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Techno-economic Assessment for Integrating Biosorption into Rare Earth Recovery Process

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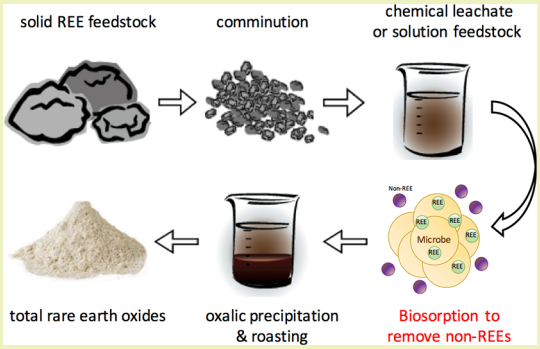
Supporting Information

ABSTRACT: The current uncertainty in the global supply of rare earth elements (REEs) necessitates the development of novel extraction technologies that utilize a variety of REE source materials. Herein, we examined the techno-economic performance of integrating a biosorption approach into a large-scale process for producing salable total rare earth oxides (TREOs) from various feedstocks. An airlift bioreactor is proposed to carry out a biosorption process mediated by bioengineered rare earth-adsorbing bacteria. Techno-economic assessments were compared for three distinctive categories of REE feedstocks requiring different pre-processing steps. Key parameters identified that affect profitability include REE concentration, composition of the feedstock, and costs of feedstock pretreatment and waste management. Among the 11 specific feedstocks investigated, coal ash from the Appalachian Basin was projected to be the most profitable, largely due to its high-value REE content. Its cost breakdown includes pre-processing (leaching primarily, 77.1%), biosorption (19.4%), and oxalic acid precipitation and TREO roasting (3.5%). Surprisingly, biosorption from the high-grade Bull Hill REE ore is less profitable due to high material cost and low production revenue. Overall, our results confirmed that the application of biosorption to low-grade feedstocks for REE recovery is economically viable.



KEYWORDS: *Low-grade feedstock, Airlift bioreactor, Mineral recovery, TEA, Mining*

INTRODUCTION

There is an ever-increasing demand for rare earth elements (REEs) in renewable energy, consumer product, and defense applications. For example, REE-based neodymium−iron−boron magnets play a key role in wind turbines, electric vehicle motors, and electronics, and the demand for the magnets continues to increase. China dominates the global REE supply, and countries such as the United States are highly dependent on this supply for rare earth products. The current uncertainty regarding REE availability in the global market hinders the growth of U.S. industries that rely on affordable REEs. The supply risk of REEs, environmental concerns associated with the extraction and processing of ores containing REEs, and economic benefits of having a stable REE supply chain have motivated research into the processing of nontraditional REE feedstocks such as mine tailings, geothermal brines, and coal byproducts.[1] Given their abundance in the U.S., these resources offer an attractive means to diversify the REE supply.[2−5] However, current hydrometallurgical processes, in particular solvent extraction, are not efficient with low-grade feedstocks, highlighting the need for new technologies that can cost-effectively extract REEs from these feedstocks.

To address the technology gap for REE extraction from low-grade feedstocks, biosorption represents a promising alternative

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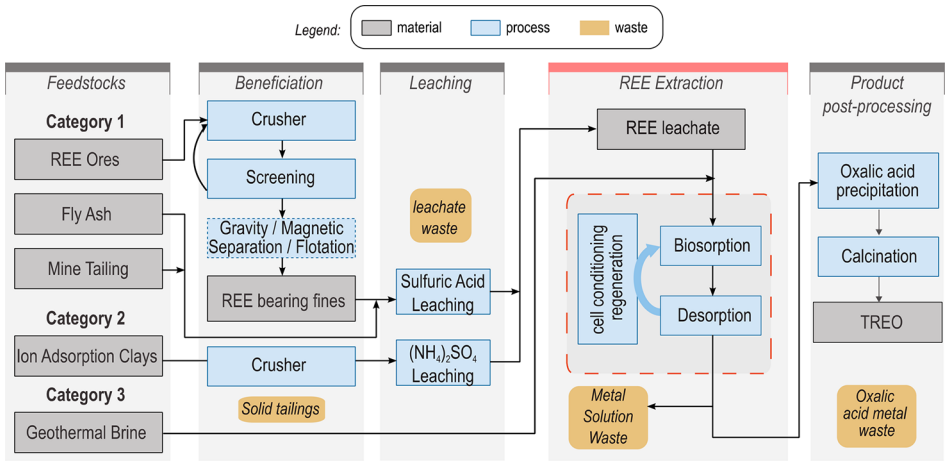

