 48 hours at ambient temperature.
3. After 48 hours, use a sieve to strain the mixture of water and ash from the ceramic particles.
4. Dry the ash at approximately 150°C, until it is completely dried. The milled ash will be used for the next step (caustic leaching).

Caustic Leaching

The milled ash will be leached using a caustic solution (15%wt. Sodium Hydroxide) to leach silica and alumina from ash particles. This will enhance the recovery of the REEs in the acid leaching step:

1. Prepare 25 liters of 15% wt. sodium hydroxide solution and add it to a 50-liter round-bottom flask (leaching reactor). See Figure 3 for reactor set up.
2. Heat the solution to 90°C and add 3.75 kg of milled ash.
3. Mix for 1 hour at 800-820 rpm, using a controlled overhead mixer with stainless steel impeller.
4. After the reaction period, allow the ash to settle and use a heavy duty peristaltic pump to filter the caustic solution through a pressure filter system using a 0.45 µm polyvinylidene fluoride (PVDF) filter. The caustic solution will be pumped into a high pH residual container.
5. Wash the remaining ash with 30 liters of DI water for 5 minutes. Repeat this step three times or until the filtered solution pH is equal to or less than 12.5.
6. Remove and dry a 5-gram sample. The sample will be sent for analysis by ICP-MS. Leave the wet, pretreated ash in the 50-liter reactor for use in the nitric acid leaching step.
7. Prior to the acid leaching process, a 2-gram sample of the wet, pretreated ash will be taken for moisture analysis using an infrared moisture analyzer. This will determine how much water and acid needs to be added to generate the desired acid volume and concentration.

Nitric Acid Leaching and Roasting

Nitric acid (34%wt.) will be used for leaching and the reaction temperature will be 90°C. After the acid leaching steps, the acid solution should be loaded with REEs. However, there will be other mixed salts in the solution, such as: sodium nitrate, calcium nitrate, aluminum nitrate and iron nitrate, with aluminum nitrate and iron nitrate being the major contaminants. The next step is roasting.

Roasting is an important step to recover REE because iron and aluminum can be oxidized at temperatures between 100°C and 200°C, generating an insoluble oxide material. For the roasting process, the temperature will be set at 175°C.

Nitric Acid Leaching

The same set up and test apparatus used in the caustic leaching process will be used for the acid leaching process (See Figure 3). Reactions will be performed in a 50-liter round-bottom flask (leaching reactor), in a temperature-controlled heating mantle with forced air in the headspace, which exhausts hot fumes through a stainless-steel condenser. A portion of acid is recovered. The cooled fumes from the condenser go into a carbonate solution scrubber. The scrubber neutralizes any noxious fumes that may be generated in the reaction. The tests will be also run inside a fume hood.
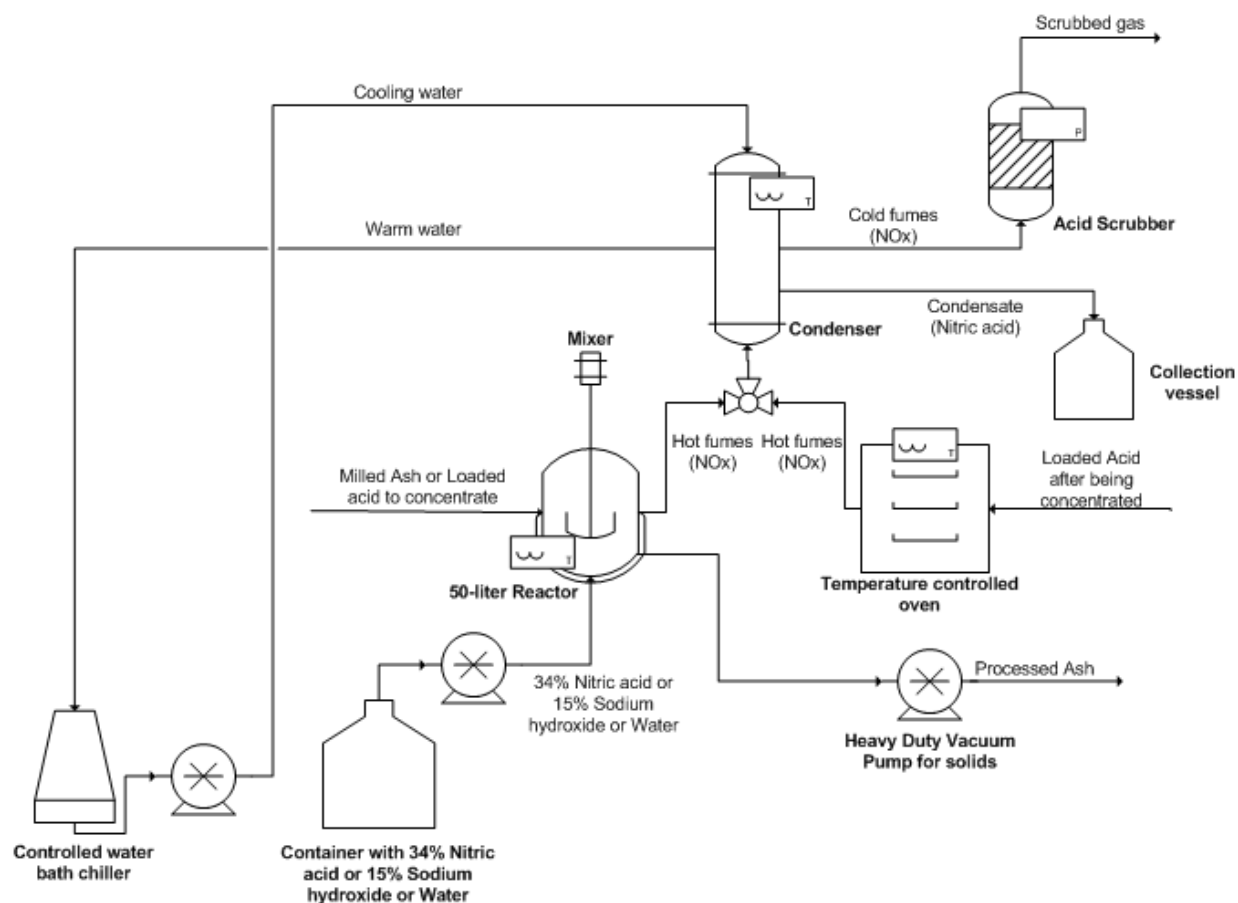
**Figure 3: Experimental set up for caustic leaching, acid leaching, and roasting experiments.**

Leaching with nitric acid will follow the procedure listed below:

1. In a fume hood, add 25 liters of 34%wt. nitric acid solution to a 50-liter round-bottom flask with a running air purge to an acid scrubber and a thermocouple in the top stem. A controlled overhead mixer with stainless steel impeller will be used for the reaction.
2. Pretreated ash is already in the 50-liter reactor from the caustic leaching.
3. Set the temperature controller to 90°C and heat the acid until it reaches 90°C (this will be the starting point of the reaction).
4. End the process after 30 minutes of reaction time by turning off the heater.
5. Add 12.5 liters of DI water and mix for 5 more minutes. Allow the ash to settle. Use a heavy duty peristaltic pump to filter 12.5 liters of acidic solution through a pressure filter system using a 0.45 µm polyvinylidene fluoride (PVDF) filter. Repeat this step 5 times.
6. Recover the loaded acid solution and take a 12 mL sample to send for analysis by ICP-MS.
7. Using a heavy-duty vacuum pump, discard the remaining ash into an appropriate waste container for low pH, oxidizing waste.

Roasting
During the roasting process, the loaded acid solution will be concentrated using the acid leaching set up (See Figure 3). After the loaded acid is concentrated to a volume of ~5 L, the solution will be roasted using a temperature-controlled oven in a fume hood. Any fumes out from the oven will be directed into a condenser followed by a carbonate scrubber, prior to being discharged into the hood. The roasting temperature for this process will be 175°C, using the following steps:

1. Take loaded acid solution obtained from nitric acid leaching step and concentrate it by boiling to about 5 liters of volume using the acid leaching set up.
2. Put the concentrated solution in the controlled oven for 36 hours.
3. Put the residual material into a 50-liter round-bottom flask and add ~5 L of DI water.
4. Mix the residual material for 24 hours. Allow the residual material to settle. Use a heavy duty peristaltic pump to filter the loaded water solution through a pressure filter system using a 0.45 µm polyvinylidene fluoride (PVDF) filter.
5. The loaded water solution should contain REE (take a 12 mL sample) and most of the residual insoluble material will be iron oxide (save the residual material). This loaded water solution will be used for the solvent extraction step.

Solvent extraction

Solvent extraction will be used for the removal of monovalent and divalent cations, along with select transition metals. The solvent extraction testing will be divided into two sets of experiments. The first set of experiments will be an experimental design where mixing time, extraction and stripping pH, and the addition of sodium metabisulfite (SMBS, used to reduce iron) will be studied. The second set of experiments will study loading of the extractant and strip solution, using optimal conditions for mixing time, extraction pH, and stripping pH discovered in first set experiments.

All factors studied in the first and second set of experiments are essential to determine optimal conditions for the SX process. Using these optimal conditions, SX will be performed to generate a high purity stream of REEs. This stream will be the feedstock for RES's electrowinning process for further purification into individual rare earth oxide products.

All solvent extraction testing will be performed in a batch set up, and the experimental procedure will be as follows:

Extraction

1. pH of loaded water solution recovered from roasting step is adjusted to a desired pH using 37.2% hydrochloric acid or 10% sodium carbonate solutions (Note: if addition of SMBS is required for testing, it will be added before the pH adjustment).
2. After adjusting the loaded water solution to the desired pH, add loaded water solution and 15% CYANEX 572 in Solvent 467 diluent into a beaker. The organic to aqueous (O:A) ratio will be 1:6 for all experiments.
3. Mix the two phases for the indicated time at 1200 rpm using an overhead mixing unit.
4. After mixing, centrifuge the mixture for 5 minutes to allow for complete separation between the aqueous and organic phase.
5. Take a 12 mL sample of the aqueous solution for ICP-MS analysis and save the organic phase for the stripping step.

Stripping

1. For the stripping step, make a hydrochloric acid, phosphoric acid, sulfuric acid or nitric acid solution (stripping solution) at the desired pH or molarity.
2. Add loaded organic phase collected from the extraction step and stripping solution into a beaker.
3. Mix the two phases for the indicated time at 1200 rpm using an overhead mixing unit.
4. After mixing, centrifuge the mixture for 5 minutes to allow for complete separation between the aqueous and organic phase.
5. Take a 12-mL sample of the stripped solution for ICP-MS analysis.

First set of experiments
The experimental design for evaluation of extraction performance can be divided into three separate series of tests: tests of extraction of REEs, stripping of REEs, and tests of final stripping and regeneration of the extractant. The factors and levels considered in each of the experiments are summarized in Table

1. These factors include starting pH for the contact of the extractant and aqueous phases, mixing (contact) time for the two phases, and addition of SMBS for the REE extraction tests. Mixing speed (measured as impeller RPM) and separation (phase break) times will be fixed throughout the testing. Reagents used will be from the same batch series to prevent variation between runs.

Table 1: Factors and levels considered for the REE extraction and stripping, and final stripping tests.

Extraction Test Levels			
Factor Number | Factor		Low Level (-1)	Intermediate Level (0)	High Level (1)
1	Mixing Time	1 min	5 min	10 min
2	Starting pH	3.0	3.3	3.6
3	SBMS Addition	0	1x	1.5x
REE Stripping Test Levels			
		Low Level (-1)	Intermediate Level (0)	High Level (1)
4	Mixing Time	1 min	5 min	10 min
5	Starting pH	0.5	0.75	1.0
Final Stripping Test Levels			
		Low Level (-1)	Intermediate Level (0)	High Level (1)
6	Mixing Time	1 min	5 min	10 min
7	Acid Ratio	5%:5%	10%:10%	15%:15%

As the REE extraction, REE stripping, and final stripping test sequences will be treated independently, three separate experimental designs were created. Although rare earth extraction and stripping are expected to be somewhat dependent on one another, limitations on the number of analyses available dictated that they be treated independently. A Box Behnken design was selected, incorporating factors 1-3 pertaining to the extraction test factors. Three center points are included in the design to capture experimental error and no blocking factors are identified. The REE stripping and final stripping tests will be treated independently, using the optimized factors from the REE extraction tests as the feedstock for the experiments. As the stripping tests include only two factors at 3 levels, a full factorial 3^2 experimental design, with limited replicates, was chosen. These experimental designs are expected to collect the necessary data to develop surface response models featuring all linear, quadratic, and cross-terms for use in optimizing the REE extraction process.

Table 2: REE extraction experimental design, based on a Box Behnken design.

Test Number	Mixing Time	pH	SMBS Addition
1	High	Mid	1.5x
2	High	Low	1x
3	Low	Low	1x
4	Low	Mid	0
5	Low	High	1x
6	Mid	High	1.5x
7	Mid	Mid	1x
8	Mid	Mid	1x
9	Mid	Low	1.5x
10	High	High	1x
11	Mid	Mid	1x
12	Mid	Low	0
13	Low	Mid	1.5x
14	Mid	High	0
15	High	Mid	0

Table 3: REE stripping test full factorial experimental design.

Test Number	pH	Mixing Time
1	Mid	Mid
2	High	Mid
3	Low	High
4	Mid	High
5	Low	Mid
6	Low	High

Test Number	pH	Mixing Time
7	Low	Low
8	Mid	Mid
9	Mid	Mid
10	High	Low
11	Low	High
12	High	High
13	Mid	Low

Table 4: Final stripping test full factorial experimental design.

Test Number	Acid Ratio	Mixing Time
1	Mid	Low
2	Mid	Mid
3	Mid	Mid
4	Low	Mid
5	Mid	Mid
6	Low	Low
7	Low	High
8	Low	High
9	High	High
10	High	Mid
11	Mid	High
12	High	Low
13	Low	High

Second set of experiments

In this set of experiments, extractant and strip solution loading tests will be performed. The extractant loading experiments are essential for the solvent extraction process because it is most economical to load the extractant as high as possible, but extractant loading cannot exceed 30% of extractant stochiometric capacity. If loading of the extractant exceeds 30% of its stochiometric capacity, it may lead to third phase formation, which is a common challenge for phosphonic/phosphinic acid based extractants [1]. A McCabe-Thiele diagram will be created to interpret the results from extractant loading experiments (See Figure 4 for a McCabe-Thiele diagram example). The experiments will be performed as described in Table 1Table 5.

Table 5: Description and conditions for extractant loading tests.

Test	Description	Conditions[1]
1	300 ml of loaded solution, and 50 ml of extractant (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
2	300 ml of loaded solution, loaded extractant from test 1 (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
3	300 ml of loaded solution, loaded extractant from test 2 (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
4	300 ml of loaded solution, loaded extractant from test 3 (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
5	300 ml of loaded solution, loaded extractant from test 4 (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
6	300 ml of loaded solution, loaded extractant from test 5 (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments

[1]pH and mixing time are maintained constant for all tests
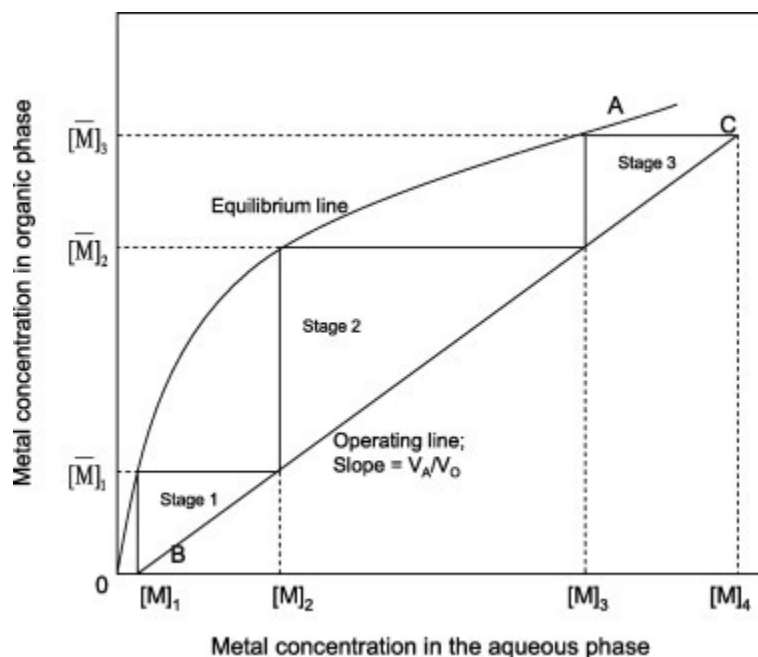
Figure 4: Example of a McCabe–Thiele diagram for extraction process [2]

Another important experiment for the solvent extraction process is the strip solution loading tests. These tests are important because stripping is the last step in production of the mixed REE concentrate solution. It is ideal to maximize the concentration of REEs before going further into the purification process. In these tests, the number of contacts needed to maximize the concentrations of REEs in the stripped solution will be estimated, and the conditions needed to fully recover REE from the extractant will be recorded. Similar to the extraction experiments, a McCabe-Thiele diagram will be used to interpret the results from stripped solution loading tests. However, in this case, the metal concentration in the aqueous (stripped solution) will be the dependent variable, while metal concentration in the organic (loaded extractant) will be in the independent variable (See Figure 5).

Table 6: Description and conditions for stripped solution loading tests.

Test	Description	Conditions[1]
1	10 ml of loaded extractant from test 6 of extractant loading test (Table 5), and 60 ml of stripping solution (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
2	Loaded extractant from test 1, 60 ml of stripping solution (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
3	Loaded extractant from test 2, 60 ml of stripping solution (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
4	10 ml of loaded extractant from test 6 of extractant loading test (Table 5), and 60 ml of stripping	pH and Mixing time = optimal conditions from first set of experiments

Test	Description	Conditions[1]
	solution dosed with REE chlorides[2] (O:A = 1:6)	
5	10 ml of loaded extractant from test 6 of extractant loading test (Table 5), and 60 ml of stripping solution dosed with REE chlorides[2] (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments
6	10 ml of loaded extractant from test 6 of extractant loading test (Table 5), and 60 ml of stripping solution dosed with REE chlorides[2] (O:A = 1:6)	pH and Mixing time = optimal conditions from first set of experiments

[1]pH and mixing time are maintained constant for all tests. [2]To obtain data for the higher spectrum of the McCabe-Thiele diagram, loaded stripped solution will be dosed with REEs chlorides.
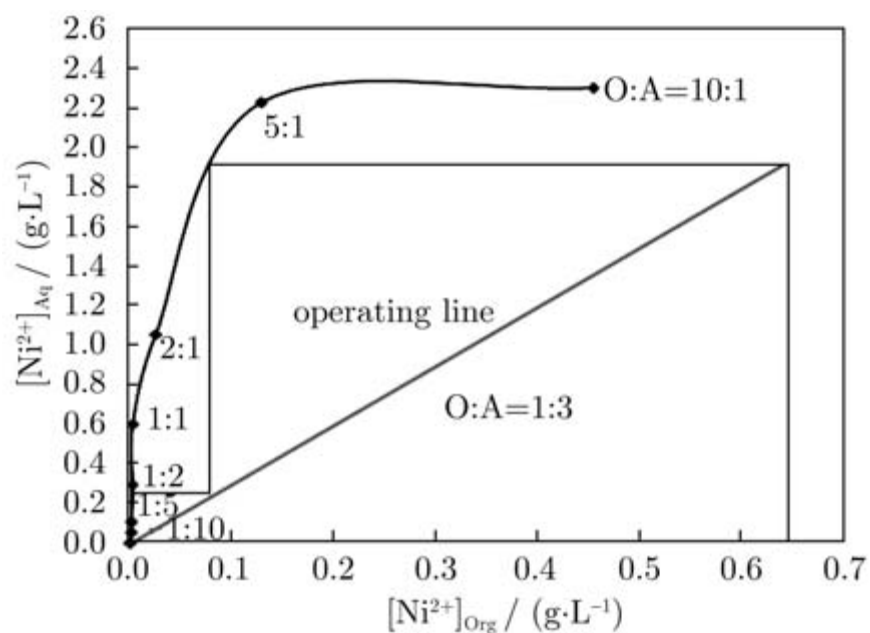
Figure 5: Example of McCabe–Thiele diagram for stripping process [3]

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Appendix C: Solvent Extraction (SX) Lab Testing Report

Recovery of High Purity Rare Earth Elements (REEs) from Coal Ash via a Novel Electrowinning Process: Solvent Extraction Laboratory Testing Report

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DUNS: 007901598

Recovery of High Purity Rare Earth Elements from Coal Ash via a Novel Electrowinning Process:

Solvent Extraction Laboratory Testing Report

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30 November 2018

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Executive Summary

The goal of this project is to produce a high purity, separated (>90%) rare earth oxide product from coal-based sources. This product will be achieved using the following three steps:

1. Battelle's ADP: The ADP leaches pretreated ash with nitric acid, and roasts the loaded acid solution containing REEs, and produces a loaded water solution which contains REEs.
2. Solvent Extraction (SX): The solvent extraction removes REEs from a loaded water solution using an organic extractant, then strips REEs from the organic phase product obtained from extraction.
3. Rare Earth Salt's (RES) Electrochemical Separation and Purification Process: The staged electrochemical process will separate rare earth oxide products from the mixed rare earth solution.

This report covers laboratory testing to determine proper operational parameters in the solvent extraction circuit, or Step 2 above. The laboratory testing was done in three stages – range finding to inform the design of experiments, extraction tests, and stripping tests. All testing in this report was performed starting from a pulverized coal combustion power plant ash, which had an average REE+Y+Sc concentration of 513 ppm.

At the outset of the project, the target for REE purity out of the solvent extraction step was 60% of the measured solutes. The best result empirically achieved was 55% and the best projected result from the model is 58%. The primary contaminants are zinc and aluminum. Based on work done by RES, the zinc is a known challenge in the separation and purification process, whereas the aluminum can be easily handled. With this information, Battelle selected a new extractant composition that was demonstrated in this work to be selective for zinc over the REEs and can be implemented prior to the traditional solvent extraction steps as a pretreatment to remove zinc. With zinc removed beforehand, we have confidence that REE purity out of the stripping step can exceed 60% of the measured solutes.

Surface response models were generated for extraction and stripping of REEs from leach solutions derived from pulverized coal combustion ash. These models can be used to estimate optimal operational points for the extraction and stripping processes, where high selectivity for REEs is accomplished. Recovery in single stage operations are generally low for the stripping sections, on the order of 30-40%, but it is expected that this can be overcome by running in multiple stages with careful control of pH.

The next step for the project is to prepare a solution containing coal derived REEs for RES to demonstrate separation and purification of individual rare earth products. Larger volumes (roughly 60kg) of PCC fly ash from an operating power plant have been leached using Battelle's ADP process, and the concentrated leach solution is being roasted prior to solvent extraction steps. After roasting, the solids will be leached with water to recover rare earth nitrates, then zinc will be removed using the zinc selective extractant composition. The remaining solution can then either be roasted again and upgraded through a proprietary RES process or through the solvent extraction scheme presented in this report, followed by separation and purification using Rare Earth Salts' technology to greater than 90% purity, meeting the objectives of this study.

From a technical standpoint, there are a few potential next steps that are beyond the scope of this project. Review of the USGS COALQUAL database suggested that zinc concentrations are likely to be high in all coal sources that contain REE, so further work on zinc removal and selectivity could benefit multiple methods for REE recovery. The current work focused on nitrate solutions with high iron and aluminum contents, but the extraction may be very different in chloride or sulfate solutions that could be used in other processes. Additionally, zinc removal may enable better recovery of scandium. Rare Earth Salts' proprietary process would be able to selectively recover scandium in the roasted solids, provided the zinc is removed. An improved process could feasibly leach all of the zinc from the first roasted solids, extract the zinc while leaving the REEs in solution, and allow all of the REE and scandium to be recovered from a single solid concentrate.

1.0 Introduction

As directed by Congress, the United States (U.S.) Department of Energy (DOE) is investigating the economic feasibility of recovery of rare earth elements (REEs) from domestic U.S. coal and coal byproducts. The Department of Energy's National Energy Technology Laboratory (NETL) has characterized a number of REE-bearing samples of coal and coal-related materials. Rare earth elements have been found in varying concentrations ranging up to 1,000 parts per million (ppm) by weight in the following materials in the United States: coal mine roof and floor materials, run-of-mine coal, prepared coal, partings, pit cleanings, coal preparation refuse, and tailings. REEs can be found in coal byproducts, including ash, coal-related sludge, and mine drainage. Certain coals can contain a higher ratio of heavy (generally more valuable) REEs than found in other sources of REEs such as natural ores, and DOE is particularly interested in sources that have higher than 300 ppm REEs. Since most coal materials start at REE concentrations well below 1,000 ppm, the yield of REEs from any separation process is likely to be low, and minimizing costs associated with recovery is a key challenge. The Department of Energy has therefore funded groups with novel processes able to recover REEs from coal sources while minimizing the processing costs.

The REEs are the 14 naturally occurring elements between lanthanum and lutetium on the periodic table, along with yttrium and scandium which have similar chemical properties. Their symbols and atomic numbers are listed in Table 1 for reference. They have become critical in renewable energy and defense applications, where they are used to make magnets for motors and generators, metal alloys, and in various sensor components. Occasionally, yttrium and scandium are considered separately, and so the group of rare earth elements is sometimes referred to as REE+Y+Sc for clarity in this report. Element 61, promethium, is not naturally occurring and not included in the analyses for this report.

Table 1: List of rare earth elements, their symbols, and their atomic numbers.

Rare Earth Elements, Symbols, and Atomic Numbers											
Sc	Scandium	21	Pr	Praseodymium	59	Gd	Gadolinium	64	Er	Erbium	68
Y	Yttrium	39	Nd	Neodymium	60	Tb	Terbium	65	Tm	Thulium	69
La	Lanthanum	57	Sm	Samarium	62	Dy	Dysprosium	66	Yb	Ytterbium	70
Ce	Cerium	58	Eu	Europium	63	Ho	Holmium	67	Lu	Lutetium	71

Battelle has been validating the economic viability of recovering REEs from coal ash using its patented (US6011193) closed-loop Acid Digestion Process (ADP). Based on results from the sampling and characterization work, a Pulverized Coal Combustion (PCC) plant fly ash was selected as the target feedstock for the process. The plant selected for this study is operating in Ohio on primarily Appalachian Basin coals and had a high total REE+Y+Sc concentration at 545 ppm +/- 13 ppm. A preliminary technoeconomic analysis (TEA) done on Battelle's ADP process suggested that it could be economically applied to between 5% and 47% of U.S. coal sources.

The goal of this project is to produce a high purity (>90%) rare earth oxide product. This product will be achieved using the following three steps:

1. Battelle's ADP: The ADP process involves pretreatment of ash (milling and caustic leaching), leaching of pretreated ash with nitric acid, roasting of loaded acid solution containing REEs, and water leaching of residual from roasting step, resulting in a loaded water solution which contains REEs. Figure 1 shows a schematic representation of the first two steps.

2. Solvent Extraction (SX): The solvent extraction involves the extraction of REEs from a loaded water solution using an organic extractant (note after extraction, the aqueous phase will be a residual solution and the organic phase will contain REEs), and stripping of REEs from organic phase product obtained from extraction using hydrochloric acid solution (the stripped solution will be the final purified product containing REEs, organic traces, and traces of other metals for further separation in the electrowinning process).

3. Rare Earth Salt's (RES) Electrochemical Separation and Purification Process: The staged electrochemical process will separate rare earth oxide products from the mixed rare earth solution. Testing by RES will also include investigation of options to minimize the solvent extraction steps.

Figure 1: Schematic representation of Battelle's ADP and Solvent Extraction.

