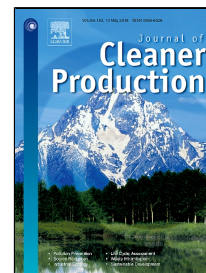


Accepted Manuscript

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PII: S0959-6526(18)30933-8
DOI: 10.1016/j.jclepro.2018.03.252
Reference: JCLP 12510
To appear in: *Journal of Cleaner Production*

Received Date: 21 November 2017
Revised Date: 23 March 2018
Accepted Date: 24 March 2018

Please cite this article as: Saptarshi Das, Gabrielle Gaustad, Ashok Sekar, Eric Williams, Techno-Economic analysis of supercritical extraction of rare earth elements from coal ash, *Journal of Cleaner Production* (2018), doi: 10.1016/j.jclepro.2018.03.252

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Techno-economic analysis of supercritical extraction of rare earth elements from coal ash

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Abstract

Given increasing demand and importance of rare earth elements (REE), exploration is underway to find alternatives to ore-extracted product. With REE concentrations varying between 270 and 1,480 ppm, coal ash has been deemed as one such potential source. A number of research groups are exploring technologies to separate REEs from coal ash and super critical extraction has emerged as a high yield contender. Estimating the economic viability of this lab-scale process at the industrial scale is both important and challenging. In this study we estimate industrial scale cost and revenues of production of REEs from coal ash by combining prior laboratory results, scaling models, combinatorial scenarios and sensitivity analysis. The processing cost of extracting REEs from one ton of coal ash using super-critical CO₂ and tributylphosphate (TBP) is found to vary between \$380 and \$1,200 for 550 grams of REE. The value of REE oxides that may be obtained per ton of ash is estimated to vary between \$6 and \$557, with a median of \$250. Scandium is the most expensive REE and can account for up to 90% of the value of the yield. The results suggest that factors critical to the economic viability of the process include scandium content & yield, reagent use, and processing time.

Key Words – Rare earth elements, coal ash, super-critical extraction, techno-economic analysis

1. Background

1.1 Coal ash as a source of rare earths

Rare earth elements (REEs) are a relatively abundant group of 17 elements consisting of scandium, yttrium, and the lanthanides. REEs have received special attention in recent years due to their critical role in electronics and energy technologies and the geographic concentration of production activities. Although REEs are relatively abundant in the Earth's crust, most mining activities occur in China. In 2015, China was responsible for 85% of global production. Some other countries that produce REEs include Australia, Russia, Malaysia and Thailand. In the USA, only one company was active in REE extraction in 2015, mining and processing Bastnäs site, a fluorocarbonate mineral, from a site in Mountain Pass, California. The United States continues to be an importer

of rare earths, importing about 70% of rare earth compounds and metals used in 2015, at an estimated expense of \$150 million (USGS, 2016). Many other countries are in a similar situation, leading to concerns over resource security and criticality of REEs, motivating a search for alternative sources to augment domestic production and reduce import dependency.

Coal ash has been found to be a source of REEs (Całus Moszko, et al., 2016; Hower, et al., 2013; Mayfield & Lewis, 2013; Smolka-Danielowska, 2010; Zhang, et al., 2001). Given that the USA generates about 78 million tons of fly ash per year (ACAA, 2016), it is also a source that is relatively abundant. In addition to tackling the problem of resource scarcity, using coal ash for REE production has the potential to turn the waste of one industry into the feedstock of another, contributing to a more circular economy (Andrews, 2015) linking coal mining, power and rare earth elements industries.

Although coal ash has a lower total concentration of REEs compared to commercially processed ores, it has higher concentrations of some high value elements such as scandium and neodymium (see Table 4) (Peiro & Mendez, 2013). The low concentrations of these REEs in mineable ores contributes to their high prices. The presence of these valuable elements in coal ash is another reason why it is considered as a potential source of REEs. These considerations were motivations for the U.S Department of Energy to fund research and development of processes to enable extraction of REEs from coal ash (NETL, 2016). REEs may be extracted from coal ash using a variety of methods. Kermer, et al., 2016 conducted an extensive study comparing different methods of extracting metals from lignite ash in Germany. In order to enrich, separate and mobilize valuable substances from lignite ash, mechanical and thermal pre-treatment methods, along with chemical and biological leaching were applied. Mechanical pre-treatment provided enriched fractions but still suffered from low yields. Thermal ash processing showed multiple significant phase changes compared to original ash. Extraction with SC-CO₂ and chemical leaching (using aqueous HCl) of untreated and thermally treated ash provided high extraction for metals like Al, Ca, Fe, Mg, etc. The highest yields were obtained with thermally treated ash.

Biological leaching experiments have been conducted with acidophilic chemolithoautotrophic micro-organisms as well as acidophilic or neutrophilic heterotrophic bacteria. Acidophilic cultures comprised mesophilic, moderate-thermophilic and thermophilic Fe-/S-oxidizing strains. Bioleaching could achieve high extraction efficiency for aluminum (75%) and magnesium (79.2%) as well as some lanthanides like erbium (75.6%), thulium (77.9) and ytterbium (79.2%) (Kermer, et al., 2016).

Acid leaching is often used in the extraction of REEs from their ores. In China, extraction processes like the Bayan Obo process use a vessel or heap leaching and are often accomplished in situ (Chi, et al., 2013). The Molycorp process and the Goldschmidt Process are additional examples of acid leaching. Acid leaching is usually used for extraction from bastnasite, monazite, and xenotime where the ores are in the form of fluoroarbonates (Peiro & Mendez, 2013).

Super-critical fluid extraction is also a leaching process where instead of large quantities of acid, super-critical fluid is used. Carbon dioxide (CO₂) is a widely used super-critical fluid as CO₂ has low viscosity (10^{-5} – 10^{-4} Pa.s) and high diffusivity (10^{-8} – 10^{-7} m²s), appropriate properties for an

extraction solvent (Sawada, et al., 2004). Supercritical CO₂ (SC-CO₂) can easily be separated from the solutes. Upon depressurization, the super-critical fluid turns into non-hazardous CO₂ gas. Moreover, CO₂ is readily available in high purity and is inexpensive to purchase. Finally, since it is non-toxic and non-combustible, CO₂ is considered to be environmentally benign. Supercritical CO₂ is therefore a popular solvent used in industry today.

There are many applications of supercritical CO₂, one of its main uses is in the food and agriculture industry for the extraction of organics. Examples include extraction of essential oils from herbs (Zabot, et al., 2015; Carvalho, et al., 2015; Pereira & Meireles, 2010), flowers (Scaliaa, et al., 1999), and coffee (Peker, et al., 1992). More recently, supercritical fluids have also been used in the extraction of metals and non-organics including rare earth elements, under laboratory conditions (Baek, et al., 2016; Thriveni, et al., 2015; Duan, et al., 2012; Shimizu, et al., 2005; Sawada, et al., 2004).

From an economics perspective, supercritical extraction may be expected to have two important advantages over other extraction techniques. Since supercritical CO₂ has low viscosity and high diffusivity, it has very high solvation strength (Abbas, et al., 2008) and may be expected to require relatively low reagent input. Secondly, super-critical CO₂ can be reused over several cycles. It can be separated from a solution simply by releasing the pressure to vaporize it and then condensed for the next cycle (Abbas, et al., 2008). The objective of this article is to explore the economic feasibility of supercritical extraction as a process to extract REEs from coal, focusing on the U.S.

1.2 Context for supercritical extraction of coal ash

Before describing the specifics of process modeling, we first review the economic and technical context of current disposition of coal ash in the U.S. In 2013, The US generated around 53 million tons of ash out of which 23 million tons or 43% were re-used (ACAA, 2016), 36% was stored in landfills, and 21% in wet storage facilities (PEI, 2015). The lowest disposal cost occurs when a disposal site is located near the point of production. If the material can be piped, rather than trucked, costs are usually lower and may be as low as \$3.00 to \$5.00 per ton. In other cases if the ash has to be transported long distances or must be handled several times due to its moisture content or volume, costs can range between \$20 and \$40 per ton. In some areas, the costs are even higher. If new sites are required and extensive permitting processes take place, the total cost of the facility may be increased, resulting in higher disposal costs over time (ACAA, 2015)

Re-use usually takes place in construction where fly ash is used as a direct substitute for Portland cement (EPA, 2017). It has been estimated that use of coal ash in transportation infrastructure construction saves nearly \$5.23 billion annually (ARTBA, 2011). Additionally coal ash is also used in soil for the production of food crops (Cimitile, 2009). There is therefore a possibility of recovering some of the disposal costs from secondary applications.

The price of fly ash varies depending on quality of ash, distance to market location and time of year, which impacts both demand and supply. Fly ash that meets concrete quality engineering standards is the most valuable and can sell for \$20 to \$45 a ton. Self-cementing fly ash used for soil stabilization sells for \$10 to \$20 a ton. Fly ash for flowable fill on the other hand can sell for as little as \$1 a ton (EPA, 2017).