Figure 1. Process flow diagram. Three feedstock categories that differ in their required preprocessing steps are included. Following pre-processing, REE-bearing solutions are run through a biosorption/desorption process where REEs are separated from contaminating metal ions and concentrated rare earth solutions are derived. Post-processing of rare earth solutions via oxalic acid precipitation and roasting produces salable total rare earth oxides.

Table 1. Feedstock Categories, Processing Steps, and REE Characteristics

	category 1					
	low-grade			high-grade	category 2	category 3
feedstock sources	coal ash	mine tailings	Round Top	Bull Hill	ion exchange clay	geothermal brine
location	Appalachian, Illinois, Powder River	Lower Radical, Togo (CO)	Texas	Wyoming	Lower Kittanning bed (PA)	Mount Taftan (Iran)
mining	none	none	yes	yes	occasional	none
beneficiation	none	none	yes	yes	minimal	none
leaching	sulfuric acid	sulfuric acid	sulfuric acid	sulfuric acid	ammonia sulfate	none
waste management	yes	yes	yes	yes	yes	minimal
REE content (ppm)[a]	337–603[20]	178–232[11,16]	633[19]	2,800[26]	131–293[3]	0.6–3.2[25]
REE value ($/(kg of TREO))[b]	437–526	93–215	40	19	18	25–31

[a]REE content refers specific samples from the listed locations. Coal ash, for example, has 603 ppm REEs in Appalachian basin, 365 ppm in Illinois basin, and 337 ppm in Powder River basin, so REE content in coal ash was noted as 337–603 ppm. [b]Individual REO prices (≥99% purity) were quoted from several sources (UCORE, accessed on May 16, 2017; mineralprices.com, prices of Mar. 31, 2017; informal communication with an industrial partner in September, 2016 for Ho, Lu, and Yb prices). REE values for the listed locations were calculated based on data from citations.[3,16,19,20,25,26]

to traditional methods.[6−9] Biosorption has been successful in bioremediation applications to remove toxic heavy metals—such as As, Cd, and Cr—due to its inexpensive operation and effectiveness with low metal ion concentrations.[9−12] Considering the high capacity and affinity of cell surface−metal binding, biosorption is well-suited for extracting precious metals including REEs. Selective adsorption of REEs over non-REEs has been observed with different microbial species via their native surfaces[9,13,14] and a pH-dependent REE desorption scheme has achieved separation factors for certain REE pairs that exceeded solvent extraction standards.[15] By combining native microbial cell surface features with advanced bioengineering, we recently generated two REE-adsorbing bacterial species *Caulobacter crescentus* (*C. crescentus*) and *Escherichia coli* (*E. coli*) with increased capacity and selectivity toward REEs.[11,16] These results highlight the technical feasibility of applying biosorption toward biomining of REEs. However, it remains unknown whether a large-scale process utilizing a biosorption approach permits a cost-effective operation for materials with low REE content.

Prior reports indicate that, for bioremediation applications, the use of biosorbents for metal extraction from aqueous systems is at least an order of magnitude cheaper than traditional technologies while also minimizing chemical waste generation.[17] However, other factors, such as establishment of a cost-effective supply chain for a large-scale operation and an efficient and optimized production engineering system are paramount in determining the sustainability of the process. Here, we performed a techno-economic assessment (TEA) for a biosorption-based approach that uses previously bioengineered bacteria for REE refinement. The entire process for converting the feedstock to salable total rare earth oxide (TREO) is discussed, with an in-depth analysis performed for biosorption. Our derived production costs for three general feedstock categories were compared, with commercial viabilities predicted based upon the current REE prices. Our results highlight the potential of integrating biosorption into a variety of industrial-scale mineral recovery systems to biomine REEs.