This report covers laboratory testing to determine proper operational parameters in the solvent extraction circuit. The laboratory testing was done in three stages – range finding to inform the design of experiments, extraction tests, and stripping tests. All testing in this report was performed starting from a PCC power plant ash, which had an average REE+Y+Sc concentration of 512.84 ppm. It was milled in water, then leached with nitric acid to extract the REEs, roasted to omit iron, aluminum, and most heavy transition metals, then leached back into water before solvent extraction testing.

2.0 Range Finding Tests

2.1 Roasting Tests

Battelle performed roasting experiments to find the optimal temperature at which iron and aluminum nitrates oxidize to insoluble materials and can thus be separated from REE nitrates using a water wash. Roasting tests were conducted at four temperatures between 140°C and 190°C (140, 157, 173, and 190°C). These temperatures were chosen based on the results of roasting experiments performed during the project's second quarter. Figure 2 shows the results from these roasting experiments.
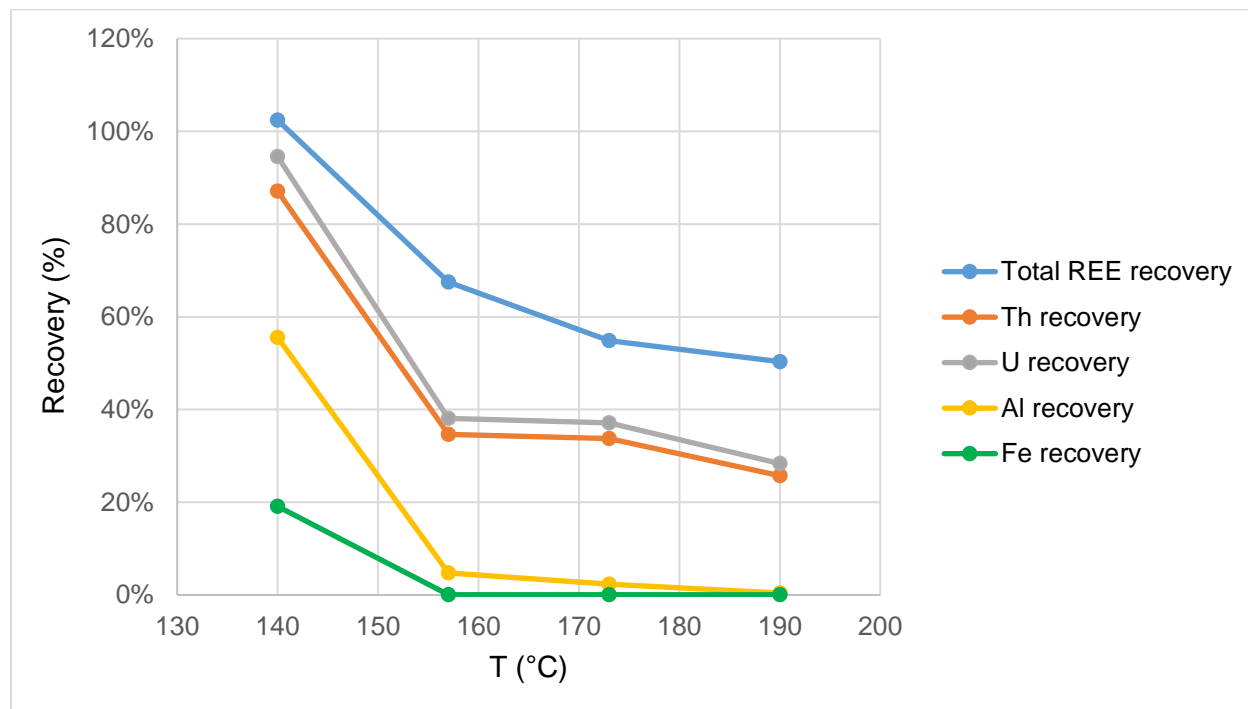
Figure 2: Roasting temperature vs. recovery of REEs and different contaminants in loaded water (feed to solvent extraction)

At temperatures below 157°C, an increase in REE recovery is observed along with an increase in the recovery of major contaminants (e.g. Fe, Al) and other contaminants of concern (e.g. Th, U), and at temperatures above 157°C, a decrease in REE recovery is observed as well as a decrease in the recovery of major contaminants. Based on these results, ~157°C is a near ideal roasting temperature at which most of the iron (0.07% of the iron is recovered) and aluminum (4.7% of the aluminum is recovered) are oxidized and rare earths remain as nitrates (68% of the REE are recovered, with much of the loss as low value cerium oxide).

2.2 Extraction and Stripping Tests

The main objectives of the solvent extraction range finding tests were to tailor the pH ranges and acid combinations that will be used in the experimental design, and to understand the effect of adding reducing agents in the solvent extraction process (see Table 2). The reducing agent was to be added before the extraction step, which would reduce the iron remaining in the solution from ferric to ferrous iron, making the reduced iron less likely to be extracted. In the extractant regeneration step (which takes place after REE have been stripped from the extractant), the acid formulation used was a key parameter to optimize for the stripping of heavy metals (Ti, Fe, As, Zr, U, and Th). This step is important because the

extractant needs to be cleaned prior to being recycled to ensure good extraction performance and extractant life.

Table 2: Solvent extraction range finding tests

Description	Test 1	Test 2	Test 3
Reducing Agent	Sodium Metabisulfite	Sodium Thiosulfate	Iron Powder
Extraction	pH 3.35	pH 3.35	pH 3.35
REE Stripping	pH 0.75	pH 0.75	pH 0.75
Extractant Regeneration	H_3PO_4:H_2SO_4 = 5%:5%	H_3PO_4:HNO_3 = 5%:5%	H_3PO_4:HCl = 5%:5%

The results obtained showed that the addition of sodium metabisulfite, sodium thiosulfate, and iron powder didn't impact the high percent of iron extracted (see Table 3). However, it was also discovered that iron won't strip in the REE stripping step pH (pH 0.75) as originally expected. Therefore, REE are able to be recovered in the stripped solution, and iron will remain in the extractant, which then will be stripped during extractant regeneration step (see Table 4).

Table 3: Percent extracted of iron after addition of different reducing agents

Reducing agent	Conditions	% of Iron Extracted
Sodium Metabisulfite	Starting pH 3.34 (Equilibrium pH 2.38)	96.9%
Sodium Thiosulfate	Starting pH 3.34 (Equilibrium pH 2.39)	97.3%
Iron Powder	Starting pH 3.35 (Equilibrium pH 2.41)	99.5%

During the extractant regeneration step, three different acid combinations were tested. The best combination based on the results obtained was the combination of phosphoric acid and sulfuric acid (H_3PO_4:H_2SO_4 = 5%:5%). This combination yielded a high percent stripped of heavy metals (see Table 5).

Table 4: Percent stripped of REE and iron during REE stripping step at starting pH 0.74 (equilibrium pH 0.84).

Species	% Stripped
Fe	0.61%
REE+Y+Sc out of total available	87.60%
REE+Y+Sc out of total measured	15.68%

Table 5: Percent stripped of some heavy metals during the extractant regeneration step.

Conditions	% Stripped			
	Fe	As	Th	U
H_3PO_4:H_2SO_4 = 5%:5%	95.19%	100%	100%	19.85%
H_3PO_4:HNO_3 = 5%:5%	84.51%	67.14%	19.81%	8.31%
H_3PO_4:HCl = 5%:5%	74.77%	Detection limit	100%	18.51%

One complication encountered during the above range finding tests was the slow disengagement of the aqueous and organic phases in the extraction step. The addition of a modifier to the extractant (15% Cyanex 572 in Solvent 467) provided improved phase disengagement. The modifiers studied were isodecanol (Exxal 10) and tributyl phosphate (TBP). The amount of modifier added to the extractant was

chosen knowing that if the amount of modifier exceeded the amount of current active ingredient (Cyanex 572), disengagement between active ingredient and modifier might occur, causing operational problems during the extraction process.
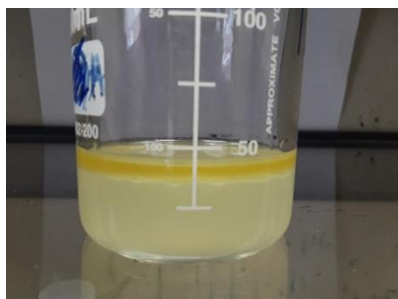
Figure 3: After extraction with 15% Cyanex 572 extractan
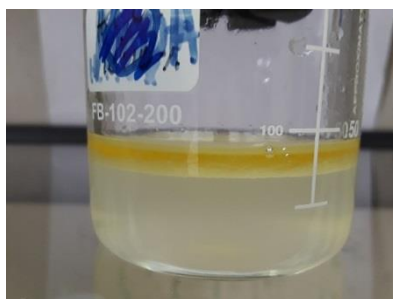
Figure 4: After extraction with 13.2%:12% Cyanex 572:Exxal10 extractant
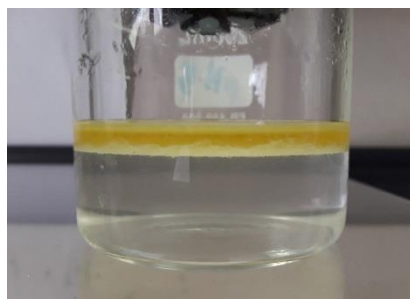
Figure 5: After extraction with 13.2%:12% Cyanex 572:TBP extractant

Figure 3, Figure 4, and Figure 5 show disengagement between the organic and aqueous phases after extraction using the current extractant (15% Cyanex 572) and the two modifiers studied (Exxal 10 and TBP). For each case, extraction was performed at starting pH 2.5, with a mixing time of 10 minutes, and mixing speed of 600 to 800 rpm. Notice that the best phase disengagement between the organic and aqueous phase occurs after extraction with 13.2%:12% Cyanex 572:TBP extractant (see Figure 5). After this testing, Battelle performed two more extraction tests to investigate the difference between the performance of the current extractant (15% Cyanex 572) and the new modified extractant (13.2%:12% Cyanex 572:TBP). The extraction tests were performed at starting pH 3.3, with a mixing time of 20 minutes, and mixing speed of 600 to 800 rpm. The results obtained are shown in Table 6. The results show that the Cyanex:TBP extractant performance is superior than the Cyanex 572 extractant alone. Tributyl phosphate was incorporated into the extraction part of the design of experiments to further investigate the performance of Battelle's modified extractant (see Table 7).

Table 6: Extraction results for 15% Cyanex 572 and 13.2%:12% Cyanex 572:TBP

Elements	% Extracted	
	15% Cyanex 572 (equilibrium pH 2.43)	13.2%:12% Cyanex 572:TBP (equilibrium pH 2.29)
Sc	93.2%	93.2%
Y	84.2%	99.1%
La	10.2%	12.8%
Ce	24.1%	43.3%
Pr	24.8%	53.7%
Nd	24.6%	61.3%
Sm	50.5%	93.8%
Eu	58.8%	96.9%
Gd	54.3%	96.5%
Tb	76.7%	98.7%
Dy	85.6%	99.4%
Ho	86.6%	99.4%
Er	90.4%	99.2%
Tm	95.8%	99.4%
Yb	97.9%	99.4%
Lu	97.7%	99.3%
REE+Y+Sc out of total available	43.89%	63.9%
REE+Y+Sc out of total measured species	18.08%	20.28%

3.0 Extraction Tests

3.1 Methods and Approach

3.1.1 Rare Earth Extraction

All solvent extraction testing was performed in a batch set up, and the experimental procedure was as follows:

Extraction

1. pH of loaded water solution recovered from roasting step was adjusted to a desired pH using 37.2% hydrochloric acid or 10% sodium carbonate solutions.
2. After adjusting the loaded water solution to the desired pH, loaded water solution and desired extractant in diluent are added into a beaker. The organic to aqueous (O:A) ratio was 1:6 for all experiments unless stated otherwise.
3. The two phases were mixed for the indicated time between 600-800 rpm using an overhead mixing unit.
4. After mixing, the mixture was left to separate for 10 minutes (unless stated otherwise).
5. A 12 mL sample of the aqueous solution was taken for ICP-MS analysis and the organic phase saved for the stripping step.

Table 7 shows the factors and levels selected in the extraction testing. Mixing time, starting pH, and modifier concentration were selected for investigation since they are expected to be the most impactful factors in the REE extraction operation.

Table 7: Factors and levels investigated in the REE extraction tests.

Extraction Test Levels			
Factor Number | Factor	**Low Level (-1)**	**Intermediate Level (0)**	**High Level (1)**
1	Mixing Time	1 min	10 min	20 min
2	Starting pH	2.5	3.3	4.0
3	Addition of TBP (Cyanex 572:TBP)	15%:0%	14.1%:6%	13.2%:12%

A Box Behnken design was selected, incorporating factors 1-3 pertaining to the extraction test factors. Three center points are included in the design to capture experimental error and no blocking factors are identified. The REE stripping tests will be treated independently, using the optimized factors from the REE extraction tests as the feedstock for the experiments. This experimental design is expected to collect the necessary data to develop surface response models featuring all linear, quadratic, and cross-terms for use in optimizing the REE extraction process (see Table 8).

Table 8: REE extraction experimental design, based on a Box Behnken design.

Test Number	Mixing Time	pH	Addition of TBP (Cyanex 572:TBP)
1	High	Mid	13.2%:12%
2	High	Low	14.1%:6%
3	Low	Low	14.1%:6%
4	Low	Mid	15%:0%
5	Low	High	14.1%:6%
6	Mid	High	13.2%:12%
7	Mid	Mid	14.1%:6%
8	Mid	Mid	14.1%:6%
9	Mid	Low	13.2%:12%
10	High	High	14.1%:6%
11	Mid	Mid	14.1%:6%
12	Mid	Low	15%:0%
13	Low	Mid	13.2%:12%
14	Mid	High	15%:0%
15	High	Mid	15%:0%

3.1.2 Zinc Extraction

Most coal sources of REE will need to handle zinc, as it tends to follow the REE in solvent extraction and other separation processes and will impact the ability to achieve a separated, saleable product. A review of the COALQUAL database shows that the median zinc concentration on an ash basis for all samples is

113 ppm, with an average of 317 ppm. Further, the ratio of zinc to REE has a median of 0.35. The coal ash used in Battelle's process has a zinc concentration of 160 ppm with a ratio of zinc to REE of 0.31. Although the zinc concentration is higher than the median, it is still in the range of many coal sources, and the ratio of zinc to REE is near the median, but slightly lower. This suggests that our experience with zinc is likely to be representative of other REE sources, and development of a simple scrubbing step to remove zinc from REE pregnant leach solutions will enable commercial development of coal based REE sources. Therefore, during this solvent extraction laboratory testing, a commercially available cationic extractant compound was investigated to selectively extract Zn from REE.

First, range finding tests were performed at different pH and concentration ranges. The most promising results were obtained at the following conditions: starting pH 4.01, 15 minutes of mixing time, 15% active ingredient in diluent, and an organic to aqueous (O:A) ratio of 1:4 (see Table 9). Roughly 25% of Zn was extracted while only extracting ~2.6% of REE (excluding Sc). Therefore, this approach is a promising discovery for the selective separation of Zn from REE. Even though ~92% of Sc was extracted, Battelle believes that Sc could be selectively stripped using high molarity stripping solutions and different acid combinations.

Table 9: Results of a selectively extraction of Zn from REE using a commercially available cationic extractant compound.

Element	%Extracted
Sc	91.8%
Y	0%
La	3.6%
Ce	4.1%
Pr	0%
Nd	0%
Sm	5.9%
Eu	11.8%
Gd	8.9%
Tb	7.1%
Dy	4.5%
Ho	7.3%
Er	5.7%
Tm	8.4%
Yb	12.3%
Lu	9.1%
REE excluding Sc	2.6%
Zn	25.1%

Because of the promising results obtained from this range finding tests, three more tests were performed at different pH and a different O:A ratio (see Table 10). The different ratio was chosen because at a larger scale process, a ratio of 1:6 (O:A) will make the extraction of zinc more economically viable since less extractant will be utilized.

Table 10: Experiments for the selective extraction of Zn using a commercially available cationic extractant compound.

Test Number	Starting pH	Mixing time	Extractant concentration	O:A ratio
1	3.0	15 min	15%	1:6
2	4.0	15 min	15%	1:6
3	5.5	15 min	15%	1:6

3.2 Results

3.2.1 Rare Earth Extraction Results

The design of experiment for REE extraction consisted of 15 tests. The results obtained are shown in Table 11 with best results highlighted in green. The experimental conditions for the best results were the following: equilibrium pH 2.65 and pH 2.64, mixing time of 10 minutes, and extractant composition of 14.1%:6% Cyanex 572:TBP. The data obtained from this experimental design were used to develop surface response models for REE recovery and REE purity (Table 12 and Table 13 show a summary of the models for REE recovery and REE purity respectively). These two response models will allow the prediction of the maximum REE recovery and purity that can be obtained in the extraction process within the conditions investigated in this experimental design, equilibrium pH, mixing time, and Cyanex 572:TBP concentration. Based on the two models ~97% recovery of REE can be achieved at equilibrium pH 3.06, mixing time 10.4 mins, and Cyanex 572:TBP = 13.9%:7.6% while a maximum REE purity of ~25% can be achieved at equilibrium pH 2.46, mixing time of 1 minute, and Cyanex 572:TBP = 13.9%:7.5%   (see Table 14).

For the validation of the response models for REE recovery and REE purity, fitted line plots of the models were graphed (Figure 6 and Figure 7 are the fitted line plots for the REE recovery and REE purity model respectively). It can be observed that the response model for REE recovery is a good fit to the data gathered in the experimental design validating the second order model obtained. The response model for REE purity shows potential non-random scattering of the empirical versus model data which could be improve with further testing. However, the second order model for REE purity was also the model yielding the best linear fit.

Table 11: Results obtained from the extraction design of experiments (single stage).

Test Number	Starting pH	Equilibrium pH	Mixing time (min)	Addition of TBP (Cyanex 572:TBP)	REEs Recovery	REEs Purity
1	3.28	2.51	20	13.2%:12%	69.7%	12.1%
2	2.52	2.34	20	14.1%:6%	69.2%	19.5%
3	2.52	2.48	1	14.1%:6%	24.1%	26.6%
4	3.28	2.86	1	15%:0%	37.3%	7.5%
5	4.03	3.06	1	14.1%:6%	75.2%	9.4%
6	4.03	2.73	10	13.2%:12%	78.0%	14.3%
7	3.26	2.65	10	14.1%:6%	79.6%	17.7%
8	3.26	2.65	10	14.1%:6%	79.2%	22.6%
9	2.51	2.43	10	13.2%:12%	65.6%	17.4%
10	4.02	2.74	20	14.1%:6%	84.3%	13.4%
11	3.27	2.64	10	14.1%:6%	77.8%	24.8%
12	2.49	2.37	10	15%:0%	35.7%	12.7%
13	3.26	2.74	1	13.2%:12%	65.7%	13.0%
14	4	2.79	10	15%:0%	71.2%	7.4%
15	3.26	2.56	20	15%:0%	58.9%	15.3%

Table 12: Summary of the REE recovery response model (second order model) for REE extraction showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-6.565
pH	3.892
t	0.172
TBP	1.663
pH:t	-0.040
pH:TBP	-0.289
t :TBP	-0.019
pH^2	-0.519
t^2	-0.002
TBP^2	-0.524
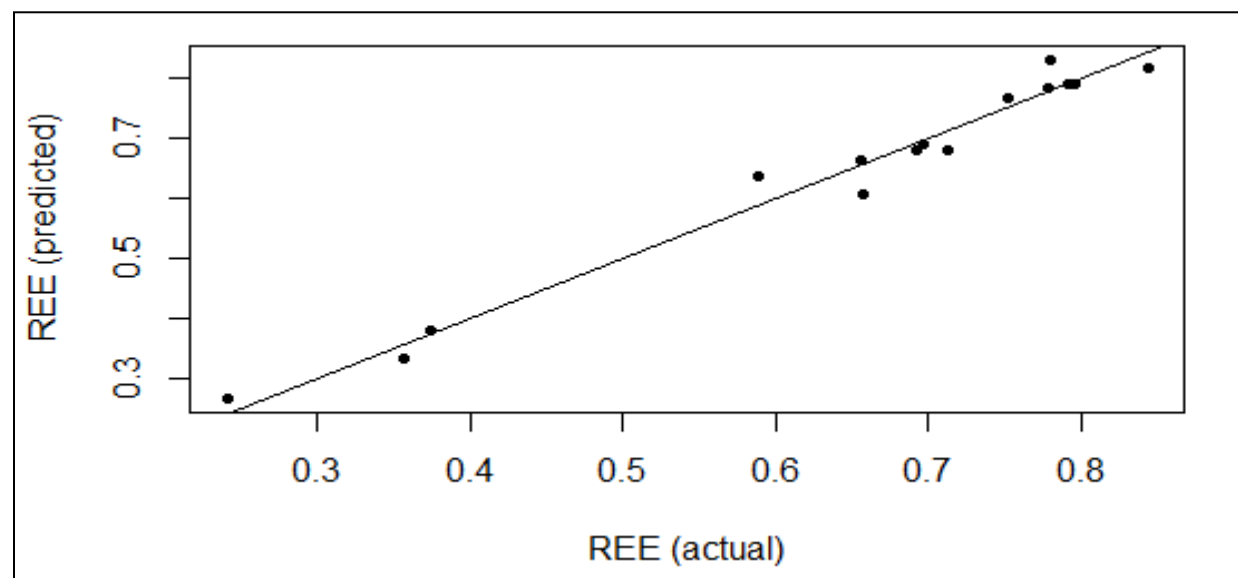
Figure 6: Fitted line plot of the REE recovery response model (second order model) for REE extraction

Table 13: Summary of the REE purity response model (second order model) for REE extraction showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-2.842e+00
pH	2.386e+00
t	1.0099e-02
TBP	5.6446e-01
pH:t	-3.628e-03
pH:TBP	-5.600e-02
t :TBP	-3.900e-03
pH^2	-4.775e-01
t^2	-7.761e-05
TBP^2	-3.926e-01
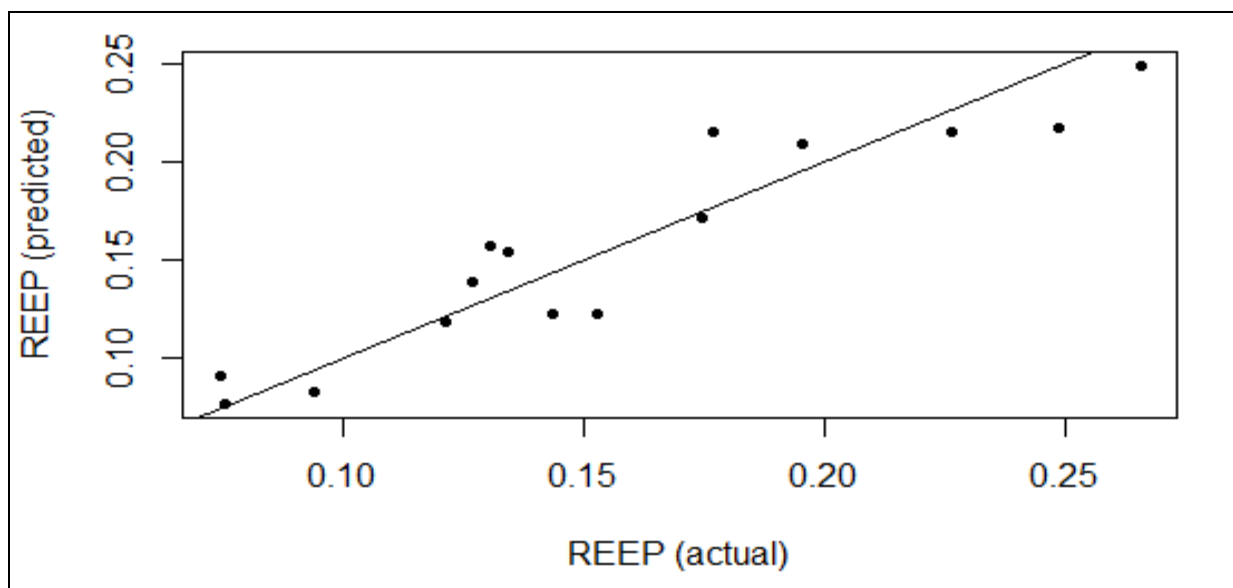
Figure 7: Fitted line plot of the REE purity response model (second order model) for REE extraction

Table 14: Optimized factors for one stage REE extraction, equilibrium pH (pH), mixing time (t), and Cyanex 572:TBP concentration (TBP)

Results	Estimates
Maximum REE recovery	~97% at equilibrium pH 3.06, mixing time 10.4 mins, and TBP of 0.55 (Cyanex 572:TBP = 13.9%:7.6%)
Maximum REE purity	~25% at equilibrium pH 2.46, mixing time 1 min, and TBP of 0.54 (Cyanex 572:TBP = 13.9%:7.5%)

3.2.2 Zinc Extraction Results

The use of a commercially available cationic extractant for the selective separation of Zn from REEs was further investigated during this solvent extraction testing. Three tests were performed at different pH and a different O:A (1:6) than the range finding tests performed earlier. Mixing time and extractant concentration where constant for all tests. The results obtained from these tests are shown in Table 15. It is worth mentioning that these tests are a single stage extraction. Therefore, recovery would be improved if multiple stage extraction was to be performed.

Table 15: Results for the selective extraction of Zn using a commercially available cationic extractant compound (single stage).

Element	% Extracted					
	Test 1		Test 2		Test 3	
	Actual starting pH 3.15	Equilibrium pH 2.73	Actual starting pH 4.00	Equilibrium pH 3.81	Actual starting pH 5.64	Equilibrium pH 5.35
Sc	95.6%		90.6%		33.4%	
Y	0%		1.9%		29.0%	
La	0%		0.9%		10.2%	
Ce	0%		0%		10.4%	
Pr	0%		0%		12.7%	
Nd	0%		0%		11.5%	
Sm	0%		0%		18.2%	
Eu	0%		0%		20.4%	
Gd	0%		0%		21.2%	
Tb	0%		3.0%		27.1%	
Dy	0%		4.5%		28.1%	
Ho	0%		5.4%		28.4%	
Er	0%		6.5%		30.3%	
Tm	0%		9.9%		30.0%	
Yb	0%		13.0%		30.5%	
Lu	0%		11.1%		30.7%	
REE excluding Sc	0%		1.31%		17.8%	
Zn	0%		8.3%		71.7%	

At equilibrium pH of 3.81 the extraction of Zn is significantly higher that the REE (excluding Sc). Most importantly, there is not extraction of some of the most valuable REE (e.g. Nd, Pr), and the separation factor for zinc over the combined REEs is high. Therefore, if this extraction was to be performed in multiples stages, a successful separation of Zn from REE (excluding Sc) would be achievable. Also, at an equilibrium pH of 3.81, the extraction of Zn is ~8.3% compare to just ~1.3% of the REEs (excluding Sc) showing the high selectivity of the cationic extractant used for Zn over the REEs (excluding Sc). This high selectivity is also observed in Figure 8. High selectivity is also observed at higher pH values, however, during this test, REE, Zn, and other elements precipitated when pH was adjusted to 5.35, leading to reduced recovery in the extractant. In practice, the zinc extraction will likely be limited to the pH of the leachate solution (typically above 4) to avoid loss of materials in precipitates but will be done in multiple stages to increase zinc recovery. Furthermore, even though ~92% of Sc was extracted during the selective separation of Zn from REE, Battelle believes that Sc could be selectively stripped using high molarity stripping solutions and different acid combinations.
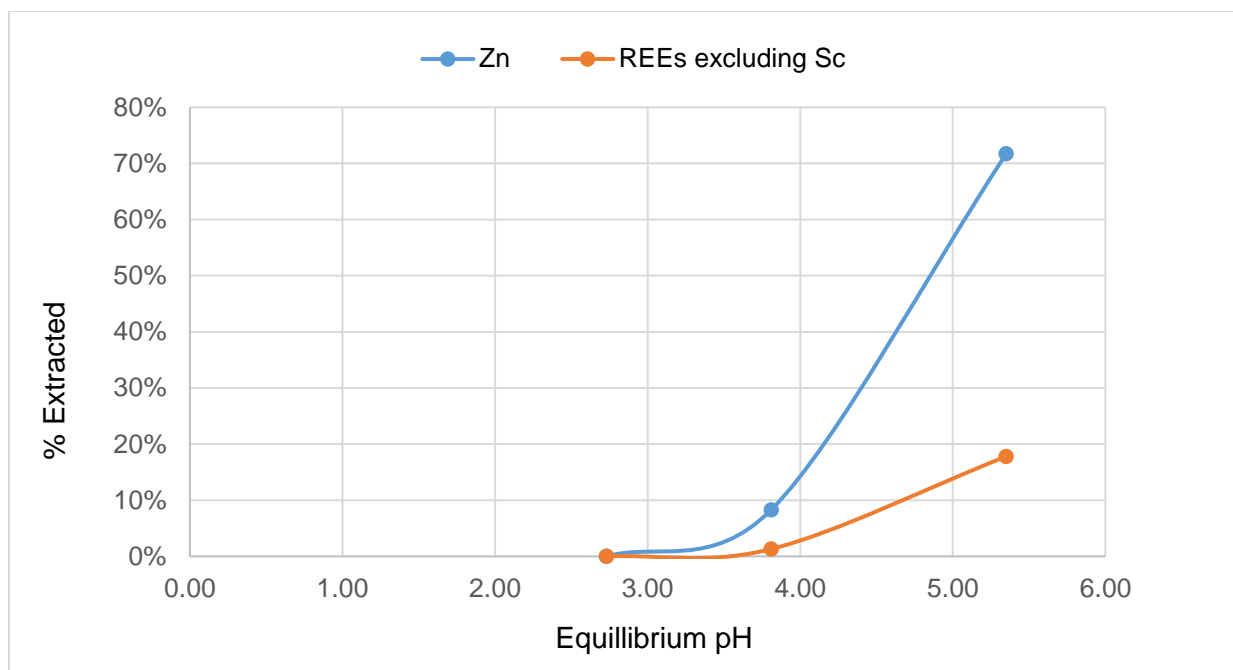
Figure 8: Relationship between equilibrium pH and percent extracted of Zn and REEs excluding Sc

4.0 Stripping Tests

4.1 Methods and Approach

All solvent extraction testing was performed in a batch set up, and the experimental procedure was as follows:

1. For the stripping step, hydrochloric acid stripping solution was made at desired pH.
2. Loaded organic collected from the extraction step and stripping solution were added into a beaker. The organic to aqueous (O:A) ratio was 1:4 for all experiments.
3. The two phases were mixed for the indicated time between 600-800 rpm using an overhead mixing unit.
4. After mixing, the mixture was left to separate for 10 minutes.
5. A 12-mL sample of the stripped solution was taken for ICP-MS analysis.