Having summarized current coal ash disposition in the U.S., we next describe how supercritical extraction would fit into this context. The process is not expected to redirect coal ash from its traditional uses, rather introduce an extra step in-between, i.e. after supercritical extraction of the rare earth elements, the coal ash can be disposed of via traditional means. Supercritical extraction is thus not expected to significantly affect the waste management of coal ash, rather to provide a new source of rare earth materials along the chain. The economic role of waste management on the supercritical process is treated by adding an expense or income associated with final disposal of coal ash. Following the above, the expense of disposing of coal ash is as high as \$40/ton, the income as a co-product as high as \$45/ton. The income/expense of final disposal depends on the as yet unknown quality of the coal ash post supercritical extraction. As will be seen (figure 6), a final disposal expense/income of -\$40/ton to +\$45/ton is small compared to process expenses and revenues from REE extraction and is therefore not expected to qualitatively affect profitability.

1.3 Need for techno-economic analysis

Since supercritical extraction of REEs from coal ash has yet to be done on an industrial scale, techno-analysis is needed to explore economic feasibility. Techno-economic analysis (TEA), or sometimes techno-economic assessment, is a modeling framework used to estimate the economic performance of a technology not yet at industrial scale. Despite a long history of TEA case studies, e.g. (Bosley, et al., 1987), there is no synthetic review describing what TEA is and the methods used to conduct it. In order to position our methodological contribution, we attempt a brief review here.

TEA is done for a number of reasons. In the public sector, TEA is most often used to inform governmental decisions on research and development (R&D) investments. The U.S. Department of Energy (DOE), for example, frequently sponsors TEA studies of technologies as part of evaluating and adjusting its R&D portfolio, e.g. (Bosley, et al., 1987; Zhu, et al., 2011; Wright, et al., 2010). In the private sector, TEA is used to improve the process of technological development by testing project feasibility and informing research and development activities for new production processes. Some examples of TEA in published literature include enzymatic biomass conversion processes (Nguyen & Saddler, 1991), production of polymers like poly(3-hydroxybutyrate) using the process of fermentation (Choi & Yup Lee, 1997), biogas upgrading process using polyvinylamine/polyvinylalcohol blend membrane (Deng & Hägg, 2010), and super-critical fluid extraction of grape seed (M. Prado, et al., 2012).

Techno-economic analysis combines process modeling, project economics and uncertainty analysis. Process modeling is done via some combination of empirical data, often from a laboratory scale process, mass-flow balance, and physico-chemical simulation, e.g. using tools such as Aspen (Withag, et al., 2012; Donatini, et al., 2009). The result of process modeling is characterization of equipment and materials needed to implement the process. The project economic analysis part models revenues and costs. In addition to the usual cash flow and discounting methods, e.g. (Newnan et al, 2009), TEA also draws on models to extrapolate early stage costs of scaled up versions, e.g. scaling models (Haldi & Whitcomb, 1967) and learning curves (Wright, 1936). TEAs are forecasts based on simulated or extrapolated process data, thus uncertainty analysis is critical and are typically done through scenario and/or sensitivity analysis. In scenario analysis, ranges of values for important parameters are developed and used (Wright, et

al., 2010). Sensitivity analysis determines how profitability varies as certain parameters are changed (Wright, et al., 2010; Kazi, et al., 2010; Aden & Foust, 2009).

Grappling with uncertainty is a primary challenge for techno-economic analysis. In this work we combine standard sensitivity analysis (in the form of tornado diagrams) with what we shall term combinatorial scenario analysis. A primary challenge in TEA is significant uncertainty in multiple process parameters. One thus needs to explore a multi-dimensional space of uncertain parameters in order to determine combinations of values that will lead to economic feasibility. Combinatorial scenario analysis supports this process as follows. Starting with N uncertain process parameters, each with a set of potential value scenarios, combinatorial scenario analysis involves estimating project economics for all possible combinations and separate combinations into economically feasible and infeasible sets. The results for economically feasible combinations of process and input quality parameters can then be used to inform R&D priorities.

To scope the paper, we explore the economic viability of REE extraction from coal ash using supercritical extraction. We built a process model, assess its economics and explore its uncertainty with combinatorial scenario and sensitivity analyses. Critical process variables are found to be REE yield, REE content of input coal ash, reactor size, reagent requirement, and reagent cost. The contributions of this work are, we argue: To present the first economic feasibility analysis of extraction of REE from coal ash and to explore the utility of the combinatorial approach in techno-economic analysis.

2. Literature Review

One of the early examples of extraction of rare earth elements using super critical materials is by Kayo Sawada and collaborators. They used a complex of tributylphosphate (TBP), HNO_3 and H_2O in supercritical CO_2 to extract uranium from UO_2 powder (Sawada, et al., 2005). The TBP complex was mixed with UO_2 powder in supercritical fluid CO_2 at 25 MPa and 323 K. `

It was found that UO_2 reacts with HNO_3 contained in the TBP complex at a HNO_3/U ratio of approximately 4:1. TBP complex forms a reversed micelle structure in SF-CO_2 and the chemical stoichiometry of UO_2 dissolution depends on the concentration of HNO_3 in the water cores in the complex. In designing a supercritical fluid extraction process, the dissolution stoichiometry of one mole of uranium reacting with four moles of HNO_3 can be used to describe the overall dissolution of UO_2 using the TBP complex in supercritical CO_2 .

Duan, et al., 2012 described a supercritical extraction process for recovery of uranium oxides and cerium oxide using TBP- HNO_3 complex in supercritical CO_2 from spent nuclear fuel. Cerium was used to simulate plutonium (Pu^{239}) found in spent nuclear fuel. They tried extraction at 50°C and 60°C and found extraction at 60°C to be more effective. It was difficult to extract CeO_2 with the TBP- HNO_3 complex in supercritical CO_2 because CeO_2 is not easily dissolved by HNO_3 . The extraction efficiency from the simulated spent nuclear fuel (U, CeO_2), prepared by electroreduction–coprecipitation method was higher. The extraction efficiency of U and Ce in (U, Ce) O_2 was found to be 98.6% and 98.1% respectively at 60°C .

This result corroborated the findings of Samsonov, et al., 2007 who used TBP-HNO₃ in supercritical CO₂ to recover actinides from a solid solution of their oxides and achieved yields of 89% (uranium) to 98% (plutonium) for various actinides. Based on Samsonov's results, Duan concluded that cerium is a good substitute in studying the recovery potential of plutonium as the behavior of a (U, Ce)O₂ solid solution and a (U, Pu)O₂ solid solution with TBP-HNO₃ complex in SC-CO₂ are similar.

Samsonov's sample contained UO₂, PuO₂, Eu₂O₃ and AmO₂ in the ratios 6.14:2.2:0.4:0.004. The yield of the four metals were 89.6, 93.1, 91.0 and 88 percent respectively. He conducted three experiments with TBP:HNO₃ ratios of (1) 1:3, (2) 1:8 and (3) 1:12. The best results were obtained when using a TBP:HNO₃ molar ratio of 1:12. The actinide to complex molar ratio was approximately 1:20. The experiment assumed an extraction time of 90 minutes and CO₂ flow of 0.5 cm³/min.

Shimizu, et al., 2005 extracted rare earth elements from luminescent material in waste fluorescent lamps using supercritical carbon dioxide containing TBP complexes with HNO₃ and H₂O. By controlling of the molecular ratio of TBP:HNO₃:H₂O in the complex, they were successfully able to prevent the formation of aqueous droplets that would lead to low recovery yields. In doing so, the yield of yttrium and europium increased to over 99% after the static extraction for 120 min at 15MPa, 333 K (Shimizu, et al., 2005). Y, Eu, La, Ce and Tb were the major elements identified in the sample, and the contents were 29.6, 2.3, 10.6, 5.0 and 2.6 wt%, respectively. REEs amounted to 50% of the luminescent material by weight. Y and Eu were present as oxides, whereas La and Ce were present as phosphates. The reactant was a combination of TBP-HNO₃-H₂O. The study experimented with two molecular ratios of TBP:HNO₃:H₂O in the reactant complex. The ratio in complex A was 1.0:1.8:0.6 while that in complex B it was 1.0:1.3:0.4. The experiment assumed an extraction time of 120 minutes and CO₂ flow of 2 cm³/min. The experiment used 2cm³ of complex A/ B per 20mg of sample. The dissolution yields of Y, Eu, were >99, >99 respectively, while that for La, Ce and Tb were <7% each.

All prior studies of supercritical extraction of REEs describe laboratory results and do not investigate economics. The above laboratory work informs our economic analysis. There is no prior work that estimates the economics of REE extraction from coal ash using any technology.

3. Methodology

We model the economics of supercritical extraction of REE from coal ash using a combination of material flow analysis, process economics, scale-up model, sensitivity analysis and combinatorial scenario approaches.

3.1 Process configuration and analytical approaches

Material flow analysis is used to quantify all inputs into, and outputs from the processes and ensures that the mass of inputs and outputs are balanced. The system boundary and mass flows have been elucidated in figure 1.