PROCESS DESCRIPTION

Using previously bioengineered REE-adsorbing microbes, for which the adsorption performance is well-characterized, the economic feasibility of a streamlined and environmentally friendly biosorption process was tested for extracting REEs from multiple sources. Figure 1 shows the overall process flow. Feedstocks are divided into three general categories based on their distinctive leaching requirements. We

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included both upstream feedstock preprocessing and downstream processes that collectively produce salable TREO products. Mining and beneficiation were considered for some feedstocks, such as REE ores and ion exchange clays, due to innate mineralogical features commonly associated with those feedstocks. Following preprocessing, REE-bearing solutions are run through a biosorption/desorption process where REEs are separated from contaminating metal ions and concentrated rare earth solutions are derived. Post-processing of rare earth solutions via oxalic acid precipitation and roasting produce salable TREOs.

Feedstock Description. A variety of REE-containing feedstocks, ranging from solid to liquid and low grade to high grade, are considered for the REE extraction pipeline. Based on their preprocessing needs, feedstocks are divided into three general categories: acid-leaching, salt-leaching with ammonium sulfate, and no-leaching-required, as shown in Table 1. The category 1 and 2 leachates and the category 3 solutions, which do not require leaching, are adjusted, if necessary, to pH 5−6 prior to biosorption.[11] More detailed material flow information is depicted in Supporting Information Figures S2−S5. REE concentrations and compositions vary significantly both within and across feedstock categories. The specific feedstocks were selected based on available information in the literature regarding REE content and extractability.

Category 1 feedstocks include REE ores/sediments, coal combustion byproducts (e.g., coal ash), and legacy mine tailings that require a strong acid leaching step to dissolve REEs bound in a solid matrix to produce an aqueous solution. Potential rare earth reserves in the U.S. include Bear Lodge (which includes Bull Hill)[18] and Round Top[19] that are recognized as "traditional" REE feedstock. Coal combustion products (e.g., coal ash) represent an emerging "non-traditional" REE feedstock, owing to high REE levels[3] in the ash produced via combustion.[2,20] Currently, about half of coal ash is recycled in the U.S. for the construction and transportation sectors, with the other half discarded as landfills.[21] Mine tailings are unwanted materials from mining and screening operations whose disposal creates environmental and safety challenges.[22]

Category 2 includes ion exchange clays with loosely associated REEs that can be solubilized through salt leaching (i.e., ion exchange with NH_4^+ in an ammonium sulfate salt). Without the need for harsh acids, salt leaching is arguably a more environmental friendly method.[3,23,24] There is a significant production of REEs from ion exchange clays in China, and information about the size of the reserve in the U.S and its extractability is only starting to become available.[2,20] Ion exchange clays in the U.S are mostly found in coal byproducts such as coal partings, coal seams, refuse, and run-of-mine, with elevated concentrations of REEs discovered recently in the Northern Appalachian Region of the U.S.[2,3,20]

Category 3 includes all forms of aqueous feedstock where REEs are present in solution. Geothermal brines, natural waters/lakes, and wastewater from fracking are known to contain elevated REE content due to long-term exposure to rare earth-rich rocks under geological settings.[25] With a global increase in geothermal energy and the exploration of unconventional oil and gas resources, large volumes of geothermal brine and produced water are being generated. Due to its abundance and availability, as well as its soluble form that is amenable to extraction without leaching, category 3 feedstocks represent an attractive mineral source for exploitation.[4,5] However, compared to solid feedstocks from the first two categories, REE concentrations in geothermal brines are generally low, ranging from 1.7 ppb to 3.2 ppm.[25]

Estimates of REE feedstock availability indicate a predictable and dependable U.S. domestic supply for all three feedstock categories. According to a report from the American Coal Ash Association,[21] over 51 million tonnes of coal ash was produced in the U.S. in 2015, which is 102 times our target feedstock level of 500,000 tonnes/year. The Bear Lodge project, which includes Bull Hill, has an ore throughput potential of 350,000 tonnes/year for 38 years.[26] Round Top Mountain plans to process 7.3 million tonnes per year of rhyolite,[19] which is almost 15 times that of our target feedstock. Geothermal brine volume is adjusted to match an industrial-scale flow rate available for mineral recovery from geothermal power plants (i.e., 9 million kg/h available at CalEnergy[27] versus 6 million kg/h used for our analysis). With the given flow rate, our target throughput for geothermal brine is 50,000,000 tonnes/year.