Table 16 shows the factors and levels selected in the stripping testing. Mixing time and starting pH were selected for investigation because they were expected to be the most impactful factors in the stripping operation. Two design of experiments were selected for REE stripping. The first design investigates REE stripping at low pH levels, and the second design investigates REE stripping at high pH levels.

Table 16: Selected factors and levels for the stripping design of experiment

Low pH REE Stripping Test Levels			
Factor Number | Factor	Low Level (-1)	Intermediate Level (0)	High Level (1)
1.Mixing Time	1 min	10 min	20 min
2. Starting pH	0.5	0.75	1.0
High pH REE Stripping Test Levels			
Factor Number | Factor	Low Level (-1)	Intermediate Level (0)	High Level (1)
1.Mixing Time	1 min	10 min	20 min
2. Starting pH	1.5	2.0	2.5

A Box Behnken design was selected, as in the extraction tests. However, the stripping tests include only two factors at 3 levels, a full factorial 3^2 experimental design, with limited replicates, was chosen. These experimental designs are expected to collect the necessary data to develop surface response models featuring all linear, quadratic, and cross-terms for use in optimizing the REE stripping operations (see Table 17 and Table 18).

Table 17: Low pH REE stripping test full factorial experimental design.

Test Number	pH	Mixing Time
1	Mid	Mid
2	High	Mid
3	Low	High
4	Mid	High
5	Low	Mid
6	Low	High
7	Low	Low
8	Mid	Mid
9	Mid	Mid
10	High	Low
11	Low	High
12	High	High
13	Mid	Low

Table 18: High pH REE stripping test full factorial experimental design.

Test Number	pH	Mixing Time
1	Mid	Low
2	Mid	Mid
3	Mid	Mid
4	Low	Mid
5	Mid	Mid
6	Low	Low
7	Low	High
8	Low	High
9	High	High
10	High	Mid
11	Mid	High
12	High	Low
13	Low	High

4.2 Results

Rare earth element stripping is an important step in the solvent extraction process since it performs much of the purification of the REE. Therefore, two different experimental designs were performed. One experimental design investigated the stripping of REE from the loaded extractant at low pH (0.5-1.0), and the other one at high pH (1.4 – 2.4). The results obtained are shown in Table 19 and Table 21 (low pH stripping and high pH stripping respectively). For low pH stripping the best result (~49% REE purity) was obtained at the following conditions: Equilibrium pH 1.06 and mixing time of 1 minute. At high pH stripping a slightly greater REE purity (~55%) was obtained at equilibrium pH 1.86 and mixing time of 10 minutes.

Similar to the REE extraction design, the data obtained from these two experimental designs were used to develop surface response models for REE purity (Table 20 and Table 22 show a summary of the REE purity response models for the low pH REE stripping and high pH REE stripping, respectively). These two response models will allow the prediction of the maximum REE purity that can be obtained in the stripping process within the conditions investigated in the two experimental designs, equilibrium pH and mixing time. The model that predicted the highest purity was the model for high pH REE stripping yielding a purity of approximately 58% at equilibrium pH 1.61 and mixing time 6 minutes.

For the validation of the response models, fitted line plots were also graphed (Figure 9 and Figure 10 are the fitted line plots of the REE purity response models for the low pH REE stripping and high pH REE stripping, respectively). It can be observed that both response models are strong fits to the data gathered in the experimental designs validating the second order models obtained.

4.2.1 Low pH REE Stripping Results

Table 19: Results obtained from the low pH REE stripping design of experiments (single stage).

Test Number	Starting pH	Equilibrium pH	Mixing time (min)	REEs Purity
1	0.74	0.76	10	30.5%
2	1.03	1.12	10	45.3%
3	0.52	0.57	20	19.0%
4	0.76	0.75	20	29.2%
5	0.52	0.59	10	22.4%
6	0.52	0.52	20	17.9%
7	0.50	0.60	1	35.4%
8	0.72	0.77	10	35.4%
9	0.72	0.76	10	35.5%
10	1.00	1.06	1	48.5%
11	0.52	0.59	20	19.6%
12	1.00	0.99	20	37.7%
13	0.74	0.78	1	41.0%

Table 20: Summary of the REE purity response model (second order model) for low pH REE stripping showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-0.0109
pH	0.7713
t	-0.0155
pH:t	0.0055
pH^2	-0.2715
t^2	0.0002
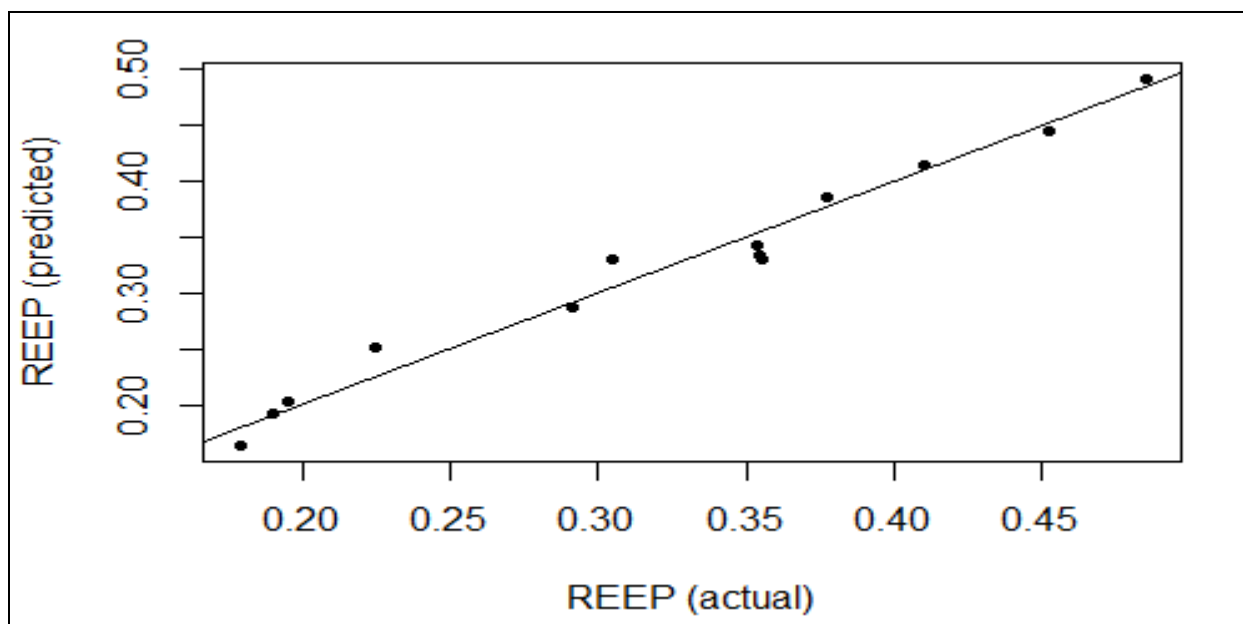
Figure 9: Fitted line plot of the REE purity response model (second order model) for low pH REE Stripping

4.2.2 High pH REE Stripping Results

Table 21: Results obtained from the high pH REE stripping design of experiments (single stage).

Test Number	Starting pH	Equilibrium pH	Mixing time (min)	REE Purity
1	1.80	1.86	1	53.7%
2	1.80	1.87	10	53.7%
3	1.80	1.86	10	55.1%
4	1.31	1.37	10	52.6%
5	1.79	1.84	10	53.0%
6	1.31	1.35	1	53.2%
7	1.29	1.28	20	34.6%
8	1.29	1.21	20	37.4%
9	2.32	2.35	20	21.8%
10	2.31	2.41	10	24.7%
11	1.78	1.70	20	46.2%
12	2.31	2.40	1	20.5%
13	1.28	1.25	20	38.9%

Table 22: Summary of the REE purity response model (second order model) for high pH REE stripping showing the estimated coefficient for each variable of the model.

Variables	Estimates
Intercept	-0.7738
pH	1.6824

Variables	Estimates
t	-0.0008
pH:t	0.0046
pH^2	-0.5311
t^2	-0.0006
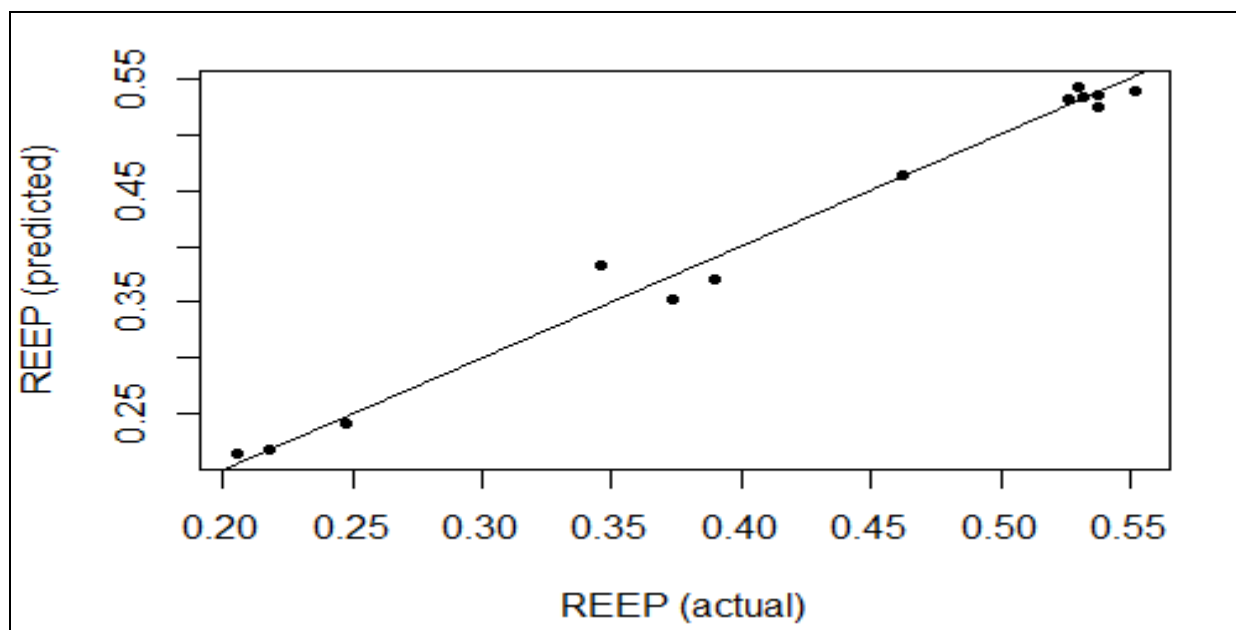
Figure 10: Fitted line plot of the REE purity response model (second order model) for high pH REE Stripping

5.0 Conclusions and Next Steps

Surface response models have been generated for extraction and stripping of REEs from leach solutions derived from pulverized coal combustion ash. These models can be used to estimate optimal operational points for the extraction and stripping processes, where high selectivity for REEs is accomplished. Recovery in single stage operations are generally low for the stripping sections, on the order of 30-40%, but it is expected that this can be overcome by running in multiple stages with careful control of pH.

At the outset of the project, the target for REE purity out of the solvent extraction step was 60% of the measured solutes. The best result empirically achieved was 55% and the best projected result from the model is 58%. The primary contaminants are zinc and aluminum. Based on work done by RES, the zinc is a known challenge in the separation and purification process, whereas the aluminum can be easily handled. With this information, Battelle selected a new extractant composition that was demonstrated in this work to be selective for zinc over the REEs and can be implemented prior to the traditional solvent extraction steps as a pretreatment to remove zinc. With zinc removed beforehand, we have confidence that REE purity out of the stripping step can exceed 60% of the measured solutes.

The next step for the project is to prepare a solution containing coal derived REEs for RES to demonstrate separation and purification of individual rare earth products. Larger volumes (roughly 60kg) of PCC fly ash from an operating power plant have been leached using Battelle's ADP process, and the concentrated leach solution is being roasted prior to solvent extraction steps. After roasting, the solids will be leached with water to recover rare earth nitrates, then zinc will be removed using the next zinc selective extractant composition. The remaining solution can then either be roasted again and upgraded

through a proprietary RES process or through the solvent extraction scheme presented in this report, followed by separation and purification using Rare Earth Salts' technology to greater than 90% purity, meeting the objectives of this study.

From a technical standpoint, there are a few potential next steps that are beyond the scope of this project. Review of the USGS COALQUAL database suggested that zinc concentrations are likely to be high in all coal sources that contain REE, so further work on zinc removal and selectivity could benefit multiple methods for REE recovery. The current work focused on nitrate solutions with high iron and aluminum contents, but the extraction may be very different in chloride or sulfate solutions that could be used in other processes. Additionally, zinc removal may enable better recovery of scandium. Rare Earth Salts' proprietary process would be able to selectively recover scandium in the roasted solids, provided the zinc is removed. An improved process could feasibly leach all of the zinc from the first roasted solids, extract the zinc while leaving the REEs in solution, and allow all of the REE and scandium to be recovered from a single solid concentrate.

Appendix D: Separation and Purification Report

Recovery of High Purity Rare Earth Elements (REEs) from Coal Ash via a Novel Electrowinning Process: Rare Earth Separation Laboratory Testing Report

BATTELLE

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Recovery of High Purity Rare Earth Elements from Coal Ash via a Novel Electrowinning Process:

Rare Earth Element Separation Laboratory Testing Report

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15 September 2019

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Executive Summary

The goal of this project is to produce a high purity, separated (>90%) rare earth oxide product from coal-based sources. This product will be achieved using the following three steps:

1. Battelle's ADP: The ADP leaches pretreated ash with nitric acid, and roasts the loaded acid solution containing REEs, and produces a loaded water solution which contains REEs.
2. Solvent Extraction (SX): The solvent extraction removes REEs from a loaded water solution using an organic extractant, then strips REEs from the organic phase product obtained from extraction.
3. Rare Earth Salt's (RES) Electrochemical Separation and Purification Process: The staged electrochemical process will separate rare earth oxide products from the mixed rare earth solution.

This report covers laboratory testing to determine ideal operating parameters for the successful separation of rare earth elements (Step 3 above) from the rare earth mixture produced through Battelle's SX process (Step 2 above). Testing in this report was performed on either surrogate solutions provided by the scientists at Battelle, surrogates produced in-house using commercially available chemicals, or mineral concentrates that RES has procured for its commercial demonstration plant (CDP).

Initial experiments with the surrogate obtained from the scientists at Battelle indicated an issue that RES had not previously experienced. Experiments with the surrogate solution showed no indications of separating as previously observed in similar solutions. It was determined that there two main deviations from previous samples examined at RES, the presence of an organic component (residual from the solvent extraction) and a high concentration of zinc. Experiments examining both of these components narrowed the disrupting factor to the high amount of zinc present in the sample. This prompted the scientists at Battelle to look for alternate routes to the rare earth concentrate. Parallel with that, RES examined ways to reduce the amount of zinc in the RE impregnated solution. The removal of zinc was approached from two fronts, using chemical approach (pH and complexing agents) and using RES's proprietary technology.

The process flow was also examined, determining the approximate operating conditions and expected separation flow for the system sans zinc. The initial conditions were set within the operating parameters as outlined within the patented process and few modifications were required to obtain the expected splits within the separations process. Additionally, fractions from different initial sources were combined at a specific point in the separations process to ensure that the coal-sourced material could be mixed in with other materials at various points in the process flow with no loss of efficiency in the process.

Finally, the issue with zinc initiated an investigation on how other transition metals may behave in the process stream. Mixtures containing zinc, nickel, copper, tungsten, manganese and iron were investigated to determine their behavior in our separations system. These particular materials were chosen due to their inclusion in other RE systems RES has analyzed previously (but not necessarily examined using their separations process).

1.0 Introduction

Rare Earth Salts (RES) has developed a proprietary separations technology for obtaining 99.9+% pure rare earth materials, eg. rare earth oxides. This technology is environmentally friendly and less costly than traditional means of rare earth separation such as solvent extraction. The technology has also proven to be scalable, moving from the laboratory to the pilot plant scale with relative ease.

The separations flow using this technology generally moves from heaviest to lightest, with the exception being yttrium which separates in the mid-heavies (where it tends to behave chemically). The various elements will move through the system through either the solid or liquid phase. A particular element may move with the solid phase in one step and then the liquid phase in a subsequent step. A simplified flow diagram of the process is shown in Figure 1, with the materials moving right in each step representing the solid material flow and the left being the liquid flow.
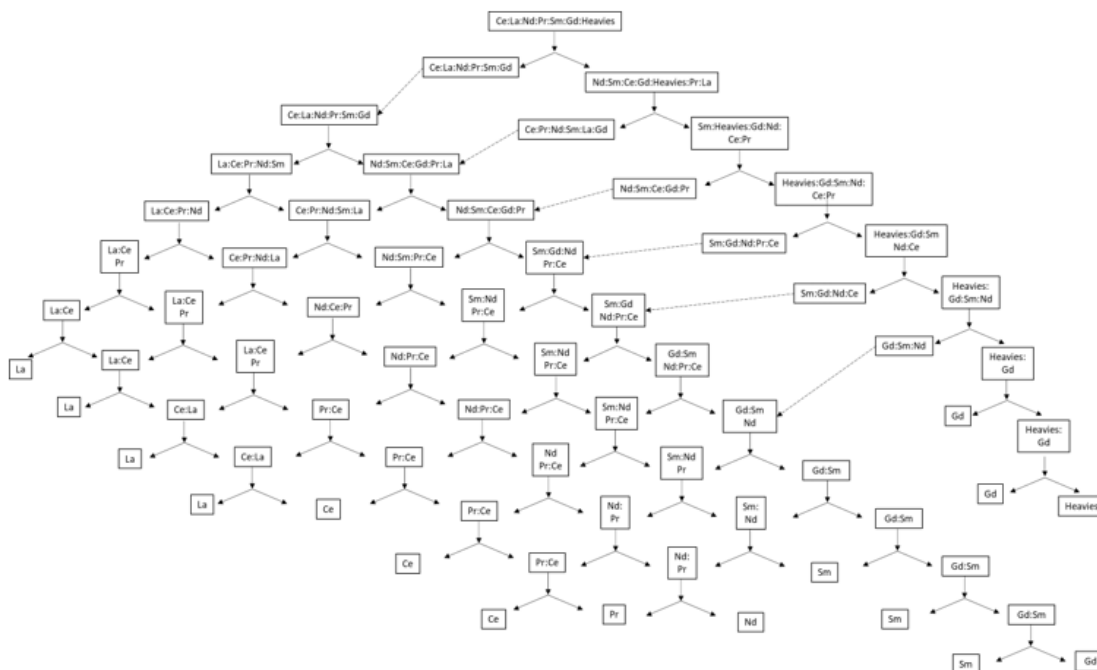
Figure 1. Example separations flow diagram with solid streams moving right and liquid streams moving left.

The goal of this project is to produce a high purity (>90%) rare earth oxide product. This product will be achieved using the following three steps:

1. Battelle's ADP: The ADP process involves pretreatment of ash (milling and caustic leaching), leaching of pretreated ash with nitric acid, roasting of loaded acid solution containing REEs, and water leaching of residual from roasting step, resulting in a loaded water solution which contains REEs.
2. Solvent Extraction (SX): The solvent extraction involves the extraction of REEs from a loaded water solution using an organic extractant (note after extraction, the aqueous phase will be a residual solution and the organic phase will contain REEs), and stripping of REEs from organic phase product obtained from extraction using hydrochloric acid solution (the stripped solution will be the final purified product containing REEs, organic traces, and traces of other metals for further separation in the electrowinning process).
3. Rare Earth Salt's (RES) Electrochemical Separation and Purification Process: The staged electrochemical process will separate rare earth oxide products from the mixed rare earth solution. Testing by RES will also include investigation of options to minimize the solvent extraction steps.

This report will focus on the third step.

2.0 Initial Testing and Zinc Removal

RES performed the initial step in the separations process on the as-received surrogate solution obtained from Battelle. The separation was performed in a newly constructed experimental apparatus within the range a normal separation would be run (proprietary). Separations performed using a newly constructed apparatus typically take a number of cycles (3-5) before solid material is obtained from the experiment. The surrogate solution indicated little to no solid development after 10 cycles, indicated there was an issue in the system. The experiment was repeated, yielding the same results.

Further analysis of the system indicated that the only two factors that RES had not addressed in previous systems was the presence of the organic fraction and the presence of a significant concentration of zinc. An experiment using a surrogate without zinc but with the presence of the organic component yielded separation as expected, narrowing the problematic variable to zinc. The experimental conditions were then changed such that much higher potentials than typically used were applied to the system yielding a small amount of material that was high in zinc but did not afford a reasonable separation of either the rare earths or the zinc from the rare earths.

Following initial attempts to separate the rare earths and zinc through our proprietary electrowinning process, more traditional wet chemical techniques were employed. The initial surrogate solution obtained from Battelle was at a substantially lower pH than typical for the starting solutions through the RES separations process. Due to the low pH, sodium hyrdroxide (either ~5M or ~10M) was used to increase the pH of the system to facilitate precipitate formation as either a hydroxide or tartrate (complexing agent used). The sodium hydroxide concentrations were chosen to minimize the change in volume and thus concentration of the original surrogate solution. The pH increase was either done by slow additions of sodium hydroxide ('Titration') or through larger additions (typically one addition, but in some cases a second or third addition was required to reach the desired pH). The experimental design utilizing pH and complexing agents that was employed is shown in Table 1.

Table 1. Zinc removal through precipitation tests

Variable	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Complexing agent	N/A	Tartaric Acid	Tartaric Acid	Tartaric Acid	Tartaric Acid	Sodium Tartrate
'Titration' or 'Single Addition'	Single	Titration	Single*	Single	Single	Single**

*A second addition of NaOH was required due to substantial pH drop upon adding the tartaric acid

**No NaOH was added due to significant pH increase and precipitation with just complexing agent

The initial experiment utilized sodium hydroxide (~5M) as the lone precipitating agent. A small amount of precipitate was formed at the three pHs examined in the experiment: 5.84, 6.06 and 6.11. The amount of precipitate collected at all three pHs was minimal and due to the fact that a) very little solid was collected to this point and b) there was little preferential precipitation at the highest pH which is at the lower edge of where the rare earth hydroxides are known to begin precipitating, the experiment was stopped and the use of complexing agents was examined.

In order to further understand the tartaric acid/zinc/rare earth system, a systematic study was undertaken examining the solution and precipitate behavior as a function of pH. The surrogate solution was mixed with tartaric acid and allowed to equilibrate, yielding a solution at pH < 0.5. Sodium hydroxide was then added in small increments with the solution allowed to equilibrate overnight before samples were taken (the precipitate was only collected at a few points in the experiment). A plot of the percentage of cerium, gadolinium, ytterbium (a light, mid and heavy rare earth respectively), as well as zinc, remaining in solution as a function of pH can be found in Figure 2.
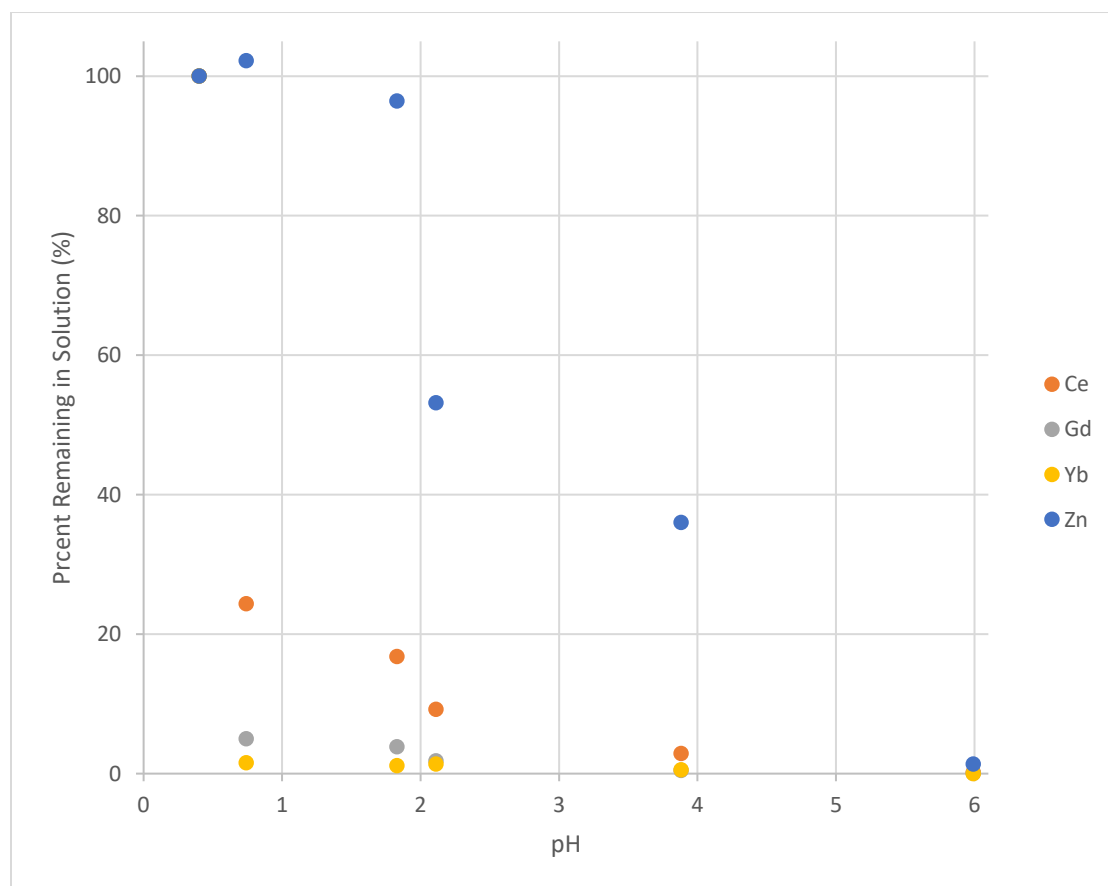
Figure 2. Plot of the percentage remaining in solution for cerium (Ce, representative of the light rare earths), gadolinium (Gd, representative of the mid rare earths), ytterbium (Yb, representative of the heavy rare earths) and zinc (Zn) as a function of pH in the system.