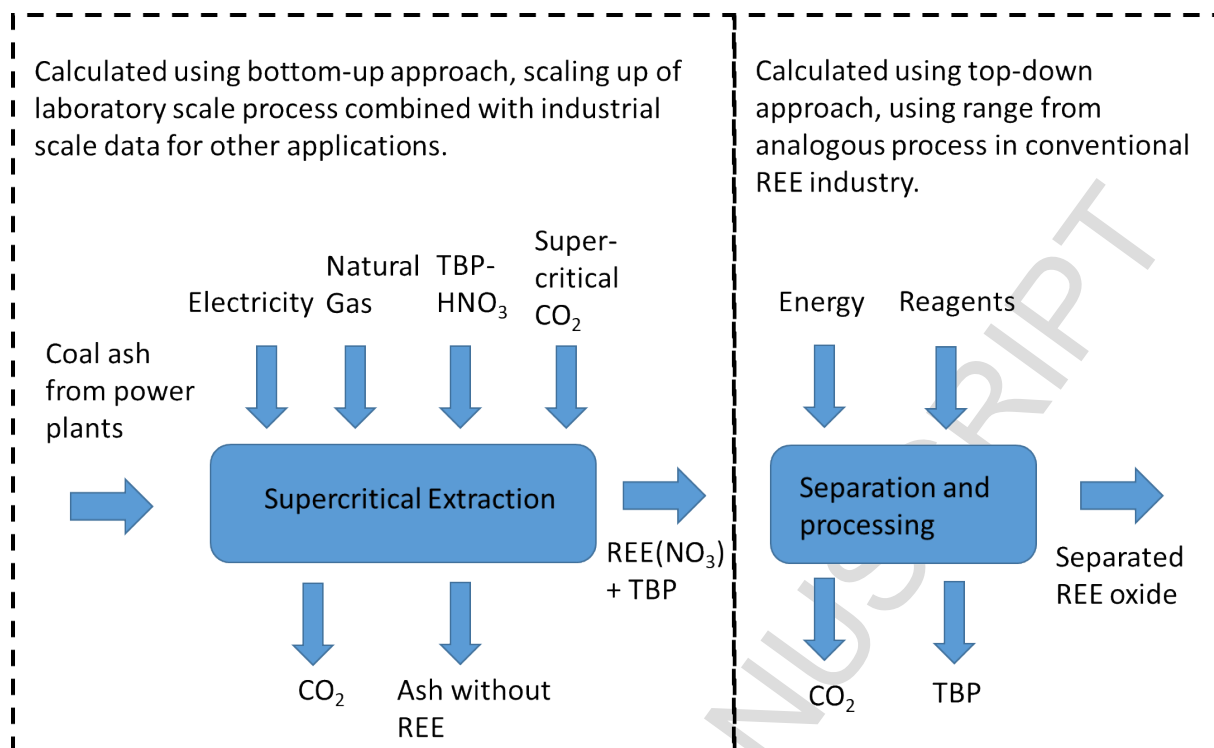


Figure 1: Representative logic flow diagram of the techno-economic analysis. The boxes show the boundary of processes and materials included in the analysis. TBP = Tributyl phosphate, REE = Rare Earth Element

The system is designed to accept coal ash from power plants, remove rare earth metals and pass it on for traditional disposal or re-use. The process takes dry coal ash as an input. In the extraction process, TBP-HNO₃ complex along with super-critical CO₂ is passed through the coal ash. TBP-HNO₃ reacts with REEs to form a REE(NO₃)+TBP complex. Both TBP-HNO₃ and REE(HNO₃)+TBP are soluble in supercritical CO₂ and are moved into a collection chamber. Once the pressure is released in the collection chamber, CO₂ vaporizes, leaving behind REE(NO₃) and the excess TBP-HNO₃. The REE(NO₃) can be precipitated with oxalic acid to get a mixture of REE oxalate (Jorjani & Shahbazi, 2016). The oxalates can then be removed for further enrichment to get individual REE oxides. TBP-HNO₃ can be separated through fractional distillation and reused (Jubin, 2008). The extraction chamber can then be cleared of the coal, which will remain dry as the super-critical CO₂ will have removed all the reagents. This coal ash can then be discarded or reused in traditional ways. The process of coal ash handling has been discussed further in section 4.5.

Figure 1 shows a dividing line between processes analyzed with a bottom up approach (supercritical extraction) and those that, due to lack of detail data, are treated using a top-down approach (separation into individual REE oxides). Details of the respective estimations are described below.

3.2 Modeling scale-up from lab to industrial scale

There is currently no industrial scale application of super-critical technologies to extract REEs from any source. To estimate the material use, energy use, cost and revenue at an industrial scale,

scaling up of laboratory and other similar industrial processes is conducted. To characterize materials flow in supercritical extraction, a literature review of prior laboratory studies was conducted, and industrial scale material and energy use was extrapolated using stoichiometric analysis. Assumptions were needed in the scale-up modeling, the process specific assumptions and literature that informed them are discussed in detail in the next three subsections.

3.3 Economic analysis

Once the material and energy use of an industrial scale process is estimated, economic analysis is required to comment on the profitability of the process.

Cost: The model follows standard process economics, including accounting for fixed and variable costs. The following cost categories are assessed (1) Capital, (2) Reagent, (3) Energy, (4) Labor, and (5) Transport. The capital cost for supercritical extraction is determined from a scaling model based on empirical data from smaller industrial scale vessels. Reagent cost assessments include individual materials shown on the left of the dashed line segment in figure 1, the boundary of the bottom up economic analysis. Reagent cost is found by multiplying material requirement by price. Energy and labor costs are determined from empirical data from other supercritical extraction processes. Transport costs are estimated by assuming distance from coal plant to extractor and assuming truck transport between the sites. The economic analysis considers the capital and energy costs related to the main equipment, but excludes rent, other energy use and the cost of ancillary equipment. In this respect this paper understates cost of production to a certain extent.

A top-down analysis is used to estimate the cost of separating REEs, which are in the form of nitrates and obtaining individual REE oxides which is the final saleable product. In this approach, the market price of a mixture of REE salts is compared to the net of their separated oxides. The difference in prices is assumed to be the cost of separation into individual oxides. Although this is a rough approximation, this is the best possible, given the availability of data. Uncertainty in the cost of enrichment is examined through scenarios.

Revenue: The saleable output of the process is rare earth oxides plus a small potential income from residue coal ash if quality is high enough for beneficial use applications. The income from REE sales is determined by multiplying REE metal content (kg/ton coal ash) by process yield (%) by price of REE oxide (\$/kg) by stoichiometric ratio of REE oxide to REE metal, summed over individual REEs. Prices are taken from five-year historical averages, we do not consider future markets for REEs.

3.4 Combinatorial scenarios and sensitivity analysis

Much of the prior method discussion addressed how to estimate the economics of a hypothetical industrial scale-up of the process. Such estimations have large uncertainties, which we analyze using combinatorial scenario analysis and sensitivity analysis. Combinatorial scenario analysis starts from the observation that the economic performance of a process depends on multiple variables whose values could change under development and scale-up. Sensitivity analysis is effective at identifying dependencies of outcomes on input variables, starting from a baseline set of values. Sensitivity analysis does not however explore the larger space of future values of

multiple process parameters. In combinatorial scenarios analysis, process parameters that may change with development are selected, such as reactor size, product yield and reagent consumption. For each parameter, a discrete set of possible values, or scenarios is selected, e.g. possible reactor sizes might be 1,000 L or 3,000 L. Outcomes are then calculated for all combination of value scenarios. By examining which combinations meet some criterion such as economic viability, combinations of process development targets emerge. The idea of combinatorial scenarios is illustrated in Figure 2.

Process parameters	A	B	C
Value Scenarios	1,2	1,2	1,2,3
Combinatorial Scenarios	A1;B1;C1	A2;B1;C1	
	A1;B2;C1	A2;B2;C1	
	A1;B1;C2	A2;B1;C2	
	A1;B2;C2	A2;B2;C2	
	A1;B1;C3	A2;B1;C3	
	A1;B2;C3	A2;B2;C3	

Figure 2: Illustrative example of combinatorial scenarios for three process parameters in which two parameters take on 2 different values and a third takes 3 possible values. There are $2 \times 2 \times 3 = 12$ different combinations

4. Data and Analysis

4.1 Supercritical Extraction - Material and energy inputs

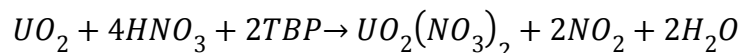
The fundamental challenge here and in other techno-economic estimates is reasonable estimation of material and energy flows of scaled up processes. Our approach to estimating reagent consumption utilizes a combination of two laboratory studies (Shimizu et al 2005; Samsonov et al 2007), stoichiometric analysis and industry experience. Needless to say, material requirements in laboratory experiments do not necessarily correlate with those for a scaled-up industrial process. In an experimental setup, scientists are usually trying to obtain maximum yield without necessarily considering how to lower reagent consumption. Results from the two laboratory studies is compared with the stoichiometric requirement and industry rules of thumb to obtain upper and lower expected values for scaled-up reagent consumption.

To recount the laboratory studies, Shimizu, et al., 2005 achieved the highest yields when using TBP, HNO₃, H₂O in the reactant complex in the ratio 1:1.3:0.4. 2 cm³ or 2.12 grams reactant complex is used per 20mg of sample. The sample contained 50% REE by weight. This translates into 212grams of reagent per gram of REE. The CO₂ flow was 2cm³ per minute and processing time was 2 hours.

Samsonov, et al., 2007 obtained the highest yields when using TBP and HNO₃ in the ratio 1:12. This is what has been used in the techno-economic model. The sample was 100% REE and the

molar ratio of sample and reagent was 1:20. This translates to 94grams of reagent per grams of REE. The CO₂ flow was 0.5cm³ per minute and processing time was 1.5 hours.