REE Biosorption. We recently reported the construction of recombinant strains of *C. crescentus*[11] and *E. coli*[16] to produce REE-adsorbing microbes with lanthanide binding tags (LBTs) anchored to the cell surface. LBTs are short peptides that have high affinity and specificity toward REEs.[28,29] The resulting LBT-displayed strains were used directly as a whole cell adsorbent with feedstock leachates of complex matrix and low REE content.[11,16] We observed that the LBT−surface display not only increased the REE adsorption capacity but also enhanced the selectivity of cell surface toward REEs. Overall, LBT display improved the ability of microbes to separate REEs from non-REEs and enabled the separation of REEs from low-grade feedstocks that contain high concentrations of non-REEs.

Based on the bioengineered REE-adsorbing microbes, a simple biosorption/desorption operation scheme is used for REE refinement through selective adsorption of REEs onto an engineered bacterial surface and produces a high-purity REE concentrate upon desorption.[11] An airlift bioreactor designed for REE biosorption (Figure 2) builds upon long-standing biosorption technology that has

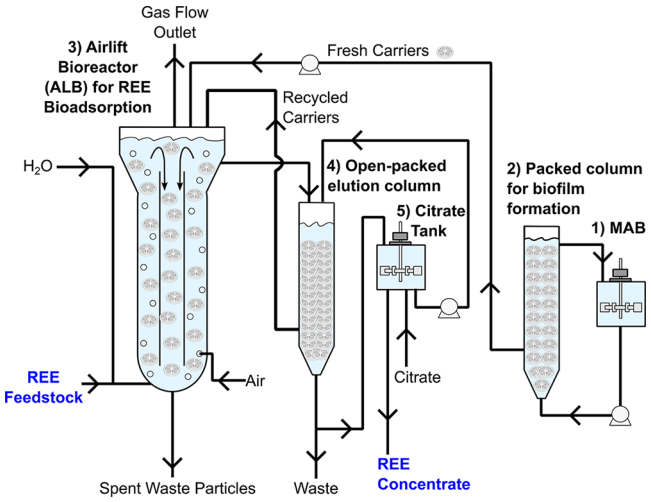

Figure 2. Airlift bioreactor design and process flow diagram. The proposed system consists of a two-stage semicontinuous process including (1) a closed mechanically agitated bioreactor (MAB) used to grow the microbes, (2) an open cylindrical container as a packed column for biofilm formation on carrier disks, (3) an airlift bioreactor (ALB) for adsorption of REE onto biofilm carrier disks, and (4) an open-packed elution column (EC) with (5) circulating citrate from a citrate tank for REE desorption and recovery.

been well-recognized in industrial-scale applications for biomining and bioremediation[30,31] (Figure S1 in the Supporting Information). It offers low shear force with high mixing to minimize potential biofilm damage and increases REE biosorption efficiency. Here we intend to assess its potential to be economically developed into an industrial-scale production system.

An important consideration for the process design is cell immobilization-enabled flow-through operation. Large-scale biosorption relies on cells that are immobilized on a supporting substrate and used to "attract" metal ions. Cell immobilization allows easy separation of the feed solution and REEs that are attached to the cell surface. It also allows continuous operation without the need of energy-intensive centrifugation or filtration. Lightweight, high-surface-area, low-cost (~$200/m^3), high-density polyethylene (HDPE) plastic disks are used as cell carriers for biofilm formation.

During biosorption, the airlift bioreactor is loaded with a REE-bearing solution and a batch of biofilm carriers with cells attached. Air is applied to the inner tube of the airlift bioreactor to enable flow

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Table 2. Cost Breakdown of Biosorption Process for Different Feedstocks Considered