The experiment resulted in a solid that was 99.2% rare earth and 0.8% zinc at pH = 1.8 with 85% of the rare earths removed from the solution (weighted percentages). The effective removal was increased to > 91% at a pH of 2.1 composed of 92% rare earths and 2% zinc.

The remaining experiments yielded results that were less satisfactory than the previous one, with the 3rd experiment yielding a solid that was 5% zinc with ~65% of RE removed. The remaining experiments showed no improvements over the previous experiments.

3.0 General Separation Flow

Given the difficulties in using the surrogate solution supplied by Battelle with the high zinc concentration, a suitable alternate surrogate was produced in the RES laboratory using the appropriate rare earth chloride hydrates. The solution was then subjected to typical experimental conditions for the electrowinning separation of rare earths. The solid material collected will have higher concentrations of some elements (relative to the starting solution) and lower concentrations of others. The solid material can further be separated into 'lots' of various concentrations as it is collected over time. The initial separation steps group the rare earth elements into pairs or triads for separation as shown in Figures 3-5. Figure 3 shows the initial groupings for the light rare earth elements, while Figures 4 and 5 show the mid and heavy rare earths, respectively. These Figures show the amount of each element remaining in solution as a function of time, a direct correlation to the composition of the solid as a function of time. The lowest member of the group above is included in each Figure as a point of reference.
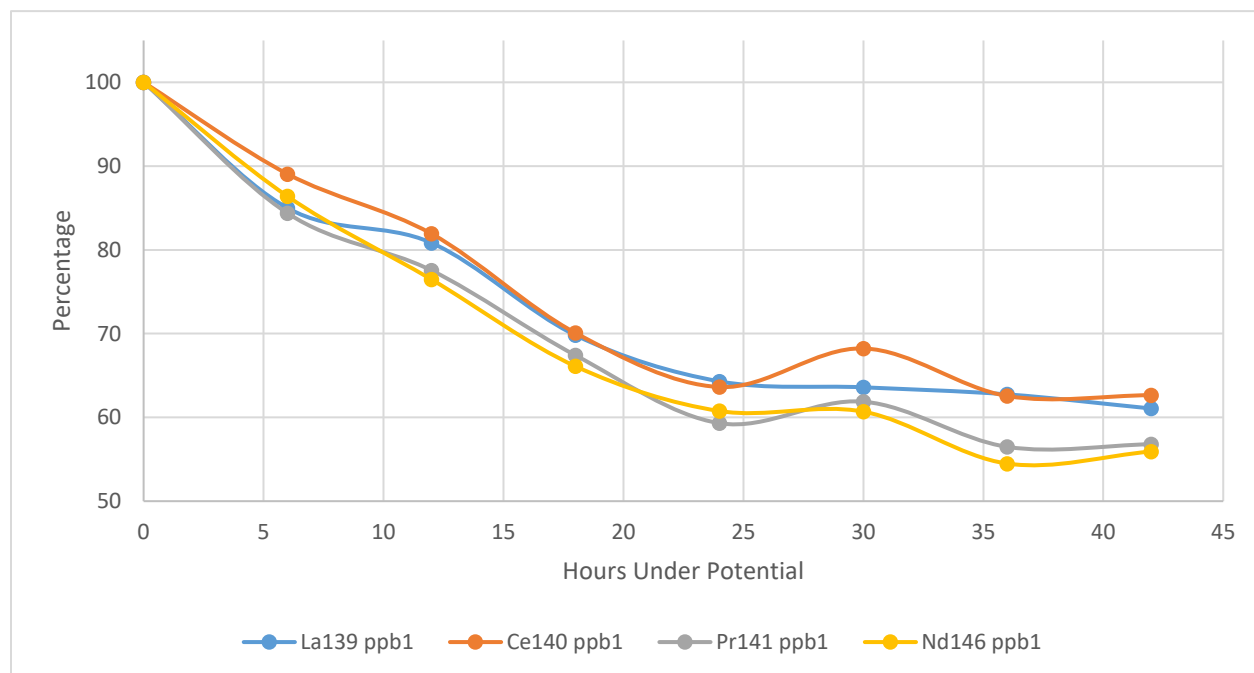
Figure 3. Percentage of original material (light rare earths) remaining in solution as a function of time spent under potential during the electrowinning process.
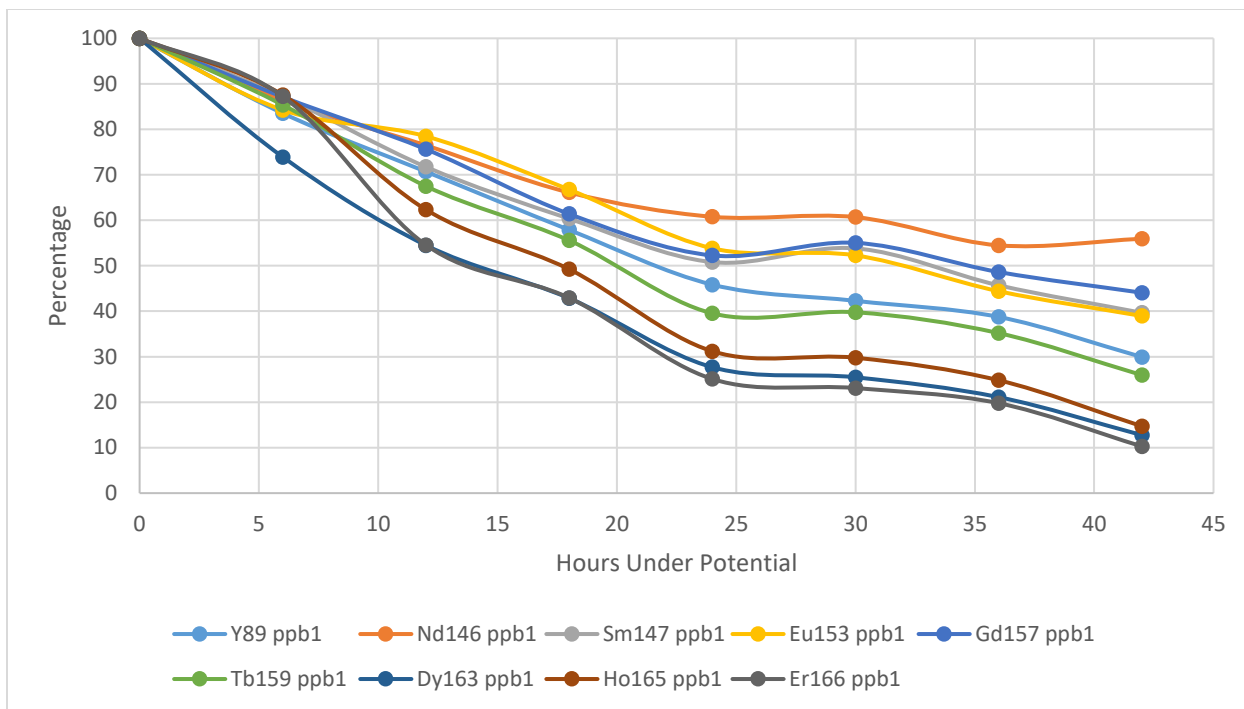
Figure 4. Percentage of original material (mid rare earths) remaining in solution as a function of time spent under potential during the electrowinning process.
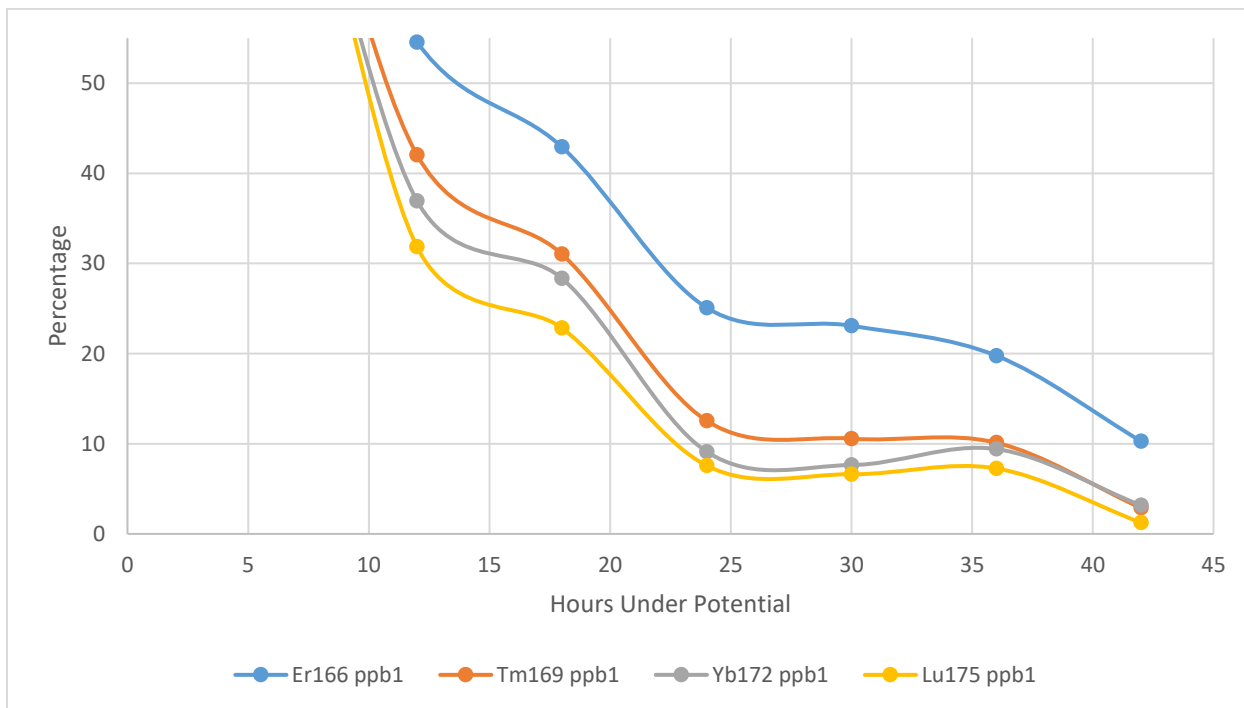
Figure 5. Percentage of original material (heavy rare earths) remaining in solution as a function of time spent under potential during the electrowinning process.

The progress of the separation can also be measured in a function our lab has defined as 'upconversion'. Upconversion or percent upconversion can be defined mathematically in equation 1 where percentage in solution is defined as the solution at the beginning of the iteration from which the solid is obtained.

$$upconversion = 100 * \frac{percentage\ in\ solid}{percentage\ in\ solution} \qquad (1)$$

Upconversion values greater than 100 indicate the material is preferentially moving into the solid phase and values less than 100 indicate that the material is preferentially remaining in solution. Figures 6 and 7 represent the upconversion values for the light and heavy rare earth elements, respectively.
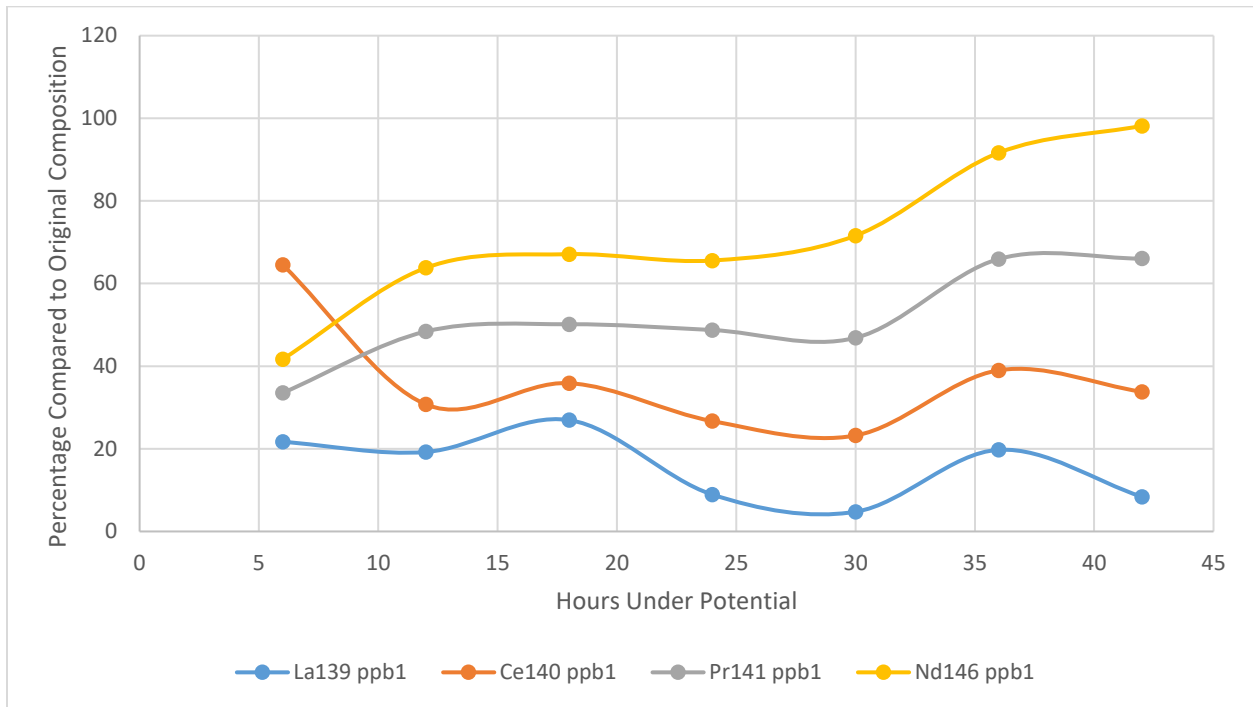
Figure 6. Percent upconversion values for the light rare earth elements as a function of time spent under potential.
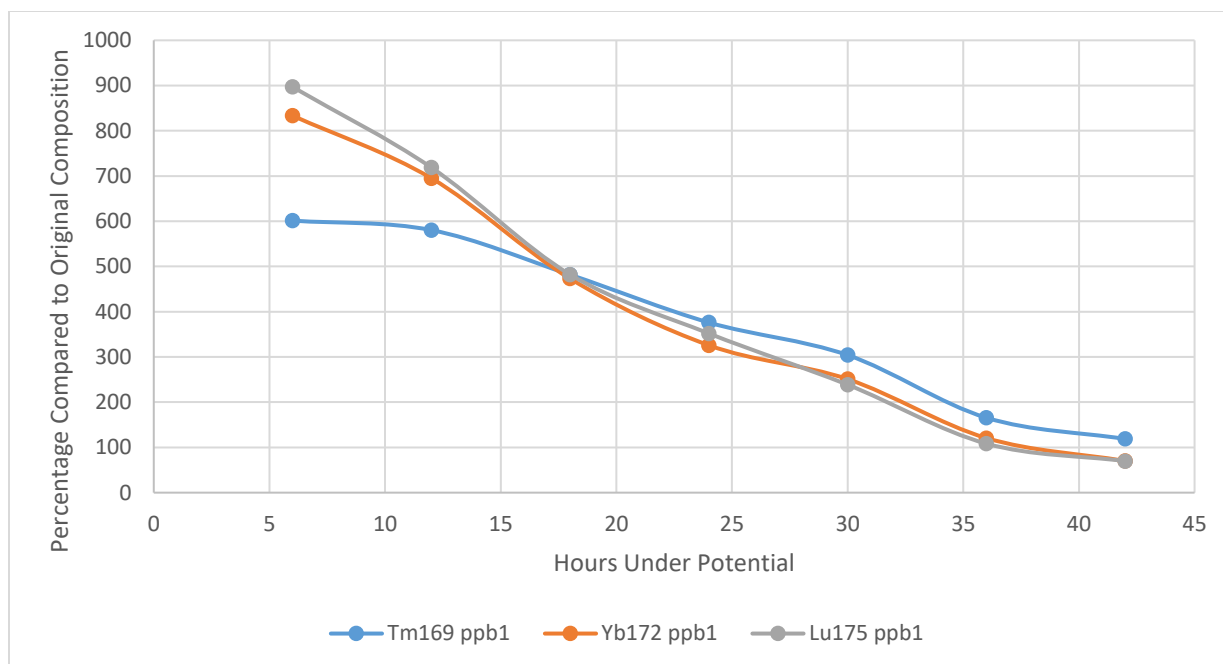
Figure 7. Percent upconversion values for the mid rare earth elements as a function of time spent under potential.

Further experiments examining the process flow in the separations scheme focused on the light rare earths (La, Ce, Nd, and Pr) as they generally comprise anywhere from 60% (the final material received from Battelle and brought into solution by RES) to 95% (a typical concentrate from a bastanite ore). Both surrogate and mineral concentrate samples were examined in this stage and intermediate products were combined to ensure that materials from multiple sources would continue to process without changes to the separation scheme.

Notable outputs from these experiments were a > 98.5% pure didymium product with a ratio of ~82% Nd to ~18% Pr and a >98.5% La product. The didymium product was one isolated for production due to the intrest from a number of rare earth magnet producers.

Scandium was found to have been removed earlier than the remaining rare earth elements during the solvent extraction process performed by Battelle. The scandium was removed along with the bulk of the iron in the sample. Rare Earth Salts received a sample of the scandium impregnated iron material and it was subjected to our proprietary conversion process. The experiment allowed us to confirm that the scandium was concentrated in the solid product while the bulk of the iron was removed from the sample. The amount of scandium present in the sample (<100 mg) was too small to allow for a quantitative assessment of the process, including determining the efficiency of the process. The amount of material was also small enough to use our larger laboratory furnace for the process, which didn't allow for the collection of the iron product for testing. It is our estimate that this process will allow for the production of a pure scandium chloride or oxide product (>99% purity) along with a substantial amount of an iron chloride or oxide by-product (also >99% purity).

4.0 Transition Metals

Due to the difficulties with zinc in the system, the behavior of a number of transition elements was examined, both through more traditional wet chemical techniques (as with the removal of zinc previously) and through the use of our proprietary electrowinning process. A system that was readily available was used, chosen for both the elements present and that there was no cost involved. The system contained manganese, iron, copper, nickel, zinc, tungsten, sodium and some other trace elements.

Traditional wet chemical techniques included straight pH manipulation using sodium hydroxide, as well as complexing (and pH manipulation) using ammonium hydroxide (or aqueous ammonia). Wet chemical techniques were able to get some preferential precipitation (to a degree) but the purities of the solids produced were insufficient.

The system was then examined using our proprietary elecrowinning process to yield surprising results. The system did not behave as traditional chemical knowledge would dictate, but did behave as expected given the results with the Battelle surrogate solution. All of the elements present had substantially positive cell potentials when coupled with a sacrificial anode; however, no plating occurred even at low applied potentials. A number of cathodic and anodic variables were examined (proprietary) along with experimental conditions under which the electrowinning was performed. Isolated elements and their purities are shown in Table 2. These results have not been optimized so expected purities for an optimized system are expected to be higher than those presented

Table 2. Unoptimized results for the separation of targeted transition metals from a mixture of six transition metals

Element	% purity (starting %)
Cu	➢ 99% (53%)
Ni	➢ 87% (16%)
Mn	➢ 99% (20%)

5.0 Separation of Rare Earths from Coal By-Products

Material was received from the scientists at Battelle in the form of a high aluminum material. The rare earths were extracted from the aluminum matrix using our proprietary conversion process, which left the majority of the aluminum matrix but did extract the majority of the transition elements (including zinc) from the matrix along with the rare earths. Due to time constraints, a 'brute force' approach was tried given the zinc levels were less than the original surrogate studied. Unfortunately, the method used did not work as intended and the grant period was extended to allow for a more thorough approach. One potential by-product of this first step in the process would be an alumina material. Depending on the type of impurity content from a more fully optimized solvent extraction process, this alumina by-product could have a purity ranging from 99% to >99.9% purity.

The fractions collected from the first attempt were recombined and dissolved using hydrochloric acid and then the rare earths were precipitated using tartaric acid under pH control of the system. The precipitated rare earths were then calcined at high temperature and redissolved using hydrochloric acid under conditions such that the final pH was approximately 4.

The rare earths were separated following the previously discussed scheme until the four light rare earths, lanthanum, cerium, praseodymium and neodymium were remaining. The separation parameters were then adjusted for finer control of the separation to produce two fractions; one high in lanthanum and one high in the other three remaining elements. Once the lanthanum was near the 90% target, an experimental technique for precipitating cerium from solution at high purity was used on the system. The results were as expected, producing a 90%+ purity cerium oxide product but during the procedure an accident occurred and contaminated the solution with a material high in cerium, praseodymium and neodymium (with lesser amounts of lanthanum). Further iterations of the experimental technique were performed to remove the remaining cerium from the system (given the ICP results, it is estimated that the resulting cerium material was ~60% coal material and 40% contaminate). Given the much larger amount of lanthanum in the system and the lower lanthanum content in the contaminate, it is estimated to be over 70% coal-based material.

The method produced a cerium product that each fraction was over 91% cerium and a lanthanum fraction that was ~90% lanthanum. The resulting material was precipitated from solution as an oxalate and then fired at 1100℃ for between 1 and 2 hours. The cerium product was again subject to contamination as the crucible cracked during the firing, causing it to be contaminated beyond recovery. The lanthanum was fired as two different products as a second precipitation was able to recover more of the material. The first product is ~1.1g and has a TREO >90% with a 89% +/- 2% lanthanum content (oxide basis) and the second product is ~0.2g with a TREO >95% with a 90% +/- 2% lanthanum content (oxide basis).

6.0 Conclusions and Next Steps

Initial steps in the separation of rare earth elements generated from coal courses have been completed. Process flow for the separation of the light elements (La, Ce, Nd/Pr) has been mapped in detail and proven on surrogate solutions, mineral concentrates and mixtures of the two. Limitations of the proprietary separations technology have been identified and means to overcome or avoid these limitations have been examined. Zinc is still problematic in these systems but it can be removed either through wet chemical means or through the use of a different extraction and concentrating process at Battelle.

Using surrogates and mineral concentrates, two rare earth products have been taken to near commercially viable products. Lanthanum was produced at greater than 98% while didymium was also produced at greater than 98%.

Transition elements were examined in our laboratory scale separations apparatus and were found to behave differently than expected (eg. calculated E_{cell} was different than experimental E_{cell}). Even with the difference between experimental and expected conditions, three transition elements were able to be separated (from a mixture of six) at reasonable purities.

The next step in the process is to map out the process flow in more detail for the SEG (samarium, europium and gadolinium) group and then the heavy rare earth elements. The SEG group is currently being examined in detail and the same study will ideally provide enough of the heavy rare earths (or a minimum of the mid-heavy rare earths) to continue to map the process flow through those elements.

Appendix E: Technology Development and Commercialization Plan

Recovery of High Purity Rare Earth Elements (REEs) from Coal Ash via a Novel Electrowinning Process: Technology Development and Commercialization Plan

BATTELLE

Recovery of High Purity Rare Earth Elements from Coal Ash via a Novel Electrowinning Process:

Technology Development and Commercialization Plan

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15 September 2019

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1.0 Executive Summary

A technoeconomic assessment was performed on Battelle and Rare Earth Salts' processes to recover high purity rare earth oxides from coal fly ash. The assessment was informed by a chemical process model based upon laboratory testing results, preliminary sizing estimates for the equipment, and a factored capital cost estimation. This technoeconomic assessment suggested that for a 20 year project, the rate of return is 27.6% on a capital investment of $76.4 million, with a simple payback period (FCI/annual cash flow) of 3.8 years. However, the process is dependent upon a ferric chloride co-product for profitability, and scandium is the bulk of the rare earth revenue stream. The availability of co-products from coal based sources may actually be a benefit compared to other marginal sources, such as monazite sands, which have minimal other mineral values to subsidize the rare earth recovery.

Looking toward commercialization, the process needs to be scaled to an integrated bench scale size that is able to produce sample quantities to engage potential offtake partners for rare earth oxides and byproducts. A shift in the development needs to be made toward development of co-products that subsidize rare earth element recovery from coal sources, and validation of the marketability of the key products. In particular, high purity scandium oxide product needs to be generated from coal sources so that end users can validate whether it is usable in their processes and what they are willing to pay. Additionally, key byproducts from the process such as ferric chloride and aluminum oxide need to be generated in quantities that can be tested by commercial end users. As feedback from end users is received on the samples, the integrated bench scale unit can be adjusted to meet end user requirements.

Once the rare earth products and byproducts have been validated by end users at the integrated bench scale, the process will be scaled through two stages of piloting, first at 0.5 tonnes per hour, then 15 tonnes per hour before a commercial plant is built. Rare Earth Salts has an existing 18 ton per day of rare earth oxides plant operating, and has made significant headway in placing the rare earth products from this system into the market. It is expected that the coal based rare earth elements from the pilot plants can be processed in their existing system with minimal adjustments, and even blended with current feed streams so that customer validation of the coal based rare earth elements can be accomplished quickly with minimal process interruptions.

2.0 Process Description and Economics

This section describes the overall REE recovery process through purified REO products, and provides preliminary process economics that are the basis for the forward looking Technology Development and Commercialization Plan. Process flow diagrams and stream tables upon which the economics are based are provided in Appendix A, and are referenced in this section.

2.1 Battelle's Acid Digestion Process (ADP) Description

The continuous rare earth recovery process (see Figure 2 in the Appendix) starts with four distinct steps: pretreatment and aluminosilicate byproduct generation (caustic blowdown 1-06 stream in Figure 2 feeds the byproduct generation process), acid leaching, acid recovery and preliminary product generation. Acid leaching to access the rare earth element (REE) content of the ash is operated in a closed loop process, allowing for the recovery and reuse of the bulk of the nitric acid used in the process. Primary process feeds include the REE containing fly ash material sourced from a pulverized coal combustion electricity generating unit (PCC EGU), a caustic hydroxide feed (nominally sodium hydroxide), makeup nitric acid, and process water. The primary process outputs are fly ash stripped of REE, an aluminosilicate (zeolite) byproduct generated during the pretreatment process (caustic blowdown 1-06 stream), wastewater blowdown, and the REE concentrate stream. The proposed design production scale plant will process 30,000 kg (30 tonnes) of ash per hour.

The pretreatment begins with a milling step, which reduces the median ash particulate size from 55 μm to 4.5 μm. This size reduction provides better access to the particle for leaching and may be performed in a jet mill or stirred media mill. Once the ash has been milled, it is treated with a sodium hydroxide solution to remove some of the silica and alumina present in the ash. This allows improved access to REE in the acid leaching step. A caustic leaching residence time of one hour in 10% sodium hydroxide solution at 90°C is sufficient to liberate REE in the acid step based on preliminary laboratory data. The ash is filtered out of the caustic solution and rinsed with water to remove entrained caustic before proceeding to the acid leaching operation. After the leach step, the caustic solution is loaded with silicate and aluminate, which can be precipitated into zeolite material. Separation of the ash from the pretreating caustic solution is accomplished using a rotary drum filter with a water rinse. After the pretreatment, the ash is fed to the Acid Digestion Process and mixed with a nitric acid stream (approximately 34 wt.%) before being pumped through a heater to an elevated, sub-boiling temperature, and into the leaching reactor. The leaching temperature is expected to be 80-90°C. Total flow rate, temperature, and stream composition for the caustic pretreatment and acid leaching process are shown in Table 16 and Table 17. PFD stream numbers are also shown in tables.