To follow with stoichiometric analysis, an example reaction of uranium oxide and nitric acid is illustrated in the following equation:



The stoichiometric molar ratio of REO:HNO₃:TBP would therefore be 1:4:2. With a scaled-up industrial process, reagent requirement may be expected to be 20 times the stoichiometric minimum (Prado, et al., 2012; Prado, et al., 2011). Reagent requirement by Shimizu, et al., 2005 is higher than this, while reagent requirement by Samsonov, et al., 2007 is slightly less. The two studies therefore provide a range for possible reagent requirements. Variabilities beyond this range is explored using sensitivity analysis. These two studies were referred to in particular as they explored the extraction requirement for several REEs, compared to other studies that only look at one or two. The reagent requirements for stoichiometric case, industry rule of thumb and the two boundary scenarios from laboratory experiments are summarized in table 1.

Table 1: Scenarios for reagent use - Stoichiometric minimum reflects every REE atom bound in TBP:HNO₃ complex. Industry rule of thumb is 20 times stoichiometric minimum. High and low reagent scenarios reflect two different laboratory scale results (Shimizu, et al., 2005) and (Samsonov, et al., 2007). Note that the high consumption of HNO₃ in the low reagent scenario will not significantly affect process costs (see section 4.2 and 5.1)

Reaction scenario	REO:TBP:HNO ₃ Molar ratio	REO:TBP:HNO ₃ Weight ratios
Stoichiometric minimum	1:2:4	1:2:1
Industry rule of thumb (Prado, et al., 2012)	1:40:80	1:39:20
High reagent Scenario (Shimizu, et al., 2005)	1:161:209	1:159:52
Low reagent Scenario (Samsonov, et al., 2007)	1:20:240	1:20:60

While the consumption of HNO₃ in the high and low scenarios is much higher than expected from an industry rule of thumb, this should not pose a problem for economic estimation. The economics of reagent use is dominated by the consumption of TBP, the cost of other reagents, including HNO₃, is insignificant compared to TBP, due to the large mass consumed and high price. We therefore choose two scenarios, one of which reflect TBP use higher than industry expectations and another that reflect TBP use lower than industry expectations.

The amount of reactant complex per ton of coal ash was calculated by multiplying the REE content per ton of coal ash with the amount of reagent required per unit of REE in the experiments. This study maintains solvent mass to feed ratio (S/F) as constant, a method often used to study the scale up of bench technologies (Prado, et al., 2011; Prado & Meireles, 2010; Prado, et al., 2012).

The extraction efficiency was considered to be the same as that provided in literature for REEs that were present in the solutions experimented with. These include Uranium, Plutonium, Americium, Europium, Yttrium, Lanthanum, Cerium and Terbium. REEs not studied in the experiment, e.g. Erbium, Gadolinium, Holmium, Terbium, Scandium etc. were assumed to have

an extraction efficiency of 90%. As will be seen in Section 5, results are not sensitive to this assumption except for the case of scandium, due to the dominance of scandium in net income.

CO₂ consumption was taken from experimental data; the data is reported by volume. In order to determine the mass, we found the density of CO₂ at the temperature and pressure at which the process was taking place. In the two processes considered, the temperature ranged between 315K and 325K and pressures between 15 and 25 MPa. Between this range of temperature and pressure, the density of CO₂ is around 0.662 grams per cm³ (Zorca, et al., 2007) and has been assumed to be so.

The energy consumption of supercritical extraction processes has been discussed by several authors. The size of commercial extractors covered in the literature ranged between 400 to 1,300 liters (Osorio-Tobón, et al., 2016; Rocha-Urbe, et al., 2014; Shariaty-Niassar, et al., 2009; Danisco, 2009; Paulo, et al., 2005; del Valle, et al., 2005). The energy consumption per liter of capacity was calculated based on the finding of del Valle, et al., 2005, who calculated the hourly energy consumption for a 1,300 liter extractor. We use an assumption consistent with prior work that super critical extraction would use electricity at 0.61 KW/L and thermal energy, which in this case come from gas, at 230 Kcal/hr/L (962 KJ/hr/L). (del Valle, et al., 2005).

4.2 Supercritical Extraction - Material and energy prices

It is assumed that processing will take place near coal power plants to reduce transportation. The fuel price in Wyoming, home of the Powder River Basin coal deposits, is chosen for this example.

Table 2: Price assumptions for energy and transportation

Item	Price	Unit	Source
Natural Gas	\$5.89	/1000 Cu Ft	(EIA, 2017)
Electricity	\$77.6	/MWh	(EIA, 2017)
Transportation of ash	\$0.26	/ton mile	(Edgar, 1983)

Table 3: Price assumptions for reagents

Item	Price	Unit	Source
Water	\$5.00	/1000 gallon	(BOPU, 2017)
Nitric Acid	\$400	/ton	(KEMCORE, 2017)
TBP	\$4,200	/ton	(KEMCORE, 2017)
Liquid CO ₂	\$460	/ton	(del Valle et al., 2005)

The process is assumed to be run 20 hours a day for 365 days a year. The equipment would be manned by two individuals. Wage rate is assumed to be \$25 per hour which is the median salary of a chemical plant operator in the USA in 2016. (Salary.com, 2016; Recruiter, 2016). Also, the coal ash is transported over a distance of 100 miles. The sensitivity of results to many of these values is analyzed in Section 5.3.

4.3 Supercritical Extraction - Capital costs

The capital cost and energy consumption of super-critical extractors was obtained through literature review of papers estimating the same for extraction of essential oils from herbs (Osorio-Tobón, et al., 2016; Rocha-Urbe, et al., 2014; Shariaty-Niassar, et al., 2009; Danisco, 2009; Paulo, et al., 2005; del Valle, et al., 2005). Although the literature review was unable to fix the maximum possible size of a supercritical extractor, most analysis considered relatively small plants ranging between 400 and 1000 liters with 1300 liters being the largest. As economies of scale imply lower marginal costs for larger reactors, we choose a reactor size on the upper end from current industrial scale supercritical facilities. The main factor determining reactor size is the need to accommodate the volume of coal ash processed per batch. We assume a reactor size exactly equal to the volume occupied by the coal ash. Volume depends on density, which for PRB bottom ash can vary between 720 and 1600 kg/m³ (US DOT, 2016). In order for the process to work efficiently, the super critical fluid should be able to flow through the ash and dissolve the REEs. The coal ash should therefore not be packed too tightly. We therefore assume the lower limit of coal ash density of 720 kg/m³. The required reactor capacity to process one ton of ash is thus 1,390 liters. If headroom for the TBP complex were accounted for, the size of extractor required to process 1 ton coal ash would be larger, leading to an increased capital cost. Such cases have been discussed in sensitivity analysis in section 4.5.

The cost of extractors of different sizes were obtained and the relation between capacity of extractor and cost for the same was estimated (figure 3). Cost data from various sources were made comparable using appropriate exchange rate and discount rates.

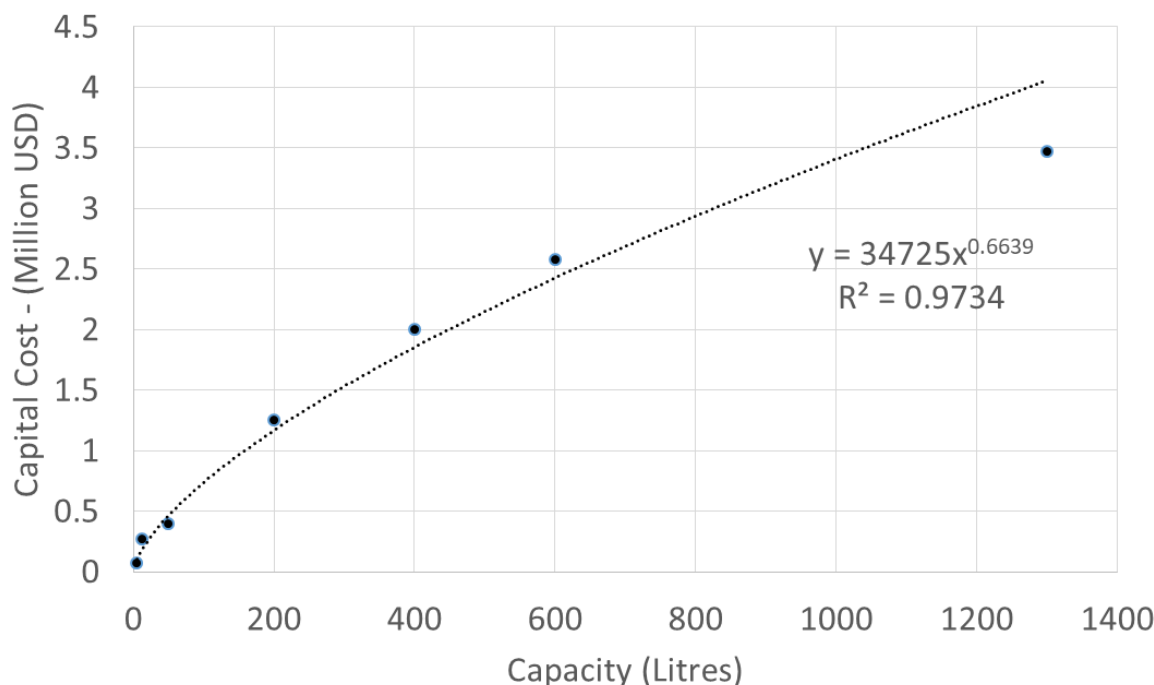


Figure 3: Relation between capacity of extractor and capital cost plotted based on data obtained from literature (USD = U.S. Dollar) (Osorio-Tobón, et al., 2016; Rocha-Urbe, et al., 2014; Shariaty-Niassar, et al., 2009; Danisco, 2009; Paulo, et al., 2005; del Valle, et al., 2005).