After the leach process, the ash is filtered out in a vacuum drum filter and transferred to an ash drying operation. The leachate, containing unreacted nitric acid, is recycled to the reactor to ensure complete utilization of the acid fed to the process. The ash dryer is important for economic recovery of REE since the high temperatures will boil off and convert any entrained nitrates, allowing them to be recovered in the closed loop process. Additionally, this drying step ensures removal of any nitrates from the ash, preventing the discharge of nitrates from the ash allowing for safe storage of the ash, or for use as a pozzolan. The ash dryer is a rotary-type drum dryer, indirectly heated to a temperature of up to 155°C (see Table 18 and Table 19).

Off gases from the acid leach process, consisting of nitric acid and other NOx species, are swept with an air stream and fed along with the REE-loaded leachate into a roasting operation. The roaster will operate in two stages, the first to concentrate the liquid feed into a slurry, and the second to crystallize the REE salts. The concentration step will use a conventional evaporation unit heated to 120°C, while the crystallization step will be done in a spray dryer, reaching temperatures high enough (between 120°C and 155°C) to convert some of the metal nitrates to oxides. By roasting the metal nitrate salts to dryness and then to a temperature around 155°C, many non-rare earth metal salts (such as iron and

aluminum) are converted to metal oxides, releasing NOx gases, which are swept along with other process off-gases to the absorption column. Based on laboratory testing, rare earth nitrates, however, are not converted to oxides at temperatures less than approximately 250°C and will therefore remain in their nitrate salt form. This step provides a water-soluble rare earth concentrate, enriched in rare earth materials, suitable for feed to Battelle's upgraded solvent extraction and Rare Earth Salts purification processes. Table 20 and Table 21 are the stream tables for the roasting process.

As discussed, all off-gases of the process, consisting of nitric acid vapor and NOx gases, will ultimately be swept to an absorption column system for recovery. Optionally, these vapors may be compressed and fed through a heat exchanger to preheat the acid feed to the roaster, then to a condenser to recover nitric acid for recycle, prior to being fed to the column. Any NO gas generated in the roaster, leaching, and ash drying processes needs to be oxidized to NO_2 prior to being absorbed back into the acid stream. This oxidation rate is improved at higher temperatures and can occur in the drying and roasting processes with the presence of air. As the gas passes through the condenser, it is then cooled, which is preferable for the absorption of the NO_2 back into the liquid phase. Gas will flow through the absorption column in a single pass, where it is contacted with recycled nitric acid as an absorbent. The liquid recirculated in the column consists of acid recovered from the roaster. Nitric acid recovered in the column will be recycled back to the leach reactor to complete the acid recycle process. A small fraction of this stream will be sent to a distillation column, which will distill and separate the water-nitric acid mixture, allowing for the proper concentration of nitric acid to be maintained in the reactor. The concentrated nitric acid recovered in the distillation column will be recycled to the acid leaching process, while the water recovered in the distillate will be treated to a neutral pH and purged from the system, ensuring that a buildup of water does not occur in the process (see Table 22 for acid recovery steps).

Overall ADP Energy Balance

Table 1 and Table 2 show the overall energy balance; heating and cooling requirements for the Battelle ADP. The lower heating value of natural gas was used for the calculations and assuming 30% energy efficiency. Inlet temperature and outlet temperature of the cooling water was assumed to be 25°C (at 30 psig) and 40°C, respectively.

Table 1: Preliminary Heat Duty for ADP 30,000 kg/hr Full-scale Process.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
Acid Leach Reactor Preheater (HX-201)	63.62	Natural gas	16.21
Rotary Kiln Roaster Ash Dryer (K-1)	12019.92	Natural gas	3062.40
Roasting Process Evaporator (EVAP-1)	35917.50	Natural gas	9150.96
Roasting Process Roaster (K-2)	2797.44	Natural gas	712.72

Table 2: Preliminary Cooling Duty for ADP 30,000 kg/hr Full-scale Process.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
ESP Condenser (COND-1)	10691.67	Cooling water	613880.00
Evaporator Condenser (COND-2)	35682.50	Cooling water	2048651.00
Roasting Process Condenser (COND-3)	5540.83	Cooling water	318200.00
Absorption Column HTXR (HX-501)	79.23	Cooling water	4549.30
Caustic Scrubber HTXR (HX-502)	61.85	Cooling water	3551.46
Distillation Column Water Product HTXR	6970.89	Cooling water	400298.00
Distillation Column Acid Product HTXR	2491.29	Cooling water	143064.00

2.2 Upgrading Solvent Extraction (SX) and Purification Processes

Solvent extraction (SX) followed by a high temperature roasting step was used to further concentrate REE and produce a mixed REE concentrate of 50-60% REE oxides, which is able to be further separated into individual rare earth oxides for sale in the market using RES' electrowinning process. It is expected that SX and the high temperature roasting step will remove monovalent and divalent cations, as well as select transition metals, especially zinc (an undesired species for the electrowinning process), from the REE feed stream. This combined REE oxide stream will be the feedstock to the electrowinning process, which consists of a conversion (potential iron chloride by-product is made during this process) step followed by the final separation of salable REE oxide products. Primary process feeds include the REE product collected from ADP, extractant and stripping solutions for SX steps, conversion reagent for RES conversion process, and process water. The primary process outputs are a potential iron chloride byproduct generated during the conversion process, wastewater and strip solutions blowdown, and the final sealable REE oxide products (see Figure 3 in the Appendix).

Upgrading Solvent Extraction

The REE product collected from the ADP process is mixed with water and then filtered using a drum filter to remove major impurities converted into oxides during the roasting process, such as aluminum, iron, uranium, and thorium. In the roasting step, most of the scandium will also be converted to oxide staying with iron and other impurities in the solid product. However, this product is treated later, recovering scandium and making iron chloride as a by-product during RES' conversion process. After this wash step, the leach solution will go into the upgrading SX process (see Table 23 for streams composition of the washing process).

The leach solution from water wash step will be extracted at pH 2-3 using a commercially available extractant. This extractant will selectively extract REE from other metals, especially zinc. The laboratory test results suggest a ~73% extraction of total REE with just ~7% of zinc extracted in one stage. At this larger scale multiple stages are used resulting in >95% of REE and <20% of zinc extracted. The selective separation of zinc from REE is of high importance due to the tendency of zinc to follow the REE in solvent extraction and other separation processes impacting the ability to achieve a separated, saleable product. After extraction, REE will be stripped using 10% nitric acid solution yielding a concentrated REE solution that then will be roasted at high temperature. Most of the striping solution will be recovered in the condenser of the high temperature roasting process. After REEs have been stripped, the extractant will be regenerated using a combined acid solution to clean extractant before being recycle back to the extraction step. Based on preliminary laboratory testing, the extractant loss during the SX process is less than 200 ppm of the active ingredient (see Table 24 and Table 25 for streams composition).

After the SX process, the loaded strip solution will be roasted at ~250°C to convert REE nitrates into oxides. At this temperature, most of the alkali and alkali earth metal nitrate salts, such as, barium, calcium, potassium, and sodium nitrates are not converted to oxides facilitating the separation of these impurities from REE oxides by performing a water washing step follow by a filtration step using a drum filter. This step provides a high purity combined REE oxide material suitable for RES' conversion process followed by electrowinning process for the final separation of salable REE oxide products. Additionally, the loaded stripped solution is recovered using a condenser which recovers about ~93% of the solution. The non-condensable from this step will be directed to the absorption column in the ADP (see Table 26 for streams composition).

Purification Process

The purification process consists of two steps. First, REE oxides from upgrading solvent extraction and solids from the roasting step will be directed into the RES conversion process. In this process, REE, including scandium left behind in the roasting step, are converted to water soluble salts leaving other impurities as insoluble oxides. A water wash step is performed follow by a filtration step using a drum

filter to remove the oxides from REE salts. The resulting product is a high purity REE solution suitable for RES' electrowinning process. Additionally, a potential iron chloride by-product is produced during the conversion process helping to offset the cost of the overall REE recovery process (see Table 27 and Table 28 for streams composition). The final step will be the RES electrowinning process where the concentrated REE solution will be separated into individual saleable REE oxide products in several stages (see Table 29 for streams composition).

Overall Energy Balance for SX and purification process

Table 3 and Table 4 show the overall energy balance (heating and cooling requirements for Battelle's SX and RES' purification process). The lower heating value of natural gas was used for the calculations and assuming 30% energy efficiency. Inlet temperature and outlet temperature of the cooling water was assumed to be 25°C (at 30 psig) and 40°C, respectively.

Table 3: Preliminary Heat Duty for Upgraded Solvent Extraction and Purification Processes.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
Oxide Conversion Spray Dryer (SD-1)	824.50	Natural gas	210.06
Pre-Conversion Spray Dryer (SD-2)	8379.63	Natural gas	2134.94
Salt Conversion Furnace (FUR-1)	12661.17	Electricity	
Separation Process Heat Required	5903.72	Electricity	

Table 4: Preliminary Heat Duty for Upgraded Solvent Extraction and Purification Processes.

Unit Operation	Heat Duty (kW)	Source	Flow Rate (kg/h)
Stripping Solution Condenser (COND-4)	685.41	Cooling water	39354.82
Water Product Cooling (9-11) Duty	6719.72	Cooling water	385836.00
Water Product Cooling (10-07) Duty	397.38	Cooling water	22816.78
Iron Chloride Cooling (10-08) Duty	2109.31	Cooling water	121112.70
Conversion Reagent Recycle Cooling (10-09) Duty	701.46	Cooling water	40275.25
Water Product Cooling (11-03) Duty	6779.39	Cooling water	383004.00

2.3 Process Economics

Preliminary economics were run for the process to inform the technology transfer and commercialization plan. The intent of this economic study was to identify key economic hurdles to commercialization so that a rational development plan can be constructed. Accordingly, contingencies are lower than would be expected for a process design at this phase, and the ultimate costs reflect what one would expect for a mature, commercial plant operation assumed to operate well under the currently understood process parameters.

Summary of TEA Method

The procedure used in this work follows the Electric Power Research Institute's (EPRI) Technical Assessment Guide (TAG™) guidelines for cost estimation of emerging technologies. The total capital requirement (TCR) of a rare earth recovery system takes into account the direct costs of purchasing and installing all processing equipment (denoted as the Process Facilities Capital, PFC), plus a number of indirect costs such as the general facilities cost, engineering and home office fees, contingency costs, and several categories of owner's costs. These costs are used to determine the overall cost of Battelle's Acid Digestion Process for recovery of REE. Figure 1 outlines the TAG method developed by EPRI.

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┌─────────────────────────────────────────────────────┐
│   Inputs from ChemCAD™ process performance model    │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
        ┌──────────────────────────────────────┐
        │       Process facilities capital =   │
        │  Sum of direct costs of all the processes │
        └──────────────────────────────────────┘
                          │
                          ▼
              ┌──────────────────────────┐
              │  Indirect cost calculations │
              └──────────────────────────┘
                          │
                          ▼
        ┌──────────────────────────────────────┐
        │          Total plant cost (TPC) =    │
        │  Direct costs + Indirect costs + Initial costs │
        └──────────────────────────────────────┘
                          │
                          ▼
        ┌──────────────────────────────────────┐
        │   Fixed and variable O&M costs, revenues │
        │    from sale of byproducts calculations │
        └──────────────────────────────────────┘
                          │
                          ▼
        ┌──────────────────────────────────────┐
        │     Total revenue requirement (TRR) = │
        │  (TPC)*FCF + O&M cost – byproduct revenue │
        └──────────────────────────────────────┘
                          │
                          ▼
        ┌──────────────────────────────────────┐
        │             Output cost =            │
        │  TRR/(CF*daily REE concentrate output*365) │
        └──────────────────────────────────────┘
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Figure 1: Method of cost assessment (Electric Power Research Institute (EPRI), 1986)

Capital Cost

The process facilities capital (PFC) of a component refers to the capital required to purchase and install a major process at the facility. Ideally, these costs are known and come from prices quoted from an equipment manufacturer. When manufacturer data is not available, installed cost data is derived from references describing costs for installing similar processes. Equipment costs are then scaled using well-documented cost correlations[1]. Table 5 lists the nominal cost values for a rare earth recovery system using the process in this project.

The total direct capital cost of the rare earth recovery system is approximately $55 million. The most capital intensive process area is the evaporator-condenser associated with the acid recovery system, which accounts for approximately one quarter of the total direct capital costs of the system. The evaporator-condenser is used to recover nitric acid from the leached stream and reduces the annual operating expenses associated with reagent cost.

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[1] Tribe, M. A., & Alpine, R. L. (1986). Scale economies and the "0.6 rule". *Engineering costs and production economies*, 271-278.

Table 5: Installed costs for major process areas of the rare earth recovery plant.

Direct Costs for All Major Process Areas ($1000, 2015)			
Coal Ash Handling	$361	Reactor Recirc. Pump	$20
Caustic Pretreat CSTR	$60	Column Sump Pump	$16
Pretreat Rotary Filter	$3,401	Filter Pump	$25
Pretreat CSTR Acid	$60	Evaporator Feed Pump	$8
Pretreat Zeolite Filtration	$60	Acid Recycle Pump	$8
Pretreat water wash	$224	Acid Makeup Pump	$8
Leach Reactor	$271	Column Blower	$104
Knockout Vessel	$187	Distillation Column	$3,911
Filter	$4,040	Oxide/Nitrate Separation	$970
Rotary Dryer	$2,277	Solvent Extraction	$747
Crystallizer/Custom Rotary Dryer	$3,402	Pre-Stripper	$1,196
Column	$263	Stripper	$2,391
ESP	$1,329	Scrubber	$2,391
Reactor Heat Exchanger	$215	Scandium Scrub	$297
Column Heat Exchanger	$218	Post SX Leach	$970
Evap. Condenser	$13,234	Spray Dryers	$2,348
Roaster Condenser	$766	Furnace Items	$3,427
Reactor Feed pump	$25	REO Purification	$6,322
Process Facilities Capital			**~$55,554**

In addition to the Process Facilities Capital costs, there are a number of other capital cost items (often referred to as indirect costs) that are applied. Traditionally, these are estimated as percentages of the total PFC. These additional costs are divided into the following categories:

- Engineering and home office fees (EHO)

- General facilities capital (GFC)

- Process contingency

- Process contingency

- Royalty charges

The sum of these costs, called the total plant cost (TPC), is developed on the basis of overnight construction. Overnight cost is the cost of a construction project if no interest was incurred during construction, as if the project was completed "overnight." (Stoft, 2002) These costs are summarized in Table 6.

Table 6: Summary of estimated direct and indirect capital costs for the rare earth recovery process. These costs are the basis for estimating the total plant cost—a major component of the total capital requirement of the plant.

Capital cost elements	Nominal Value	Component Cost ($Million, 2015)
Process Facilities Capital (PFC)		$55.5
Engineering and Home Office Fees	7% PFC	$3.9
General Facilities	10% PFC	$5.6
Project Contingency	10% PFC	$5.6
Process Contingency	10% PFC	$5.6
Total Plant Cost (TPC) = Sum of the above		**$76.1**

General facilities capital (GFC) is the capital required for the construction of general facilities such as buildings, roads, shops, etc. This cost is usually estimated to be between 5 and 20% of the PFC. Engineering and home office overhead is included if the cost estimates for the general facilities capital do not include these fees as part of the equipment costs. For these fees, 7 and 15% of the PFC is typical. Royalty charges are included as indirect capital costs and typically range from 1 to 10% of PFC.

The EPRI TAG method uses two types of contingencies: the process contingency and the project contingency. The process contingency is a capital cost contingency factor applied to a new technology in an effort to quantify the uncertainty in the technical performance and cost of commercial scale equipment[2]. Therefore, a higher process contingency factor is used for more basic cost estimates. Table 7 shows how the maturity of the technical design influences the process contingency.

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[2] Electric Power Research Institute (EPRI). (1986). *Technical Assessment Guide (TAG) Vol. 1: Electricity supply.* Palo alto: Electric Power Research Institute.

Table 7: Process contingency cost guidelines[3].

Technology status	Process contingency cost (%PFC)
New concept with limited data	40+
Concept with bench-scale data	30-70
Small pilot plant data	20-35
Full-sized modules have been operated	5-20
Process is used commercially	0-10

EPRI recommends that separate process contingencies be given for each major process systems. For the REE recovery and purification processes, this work uses a default process contingency of 10% for a commercial process, as this commercialization plan aims to identify future-looking economic hurdles, rather than considering costs if built today.

The project contingency is a capital cost contingency factor that is intended to cover the cost of additional equipment or other costs that would result from a more detailed design of a definitive project specific to the actual site[5]. Specifically, the project contingency addresses the need for site preparation, building construction, ancillary process equipment, structural support, and miscellaneous equipment required when the actual plant is built. Table 8 lists the project contingency cost guidelines as suggested by EPRI. This work uses a simplified design intended to be applicable for a range of equipment options.

Table 8: Project contingency costs[6]. The contingency costs are compared to the American Association of Cost Engineers (ACEE) technology Class ranking system.

EPRI cost calculation	Design effort	Project contingency
Class I (~AACE Class 5/4)	Simplified	30-50
Class II (~AACE Class 3)	Preliminary	15-30
Class III (~AACE Class 3/2)	Detailed	10-20
Class IV (~AACE Class 1)	Finalized	5-10

Like the process contingency, EPRI recommends that project contingencies be applied for each plant selection and this work uses finalized design effort values for each supply chain step outside of the recovery process. Regarding Battelle's recovery process, a project contingency factor of 10% is used

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[3] Electric Power Research Institute (EPRI). (1993). *TAG(tm) Technical Assessment Guide Volume 1: Electricity Supply.* Palo Alto: EPRI.

as the default value. As with the process contingency, this is a low value, but intended to allow for forward looking identification of economic hurdles rather than the anticipated cost of building a plant today.

The total capital requirement (TCR) includes all the capital necessary to complete the entire project. These items include:

- Total plant cost (TPC)

- Allowance for funds used during construction (AFUCC)

- Prepaid royalties

- Inventory capital

- Pre-production costs

Table 9 summarizes the steps required to calculate the total capital requirement. The total capital requirement for the rare earth recovery process is approximately $80 million. This includes all direct and indirect capital costs associated with the project.

Table 9: Indirect capital costs for a rare earth element recovery plant.

Capital cost elements	Nominal Value	Component Cost ($1000, 2015
Total Plant Cost (TPC)		**$76,109**
AFUDC (interest during construction)	0.5% TPC	$381
Royalty Fees	0.5% PFC	$278
Pre-Production (fixed)	1 month fixed O&M	$729
Pre-production (variable)	1 month variable O&M	$2,433
Inventory Capital	0.5% TPC	$381
Total Capital Requirement (TCR)		**$80,311**

Operating Costs

The operating and maintenance (O&M) costs are usually estimated for one year of operation. These can be divided into fixed O&M and variable O&M costs. These costs are discussed in this section. The fixed O&M (FOM) costs include the costs of plant maintenance (materials and labor) and labor (operating labor, administrative, and support labor). Operating labor costs are estimated based on correlations between labor hour requirements and the plant's daily capacity[4].

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[4] Peters, T., Timmerhaus, K., & West, R. (2003). *Plant Design and Economics for Chemical Engineers* (5th ed.). New York: McGraw Hill.

Table 10: Fixed operating and maintenance cost parameters and their deterministic values.

Fixed O&M Costs	Units	Nominal Value
Major processing steps	#	19
Cor'l'n for Op. Labor	Hrs./day-step	14
Operating Labor Rate	$/hr	$46.43
Total Maintenance Cost	%TPC	2.5%
Maint. Cost allocated to labor	% FOM maint.	40%
Admin. & Support labor cost	% total labor	30%

The variable O&M (VOM) costs include the cost of materials consumed (make-up acid, process water, etc.), utilities, and services used (waste transport and disposal). These quantities are determined in the CHEMCAD performance model. The unit cost of each item (e.g. dollars per tonne of coal ash) is a parameter specified as a cost input to the model. The total annual cost of each item is then calculated by multiplying the unit cost by the total annual quantity used or consumed. Total annual quantities are dependent upon the facility's annual operating capacity factor. The individual components of variable O&M costs are explained in more detail below. Note that the unit costs for all of the consumables are based on publicly available sources.

Table 11: Variable operating and maintenance cost components and their deterministic values.

Variable O&M Costs	Units	Nominal Value
Coal Ash	$/tonne	$-
Makeup Nitric Acid	$/tonne	$600
Dilution Water	$/tonne	$0.3
Leached Ash Disposal	$/tonne	$10.3
Natural Gas	$/GJ	$1.26
Electricity	$/MWh	$6.73
SMBS Price	$/tonne	$280
HCl Price	$/tonne	$115
NaOH Price	$/tonne	$320
Extractant Price	$/kg	$8.30
Wastewater Disposal	$/kliter	$0.30
Hazardous Wastewater Disposal	$/kliter	$18.79
Avg. Price for Salable Ash	$/tonne	$(30.00)
Selling Price for Ferric Chloride	$/tonne	$(400.00)
Conversion Reagent Price	$/tonne	$200.00

The nominal (default) values of all major operating and maintenance (O&M) costs in the REE recovery process model are summarized in Table 12. Note that the cost of coal ash is zero for the deterministic case.

Table 12: Variable and fixed operating cost component results for a rare earth recovery plant.

Variable Cost Component	Variable O&M Cost ($1000/yr)	Fixed Cost Component	Fixed O&M Cost ($1000/yr)
Coal Ash	$0	Operating Labor	$4,508
Makeup Nitric Acid	$10,678	Maintenance Material	$1,903
Makeup Water	$95	Maintenance Labor	$761
Solid waste disposal	$787	Admin. & Support Labor	$1,581
Natural Gas	$894	**REE Process Total Fixed Costs ($1000/yr)**	**$8,753**

Variable Cost Component	Variable O&M Cost ($1000/yr)	Fixed Cost Component	Fixed O&M Cost ($1000/yr)
Electricity	$2,628		
Solvent Extraction Reagent	$24		
Caustic	$197		
Hydrochloric Acid	$2		
Conversion Reagent	$13,797		
Hazardous Disposal	$14		
Purification	$209		
REE Process Total Variable Costs ($/yr)	**~$29,325**	**Total O&M Costs ($/yr)**	**~$38,078**

A discounted cash flow model was constructed using the capital and manufacturing costs presented. This model used the rare earth oxide selling prices listed in Table 13, which has some prices redacted as they are values proprietary to the marketing consultant source.

Table 13: Rare earth oxide prices used in the economic assessment

Element	Value US$/kg, Oxide Basis
Lu	XXX.x (proprietary price)
Sc	4200.0
Ce	2.0
Dy	230.0
Er	34.0
Eu	150.0
Gd	32.0
Ho	XX.x (proprietary price)
La	2.0
Nd	42.0
Pr	52.0
Sm	2.0
Tb	400.0
Tm	XX.x (proprietary price)
Y	6.0
Yb	XX.x (proprietary price)

The discounted cash flow model used assumptions as shown in Table 14. For a 20 year project, the net present value equates to about $54 million, with a simple payback period (FCI/annual cash flow) of 3.8 years. The rate of return is 27.6%. The discounted payback period is just over 12 years.

Table 14: Financial assumptions used in the discounted cash flow model

Capital Cost Escalation (nominal annual rate)	3.6%
Equity	50%
Loan Interest	6%
Loan Term, years	10
Working Capital (% of FCI)	0.00%
Type of Depreciation	DDB
General Plant	150
Depreciation Period (Years)	20
Construction Period (Years)	3
% Spent in Year -3	10.00%
% Spent in Year -2	60.00%
% Spent in Year -1	30.00%
Internal Rate of Return	15.00%
Income Tax Rate	38.00%
Cost Year Increment	annual average

A key takeaway from the economic analysis is that rare earth oxide sales alone are not sufficient to cover costs for the process. Revenues from REO sales are roughly $34 million against O&M costs of $38 million, so profits are entirely dependent upon the sale of byproducts; primarily the ferric chloride byproduct. Lesser revenue is also realized from sales of upgraded fly ash after leaching (assuming 50% of the fly ash is placeable), and sales of zeolite which are assumed only to cover the cost of pretreatment of the fly ash with caustic. Another item of note is the high value of scandium, which represents over 90% of the value of REO in this feedstock. Scandium is a very small market with niche applications, and the placement of large volumes of scandium at the estimated price needs to be validated.

3.0 Technology Development and Commercialization Plan

The economic analysis performed suggests that byproducts are critical to the economic sustainability of REE from coal sources. In fact, when considering marginal REE sources, the potential byproducts available from coal sources may make it more attractive than higher grade sources such as monazite sands. Beyond scale up of the coal REE recovery technology, there needs to be a transition to development and validation of co-products that are easily placed in the market to subsidize REE recovery. Obvious targets from coal sources include aluminum and iron products due to their prevalence in the mineral composition of coal, and Battelle and Rare Earth Salts' processes are capable of generating high purity ferric chloride and aluminum oxide products. Future work should place equal emphasis on these subsidizing co-products as the rare earth products.

3.1   Product Validation

As with any new technology, validation of the generated products with potential offtake groups is critical to commercialization because it resolves purity or product issues early in the development process and begins to form relationships with key commercialization partners. The most important products in this process, from a revenue standpoint, are scandium oxide and ferric chloride. Scandium is critical due to its high value, and ferric chloride is critical due to its high volume. We expect to be able to generate a high purity aluminum oxide product at high volumes which could be another important product. Other rare earth oxides, some base metals such as copper, zeolite products, and high-quality fly ash are lesser byproducts that can contribute to the process profitability.

On this project, products have been produced at a commercially relevant purity, and outreach to potential offtake groups can begin. Offtake groups will generally ask for independent analysis along with samples, which are easily handled under non-disclosure and material transfer agreements that the project team is familiar with implementing. Feedback from these groups on the purity and quality is a critical part of the sample process, and will be used to improve and tailor the process for production of salable products.

3.2   Technology Readiness Level

RES' electrowinning technology for the purification of REEs recovered from recycled fluorescent light bulbs to a standard purity of 99.9% is currently classified as a TRL 7, with a fully integrated prototype validated for recycling of REE from lightbulbs. RES's process is among the first low-cost, REE separation units recycling REEs from feedstock materials, and is expected to operate at a production rate of 18 metric tons per month. However, the process concept for using electrowinning purification technology capable of separating and purifying REEs and critical materials (CM) recovered from coal-based feedstocks to concentrations exceeding 90% purity is currently being implemented by Battelle and RES, and therefore is a TRL of 3.

Battelle's ADP and solvent extraction are currently classified as a TRL 3 technology, with preliminary design in place to build a high-fidelity, bench-scale integrated system for advancement to TRL 5. The full, combined process of ADP, SX, chloride conversion and electrowinning will be advanced to TRL 5 after bench scale integrated work. It will be the first time that they are integrated in a continuous bench-scale unit, with ADP feeding SX, and SX feeding RES's chloride conversion and electrowinning processes to generate 90% purity or higher separated rare earth oxide (REO) and CM products. The technology maturation plan presented is outlined in Table 15.

The ultimate goal for this integrated technology is advancement from TRL 3 to TRL 9, which is a commercially operated plant capable of producing salable REO (including scandium oxide) and CM products at a concentration of 90 to 99.9% in an economical and environmentally benign manner.

Battelle anticipates commercialization will be in REE and CM recovery from coal sources, enabling domestic REE/CM sources and new outlets for coal products. Furthermore, the recycling acid leach of the ADP process, coupled with SX upgrading and RES's purification steps, can be applied to many other resource recovery or recycling operations.

Table 15: Expected technology maturation plan.

Year	Milestones	Performance Targets	TRL Achieved at Milestone
2019	Complete laboratory bench testing and bench-scale process design	Determine process parameter influence on bench-scale performance	3
2021	Complete continuous bench process demonstration (~12.5 lb/hr ash feed)	Integrated system performance on coal ash feedstocks at bench scale and demonstrate REE/CM product of 90-99.9% purity	5
2023	Execute pilot demonstration (~0.5 ton/hr, ~80x scale up)	Validate system performance, including REE/CM purity greater than 99.9%	6
2026	~30x (~15 ton/hr) scale-up pilot plant demonstration	Technology scale-up issues addressed	7
2027	Commercial unit demonstration (~15-30 ton/hr)	Technology commercial start-up	8
2027+	Long-term commercial operating system	Long-term, cost-efficient, and environmentally benign REE/CM supply technology	9

3.3 Future Technical and Commercial Development Work

The first step in the development of the integrated technology is to further develop Battelle's SX process for REE concentration. In previous research, coal fly ash has been fed to Battelle's ADP, reaching a combined REE product of 2% purity and a Fe/Al+Sc oxide material. The combined REE product contains some aluminum which will be selectively remove from REE during extraction step of the SX process producing two streams, a loaded organic extractant stream containing the REE and an aluminum nitrate stream at >50% purity. Next, the loaded organic extractant stream is stripped with acid to yield a purified REE solution. This solution is then roasted at 250°C to calcine REE, separating them from calcium and sodium (undesired species in the purification process). The result will be a purified mixed REO product at 40 to 50% purity. To achieve these purity results, Battelle plans to optimize extractant formulation and process variables such as residence time and stripping conditions to develop a set of operating conditions for bench-scale testing. Optimization will allow advancement of the SX technology to a TRL of 4. Continuous bench-scale testing using these process parameters will be conducted to further advance the TRL to 5. Battelle maintains two sets of bench-scale SX circuits for this research.

To advance RES's chloride conversion and electrowinning technologies for coal-ash applications from a TRL 3 to a TRL 5, RES will work first with a surrogate material with similar chemical composition that is representative of the effluent of Battelle's ADP and SX process. Research will be conducted to optimize the chloride conversion and electrowinning process parameters specifically for the SX process effluent, removing contaminants commonly associated with coal-ash REE/CM feedstocks while maintaining a salable REO (including scandium oxide) and aluminum oxide products of 90 to 99.9% purity, and producing ferric chloride as a key byproduct. After optimization of the chloride conversion and electrowinning processes using a surrogate material, Battelle will provide a derived material from a coal ash source that was processed using Battelle's ADP and SX technologies. In future efforts, RES

maintains the ability to operate continuous small-scale electrowinning cells, capable of demonstrating the optimized technology at a TRL of 5. Throughout this step, it will be important to monitor the enrichment of radionuclides like uranium and thorium, as avoiding enrichment to actionable levels will be a key step in maintaining an environmentally benign process. The ferric chloride byproduct is a key revenue source to support REE recovery from coal sources, and its development will contribute heavily to future commercialization.

It is expected that funding for the advancement to TRL 5 will come primarily from government sources, with some commercial investment supporting the project. At TRL 5, interaction will begin with mining/commodity groups who could be potential licensees/operators of the technology at the commercial scale. These interactions will include sharing of economic projections and models, samples, and demonstrations of the technology operating on coal feedstocks. Rare Earth Salts has already made significant progress in placing their REO products in the market, and as the owners of the purification process, it is expected that they will be able to add coal based sources into their product stream for sale with minimal modifications. This will be validated with outputs from the integrated bench scale system.

After bench scale integration, the proposed integrated technology will have advanced from TRL 3 to TRL 5. Advancement from a TRL of 5 to a TRL of 7 will be executed in two pilot demonstrations, each building upon the scale and complexity of the previous. Anticipated pilot scales are shown in Table 15. Battelle has operated the ADP technology in pilot-scale applications of 70 lb/hr in previous projects, and would follow a similar development approach for the scale-up of the ADP REE/CM recovery process. Similarly, Battelle has process development experience in piloting SX processes, as Battelle previously led the startup of a novel 100-gpm pilot SX system for treatment of mine drainage waters. RES has scale-up experience of its electrowinning process, as the process is currently being operated at an 18-ton/day scale for recovery of REEs from recycled lightbulbs[5]. RES will use a similar scale-up process for the electrowinning technology developed for recovery of REEs from coal sources.

The primary parameters to be evaluated in the two pilot-scale plants are stream scaling factors and process control conditions. The scales of the pilot plants to advance the integrated technology from TRL 5 to TRL 6, and subsequently from TRL 6 to TRL 7, will be chosen to allow for common process equipment design calculations to be used to size and specify the required unit operations, allowing for scale-up data to be confidently collected without requiring a capital-intensive plant to be built. At this point in the technology development process, industrial partners interested in operating the technology will be identified, and required funding for these pilots will gradually transition from primarily government sources to commercial partners. It is anticipated that the industrial groups most interested in the technology will be REE commodity producers, mining companies, and potentially large REE and CM product end users. Throughout the pilot demonstration, maintaining a salable REE and CM product of high purity (90 to 99.9%) will be a key pilot parameter to monitor, along with reagent feed rates and waste production rates.

Demonstrating that this integrated technology will be a cost-efficient and environmentally benign REE and CM supply technology will be key to identifying and securing investors in the technology. It is anticipated that a TRL of 7 would be reached by 2026, which is a time when REEs are anticipated to increase greatly in demand. This demand is expected to accelerate exponentially between 2020 and 2025, and China, which is the current primary supplier of REEs, will not be able to keep up with this demand, in turn allowing for alternative sourcing technologies to enter the market.

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[5] Rare Earth Salts, "Rare Earth Salts Commences Initial Production of Rare Earth Oxides in United States," 10 July 2017. [Online]. Available: http://rareearthsalts.com/.

APPENDIX A: Process Flow Diagrams and Stream Tables
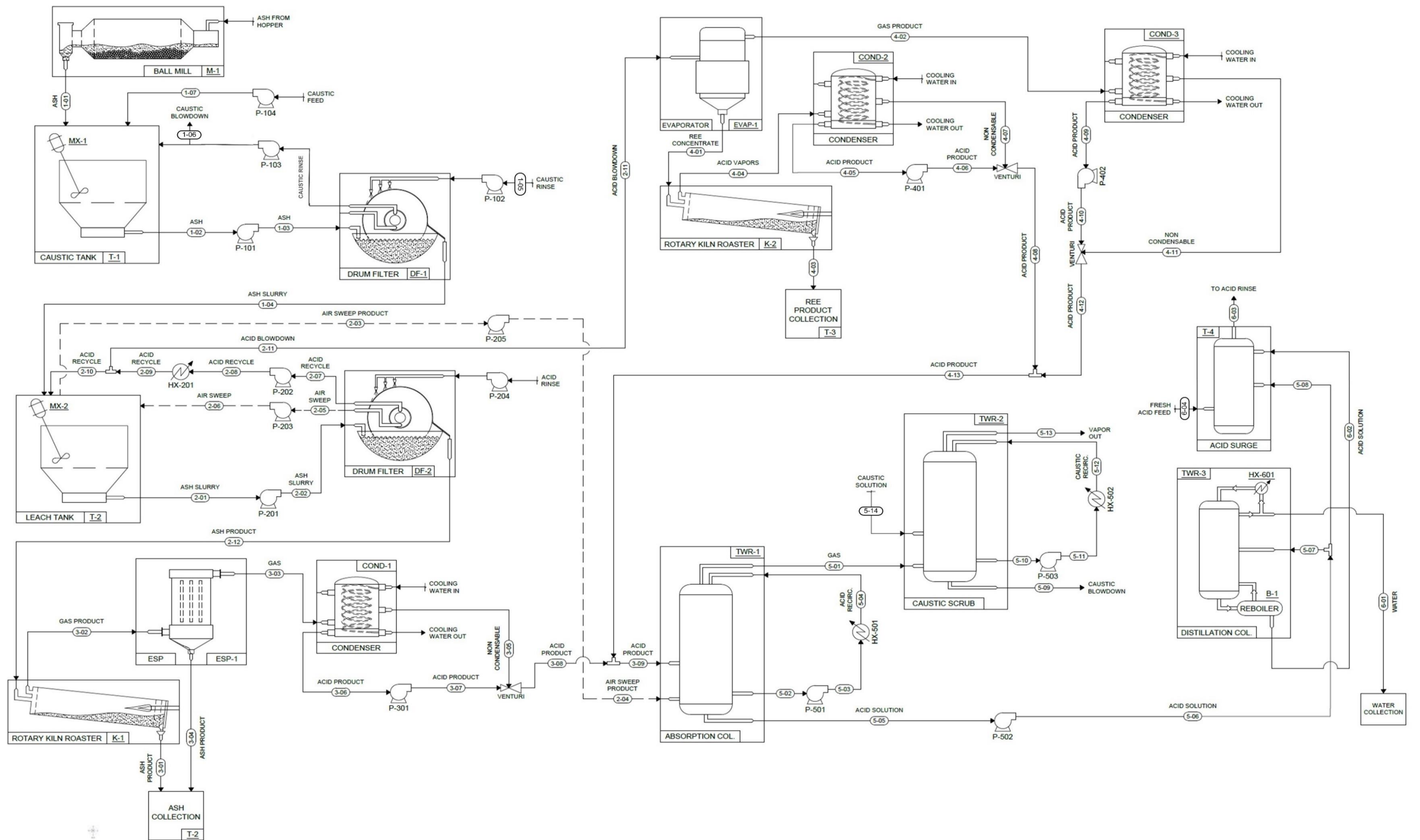
Figure 2: Preliminary PFD for Battelle's ADP Full-scale Process.

Table 16: Stream Table for Caustic Pretreatment and Acid Leaching Process.

PFD Stream No.	1-01	1-02	1-03	1-04	1-05	1-06	1-07	2-01	2-02	2-05	2-06	2-07	2-08	2-09	2-10	2-11	2-12
Stream Name	ASH	ASH	ASH	ASH SLURRY	CAUSTIC RINSE	CAUSTIC BLOWDOWN	CAUSTIC FEED	ASH SLURRY	ASH SLURRY	AIR SWEEP	AIR SWEEP	ACID RECYCLE	ACID RECYCLE	ACID RECYCLE	ACID RECYCLE	ACID BLOWDOWN	ASH PRODUCT
Temperature (°C)	25.0	90.0	90.0	77.3	25.0	84.4	25.1	79.8	79.9	25.0	153.7	79.9	79.9	80.0	80.0	80.0	79.9
Total rate (kg/h)	29984.8	43717.1	43717.1	37026.9	7418.2	17475.2	17099.1	455386.0	455386.0	841.2	841.2	413557.5	413557.5	413557.5	330846.0	82711.5	41828.6
Flow rates in kg/h																	
Aluminum Oxide	7375.9531	6638.3584	6638.3584	6638.3584	0	0	0	3171.6189	3171.6189	0	0	0	0	0	0	0	3171.6189
Antimony Trioxi	0.4681	0.4681	0.4681	0.4681	0	0	0	0.4681	0.4681	0	0	0	0	0	0	0	0.4681
Barium Oxide	15.497	15.497	15.497	15.497	0	0	0	0.1224	0.1224	0	0	0	0	0	0	0	0.1224
Boron Trioxide	61.8966	61.8966	61.8966	61.8966	0	0	0	61.8966	61.8966	0	0	0	0	0	0	0	61.8966
Calcium Oxide	433.1048	433.1048	433.1048	433.1048	0	0	0	4.3311	4.3311	0	0	0	0	0	0	0	4.3311
Cerium Nitrate	0	0	0	0	0	0	0	58.3481	58.3481	0	0	55.5393	55.5393	55.5393	44.4315	11.1079	2.8087
Cerium Oxide	6.4837	6.4837	6.4837	6.4837	0	0	0	0.3195	0.3195	0	0	0	0	0	0	0	0.3195
Chromium(III) Ox	7.6195	7.6195	7.6195	7.6195	0	0	0	7.6195	7.6195	0	0	0	0	0	0	0	7.6195
Cobalt(II) Oxide	1.914	1.914	1.914	1.914	0	0	0	0.3741	0.3741	0	0	0	0	0	0	0	0.3741
Copper(II) Oxid	5.1798	5.1798	5.1798	5.1798	0	0	0	0.0518	0.0518	0	0	0	0	0	0	0	0.0518
Dysprosium Nitr	0	0	0	0	0	0	0	4.5504	4.5504	0	0	4.3313	4.3313	4.3313	3.4651	0.8663	0.219
Dysprosium Oxid	0.6133	0.6133	0.6133	0.6133	0	0	0	0.0332	0.0332	0	0	0	0	0	0	0	0.0332
Erbium Nitrate	0	0	0	0	0	0	0	2.7212	2.7212	0	0	2.5902	2.5902	2.5902	2.0722	0.518	0.131
Erbium Oxide	0.3651	0.3651	0.3651	0.3651	0	0	0	0.0141	0.0141	0	0	0	0	0	0	0	0.0141
Europium Nitrat	0	0	0	0	0	0	0	1.1252	1.1252	0	0	1.0711	1.0711	1.0711	0.8569	0.2142	0.0542
Europium Oxide	0.1434	0.1434	0.1434	0.1434	0	0	0	0.0038	0.0038	0	0	0	0	0	0	0	0.0038
Gadolinium Nitr	0	0	0	0	0	0	0	5.1218	5.1218	0	0	4.8752	4.8752	4.8752	3.9002	0.975	0.2465
Gadolinium Oxid	0.646	0.646	0.646	0.646	0	0	0	0.0017	0.0017	0	0	0	0	0	0	0	0.0017
Gallium(III) Ox	2.7155	2.7155	2.7155	2.7155	0	0	0	0.0272	0.0272	0	0	0	0	0	0	0	0.0272
Germanium Dioxi	4.334	4.334	4.334	4.334	0	0	0	4.334	4.334	0	0	0	0	0	0	0	4.334
Holmium Nitrate	0	0	0	0	0	0	0	0.8972	0.8972	0	0	0.854	0.854	0.854	0.6832	0.1708	0.0432
Holmium Oxide	0.1269	0.1269	0.1269	0.1269	0	0	0	0.0118	0.0118	0	0	0	0	0	0	0	0.0118
Iron(iii) oxide	5497.0918	5497.0918	5497.0918	5497.0918	0	0	0	3891.5186	3891.5186	0	0	0	0	0	0	0	3891.5186
Lanthanum Nitrat	0	0	0	0	0	0	0	22.5458	22.5458	0	0	21.4605	21.4605	21.4605	17.1684	4.2921	1.0853
Lanthanum Oxide	2.8276	2.8276	2.8276	2.8276	0	0	0	0.1346	0.1346	0	0	0	0	0	0	0	0.1346
Lead(II) Oxide	2.8465	2.8465	2.8465	2.8465	0	0	0	0.8674	0.8674	0	0	0	0	0	0	0	0.8674
Lithium Oxide	11.6419	11.6419	11.6419	11.6419	0	0	0	5.9554	5.9554	0	0	0	0	0	0	0	5.9554
Lutetium Nitrat	0	0	0	0	0	0	0	0.1472	0.1472	0	0	0.1402	0.1402	0.1402	0.1121	0.028	0.0071
Lutetium Oxide	0.0259	0.0259	0.0259	0.0259	0	0	0	0.0066	0.0066	0	0	0	0	0	0	0	0.0066
Magnesium Oxide	216.1247	216.1247	216.1247	216.1247	0	0	0	2.1612	2.1612	0	0	0	0	0	0	0	2.1612
Molybdenum Trio	1.0266	1.0266	1.0266	1.0266	0	0	0	1.0266	1.0266	0	0	0	0	0	0	0	1.0266
Neodymium Nitra	0	0	0	0	0	0	0	23.2669	23.2669	0	0	22.1469	22.1469	22.1469	17.7175	4.4294	1.12
Neodymium Oxide	2.8693	2.8693	2.8693	2.8693	0	0	0	0.0455	0.0455	0	0	0	0	0	0	0	0.0455
Nickel(II) Oxid	4.9758	4.9758	4.9758	4.9758	0	0	0	1.6513	1.6513	0	0	0	0	0	0	0	1.6513
Nitric Acid	0	0	0	0	0	2249.5906	0	35772.707	35772.707	0	0	34050.707	34050.707	34050.707	27240.5684	6810.1411	1722
Potassium Oxide	557.3683	557.3683	557.3683	557.3683	0	0	0	187.6458	187.6458	0	0	0	0	0	0	0	187.6458
Praseodymium Ni	0	0	0	0	0	0	0	5.8772	5.8772	0	0	5.5942	5.5942	5.5942	4.4754	1.1188	0.2829
Praseodymium Ox	0.7321	0.7321	0.7321	0.7321	0	0	0	0.0258	0.0258	0	0	0	0	0	0	0	0.0258
Rubidium Oxide	4.2047	4.2047	4.2047	4.2047	0	0	0	1.8307	1.8307	0	0	0	0	0	0	0	1.8307
Samarium Nitrat	0	0	0	0	0	0	0	4.6929	4.6929	0	0	4.467	4.467	4.467	3.5736	0.8934	0.2259
Samarium Oxide	0.5933	0.5933	0.5933	0.5933	0	0	0	0.0137	0.0137	0	0	0	0	0	0	0	0.0137
Scandium Nitrate	0	0	0	0	0	0	0	25.5296	25.5296	0	0	24.3007	24.3007	24.3007	19.4405	4.8601	1.2289
Scandium(III) Ox	1.8341	1.8341	1.8341	1.8341	0	0	0	0.0183	0.0183	0	0	0	0	0	0	0	0.0183
Silicon Dioxide	14636.8301	13173.1475	13173.1475	13173.1475	0	0	0	13173.1475	13173.1475	0	0	0	0	0	0	0	13173.1475
Strontium Oxide	39.2441	39.2441	39.2441	39.2441	0	0	0	0.3924	0.3924	0	0	0	0	0	0	0	0.3924

PFD Stream No.	1-01	1-02	1-03	1-04	1-05	1-06	1-07	2-01	2-02	2-05	2-06	2-07	2-08	2-09	2-10	2-11	2-12
Stream Name	ASH	ASH	ASH	ASH SLURRY	CAUSTIC RINSE	CAUSTIC BLOWDOWN	CAUSTIC FEED	ASH SLURRY	ASH SLURRY	AIR SWEEP	AIR SWEEP	ACID RECYCLE	ACID RECYCLE	ACID RECYCLE	ACID RECYCLE	ACID BLOWDOWN	ASH PRODUCT
Temperature (°C)	25.0	90.0	90.0	77.3	25.0	84.4	25.1	79.8	79.9	25.0	153.7	79.9	79.9	80.0	80.0	80.0	79.9
Total rate (kg/h)	29984.8	43717.1	43717.1	37026.9	7418.2	17475.2	17099.1	455386.0	455386.0	841.2	841.2	413557.5	413557.5	413557.5	330846.0	82711.5	41828.6
Flow rates in kg/h																	
Calcium Sulfate	677.8571	677.8571	677.8571	677.8571	0	0	0	2845.2681	2845.2681	0	0	2708.3044	2708.3044	2708.3044	2166.6438	541.6609	136.9635
Terbium Nitrate	0	0	0	0	0	0	0	0.8607	0.8607	0	0	0.8193	0.8193	0.8193	0.6554	0.1639	0.0414
Terbium Oxide	0.1088	0.1088	0.1088	0.1088	0	0	0	0	0	0	0	0	0	0	0	0	0
Titanium Dioxide	380.5496	380.5496	380.5496	380.5496	0	0	0	380.5496	380.5496	0	0	0	0	0	0	0	380.5496
Thorium(IV) Oxi	0.8342	0.8342	0.8342	0.8342	0	0	0	0.0001	0.0001	0	0	0	0	0	0	0	0.0001
Thulium Nitrate	0	0	0	0	0	0	0	0.3263	0.3263	0	0	0.3106	0.3106	0.3106	0.2485	0.0621	0.0157
Thulium Oxide	0.0484	0.0484	0.0484	0.0484	0	0	0	0.0061	0.0061	0	0	0	0	0	0	0	0.0061
Uranium(IV) Oxi	0.7078	0.7078	0.7078	0.7078	0	0	0	0.2656	0.2656	0	0	0	0	0	0	0	0.2656
Vanadium(V) Oxi	15.6466	15.6466	15.6466	15.6466	0	0	0	15.6466	15.6466	0	0	0	0	0	0	0	15.6466
Water	0	10399.2119	10399.2119	7345.1577	7418.1816	12669.6436	12581.29	289130	289130	0	0	275212	275212	275212	220169.4688	55042.3633	13917.9248
Ytterbium Nitra	0	0	0	0	0	0	0	1.9862	1.9862	0	0	1.8906	1.8906	1.8906	1.5125	0.3781	0.0956
Ytterbium Oxide	0.3117	0.3117	0.3117	0.3117	0	0	0	0.052	0.052	0	0	0	0	0	0	0	0.052
Yttrium Oxide	4.5102	4.5102	4.5102	4.5102	0	0	0	0.0451	0.0451	0	0	0	0	0	0	0	0.0451
Yttrium(III) Nit	0	0	0	0	0	0	0	45.6364	45.6364	0	0	43.4396	43.4396	43.4396	34.7517	8.6879	2.1968
Zinc Oxide	6.8935	6.8935	6.8935	6.8935	0	0	0	0.0689	0.0689	0	0	0	0	0	0	0	0.0689
Barium Nitrate	0	0	0	0	0	0	0	109.9911	109.9911	0	0	104.6964	104.6964	104.6964	83.7571	20.9393	5.2947
Calcium Nitrate	0	0	0	0	0	0	0	5266.146	5266.146	0	0	5012.6475	5012.6475	5012.6475	4010.1179	1002.5295	253.498
Potassium Nitrat	0	0	0	0	0	0	0	3331.3743	3331.3743	0	0	3171.011	3171.011	3171.011	2536.8091	634.2022	160.3634
Magnesium Nitrat	0	0	0	0	0	0	0	3304.9312	3304.9312	0	0	3145.8408	3145.8408	3145.8408	2516.6729	629.1681	159.0905
Nitrogen Dioxide	0	0	0	0	0	0	0	850.6254	850.6254	0	0	809.6785	809.6785	809.6785	647.7429	161.9357	40.9468
Aluminum Nitrat	0	0	0	0	0	0	0	60795.7031	60795.7031	0	0	57869.1641	57869.1641	57869.1641	46295.332	11573.832	2926.5405
Arsenic Acid	0	0	0	0	0	0	0	0.0313	0.0313	0	0	0.0297	0.0297	0.0297	0.0238	0.0059	0.0015
Cobalt(II) Nitr	0	0	0	0	0	0	0	15.7802	15.7802	0	0	15.0206	15.0206	15.0206	12.0165	3.0041	0.7596
Copper(II) Nitr	0	0	0	0	0	0	0	50.7519	50.7519	0	0	48.3088	48.3088	48.3088	38.6471	9.6618	2.4431
Iron(III) Nitra	0	0	0	0	0	0	0	20414.041	20414.041	0	0	19431.3652	19431.3652	19431.3652	15545.0928	3886.2727	982.6768
Gallium(III) Ni	0	0	0	0	0	0	0	30.7912	30.7912	0	0	29.309	29.309	29.309	23.4472	5.8618	1.4822
Nickel(II) Nitr	0	0	0	0	0	0	0	34.1317	34.1317	0	0	32.4887	32.4887	32.4887	25.991	6.4977	1.643
Lead(II) Nitrat	0	0	0	0	0	0	0	12.3271	12.3271	0	0	11.7337	11.7337	11.7337	9.387	2.3467	0.5934
Uranyl Nitrate	0	0	0	0	0	0	0	2.7089	2.7089	0	0	2.5785	2.5785	2.5785	2.0628	0.5157	0.1304
Zinc Nitrate	0	0	0	0	0	0	0	66.6663	66.6663	0	0	63.4571	63.4571	63.4571	50.7657	12.6914	3.2091
Lithium Nitrate	0	0	0	0	0	0	0	110.1456	110.1456	0	0	104.8435	104.8435	104.8435	83.8748	20.9687	5.3021
Rubidium Nitrat	0	0	0	0	0	0	0	15.7223	15.7223	0	0	14.9655	14.9655	14.9655	11.9724	2.9931	0.7568
Strontium Nitra	0	0	0	0	0	0	0	333.0667	333.0667	0	0	317.0337	317.0337	317.0337	253.627	63.4067	16.0329
Thorium(IV) Nit	0	0	0	0	0	0	0	6.3657	6.3657	0	0	6.0593	6.0593	6.0593	4.8474	1.2119	0.3064
Nitrogen	0	0	0	0	0	0	0	0.0135	0.0135	645.2747	645.2747	0.0129	0.0129	0.0129	0.0103	0.0026	0.0007
Oxygen	0	0	0	0	0	0	0	2.1136	2.1136	195.9254	195.9254	2.0119	2.0119	2.0119	1.6095	0.4024	0.1017
Nitric Oxide	0	0	0	0	0	0	0	1.5943	1.5943	0	0	1.5176	1.5176	1.5176	1.2141	0.3035	0.0767
dinitrogen pent	0	0	0	0	0	0	0	199.7424	199.7424	0	0	190.1274	190.1274	190.1274	152.1019	38.0255	9.6151
Nitrous Acid	0	0	0	0	0	0	0	896.2382	896.2382	0	0	853.0957	853.0957	853.0957	682.4766	170.6191	43.1425
Sodium Hydroxide	0	1644.4791	1644.4791	564.0563	0	1427.9097	4517.8169	5.6838	5.6838	0	0	5.4102	5.4102	5.4102	4.3282	1.082	0.2736
Sodium Aluminat	0	1418.7799	1418.7799	486.6414	0	1231.934	0	2058.7695	2058.7695	0	0	1959.6659	1959.6659	1959.6659	1567.7328	391.9332	99.1036
Sodium Silicate	0	2471.1018	2471.1018	847.5879	0	2145.6709	0	3585.7781	3585.7781	0	0	3413.1685	3413.1685	3413.1685	2730.5349	682.6337	172.6097
Sodium Nitrate	0	0	0	0	0	0	0	5019.1694	5019.1694	0	0	4777.5601	4777.5601	4777.5601	3822.0481	955.5119	241.6092