The usual scaling model for capital costs of industrial processes was used (Haldi & Whitcomb, 1967),

$$\frac{\text{Cost of size A}}{\text{Cost of size B}} = \left(\frac{\text{Capacity of size A}}{\text{Capacity of size B}} \right)^{\beta}$$

, where β is an empirical constant, as a general relationship to determine cost for any size plant. Regression of the data indicates a scaling factor of 0.66. This result is close to what is found in the literature, e.g. the scaling factor of chemical reactors or pressurized tanks is listed as 0.6 in (Newman, et al., 2009). Although the estimate obtained was based on relatively few data points, it closely matches that of similar technologies found in literature and therefore is used in the economic scaling model.

Based on the above modeling, a supercritical extraction process with 1,390 liter capacity is found to have a capital cost of \$4.2 million. The relationship established above however can be used to estimate the cost of larger plants. Insurance, maintenance and property tax are assumed to be 1%, 2% and 4% of capital cost (Shariaty-Niassar, et al., 2009). Interest rate has been assumed to be 4% according to the prime lending rate in the USA (Trading economics, 2016). The life of the extractor has been assumed to be 15 years (del Valle, et al., 2005).

Based on these assumptions, the annualized capital + maintenance + tax + finance cost of a 1,390L supercritical CO₂ reactor was found to be \$456,000 per year.

4.4 Separation and Processing

The output obtained from the supercritical process is a mixture of REE nitrates. The next steps are separation into individual REE oxides, which is the final saleable product considered in this study. Metallothermic reduction processes are used to extract the rare earth elements in metals under vacuum conditions with inert gas at high temperatures ($>1000\text{ }^{\circ}\text{C}$) (Haque, et al., 2014), though this step is beyond the scope of this study and has not been researched. Due to the chemical similarity of different REEs, their separation is technically challenging (McGill, 2000). The specifics of separation are firm specific and kept confidential. There is thus insufficient publicly available data to build a process-level description of the economics of separation. This leads us to a qualitatively different approach for separation and purification: analysis of market price data for REE products in different stages of processing.

The idea is to compare the price of a mixture of REEs with the net value of REEs post separation and identify the difference with the cost of separation and processing. Enriched mixtures made from bastnasite and monezite ores, 68% REE salts, are market products for which price data is available for 2008-2012 (USGS, 2016). Average prices for individual rare earth oxides are available for the same period. Because prices of rare earth oxides are volatile, a single year's data is not necessarily representative of process costs. Thus, we do the calculation for a number of years and take the lowest and highest value as a range. The price of enriched ore mixtures ranges between \$24 and \$108 per kg from 2008-2012 (USGS, 2013). Using data on the REE content of these ores (Peiro & Mendez, 2013) and global annual price data for REE oxides (USGS, 2016), we calculated the value of REE oxides contained in these mixtures to range between \$24 and \$104 per kg. Subtracting year by year, the difference in value of REE oxides contained in the mixture and the market price of the enriched ore mixture ranged between \$18 and \$97 per kg. We next assume that the cost of separating the output of the supercritical extraction process, a mixture of REE nitrates, would be similar in scale to that of enriching bastnasite and monezite, to arrive at REE oxides.

Finally, the separation costs per ton of coal ash are backed out from the above costs to process the enriched mixture as follows. We calculated the quantity of REE nitrates generated from a ton of coal ash. As an example, for the case of coal ash with global maximum REE concentration (934 ppm), approximately 1 kg of REE nitrate will be produced per ton of ash. This therefore gives us the same range of \$18-\$97 per ton of coal ash, for separation and processing cost. Further details of how these calculations are used in scenario development is shown in Table A.1 in the Appendix.

4.5 Concentrations of REEs in coal ash and prices

The potential income from REE extraction from coal ash depends on the combination of concentration, extraction yields and efficiency. For concentration, we use a substantial body of prior analytical work characterizing composition of coal ash from a variety of power plants around the world (Calus Moszko, et al., 2016; Hower, et al., 2013; Smolka-Danielowska, 2010; Zhang, et al., 2001; Mayfield & Lewis, 2013; NETL, 2017). While analytical methods varied by study, the two major techniques used to characterize REE content were wavelength dispersive X-ray

fluorescence spectrometry and inductively coupled plasma mass spectroscopy (ICP-MS). Combining the available literature into an integrated data set yields a total of 155 samples from North America, Europe and Asia, of which 126 were fly ash and the rest bottom ash. The dataset includes 86 samples for the U.S, 64 of which were flyash and 22 bottom ash.

From the elemental concentration, the value of each coal ash for each of the 155 global samples was calculated based on the five-year average price (USGS, 2016) and 100% yield. Two samples with median and max values were selected to serve as representative scenarios, the median being ash from a power plant in Poland and the max being ash from a power plant in Yunnan, China. The elemental concentrations, prices and values of ashes with minimum, median and maximum value of REE content are shown in table 4. Note that scandium is a major source of income in both cases (85% for max ash and 67% for median ash). This is a major difference between coal ash and most REE ores, the latter contains no scandium (Peiro & Mendez, 2013). Doing a similar exercise focusing only on the 86 ash samples from the U.S, the total concentration of REEs in coal ash has been observed to vary between 98.7 and 525 ppm (Całus Moszko, et al., 2016; Hower, et al., 2013; Mayfield & Lewis, 2013; Smolka-Danielowska, 2010; Zhang, et al., 2001). Appalachian basin fly ash contains on average 501 mg REE per kg. Powder River and Illinois Basin fly ash on the other hand contain, on average 403 and 337 mg REE per kg ash respectively. The three basins together are responsible for 70% to 80% of US coal production (Taggart, et al., 2016).

Globally, the total value of REE oxides that may be obtained per ton fly ash varies between \$6 and \$557 with a median of \$250 when using five-year average of prices from 2010 and 2014. Table 4 shows details of prices and REE concentrations for six sample ashes, global max, median and minimum, and the maximum, median and minimum from U.S. samples. Note that US coal ash has relatively low concentrations of valuable REEs and the US max is lower than global median.

Literature reports concentration of REE metal in coal ash, which exist as REE salts (sulfates, phosphates and nitrates). At the same time, price of metallic REEs is not available in a consistent manner from any data source. Therefore in order to determine the revenue from this process we needed to determine the value of REE oxide obtained from this process. We used the stoichiometric ratio between REE metal and REE oxide to adjust the prices, so that, when multiplied by the concentration numbers, which are reported in terms of metallic REE, it would reflect the total value of the respective REE oxides that may be obtained.

Table 4: Five year (2010-2014) average price of REEs and concentrations of REEs in 6 ash samples (from 155 global ash samples) with maximum, median and minimum value of contained REEs, globally and in the United States

	Price (USD/Kg)	Concentration (ppm)					
	(USGS, 2016)	Ash with max value, global (Moszko, et al., 2016)	Ash with median value, global (Hower, et al., 2013)	Ash with min value, global (Zhang. et al., 2001)	Ash with max value, US (NETL, 2017)	Ash with median value, US (NETL, 2017)	Ash with min value, US (NETL, 2017)
Location		Poland	China	Japan	West Virginia	Pennsylvania	Ohio

Ce 140	40.8	345	206	11.2	216	66.7	170
Dy 163	885	2.3	15.1	0.54	18.5	6.50	11.0
Er 166	223	6.8	8.6	0.31	17.0	13.0	7.00
Eu 153	2,106	1.7	3.7	0.39	7.51	5.00	3.60
Gd 157	136	13.8	18.6	0.88	122	8.25	14.4
Ho 165	859	3.5	3	0.11	7.51	13.8	2.20
La 139	40.8	175	96	6.8	117	43.0	90.7
Lu 175	3,525	1.8	1.2	0.05	9.00	5.00	1.20
Nd 146	136	135	93	4.05	105	62.5	102
Pr 141	144	39	24	1.13	74.5	22.8	23.5
Sc 45	6,719	70.9	25	3.84	45.9	15.5	4.25
Sm 147	87.4	13.9	18	0.93	21.0	17.8	15.1
Tb 159	1,826	0.9	2.6	0.35	30.5	13.0	1.90
Th 232	1,713	1.2	1.2	0.01	0	0	0
Tm 169	1,500	0	1.2	0	8.51	9.00	1.10
Y 89	87.4	121	83	8.64	114	20.5	61.8
Yb 172	470	2.4	8	0.31	11.0	5.25	6.90
Total		934	608	30.6	525	215	98.7