PFD Stream No.	3-01	3-02	3-03	3-04	3-05	3-06	3-07	3-08	3-09
Stream Name	ASH PRODUCT	GAS PRODUCT	GAS	ASH PRODUCT	NON CONDENSABLE	ACID PRODUCT	ACID PRODUCT	ACID PRODUCT	ACID PRODUCT
Temperature (°C)	155.0	155.0	155.0	155.0	40.0	40.0	40.1	40.0	40.1
Total rate (kg/h)	22229.2	20440.6	19270.6	1170.0	915.8	18354.8	18354.8	19270.6	92028.2
Flow rates in kg/h									
Aluminum Oxide	3645.2092	191.8531	0	191.8531	0	0	0	0	0
Antimony Trioxi	0.4447	0.0234	0	0.0234	0	0	0	0	0
Barium Oxide	0.1163	0.0061	0	0.0061	0	0	0	0	0
Boron Trioxide	58.8018	3.0948	0	3.0948	0	0	0	0	0
Calcium Oxide	4.1145	0.2166	0	0.2166	0	0	0	0	0
Cerium Nitrate	2.6683	0.1404	0	0.1404	0	0	0	0	0
Cerium Oxide	0.3035	0.0160	0	0.0160	0	0	0	0	0
Chromium(III) Ox	7.2385	0.3810	0	0.3810	0	0	0	0	0
Cobalt(II) Oxide	0.3554	0.0187	0	0.0187	0	0	0	0	0
Copper(II) Oxid	0.0492	0.0026	0	0.0026	0	0	0	0	0
Dysprosium Nitr	0.2081	0.0110	0	0.0110	0	0	0	0	0
Dysprosium Oxid	0.0315	0.0017	0	0.0017	0	0	0	0	0
Erbium Nitrate	0.1245	0.0066	0	0.0066	0	0	0	0	0
Erbium Oxide	0.0134	0.0007	0	0.0007	0	0	0	0	0
Europium Nitrat	0.0515	0.0027	0	0.0027	0	0	0	0	0
Europium Oxide	0.0036	0.0002	0	0.0002	0	0	0	0	0
Gadolinium Nitr	0.2342	0.0123	0	0.0123	0	0	0	0	0
Gadolinium Oxid	0.0016	0.0001	0	0.0001	0	0	0	0	0
Gallium(III) Ox	0.0258	0.0014	0	0.0014	0	0	0	0	0
Germanium Dioxi	4.1173	0.2167	0	0.2167	0	0	0	0	0
Holmium Nitrate	0.0410	0.0022	0	0.0022	0	0	0	0	0
Holmium Oxide	0.0112	0.0006	0	0.0006	0	0	0	0	0
Iron(iii) oxide	3989.7245	209.9855	0	209.9855	0	0	0	0	0
Lanthanum Nitrat	1.0310	0.0543	0	0.0543	0	0	0	0	0
Lanthanum Oxide	0.1279	0.0067	0	0.0067	0	0	0	0	0
Lead(II) Oxide	0.8240	0.0434	0	0.0434	0	0	0	0	0
Lithium Oxide	5.6576	0.2978	0	0.2978	0	0	0	0	0
Lutetium Nitrat	0.0067	0.0004	0	0.0004	0	0	0	0	0
Lutetium Oxide	0.0063	0.0003	0	0.0003	0	0	0	0	0
Magnesium Oxide	2.0531	0.1081	0	0.1081	0	0	0	0	0
Molybdenum Trio	0.9753	0.0513	0	0.0513	0	0	0	0	0
Neodymium Nitra	1.0640	0.0560	0	0.0560	0	0	0	0	0
Neodymium Oxide	0.0432	0.0023	0	0.0023	0	0	0	0	0
Nickel(II) Oxid	1.5687	0.0826	0	0.0826	0	0	0	0	0
Nitric Acid	9.1420	4910.0188	4909.5376	0.4812	33.236	4876.3018	4876.3018	4909.5381	24167.7813
Potassium Oxide	178.2635	9.3823	0	9.3823	0	0	0	0	0
Praseodymium Ni	0.2688	0.0141	0	0.0141	0	0	0	0	0
Praseodymium Ox	0.0245	0.0013	0	0.0013	0	0	0	0	0
Rubidium Oxide	1.7392	0.0915	0	0.0915	0	0	0	0	0
Samarium Nitrat	0.2146	0.0113	0	0.0113	0	0	0	0	0
Samarium Oxide	0.0130	0.0007	0	0.0007	0	0	0	0	0
Scandium Nitrate	1.1675	0.0614	0	0.0614	0	0	0	0	0
Scandium(III) Ox	0.0174	0.0009	0	0.0009	0	0	0	0	0
Silicon Dioxide	12514.4901	658.6574	0	658.6574	0	0	0	0	0
Strontium Oxide	0.3728	0.0196	0	0.0196	0	0	0	0	0

PFD Stream No.	3-01	3-02	3-03	3-04	3-05	3-06	3-07	3-08	3-09
Stream Name	ASH PRODUCT	GAS PRODUCT	GAS	ASH PRODUCT	NON CONDENSABLE	ACID PRODUCT	ACID PRODUCT	ACID PRODUCT	ACID PRODUCT
Temperature (°C)	155.0	155.0	155.0	155.0	40.0	40.0	40.1	40.0	40.1
Total rate (kg/h)	22229.2	20440.6	19270.6	1170.0	915.8	18354.8	18354.8	19270.6	92028.2
Flow rates in kg/h									
Calcium Sulfate	130.1152	6.8482	0	6.8482	0	0	0	0	0
Terbium Nitrate	0.0393	0.0021	0	0.0021	0	0	0	0	0
Titanium Dioxide	361.5221	19.0275	0	19.0275	0	0	0	0	0
Thorium(IV) Oxi	0.0001	0.0000	0	0.0000	0	0	0	0	0
Thulium Nitrate	0.0149	0.0008	0	0.0008	0	0	0	0	0
Thulium Oxide	0.0058	0.0003	0	0.0003	0	0	0	0	0
Uranium(IV) Oxi	0.2523	0.0133	0	0.0133	0	0	0	0	0
Vanadium(V) Oxi	14.8643	0.7823	0	0.7823	0	0	0	0	0
Water	38.4984	13422.4022	13420.376	2.0262	37.7919	13382.585	13382.585	13420.375	66553.3516
Ytterbium Nitra	0.0908	0.0048	0	0.0048	0	0	0	0	0
Ytterbium Oxide	0.0494	0.0026	0	0.0026	0	0	0	0	0
Yttrium Oxide	0.0428	0.0023	0	0.0023	0	0	0	0	0
Yttrium(III) Nit	2.0870	0.1098	0	0.1098	0	0	0	0	0
Zinc Oxide	0.0655	0.0034	0	0.0034	0	0	0	0	0
Barium Nitrate	5.0299	0.2647	0	0.2647	0	0	0	0	0.0001
Calcium Nitrate	240.8214	12.6763	0.0015	12.6748	0	0.0015	0.0015	0.0015	0.0028
Potassium Nitrat	152.3441	8.0191	0.0010	8.0181	0	0.001	0.001	0.001	0.0017
Magnesium Nitrat	151.1348	7.9555	0.0010	7.9545	0	0.001	0.001	0.001	0.0017
Nitrogen Dioxide	0.0068	40.9400	40.9396	0.0004	3.3457	37.5939	37.5939	40.9396	202.8738
Aluminum Nitrat	139.0096	7.3172	0.0009	7.3163	0	0.0009	0.0009	0.0009	0.0059
Arsenic Acid	0	0.0015	0.0015	0	0	0.0015	0.0015	0.0015	0.0074
Cobalt(II) Nitr	0.7216	0.0380	0	0.0380	0	0	0	0	0
Copper(II) Nitr	2.3209	0.1222	0	0.1222	0	0	0	0	0
Iron(III) Nitra	46.6768	2.4570	0.0003	2.4567	0	0.0003	0.0003	0.0003	0.002
Gallium(III) Ni	1.4081	0.0741	0	0.0741	0	0	0	0	0
Nickel(II) Nitr	1.5609	0.0822	0	0.0822	0	0	0	0	0
Lead(II) Nitrat	0.5637	0.0297	0	0.0297	0	0	0	0	0
Uranyl Nitrate	0.1239	0.0065	0	0.0065	0	0	0	0	0
Zinc Nitrate	3.0486	0.1605	0	0.1605	0	0	0	0	0
Lithium Nitrate	5.0370	0.2651	0	0.2651	0	0	0	0	0.0001
Rubidium Nitrat	0.7190	0.0378	0	0.0378	0	0	0	0	0
Antimony Pentox	0	0	0	0	0	0	0	0	0
Strontium Nitra	15.2312	0.8017	0.0001	0.8016	0	0.0001	0.0001	0.0001	0.0002
Thorium(IV) Nit	0.2911	0.0153	0	0.0153	0	0	0	0	0
Nitrogen	0.0001	645.2752	645.2752	0.0000	645.1346	0.1405	0.1405	645.2751	645.2777
Oxygen	0	196.0271	196.0271	0	195.9424	0.0847	0.0847	196.0271	196.4295
Nitric Oxide	0	0.0767	0.0767	0	0.0767	0	0	0.0767	0.3803
dinitrogen pent	0.0114	9.6037	9.6031	0.0006	0.2714	9.3317	9.3317	9.6031	47.6153
Nitrous Acid	0.7084	42.4341	42.3968	0.0373	0.0151	42.3817	42.3817	42.3968	204.0146
Sodium Hydroxide	0.2599	0.0137	0	0.0137	0	0	0	0	0
Sodium Aluminat	91.9426	7.1609	2.3218	4.8391	0	2.3218	2.3218	2.3218	3.8186
Sodium Silicate	160.1373	12.4722	4.0439	8.4283	0	4.0439	4.0439	4.0439	6.6509
Sodium Nitrate	229.5286	12.0805	0	12.0805	0	0	0	0	0

Table 20: Stream Table for Roasting and REE Product Collection Process.

PFD Stream No.	4-01	4-02	4-03	4-04	4-05	4-06	4-07	4-08	4-09	4-10	4-11	4-12	4-13
Stream Name	REE CONCENTRATE	GAS PRODUCT	REE PRODUCT COLLECTION	ACID VAPORS	ACID PRODUCT	ACID PRODUCT	NON CONDENSABLE	ACID PRODUCT	ACID PRODUCT	ACID PRODUCT	NON CONDENSABLE	ACID PRODUCT	ACID PRODUCT
Temperature (°C)	120.0	120.0	153.6	153.6	40.0	40.1	40.0	40.1	40.0	40.0	40.0	40.0	40.0
Total rate (kg/h)	27331.5	55380.0	9877.9	17453.7	17377.6	17377.6	0.0	17377.6	55380.0	55380.0	0.0	55380.0	72757.6
Flow rates in kg/h													
Aluminum Oxide	0	0	2631.6851	0	0	0	0	0	0	0	0	0	0
Cerium Nitrate	11.1079	0	7.4423	0	0	0	0	0	0	0	0	0	0
Cerium Oxide	0	0	1.6255	0	0	0	0	0	0	0	0	0	0
Cobalt(II) Oxide	0	0	0.4725	0	0	0	0	0	0	0	0	0	0
Copper(II) Oxid	0	0	3.565	0	0	0	0	0	0	0	0	0	0
Dysprosium Nitr	0.8663	0	0.8663	0	0	0	0	0	0	0	0	0	0
Erbium Nitrate	0.518	0	0.518	0	0	0	0	0	0	0	0	0	0
Europium Nitrat	0.2142	0	0.2142	0	0	0	0	0	0	0	0	0	0
Gadolinium Nitr	0.975	0	0.975	0	0	0	0	0	0	0	0	0	0
Gallium(III) Ox	0	0	0.9817	0	0	0	0	0	0	0	0	0	0
Holmium Nitrate	0.1708	0	0.1708	0	0	0	0	0	0	0	0	0	0
Iron(iii) oxide	0	0	1218.8291	0	0	0	0	0	0	0	0	0	0
Lanthanum Nitrat	4.2921	0	4.2921	0	0	0	0	0	0	0	0	0	0
Lead(II) Oxide	0	0	1.5514	0	0	0	0	0	0	0	0	0	0
Lutetium Nitrat	0.028	0	0.0265	0	0	0	0	0	0	0	0	0	0
Lutetium Oxide	0	0	0.0008	0	0	0	0	0	0	0	0	0	0
Neodymium Nitra	4.4294	0	3.889	0	0	0	0	0	0	0	0	0	0
Neodymium Oxide	0	0	0.2753	0	0	0	0	0	0	0	0	0	0
Nickel(II) Oxid	0	0	0.9059	0	0	0	0	0	0	0	0	0	0
Nitric Acid	492.9568	6317.1846	149.6147	12987.4055	12941.0566	12941.0566	0	12941.0566	6317.1846	6317.1846	0	6317.1846	19258.2422
Praseodymium Ni	1.1188	0	1.1188	0	0	0	0	0	0	0	0	0	0
Samarium Nitrat	0.8934	0	0.8934	0	0	0	0	0	0	0	0	0	0
Scandium Nitrate	4.8601	0	0.8311	0	0	0	0	0	0	0	0	0	0
Scandium(III) Ox	0	0	1.2028	0	0	0	0	0	0	0	0	0	0
Calcium Sulfate	541.6608	0	541.6608	0	0	0	0	0	0	0	0	0	0
Terbium Nitrate	0.1639	0	0.1639	0	0	0	0	0	0	0	0	0	0
Thorium(IV) Oxi	0	0	0.5439	0	0	0	0	0	0	0	0	0	0
Thulium Nitrate	0.0621	0	0.0621	0	0	0	0	0	0	0	0	0	0
Uranium(IV) Oxi	0	0	0.3336	0	0	0	0	0	0	0	0	0	0
Water	6274.0234	48768.3398	84.889	4381.7076	4364.6406	4364.6406	0	4364.6406	48768.3398	48768.3398	0	48768.3398	53133
Ytterbium Nitra	0.3781	0	0.3781	0	0	0	0	0	0	0	0	0	0

Table 21: Stream Table for Roasting and REE Product Collection Process (continue).

PFD Stream No.	4-01	4-02	4-03	4-04	4-05	4-06	4-07	4-08	4-09	4-10	4-11	4-12	4-13
Stream Name	REE CONCENTRATE	GAS PRODUCT	REE PRODUCT COLLECTION	ACID VAPORS	ACID PRODUCT	ACID PRODUCT	NON CONDENSABLE	ACID PRODUCT	ACID PRODUCT	ACID PRODUCT	NON CONDENSABLE	ACID PRODUCT	ACID PRODUCT
Temperature (°C)	120.0	120.0	153.6	153.6	40.0	40.1	40.0	40.1	40.0	40.0	40.0	40.0	40.0
Total rate (kg/h)	27331.5	55380.0	9877.9	17453.7	17377.6	17377.6	0.0	17377.6	55380.0	55380.0	0.0	55380.0	72757.6
Flow rates in kg/h													
Yttrium(III) Nit	8.6879	0	8.6879	0	0	0	0	0	0	0	0	0	0
Zinc Oxide	0	0	0.1854	0	0	0	0	0	0	0	0	0	0
Barium Nitrate	20.9393	0	20.9393	0	0	0	0	0	0	0	0	0	0
Calcium Nitrate	1002.5289	0.0004	1002.528	0.0008	0.0008	0.0008	0	0.0008	0.0004	0.0004	0	0.0004	0.0012
Potassium Nitrat	634.2018	0.0002	634.2015	0.0005	0.0005	0.0005	0	0.0005	0.0002	0.0002	0	0.0002	0.0008
Magnesium Nitrat	629.1677	0.0002	629.1674	0.0005	0.0005	0.0005	0	0.0005	0.0002	0.0002	0	0.0002	0.0008
Nitrogen Dioxide	1.1318	160.8039	2.9133	11.1975	1.1302	1.1302	0	1.1302	160.8039	160.8039	0	160.8039	161.9342
Aluminum Nitrat	11573.8301	0.0045	578.6911	0.0005	0.0005	0.0005	0	0.0005	0.0045	0.0045	0	0.0045	0.005
Arsenic Acid	0.0012	0.0047	0.0001	0.0012	0.0012	0.0012	0	0.0012	0.0047	0.0047	0	0.0047	0.0059
Cobalt(II) Nitr	3.0041	0	1.8505	0	0	0	0	0	0	0	0	0	0
Copper(II) Nitr	9.6618	0	1.256	0	0	0	0	0	0	0	0	0	0
Iron(III) Nitra	3886.271	0.0015	194.3133	0.0002	0.0002	0.0002	0	0.0002	0.0015	0.0015	0	0.0015	0.0017
Gallium(III) Ni	5.8618	0	3.183	0	0	0	0	0	0	0	0	0	0
Nickel(II) Nitr	6.4977	0	4.282	0	0	0	0	0	0	0	0	0	0
Lead(II) Nitrat	2.3467	0	0.0446	0	0	0	0	0	0	0	0	0	0
Uranyl Nitrate	0.5157	0	0.0289	0	0	0	0	0	0	0	0	0	0
Zinc Nitrate	12.6914	0	12.2599	0	0	0	0	0	0	0	0	0	0
Lithium Nitrate	20.9687	0	20.9687	0	0	0	0	0	0	0	0	0	0
Rubidium Nitrat	2.9931	0	2.9931	0	0	0	0	0	0	0	0	0	0
Strontium Nitra	63.4067	0	63.4067	0.0001	0.0001	0.0001	0	0.0001	0	0	0	0	0.0001
Thorium(IV) Nit	1.2119	0	0.223	0	0	0	0	0	0	0	0	0	0
Nitrogen	0	0.0026	0	0	0	0	0	0	0.0026	0.0026	0	0.0026	0.0026
Oxygen	0	0.4024	0.0006	2.2761	0	0	0	0	0.4024	0.4024	0	0.4024	0.4024
Nitric Oxide	0	0.3035	0	0	0	0	0	0	0.3035	0.3035	0	0.3035	0.3035
dinitrogen pent	1.3967	36.6288	0.0089	1.3878	1.3835	1.3835	0	1.3835	36.6288	36.6288	0	36.6288	38.0123
Nitrous Acid	75.0676	95.5516	8.701	66.3666	66.0663	66.0663	0	66.0663	95.5516	95.5516	0	95.5516	161.6178
Sodium Hydroxide	1.082	0	1.082	0	0	0	0	0	0	0	0	0	0
Sodium Aluminat	391.6562	0.2769	390.4306	1.2256	1.2199	1.2199	0	1.2199	0.2769	0.2769	0	0.2769	1.4968
Sodium Silicate	682.1511	0.4822	680.0169	2.1347	2.1248	2.1248	0	2.1248	0.4822	0.4822	0	0.4822	2.607
Sodium Nitrate	955.5117	0	955.5117	0	0	0	0	0	0	0	0	0	0

Table 22: Stream Table for the Acid Recovery Process.

PFD Stream No.	5-01	5-02	5-03	5-04	5-05	5-06	5-07	5-08	5-09	5-10	5-11	5-12	5-13	5-14	6-01	6-02	6-03	6-04
Stream Name	GAS			ACID RECIRC.	ACID SOLUTION	ACID SOLUTION			CAUSTIC BLOWDOWN			CAUSTIC RECIRC.	VAPOR OUT	CAUSTIC SOLUTION	WATER COLLECTION	ACID SOLUTION	TO ACID RINSE	FRESH ACID FEED
Temperature (°C)	40.3	40.3	40.3	40.0	40.3	40.4	40.4	40.4	45.0	45.0	45.1	40.0	45.0	25.0	100.0	40.0	40.3	**25.0**
Total rate (kg/h)	919.4	255282.0	255282.0	255282.0	91248.0	91248.0	18249.6	72998.4	2933.4	10909.0	10909.0	10909.0	905.9	2948.8	10789.2	7291.1	80289.5	6734.0

								Flow rates in kg/h										
Cerium Nitrate	0	0.0001	0.0001	0.0001	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nitric Acid	28.9121	69355.2188	69355.2188	69355.2188	24790.3125	24790.3125	4958.0625	19832.25	0.0668	0.2485	0.2485	0.2485	0.0031	0	0	4958.0625	24790.3125	3529.9089
Water	32.0699	185322.6719	185322.6719	185322.6719	66241.7031	66241.7031	13248.3398	52993.3594	2794.603	10392.9746	10392.9746	10392.9746	55.2987	2849.9019	10788.9307	2290.157	55283.5156	3204.063
Yttrium(III) Nit	0	0.0001	0.0001	0.0001	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barium Nitrate	0	0.0002	0.0002	0.0002	0.0001	0.0001	0	0	0	0	0	0	0	0	0	0	0.0001	0
Calcium Nitrate	0	0.0077	0.0077	0.0077	0.0027	0.0027	0.0005	0.0022	0	0	0	0	0	0	0	0.0005	0.0027	0
Potassium Nitrat	0	0.0049	0.0049	0.0049	0.0017	0.0017	0.0003	0.0014	0	0	0	0	0	0	0	0.0003	0.0017	0
Magnesium Nitrat	0	0.0048	0.0048	0.0048	0.0017	0.0017	0.0003	0.0014	0	0	0	0	0	0	0	0.0003	0.0017	0
Aluminum Nitrat	0	0.0165	0.0165	0.0165	0.0059	0.0059	0.0012	0.0047	0	0	0	0	0	0	0	0.0012	0.0059	0
Arsenic Acid	0	0.0207	0.0207	0.0207	0.0074	0.0074	0.0015	0.0059	0	0	0	0	0	0	0	0.0015	0.0074	0
Copper(II) Nitr	0	0.0001	0.0001	0.0001	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Iron(III) Nitra	0	0.0055	0.0055	0.0055	0.002	0.002	0.0004	0.0016	0	0	0	0	0	0	0	0.0004	0.002	0
Zinc Nitrate	0	0.0001	0.0001	0.0001	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lithium Nitrate	0	0.0002	0.0002	0.0002	0.0001	0.0001	0	0	0	0	0	0	0	0	0	0	0.0001	0
Strontium Nitra	0	0.0005	0.0005	0.0005	0.0002	0.0002	0	0.0001	0	0	0	0	0	0	0	0	0.0002	0
Nitrogen	645.1054	2.3214	2.3214	2.3214	0.8298	0.8298	0.166	0.6638	0.0244	0.0906	0.0906	0.0906	645.0837	0	0.1663	0	0.6638	0
Oxygen	204.0455	1.4568	1.4568	1.4568	0.5207	0.5207	0.1041	0.4166	0.0153	0.0567	0.0567	0.0567	205.4891	0	0.1067	0	0.4166	0
Nitric Oxide	9.2512	0.0977	0.0977	0.0977	0.0349	0.0349	0.007	0.0279	0	0	0	0	0	0	0	0.007	0.0349	0
Nitrous Acid	0.0125	571.0746	571.0746	571.0746	204.1248	204.1248	40.825	163.2999	0.0148	0.0549	0.0549	0.0549	0	0	0	40.825	204.1248	0
Sodium Hydroxide	0	0	0	0	0	0	0	0	62.6228	232.8907	232.8907	232.8907	0	98.9031	0	0	0	0
Sodium Aluminat	0	10.6253	10.6253	10.6253	3.7979	3.7979	0.7596	3.0383	0	0	0	0	0	0	0	0.7596	3.7979	0
Sodium Silicate	0	18.5063	18.5063	18.5063	6.6149	6.6149	1.323	5.2919	0	0	0	0	0	0	0	1.323	6.6149	0
Sodium Nitrite	0	0	0	0	0	0	0	0	30.176	112.223	112.223	112.223	0	0	0	0	0	0
Sodium Nitrate	0	0	0	0	0	0	0	0	45.8361	170.4618	170.4618	170.4618	0	0	0	0	0	0
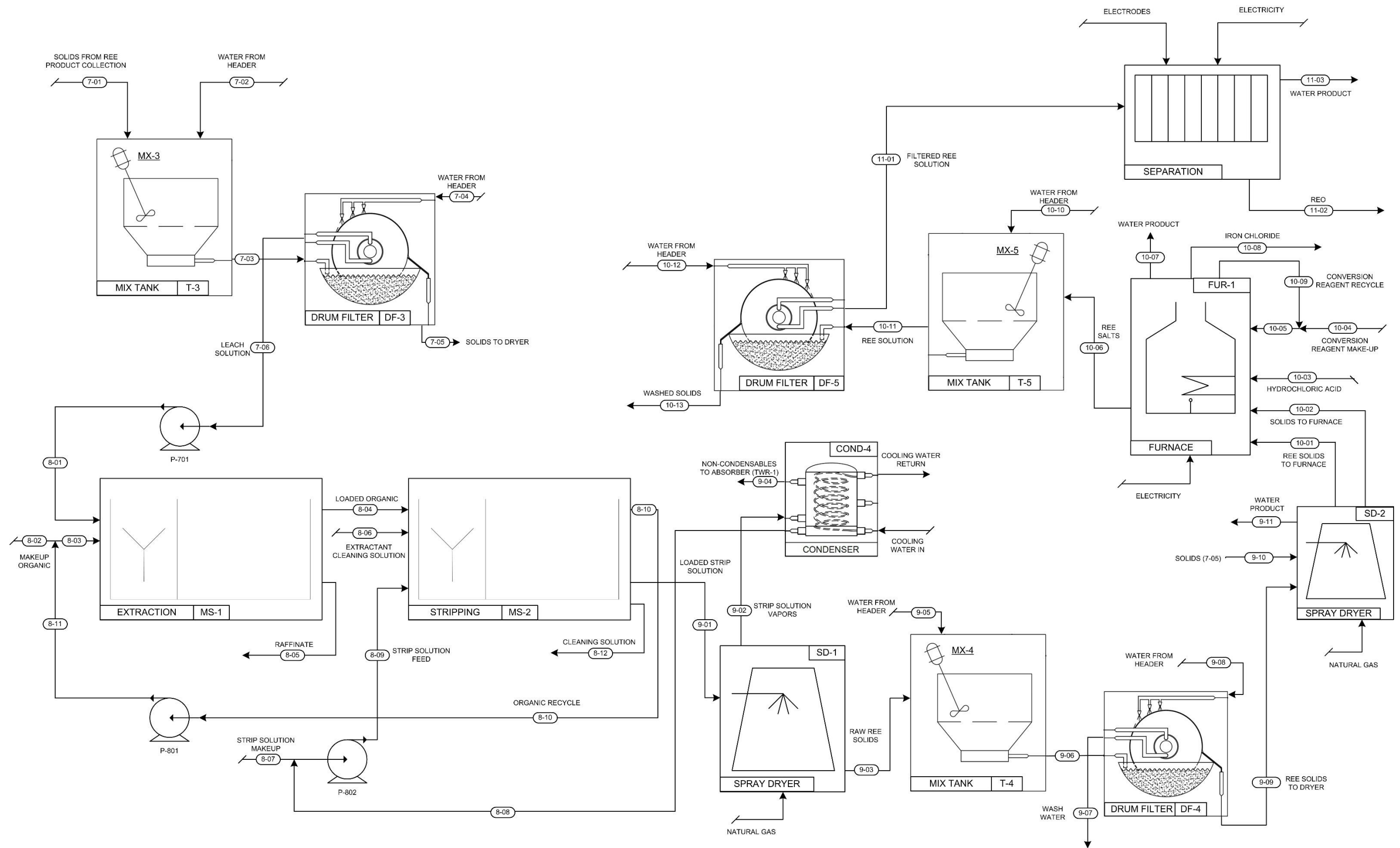
Figure 3: Preliminary PFD for Battelle's Upgrade SX and RES Purification Full-scale Processes.

Table 23: ADP Collected REE Product Washing Process.

PFD Stream No.	7-01	7-02	7-03	7-04	7-05	7-06
Stream Name	REE COLLECTION SOLIDS	WATER FROM HEADER		WATER FROM HEADER	SOLIDS TO DRYER	LEACH SOLUTION
Temperature (°C)	25	25	25	25	25	25
Total rate (kg/h)	9877.9	28460.7	33120.7	14230.4	13671.9	38897.1
Flow rates in kg/h						
Aluminum Oxide	2631.6851	0	2631.6851	0	2631.6851	0
Cerium Nitrate	7.4423	0	7.4423	0	0	7.4423
Cerium Oxide	1.6255	0	1.6255	0	1.6255	0
Cobalt(II) Oxide	0.4725	0	0.4725	0	0.4725	0
Copper(II) Oxid	3.565	0	3.565	0	3.565	0
Dysprosium Nitr	0.8663	0	0.8663	0	0	0.8663
Erbium Nitrate	0.518	0	0.518	0	0	0.518
Europium Nitrat	0.2142	0	0.2142	0	0	0.2142
Gadolinium Nitr	0.975	0	0.975	0	0	0.975
Gallium(III) Ox	0.9817	0	0.9817	0	0.9817	0
Holmium Nitrate	0.1708	0	0.1708	0	0	0.1708
Iron(iii) oxide	1218.8291	0	1218.8291	0	1218.8291	0
Lanthanum Nitrat	4.2921	0	4.2921	0	0	4.2921
Lead(II) Oxide	1.5514	0	1.5514	0	1.5514	0
Lutetium Nitrat	0.0265	0	0.0265	0	0	0.0265
Lutetium Oxide	0.0008	0	0.0008	0	0.0008	0
Neodymium Nitra	3.889	0	3.889	0	0	3.889
Neodymium Oxide	0.2753	0	0.2753	0	0.2753	0
Nickel(II) Oxid	0.9059	0	0.9059	0	0.9059	0
Nitric Acid	149.6147	0	149.6147	0	29.9229	119.6918
Praseodymium Ni	1.1188	0	1.1188	0	0	1.1188
Samarium Nitrat	0.8934	0	0.8934	0	0	0.8934
Scandium Nitrate	0.8311	0	0.8311	0	0	0.8311
Scandium(III) Ox	1.2028	0	1.2028	0	1.2028	0
Calcium Sulfate	541.6608	0	541.6608	0	541.6608	0
Terbium Nitrate	0.1639	0	0.1639	0	0	0.1639
Thorium(IV) Oxi	0.5439	0	0.5439	0	0.5439	0
Thulium Nitrate	0.0621	0	0.0621	0	0	0.0621
Uranium(IV) Oxi	0.3336	0	0.3336	0	0.3336	0
Water	84.889	28460.7402	28545.6292	14230.3701	8555.1973	34220.8008
Ytterbium Nitra	0.3781	0	0.3781	0	0	0.3781
Yttrium(III) Nit	8.6879	0	8.6879	0	0	8.6879
Zinc Oxide	0.1854	0	0.1854	0	0.1854	0
Barium Nitrate	20.9393	0	20.9393	0	0	20.9393
Calcium Nitrate	1002.528	0	1002.528	0	0	1002.528
Potassium Nitrat	634.2015	0	634.2015	0	0	634.2015
Magnesium Nitrat	629.1674	0	629.1674	0	0	629.1674
Nitrogen Dioxide	2.9133	0	2.9133	0	2.9133	0
Aluminum Nitrat	578.6911	0	578.6911	0	0	578.6911
Arsenic Acid	0.0001	0	0.0001	0	0	0.0001
Cobalt(II) Nitr	1.8505	0	1.8505	0	0	1.8505
Copper(II) Nitr	1.256	0	1.256	0	0	1.256
Iron(III) Nitra	194.3133	0	194.3133	0	0	194.3133
Gallium(III) Ni	3.183	0	3.183	0	0	3.183
Nickel(II) Nitr	4.282	0	4.282	0	0	4.282
Lead(II) Nitrat	0.0446	0	0.0446	0	0	0.0446
Uranyl Nitrate	0.0289	0	0.0289	0	0	0.0289
Zinc Nitrate	12.2599	0	12.2599	0	0	12.2599
Lithium Nitrate	20.9687	0	20.9687	0	0	20.9687
Rubidium Nitrat	2.9931	0	2.9931	0	0	2.9931
Strontium Nitra	63.4067	0	63.4067	0	0	63.4067
Thorium(IV) Nit	0.223	0	0.223	0	0	0.223
Oxygen	0.0006	0	0.0006	0	0.0006	0
dinitrogen pent	0.0089	0	0.0089	0	0.0089	0
Nitrous Acid	8.701	0	8.701	0	0	8.701
Sodium Hydroxide	1.082	0	1.082	0	0	1.082
Sodium Aluminat	390.4306	0	390.4306	0	0	390.4306
Sodium Silicate	680.0169	0	680.0169	0	680.0169	0
Sodium Nitrate	955.5117	0	955.5117	0	0	955.5117

Table 24: Battelle's Upgraded Solvent Extraction Process.

PFD Stream No.	8-01	8-02	8-03	8-04	8-05	8-06	8-07	8-08	8-09	8-10	8-11	8-12
Stream Name		ORGANIC MAKEUP		LOADED ORGANIC	RAFFINATE	EXTRACTANT CLEANING SOLUTION	STRIP SOLUTION MAKEUP		STRIP SOLUTION FEED	ORGANIC RECYCLE		CLEANING SOLUTION
Temperature (°C)	25.0		25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Total rate (kg/h)	38897.1	0.1	7516.4	7598.3	38815.1	968.0	57.8	900.2	958.0	7516.3	7516.3	1016.6
						Flow rates in kg/h						
Extractant	0	0.1125	1127.4565	1123.0704	0.0564	0	0	0	0	1127.3440	1127.3440	0.0281
Solvent 467	0	0	6388.9201	6388.9201	0	0	0	0	0	6388.9201	6388.9201	0
Nitric Acid	0	0	0	0	0	0	53.4939	42.3061	95.8000	0	0	0
WATER	0	0	0	0	0	871.2000	4.3368	857.8632	862.2000	0	0	871.2000
Phosphoric acid	0	0	0	0	0	48.4000	0	0	0	0	0	46.9057
Sulfuric acid	0	0	0	0	0	48.4000	0	0	0	0	0	46.9057
Cerium Nitrate	7.4423	0	0	0	0.0024	0	0	0	0	0	0	0
Ce+3	0	0	0	3.1964	0	0	0	0	0	0	0	0.0293
Dysprosium Nitr	0.8663	0	0	0	0.0248	0	0	0	0	0	0	0
Dy+3	0	0	0	0.3923	0	0	0	0	0	0	0	0.0002
Erbium Nitrate	0.518	0	0	0	0.0457	0	0	0	0	0	0	0
Er+3	0	0	0	0.2236	0	0	0	0	0	0	0	0.0001
Europium Nitrat	0.2142	0	0	0	0.0010	0	0	0	0	0	0	0
Eu+3	0	0	0	0.0958	0	0	0	0	0	0	0	0.0002
Gadolinium Nitr	0.975	0	0	0	0.0202	0	0	0	0	0	0	0
Gd+3	0	0	0	0.4374	0	0	0	0	0	0	0	0.0004
Holmium Nitrate	0.1708	0	0	0	0.0091	0	0	0	0	0	0	0
Ho+3	0	0	0	0.0760	0	0	0	0	0	0	0	0
Lanthanum Nitrat	4.2921	0	0	0	0.0015	0	0	0	0	0	0	0
La+3	0	0	0	1.8343	0	0	0	0	0	0	0	0.0346
Lutetium Nitrat	0.0265	0	0	0	0.0129	0	0	0	0	0	0	0
Lu+3	0	0	0	0.0066	0	0	0	0	0	0	0	0
Neodymium Nitra	3.889	0	0	0	0.0028	0	0	0	0	0	0	0
Nd+3	0	0	0	1.6973	0	0	0	0	0	0	0	0.0108
Nitric Acid	119.6918	0	0	0	390.3553	0	0	0	0	0	0	0
Praseodymium Ni	1.1188	0	0	0	0.0006	0	0	0	0	0	0	0
Pr+3	0	0	0	0.4820	0	0	0	0	0	0	0	0.0041
Samarium Nitrat	0.8934	0	0	0	0.0022	0	0	0	0	0	0	0
Sm+3	0	0	0	0.3984	0	0	0	0	0	0	0	0.0018
Scandium Nitrate	0.8311	0	0	0	0.3783	0	0	0	0	0	0	0
Sc+3	0	0	0	0.0881	0	0	0	0	0	0	0	0
Terbium Nitrate	0.1639	0	0	0	0.0040	0	0	0	0	0	0	0
Tb+3	0	0	0	0.0737	0	0	0	0	0	0	0	0
Thulium Nitrate	0.0621	0	0	0	0.0130	0	0	0	0	0	0	0
Tm+3	0	0	0	0.0234	0	0	0	0	0	0	0	0
Water	34220.8008	0	0	0	34220.8037	0	0	0	0	0	0	0
Ytterbium Nitra	0.3781	0	0	0	0.1165	0	0	0	0	0	0	0
Yb+3	0	0	0	0.1261	0	0	0	0	0	0	0	0.0001

Table 25: Battelle's Upgraded Solvent Extraction Process (continue).

PFD Stream No.	8-01	8-02	8-03	8-04	8-05	8-06	8-07	8-08	8-09	8-10	8-11	8-12
Stream Name		ORGANIC MAKEUP		LOADED ORGANIC	RAFFINATE	EXTRACTANT CLEANING SOLUTION	STRIP SOLUTION MAKEUP		STRIP SOLUTION FEED	ORGANIC RECYCLE		CLEANING SOLUTION
Temperature (°C)	25.0		25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Total rate (kg/h)	38897.1	0.1	7516.4	7598.3	38815.1	968.0	57.8	900.2	958.0	7516.3	7516.3	1016.6
Flow rates in kg/h												
Yttrium(III) Nit	8.6879	0	0	0	1.9129	0	0	0	0	0	0	0
Y+3	0	0	0	2.1910	0	0	0	0	0	0	0	0.0008
Barium Nitrate	20.9393	0	0	0	18.1466	0	0	0	0	0	0	0
Ba+2	0	0	0	1.4675	0	0	0	0	0	0	0	1.1748
Calcium Nitrate	1002.528	0	0	0	964.4615	0	0	0	0	0	0	0
Ca+2	0	0	0	9.2976	0	0	0	0	0	0	0	0.0071
Potassium Nitrat	634.2015	0	0	0	587.6963	0	0	0	0	0	0	0
K+	0	0	0	17.9842	0	0	0	0	0	0	0	12.7374
Magnesium Nitrat	629.1674	0	0	0	629.1674	0	0	0	0	0	0	0
Aluminum Nitrat	578.6911	0	0	0	451.0105	0	0	0	0	0	0	0
Al+3	0	0	0	16.1743	0	0	0	0	0	0	0	14.6577
Arsenic Acid	0.0001	0	0	0	0.0001	0	0	0	0	0	0	0
Cobalt(II) Nitr	1.8505	0	0	0	1.7393	0	0	0	0	0	0	0
Co+2	0	0	0	0.0358	0	0	0	0	0	0	0	0.0225
Copper(II) Nitr	1.256	0	0	0	1.2560	0	0	0	0	0	0	0
Iron(III) Nitra	194.3133	0	0	0	194.3133	0	0	0	0	0	0	0
Gallium(III) Ni	3.183	0	0	0	1.2438	0	0	0	0	0	0	0
Ga+3	0	0	0	0.4666	0	0	0	0	0	0	0	0.0247
Nickel(II) Nitr	4.282	0	0	0	4.2820	0	0	0	0	0	0	0
Lead(II) Nitrat	0.0446	0	0	0	0.0130	0	0	0	0	0	0	0
Pb+2	0	0	0	0.0198	0	0	0	0	0	0	0	0.0031
Uranyl Nitrate	0.0289	0	0	0	0.0001	0	0	0	0	0	0	0
U+6	0	0	0	0.0164	0	0	0	0	0	0	0	0.0163
Zinc Nitrate	12.2599	0	0	0	9.9316	0	0	0	0	0	0	0
Zn+2	0	0	0	0.8038	0	0	0	0	0	0	0	0.0106
Lithium Nitrate	20.9687	0	0	0	20.9687	0	0	0	0	0	0	0
Rubidium Nitrat	2.9931	0	0	0	2.9102	0	0	0	0	0	0	0
Rb+	0	0	0	0.0478	0	0	0	0	0	0	0	0.0098
Strontium Nitra	63.4067	0	0	0	61.9792	0	0	0	0	0	0	0
Sr+2	0	0	0	0.5910	0	0	0	0	0	0	0	0.1266
Thorium(IV) Nit	0.223	0	0	0	0.0443	0	0	0	0	0	0	0
Th+4	0	0	0	0.0864	0	0	0	0	0	0	0	0.0856
Nitrous Acid	8.701	0	0	0	8.7010	0	0	0	0	0	0	0
Sodium Hydroxide	1.082	0	0	0	1.0820	0	0	0	0	0	0	0
Sodium Aluminat	390.4306	0	0	0	390.4306	0	0	0	0	0	0	0
Sodium Nitrate	955.5117	0	0	0	851.9973	0	0	0	0	0	0	0
Na+	0	0	0	27.9992	0	0	0	0	0	0	0	22.6040

Table 26: High Temperature Roasting Process

PFD Stream No.	9-01	9-02	9-03	9-04	9-05	9-06	9-07	9-08	9-09	9-10	9-11
Stream Name	LOADED STRIP SOLUTION	STRIP SOLUTION VAPORS	RAW REE SOLIDS	NON-CONDENSABLE TO ABSORBER (TWR-1)	WATER FROM HEADER		WASH WATER	WATER FROM HEADER	REE SOLIDS TO DRYER	SOLIDS (7-05)	WATER PRODUCT
Temperature (°C)	25.0	250.0	250.0	250.0	25.0	122.8	122.0	25.0	25.0	25.0	250.0
Total rate (kg/h)	991.5	900.6	90.8	0.5	273.6	364.4	401.6	136.8	99.6	13671.9	8670.1

Flow rates in kg/h

	9-01	9-02	9-03	9-04	9-05	9-06	9-07	9-08	9-09	9-10	9-11
Extractant	0.0281	0.0281	0	0.0281	0	0	0	0	0	0	0
Aluminum Oxide	0	0	2.8656	0	0	2.8656	0	0	2.8656	2631.6851	0
Cerium Nitrate	7.3716	0	0	0	0	0	0	0	0	0	0
Cerium Oxide	0	0	3.2688	0	0	3.2688	0	0	3.2688	1.6255	0
Cobalt(II) Oxide	0	0	0.0169	0	0	0.0169	0	0	0.0169	0.4725	0
Copper(II) Oxid	0	0	0	0	0	0	0	0	0	3.565	0
Dysprosium Nitr	0.8411	0	0	0	0	0	0	0	0	0	0
Dysprosium Oxid	0	0	0.4501	0	0	0.4501	0	0	0.4501	0	0
Erbium Nitrate	0.4722	0	0	0	0	0	0	0	0	0	0
Erbium Oxide	0	0	0.2556	0	0	0.2556	0	0	0.2556	0	0
Europium Nitrat	0.2127	0	0	0	0	0	0	0	0	0	0
Europium Oxide	0	0	0.1107	0	0	0.1107	0	0	0.1107	0	0
Gadolinium Nitr	0.9539	0	0	0	0	0	0	0	0	0	0
Gadolinium Oxid	0	0	0.5037	0	0	0.5037	0	0	0.5037	0	0
Gallium(III) Ox	0	0	0.6731	0	0	0.6731	0	0	0.6731	0.9817	0
Holmium Nitrate	0.1617	0	0	0	0	0	0	0	0	0	0
Holmium Oxide	0	0	0.087	0	0	0.087	0	0	0.087	0	0
Iron(iii) oxide	0	0	0	0	0	0	0	0	0	1218.8291	0
Lanthanum Nitrat	4.2097	0	0	0	0	0	0	0	0	0	0
Lanthanum Oxide	0	0	2.1106	0	0	2.1106	0	0	2.1106	0	0
Lead(II) Oxide	0	0	0.0179	0	0	0.0179	0	0	0.0179	1.5514	0
Lutetium Nitrat	0.0136	0	0	0	0	0	0	0	0	0	0
Lutetium Oxide	0	0	0.0075	0	0	0.0075	0	0	0.0075	0.0008	0
Neodymium Nitra	3.8615	0	0	0	0	0	0	0	0	0	0
Neodymium Oxide	0	0	1.9671	0	0	1.9671	0	0	1.9671	0.2753	0
Nickel(II) Oxid	0	0	0	0	0	0	0	0	0	0.9059	0
Nitric Acid	11.9671	11.9671	0	0	0	0	0	0	0	29.9229	29.9229
Praseodymium Ni	1.1088	0	0	0	0	0	0	0	0	0	0
Praseodymium Ox	0	0	0.5593	0	0	0.5593	0	0	0.5593	0	0
Samarium Nitrat	0.8872	0	0	0	0	0	0	0	0	0	0
Samarium Oxide	0	0	0.4599	0	0	0.4599	0	0	0.4599	0	0
Scandium Nitrate	0.4528	0	0	0	0	0	0	0	0	0	0
Scandium(III) Ox	0	0	0.1352	0	0	0.1352	0	0	0.1352	1.2028	0
Calcium Sulfate	0	0	0	0	0	0	0	0	0	541.6608	0
Terbium Nitrate	0.1599	0	0	0	0	0	0	0	0	0	0
Terbium Oxide	0	0	0.0848	0	0	0.0848	0	0	0.0848	0	0
Thorium(IV) Oxi	0	0	0.0009	0	0	0.0009	0	0	0.0009	0.5439	0
Thulium Nitrate	0.0491	0	0	0	0	0	0	0	0	0	0
Thulium Oxide	0	0	0.0267	0	0	0.0267	0	0	0.0267	0	0
Uranium(IV) Oxi	0	0	0.0002	0	0	0.0002	0	0	0.0002	0.3336	0
Water	862.2	862.2	0	0	273.6038	273.6038	328.3246	136.8019	82.0811	8555.1973	8637.2784
Ytterbium Nitra	0.2614	0	0	0	0	0	0	0	0	0	0
Ytterbium Oxide	0	0	0.1434	0	0	0.1434	0	0	0.1434	0	0
Yttrium Oxide	0	0	2.7814	0	0	2.7814	0	0	2.7814	0	0
Yttrium(III) Nit	6.7725	0	0	0	0	0	0	0	0	0	0
Zinc Oxide	0	0	0.9872	0	0	0.9872	0	0	0.9872	0.1854	0
Barium Nitrate	0.5571	0	0.5571	0	0	0.5571	0.5571	0	0	0	0
Calcium Nitrate	38.0374	0	38.0375	0	0	38.0375	38.0375	0	0	0	0
Potassium Nitrat	13.5677	0	13.5677	0	0	13.5677	13.5677	0	0	0	0
Nitrogen Dioxide	0	22.5336	0	0.3834	0	0	0	0	0	2.9133	2.9133
Aluminum Nitrat	11.9723	0	0	0	0	0	0	0	0	0	0
Cobalt(II) Nitr	0.0413	0	0	0	0	0	0	0	0	0	0
Gallium(III) Ni	1.8366	0	0	0	0	0	0	0	0	0	0
Lead(II) Nitrat	0.0266	0	0	0	0	0	0	0	0	0	0
Uranyl Nitrate	0.0003	0	0	0	0	0	0	0	0	0	0
Zinc Nitrate	2.2976	0	0	0	0	0	0	0	0	0	0
Rubidium Nitrat	0.0658	0	0.0658	0	0	0.0658	0.0658	0	0	0	0
Strontium Nitra	1.1218	0	1.1218	0	0	1.1218	1.1218	0	0	0	0
Thorium(IV) Nit	0.0017	0	0	0	0	0	0	0	0	0	0
Oxygen	0	3.9183	0	0.0667	0	0	0	0	0	0.0006	0.0006
dinitrogen pent	0	0	0	0	0	0	0	0	0	0.0089	0.0089
Sodium Silicate	0	0	0	0	0	0	0	0	0	680.0169	0
Sodium Nitrate	19.9465	0	19.9465	0	0	19.9465	19.9465	0	0	0	0

Table 27: RES' Conversion Process.

PFD Stream No.	10-01	10-02	10-03	10-04	10-05	10-06	10-07	10-08	10-09	10-10	10-11	10-12	10-13
Stream Name	REE SOLIDS TO FURNACE	SOLIDS TO FURNACE	HYDROCHLORIC ACID	CONVERSION REAGENT MAKE-UP		REE SALTS	WATER PRODUCT	IRON CHLORIDE	CONVERSION REAGENT RECYCLE	WATER FROM HEADER	REE SOLUTION	WATER FROM HEADER	WASHED SOLIDS
Temperature (°C)	250.0	250.0	25.0	25.0	39.7	400.0	40.0	40.0	40.0	25.0	121.5	25.0	121.3
Total rate (kg/h)	99.6	5083.8	1666.3	49.1	2469.4	3903.7	461.8	2451.2	2420.3	7807.4	11711.2	3903.7	6221.0
					Flow rates in kg/h								
Hydrochloric acid	0	0	1666.3480	0	0	0	16.6635	0	0	0	0	0	0
Conversion reagent	0	0	0	49.1414	2469.4178	0	24.6942	0	2420.276343	0	0	0	0
Conversion reagent product	0	0	0	0	0	0	7.7838	0	0	0	0	0	0
Aluminum Oxide	2.8656	2631.6851	0	0		2634.5507	0	0	0	0	2634.5507	0	2634.5507
Cerium Chloride	0	0	0	0		6.9387	0	0	0	0	6.9387	0	0
Cerium Oxide	3.2688	1.6255	0	0		0.0489	0	0	0	0	0.0489	0	0.0489
Cobalt(II) Oxide	0.0169	0.4725	0	0		0.4894	0	0	0	0	0.4894	0	0.4894
Copper(II) Oxid	0	3.565	0	0		3.5650	0	0	0	0	3.5650	0	3.5650
Dysprosium Oxid	0.4501	0	0	0		0.0045	0	0	0	0	0.0045	0	0.0045
Dysprosium Chloride	0	0	0	0		0.6423	0	0	0	0	0.6423	0	0
Erbium Oxide	0.2556	0	0	0		0.0026	0	0	0	0	0.0026	0	0.0026
Erbium Chloride	0	0	0	0		0.3621	0	0	0	0	0.3621	0	0
Europium Oxide	0.1107	0	0	0		0.0011	0	0	0	0	0.0011	0	0.0011
Europium Chloride	0	0	0	0		0.1610	0	0	0	0	0.1610	0	0
Gadolinium Oxid	0.5037	0	0	0		0.0050	0	0	0	0	0.0050	0	0.0050
Gadolinium Chloride	0	0	0	0		0.7253	0	0	0	0	0.7253	0	0
Gallium(III) Ox	0.6731	0.9817	0	0		1.6548	0	0	0	0	1.6548	0	1.6548
Holmium Oxide	0.087	0	0	0		0.0009	0	0	0	0	0.0009	0	0.0009
Holmium Chloride	0	0	0	0		0.1237	0	0	0	0	0.1237	0	0
Iron(iii) oxide	0	1218.8291	0	0		12.1883	0	0	0	0	12.1883	0	12.1883
Iron(iii) Chloride	0	0	0	0		0	0	2451.2409	0	0	0	0	0
Lanthanum Oxide	2.1106	0	0	0		0.0211	0	0	0	0	0.0211	0	0.0211
Lanthanum Chloride	0	0	0	0		3.1074	0	0	0	0	3.1074	0	0
Lead(II) Oxide	0.0179	1.5514	0	0		1.5693	0	0	0	0	1.5693	0	1.5693
Lutetium Oxide	0.0075	0.0008	0	0		0.0001	0	0	0	0	0.0001	0	0.0001
Lutetium Chloride	0	0	0	0		0.0117	0	0	0	0	0.0117	0	0
Neodymium Oxide	1.9671	0.2753	0	0		0.0224	0	0	0	0	0.0224	0	0.0224

Table 28: RES' Conversion Process (continue).

PFD Stream No.	10-01	10-02	10-03	10-04	10-05	10-06	10-07	10-08	10-09	10-10	10-11	10-12	10-13
Stream Name	REE SOLIDS TO FURNACE	SOLIDS TO FURNACE	HYDROCHLORIC ACID	CONVERSION REAGENT MAKE-UP		REE SALTS	WATER PRODUCT	IRON CHLORIDE	CONVERSION REAGENT RECYCLE	WATER FROM HEADER	REE SOLUTION	WATER FROM HEADER	WASHED SOLIDS
Temperature (°C)	250.0	250.0	25.0	25.0	39.7	400.0	40.0	40.0	40.0	25.0	121.5	25.0	121.3
Total rate (kg/h)	99.6	5083.8	1666.3	49.1	2469.4	3903.7	461.8	2451.2	2420.3	7807.4	11711.2	3903.7	6221.0
Flow rates in kg/h													
Neodymium Chloride	0	0	0	0		3.3067	0	0	0	0	3.3067	0	0
Nickel(II) Oxid	0	0.9059	0	0		0.9059	0	0	0	0	0.9059	0	0.9059
Nitric Acid	0	0	0	0		0	0.0000	0	0	0	0	0	0
Praseodymium Ox	0.5593	0	0	0		0.0056	0	0	0	0	0.0056	0	0.0056
Praseodymium Chloride	0	0	0	0		0.8303	0	0	0	0	0.8303	0	0
Samarium Oxide	0.4599	0	0	0		0.0046	0	0	0	0	0.0046	0	0.0046
Samarium Chloride	0	0	0	0		0.6704	0	0	0	0	0.6704	0	0
Scandium(III) Ox	0.1352	1.2028	0	0		0.0134	0	0	0	0	0.0134	0	0.0134
Scandium(III) Chloride	0	0	0	0		2.9068	0	0	0	0	2.9068	0	0
Calcium Sulfate	0	541.6608	0	0		541.6608	0	0	0	0	541.6608	0	541.6608
Terbium Oxide	0.0848	0	0	0		0.001	0	0	0	0	0.0008	0	0.0008
Terbium Chloride	0	0	0	0		0.1217	0	0	0	0	0.1217	0	0
Thorium(IV) Oxi	0.0009	0.5439	0	0		0.5448	0	0	0	0	0.5448	0	0.5448
Thulium Oxide	0.0267	0	0	0		0.0003	0	0	0	0	0.0003	0	0.0003
Thulium Chloride	0	0	0	0		0.0377	0	0	0	0	0.0377	0	0
Uranium(IV) Oxi	0.0002	0.3336	0	0		0.3338	0	0	0	0	0.3338	0	0.3338
Water	0	0	0	0		0	411.6803	0	0	7807.44441	7807.4444	3903.7222	2342.2333
Ytterbium Oxide	0.1434	0	0	0		0.0014	0	0	0	0	0.0014	0	0.0014
Ytterbium Chloride	0	0	0	0		0.2014	0	0	0	0	0.2014	0	0
Yttrium Oxide	2.7814	0	0	0		0.0278	0	0	0	0	0.0278	0	0.0278
Yttrium Chloride	0	0	0	0		4.7622	0	0	0	0	4.7622	0	0
Zinc Oxide	0.9872	0.1854	0	0		1.1726	0	0	0	0	1.1726	0	1.1726
Nitrogen Dioxide	0	0	0	0		0	0.0000	0	0	0	0	0	0
Oxygen	0	0	0	0		0	0.0000	0	0	0	0	0	0
dinitrogen pent	0	0	0	0		0	0.0000	0	0	0	0	0	0
Sodium Silicate	0	680.0169	0	0		680.0169	0	0	0	0	680.0169	0	680.0169
Chlorine	0	0	0	0	0	0	0.9980	0	0	0	0	0	0

Table 29: RES' Electrowinning Process

PFD Stream No.	11-01	11-02	11-03
Stream Name	FILTERED REE SOLUTION	REO	WATER PRODUCT
Temperature (°C)	121.3	40.0	40.0
Total rate (kg/h)	9393.8	15.7	9378.2
Flow rates in kg/h			
Hydrochloric acid	0	0	12.3208
Cerium Chloride	6.9387	0	0
Cerium (III) Oxide	0	4.6201	0
Cobalt(II) Oxide	0	0	0
Copper(II) Oxid	0	0	0
Dysprosium Oxid	0	0.4456	0
Dysprosium Chloride	0.6423	0	0
Erbium Oxide	0	0.2531	0
Erbium Chloride	0.3621	0	0
Europium Oxide	0	0.1096	0
Europium Chloride	0.1610	0	0
Gadolinium Oxid	0	0.4987	0
Gadolinium Chloride	0.7253	0	0
Gallium(III) Ox	0	0	0
Holmium Oxide	0	0.0862	0
Holmium Chloride	0.1237	0	0
Iron(iii) oxide	0	0	0
Iron(iii) Chloride	0	0	0
Lanthanum Oxide	0	2.0895	0
Lanthanum Chloride	3.1074	0	0
Lead(II) Oxide	0	0	0
Lutetium Oxide	0	0.0082	0
Lutetium Chloride	0.0117	0	0
Neodymium Oxide	0	2.2200	0
Neodymium Chloride	3.3067	0	0
Nickel(II) Oxid	0	0	0
Nitric Acid	0	0	0
Praseodymium Ox	0	0.5537	0
Praseodymium Chloride	0.8303	0	0
Samarium Oxide	0	0.4553	0
Samarium Chloride	0.6704	0	0
Scandium(III) Ox	0	1.3247	0
Scandium(III) Chloride	2.9068	0	0
Calcium Sulfate	0	0	0
Terbium Oxide	0	0.0839	0
Terbium Chloride	0.1217	0	0
Thorium(IV) Oxi	0	0	0
Thulium Oxide	0	0.0264	0
Thulium Chloride	0.0377	0	0
Uranium(IV) Oxi	0	0	0
Water	9368.9333	0	9365.8894
Ytterbium Oxide	0	0.1420	0
Ytterbium Chloride	0.2014	0	0
Yttrium Oxide	0	2.7535	0
Yttrium Chloride	4.7622	0	0
Zinc Oxide	0	0	0

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It can be done