520

521 5. Results

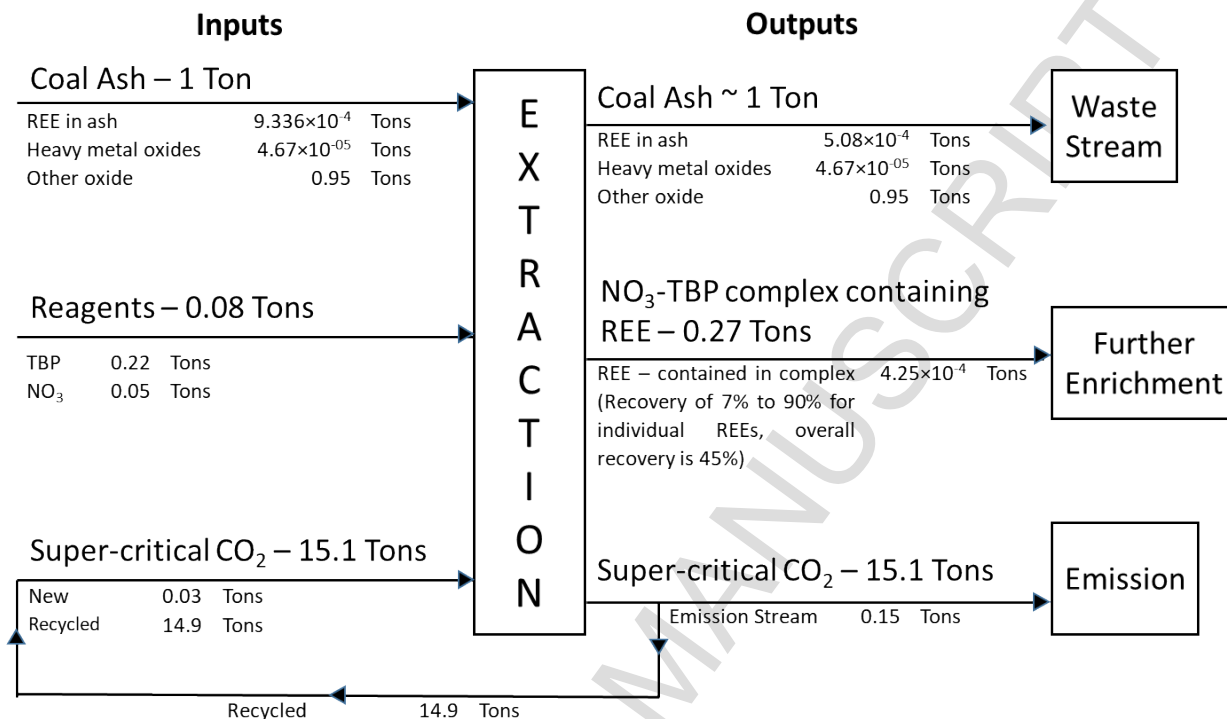
522 5.1 Mass balances

523 Mass balances of super-critical extraction of rare earth metals from coal ash, at an industrial scale
 524 was developed using data available in literature. The mass balance is designed to represent inflow
 525 of 1 ton of coal ash. The REE content of 1 ton coal ash has been obtained from literature exploring
 526 the same. In this mass balance we have used a representative coal ash that contains maximum
 527 concentration of REEs by value. The concentration of REE is 934 grams per ton coal ash valued
 528 at \$557. The reagent input has been calculated by extrapolating reagent use per unit rare earth
 529 elements in samples in lab experiments. We referred to Shimizu et al., 2005 for high reagent use
 530 scenario and Samsonov et al, 2007 for low reagent scenario. Assumptions on percentage yield of
 531 individual REEs are detailed in table 5 in section 5.2.

532
 533 *High reagent use scenario:* The detailed inputs and outputs for processing one ton of coal ash with
 534 maximum concentration of REE by value for a high reagent scenario is shown in figure 4. Heavy
 535 metals are absent from this flow. While heavy metals can also be extracted using super-critical
 536 CO₂, this requires a ligand different from the TBP-HNO₃ complex (Halili, et al., 2015; Kermer, et

al., 2016). It is therefore assumed that heavy metals are not extracted in this process and remain in the leftover ash.

Figure 4: High reagent use and max concentration of REE case -
Inputs and outputs for processing one ton of coal ash



In figure 4, inputs are all the materials going into the process, outputs are all usable materials obtained and emission/waste are all the material that are not used. Every ton of coal ash processing starts with 15.1 tons of CO₂, 99% of which is recycled, and 270 kg of TBP-HNO₃-H₂O complex. The REEs react with the Nitric acid to form REE(NO₃).TBP. REE(NO₃). TBP along with SC-CO₂ is sent to the collection chamber. Once the pressure is released, the CO₂ vaporizes, is captured and recycled for the next batch. Some of the CO₂ is lost due to leakage during this process. The assumptions behind CO₂ leakage varies between studies, ranging between 1% and 5% (Carvalho, et al., 2015; Osorio-Tobón, et al., 2016; Osorio-Tobón, et al., 2016; Pereira & Meireles, 2010). It is assumed that there is a leakage of 1% in every cycle, = the most conservative estimate. The REE(NO₃) and TBP is collected for further processing (listed under outputs). Heavy metals and other oxides remain with the coal ash which may then be sent to landfills or put to secondary uses like construction of roads or making bricks.

The extraction efficiency of different REEs varies between 7% and 99%. (Duan, et al., 2012; Samsonov, et al., 2007; Shimizu, et al., 2005; Jorjani & Shahbazi, 2016) . This has been elaborated in table 5. Cerium is the most abundant REE, contributing to around 33% by weight. Cerium oxide however has poor solubility in the TBP complex and only 7% is captured. Therefore the overall extraction efficiency of REEs only amount to 50%. CO₂ emissions from the process include grid electricity, transportation, in situ natural gas combustion and leakage. Emissions for a Wyoming grid are assumed to be 1822lb or 828 Kg CO₂ per MWh (EIA, 2017). Emissions from transportation is assumed to be 1.5Kg CO₂ per mile for a truck of 8 ton capacity (US DOT, 2017).

Emissions from natural gas is assumed to be 0.12lb per scf or 1.5grams/m³ (EPA, 1998). Leakage from the process is assumed to be 1%. Taking all the emissions into account the process is estimated to emit 0.95 tons CO₂ per ton of coal ash processed.

Low reagent use scenario: Figure 5 shows material flows for the low reagent use scenario. The low reagent scenario used 3.2 tons of CO₂ and 90kg of TBP-HNO₃ complex per ton of ash. The REE output is slightly higher in this case. Shimizu reported yield of Lanthanum as 7%. Samsonov did not report yield of Lanthanum and has been assumed to be 90%. Given the value of Lanthanum however this does not impact profitability to any significant extent, as discussed in section 4.4. The process emits 0.77 tons CO₂ per ton of coal ash processed (grid electricity + transport + in situ natural gas combustion + leakage from process).

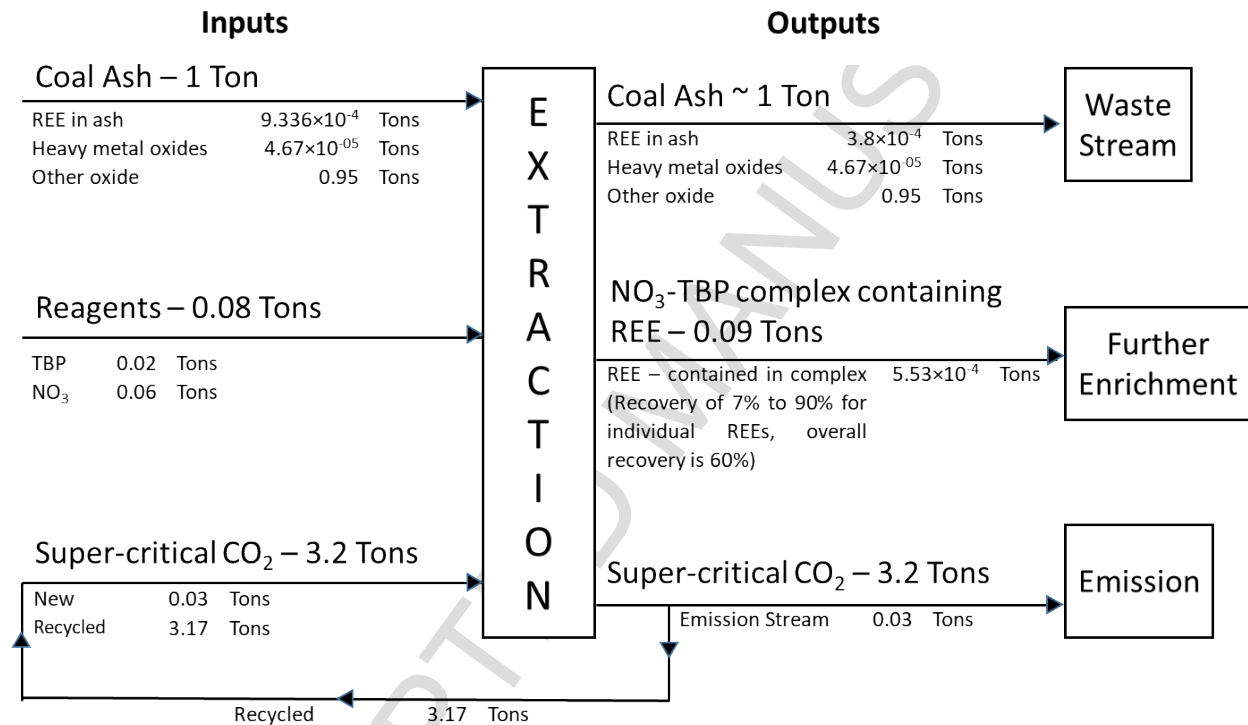


Figure 5: Low reagent use and max concentration of REE case - Inputs and outputs for processing one ton of coal ash

5.2 Income from REEs

The income from this process is determined by the price of coal ash, the REE content of coal ash and the percentage yield from the extractions. As explained earlier, we considered two yield scenarios, one with high reagent use and the other with low. The two scenarios have similar but slightly different yield results. We used the price of REEs in table 4 and the yield assumptions for high and low reagent scenarios to calculate the total revenue from a ton of coal ash with global maximum and median REE content.

Table 5: Yield from the two reagent scenarios, REE income from reagent and coal ash content scenarios (global maximum and median revenue coal ash).

Low reagent Scenario (Samsonov, et al., 2007)				High reagent Scenario (Shimizu, et al., 2005)		
REE	Yield	Global max value (USD/ton coal ash)	Global median value (USD/ton coal ash)	Yield	Global max value (USD/ton coal ash)	Global median value (USD/ton coal ash)
Ce 140	7%	0.99	0.59	7%	0.99	0.59
Dy 163	90%	1.83	12.0	90%	1.83	12.0
Er 166	90%	1.36	1.73	90%	1.36	1.73
Eu 153	91%	3.26	7.09	99%	3.54	7.71
Gd 157	90%	1.69	2.28	90%	1.69	2.28
Ho 165	90%	2.71	2.32	90%	2.71	2.32
La 139	90%	6.43	3.53	7%	0.50	0.27
Lu 175	90%	5.71	3.81	90%	5.71	3.81
Nd 146	90%	16.5	11.4	90%	16.5	11.4
Pr 141	90%	5.05	3.11	90%	5.05	3.11
Sc 45	90%	429	151	90%	429	151
Sm 147	90%	1.09	1.42	90%	1.09	1.42
Tb 159	90%	1.48	4.27	7%	0.12	0.33
Th 232	0%	0	0	90%	1.85	1.85
Tm 169	90%	0.00	1.62	90%	0.00	1.62
Y 89	90%	9.52	6.53	99%	10.5	7.18
Yb 172	90%	1.02	3.38	90%	1.02	3.38
		487	216		483	212

5.2 Analysis of expenses and revenue using combinatorial scenarios

Figure 6 lists four cost and eight revenue scenarios with different combinations of reagent use, concentration of REEs in coal ash and yield of scandium. The analysis reveals that economic viability depends primarily on use of reagents and the concentration and yield of REEs from coal ash. Scandium accounts for 90% in value in the most valuable ash and about 70% in value of median value ash. The concentration and yield of scandium is thus critical in the economic viability of the process.

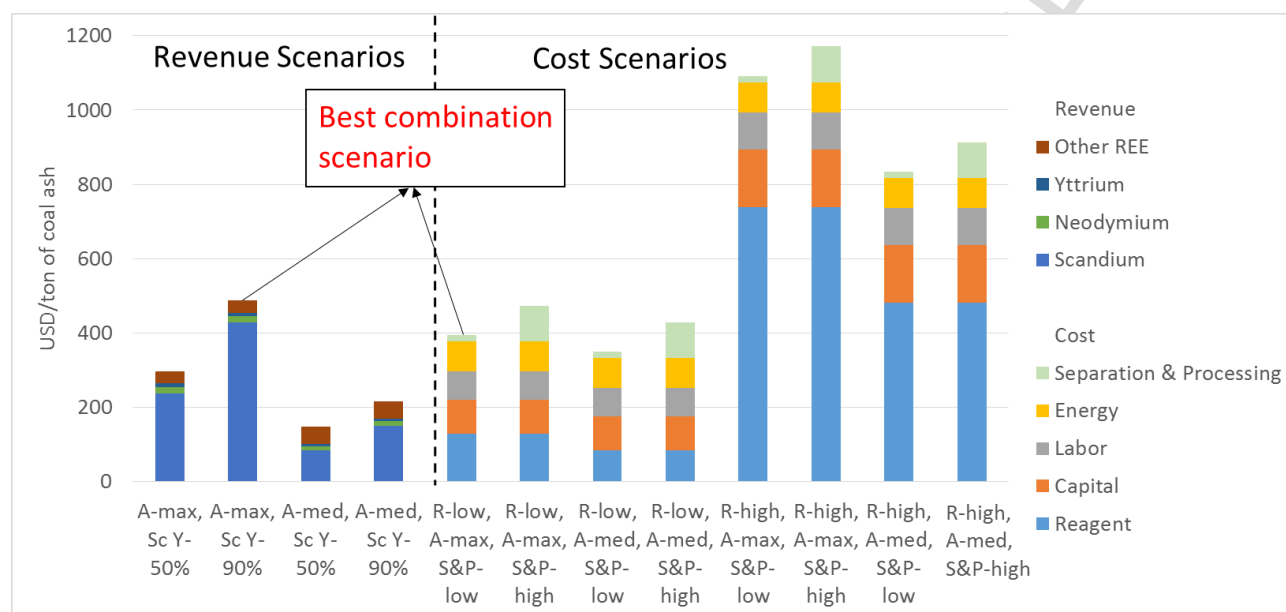


Figure 6: Revenue and cost scenarios for supercritical extraction of REE from coal ash. A-max = ash with global max REE content, A-med = ash with global median REE content, Sc Y = Scandium yield, R = Reagent use, Reagents = CO₂, TBP, HNO₃, S&P = Separation and processing. Details of the scenarios are listed in table A.1 in the appendix.

Revenue scenarios combine two alternatives of REE concentration in ash (maximum by value, or median by value) and two alternatives of Scandium yield (50% and 90%). A lack of literature exploring the yield of scandium through super-critical extraction necessitated the yield scenarios. Cost scenarios have two alternatives of reagent use (high and low). The reagent use also differs between max and median value ash because it has a stoichiometric dependence on the mass of REE. We do have to alternatives for the reagent use, in the revenue scenarios, since the value of the yield is practically the same for both high and low reagent use. Cost of separation of oxides, referred to as “separation and processing” are two more alternatives and they have either the low value of \$18 or the high value of \$97. Given the two alternatives for the four parameters, eight scenarios of cost and four scenarios of revenue has been developed.

The maximum profit can be obtained when using coal ash with a maximum concentration of REEs, 90% yield of scandium, low use of reagent and low cost of separation and processing. Under such conditions, the process stands to make a revenue of \$487 while incurring a cost of \$395, thereby making a profit of \$92 per ton of coal ash processed. If separation cost is high on the other,

assuming all other conditions remain same, the profit will reduce to \$13 per ton ash processed. All other cost and revenue combinations seem economically unviable.

Recycling of reagents is possible using methods similar to those used in recycling reagents used in the PUREX process (Jubin, 2008) (Irish & Reas, 1957). A leaching process using TBP, nitric acid and kerosene as reagents, the PUREX process reprocesses spent nuclear fuel to separate uranium and plutonium from fission products. The solvents are recovered using several stages of distillation, absorption and fractionation (Irish & Reas, 1957). Due to costs of recovery, the methods used to recycle the reagents used in the PUREX process is not expected to affect the net cost of production much, rather its role would be to reduce reagent emissions and thereby prevent potential environmental damage (Park, et al., 2015). While it is not clear if low cost recycling of TBP and HNO_3 is possible, if it could be done at zero cost the cost of the high reagent use scenario would change to \$405 per ton ash while a low reagent use scenario would then cost \$264 (excluding the cost of oxide separation). If using ash with maximum concentration of REE, both cases suggest economic viability, though in the high reagent use case, the recycling cost would have to be kept under 10% of the market price of the reagents. Neither case is likely to be viable if using ash with median REE concentration.

The annual cost and revenue of the four basic scenarios, assuming a scandium yield of 90%, have been summarized in table 6.

Cost incurred from disposal of coal ash or income from selling the coal ash would change profits from each scenario by $\pm \$40$. This has not been shown in figure 6 or table 6.

Table 6: Annual cost, revenue and output from four revenue and cost scenarios for supercritical extraction of REEs from coal ash (1,300 liter extractor)

Scenario	REE content of coal ash	Coal Ash processed annually (Tons)	Annual Processing cost (\$ Million)	Annual Revenue (\$ Million)	Annual REE output (Tons)
High Reagent	Global Max	3,650	3.70	1.76	1.53
	Global Median	3,650	2.80	0.77	1.10
Low Reagent	Global Max	4,867	1.83	2.37	2.69
	Global Median	4,867	1.61	1.05	1.82

5.3 Sensitivity analysis of super-critical extraction process

Since the high reagent use scenario is unlikely to be economically viable, sensitivity analysis was conducted with low reagent use on coal ash with maximum and median concentration of REEs. Figure 7 represents the effect of a 10% increase in nine key parameters on the revenue of the process. If using ash with maximum concentration for example, a 10% increase in scandium yield will increase profits by \$43 (46%) while a 10% increase in reagent price will reduce profits by \$10 (11%). The reverse would be true for a 10% decrease in the same parameters.

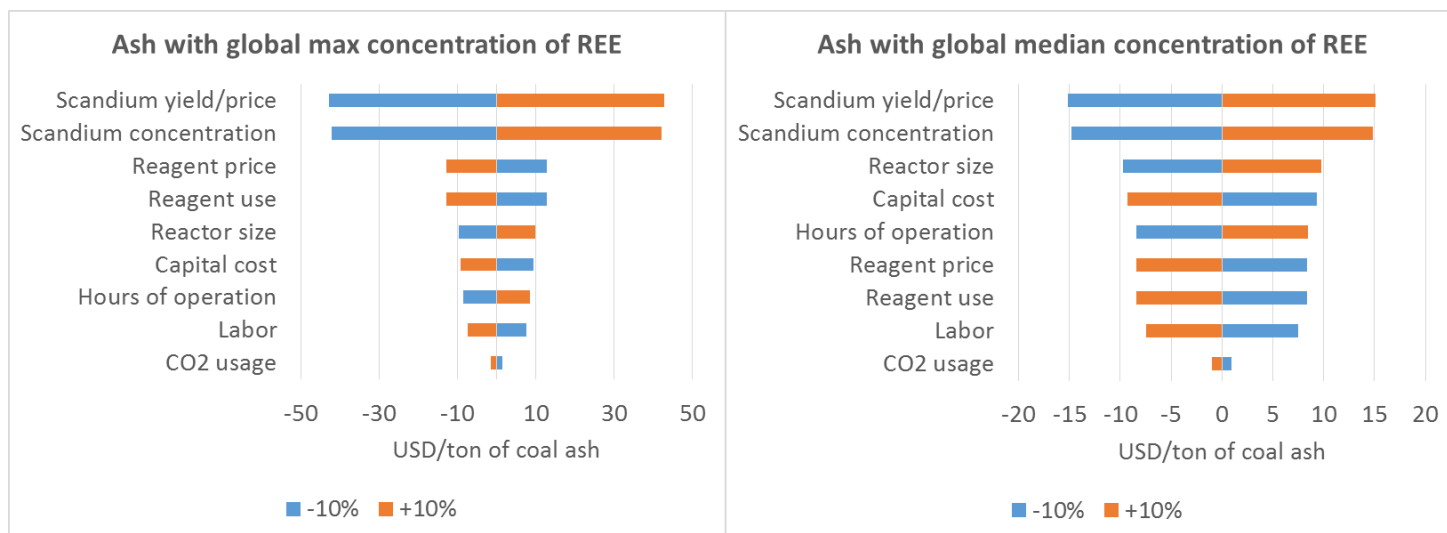


Figure 7: Impact of 10% increase (or decrease) of various factors on revenue. The base case has low reagent use, the profit from processing one ton of ash with max concentration is \$97, for ash with median concentration, profit is -\$134. Reagents = TBP, HNO_3

Analysis reveals that scandium is a key driver of overall process profitability. Changes in its yield, price, or concentration are major determinants of profitability for both types of ash. Reagent use is linked to REE concentration since it is stoichiometrically linked to the quantity of REEs. Reagent use and price is more important for ash with higher concentrations of REEs as can be seen in the case of ash with the global max REE. Reactor size, capital cost and hours of operation, factors that affect batch size are relatively more important for ashes with lower concentrations of REE. Hours of operation conflates two impacts, reducing annual output and at the same time increasing energy costs.

The cost of energy, which includes natural gas and electricity amount to \$81 per ton of coal ash processed. Incidentally, Wyoming has one of the lowest energy prices in the US. Our model uses 2014 prices of energy, the price of natural gas was \$5.89/1,000 cubic ft and that of electricity was \$77.6 per MWh. Connecticut has one of the highest energy prices in continental USA. The price of natural gas in the same year was \$8.07/ 1,000 cubic ft and that of electricity was \$170.5/MWh. If the process were to be conducted in Connecticut, the energy bill per ton would more than double to \$173 per ton. Considering US average prices (\$5.62/1,000 cubic ft natural gas and 104.4/MWh electricity) however, the energy cost per ton of coal ash processed would amount to \$101, 25% higher than in Wyoming. Having said that however, this process is mostly likely going to be conducted in states with significant coal based generation, which also tend to have low energy prices. In practice therefore, the cost of energy may be expected to be closer to the lower bound of \$81 per ton of ash processed. It should also be noted that the prices of natural gas have been decreasing and is expected to go down even further in the future. The energy cost is therefore expected to decrease.

Economies of scale become more important as concentration of REE goes down. Capital cost could also increase if the coal ash requires head room in the extractor. The increase in capital cost in

such a case would be directly proportional to the headroom required. CO₂ usage has little impact not only because it is relatively less expensive, but also because 99% of it is recycled.

There may be challenges in altering the parameters ranked in figure 7. The exercise assumes that the size of the extractor is 1,390L, based on the requirements of processing one ton of coal ash. The literature lists commercial extractors ranging from 400L to 1300L. Although larger extractors would reduce processing cost through economies of scale, super critical extractors work at very high pressure and therefore the size of the vessels is constrained. Acid resistant reactors may also cost more than those used in food processing as the reactors may have to be specially prepared to prevent metal leaching and corrosion.

The low reagent scenario is already considering the lower bound of reagent use. Reducing reagent use further might also prove to be a challenge. Other factors like price of REEs, capital, and reagents cost are exogenous to the process and the processing plant is unlikely to be able to influence these factors.

6. Conclusion

In recent years there have been studies to establish the technical feasibility of coal ash as a source of REEs (Franus, et al., 2015) and assess potential environmental impacts (Mayfield & Lewis, 2013). This is the first study to test economic feasibility. This work serves not only as an estimate of the profitability of the nascent technology, but also rank priorities for future research in this field. Our analysis suggests that super-critical extraction could be an economically viable method to extract rare earth metals from coal ash, but only under certain conditions. These conditions include:

(i) The ash will have to have a high concentration of high value REE. The value of the REE content has to be close to maximum of what is found in coal ash globally. Scandium and neodymium are the two most expensive REEs and they heavily impact the value of the content. In the literature review we found that the ash sample with the highest value of REE came from a plant in Poland. There was however no way to ascertain the origin of the coal used to produce the ash. A preliminary analysis should therefore be done to ascertain of value of the REE content before engaging in this process. Currently, US coal ash has far lower REE content and is therefore unlikely to be suitable for the process.

(ii) The molar ratio of REE oxides to TBP reagent should be close to 1:20. TBP is expensive and increase in TBP use can quickly diminish profitability. The TBP-HNO₃ complex is used to dissolve REEs, the level of solvation of various REEs depends on the ratio TBP: HNO₃. Empirical work is thus needed to achieve high yields of the most valuable REEs while at the same time managing reagent use, i.e. not exceeding a REE oxide:TBP ratio of 1:20.

(iii) Profitability is heavily dependent on scandium recovery, currently the most expensive REE. Processes must therefore have high scandium yield. Neodymium is the second most expensive REE, at about half the value. As prices change in the future, this will impact economic feasibility.

REE ores do not contain some of the more valuable REEs such as scandium, which are currently obtained from other sources like red mud. This rarity lends to their high price. Ores do however contain more of elements like cerium and lanthanum, the output of which far exceeds their current demand. This imbalance between supply and demand and the ratios in ores of individual elements leads to stockpiling of the more abundant elements and further drives down their prices (Binnemans, et al., 2018). Since initially it is unlikely that super-critical extraction will occur at a large enough scale to impact REE prices, profitability from the process will be determined by prices set by ore based production.

In addition to being a case-study, this work also contributes to TEA methodology. As is typical with TEA, data availability was a challenge due to lack of prior industrial development of the process of interest, in this case, super-critical extraction on mineral processing. Also, much of the data in the mining industry is proprietary and not easily accessed. In this work we used available data from similar industries and results from laboratory experiments, leveraging both to create scenarios for plausible industrial scale-up. The exercise here, as in all TEA, is beset with uncertainty. While there is no way to dispense the uncertainty, the combinatorial scenarios proposed here is a useful approach to clarify how outcomes depend on combinations of uncertain parameters.

Acknowledgements: This research was supported by the U.S Department of Energy under Grant Number **FE0027069**

Appendix

Table A.1 list the components of the combinatorial scenarios following the format elucidated in figure 2 in the article.

Table A.1: Components of combinatorial scenario, following from figure 2 in article. Shaded cells indicate choice of variable

Cost Scenario						
Process parameters	Reagent Use [R]		REE content of Ash [A]		Processing & Separation cost [S&P]	
Values	High	Low	Maximum [max]	Median [med]	High	Low
Combinatory Scenarios						
R - high, A-max, S&P-High						
R - high, A-max, S&P-Low						
R - high, A-med, S&P-High						
R - high, A-med, S&P-Low						
R - low, A-max, S&P-High						
R - low, A-max, S&P-Low						
R - low, A-med, S&P-High						
R - low, A-med, S&P-Low						

Revenue Scenarios						
Process parameters		REE content of Ash [A]		Scandium Yield [Sc Y]		
Values		Maximum [max]	Median [med]	50%	90%	
Combinatory Scenarios						
A-max, Sc Y-50%						
A-max, Sc Y-90%						
A-mid, Sc Y-50%						
A-mid, Sc Y-90%						

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