	category 1				category 2	category 3
feedstock sources	coal ash	mine tailings	Round Top	Bull Hill	ion exchange clay	geothermal brine
feedstock (tonnes/year)	500,000	500,000	500,000	500,000	500,000	50,000,000
TREO (tonnes/year)	127−227	67−87	184	9,270	44−98	27−133
material						
(M$/year)	1.0−1.8	0.5−0.6	1.5	62.2	0.3−0.7	0.2−0.9
(% of total cost)	24−30	16−18	31	45	11−19	1−5
electricity						
(M$/year)	0.1	0.09	0.09	0.4	0.1	1.1
(% of total cost)	2	3	2	0.3	3	7−8
utility						
(M$/year)	0.3−0.6	0.2	0.5	20.6	0.1−0.2	0.06−0.3
(% of total cost)	8−10	5−6	10	15	4−6	0.4−2
waste management						
(M$/year)	0.4−0.7	0.2	0.5	22.1	0.1−0.2	0.06−0.3
(% of total cost)	9−11	6−7	11	16	4−7	0.4−2
direct labor						
(M$/year)	0.4	0.4	0.4	0.4	0.4	0.4
(% of total cost)	6−9	11−12	8	0.3	10−14	2−3
other						
(M$/year)	0.5	0.4	0.3	2.6	0.4−0.5	4.1
(% of total cost)	8−11	13−14	7	2	14−17	25−27
capital						
(M$/year)[a]	0.2−0.3	0.2	0.2	1.9	0.2−0.3	3.0
(% of total cost)	5−6	7−8	3	1	8−9	18−20
indirect						
(M$/year)	0.4	0.4	0.4	1.4	0.4	2.1
(% of total cost)	7−10	12−13	7	1	12−15	12−14
general						
(M$/year)	0.9−1.3	0.7	1.0	27.4	0.6−0.8	4.0−4.3
(% of total cost)	21−22	22	21	20	22−23	26−27
total cost						
(M$/year)	4.2−6.0	3.0−3.3	4.9	139.1	2.7−3.6	14.9−16.5
(% of total cost)	100	100	100	100	100	100
processing cost ($/(tonne of feedstock))	8.4−12.0	6.0−6.5	9.8	278.2	5.3−7.2	0.3
production cost ($/(kg of TREO))	26−33	37−45	27	15	37−61	124−553

[a]Annualized capital cost, assuming a plant life of 20 years.

circulation and mixing to accelerate REE biosorption. Reaction time depends on carrier loading time and the REE feedstock concentration. When the adsorption capacity of the carriers reaches 90% of the REE recovery rate, the airflow is shut down to allow the biofilm carriers to float to the top of the bioreactor. Additional water is then pumped into the bioreactor to allow the biofilm carriers to overflow into the elution column. For REE desorption and recovery, citrate solution (5 mM, pH 6)[11] is circulated through the elution column to effectively strip (desorb) the REEs from the biofilm carriers. Following desorption, the biofilm carriers are fed back to the airlift bioreactor and the process repeats. Biofilm carriers can be reused multiple times without loss of adsorption capability.[11] Biofilm carriers are used for 10 adsorption/desorption cycles prior to regeneration in the biofilm formation column.

RESULTS AND DISCUSSION

The techno-economic performance of a REE extraction pipeline featuring a bacterial cell-mediated biosorption scheme is assessed with representative samples from each of the three feedstock categories. We first focused on the cost breakdown of the biosorption process, followed by analyses of the entire pipeline from mining (if applicable) to salable TREO production with comparisons among feedstocks. Finally, some recommendations are provided on additional process engineering to improve economic prospects.

TEA for Biosorption. A 20 year industrial-scale operation is planned to process 500,000 tonnes/year of category 1 and 2 feedstocks and 50,000,000 tonnes/year of category 3 feedstocks. Table 2 shows the cost breakdown of the biosorption process as applied to various feedstocks. More detailed cost and revenue information is available in Supporting Information.

The cost breakdown of biosorption varies greatly among feedstocks, depending heavily on REE concentration (Table 2). The more REEs present in the feedstock, the more materials such as cell growth nutrients, sodium citrate, and water are required. Low-grade feedstocks in categories 1 and 2, including coal ash, mine tailings, Round Top, and ion exchange clays, have similar REE concentrations, and thus share similar processing costs, ranging from $5−$12/(tonne of feedstock). A high-grade feedstock, Bull Hill ore, on the other hand, contains the highest REE concentration (2.8%), and thus biosorption cost is the highest ($278/(tonne of feedstock)). Among all the feedstocks, geothermal brine has the lowest

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Table 3. TEA Results for Each Processing Step with the Different Feedstocks

	category 1				category 2	category 3
feedstock sources	coal ash	mine tailings	Round Top	Bull Hill	ion exchange clay	geothermal brine
input feedstock (tonnes/year)	500,000	500,000	500,000	500,000	500,000	50,000,000
TREO production (tonnes/year)	127−227	67−87	184	9,270	44−98	27−133
preprocessing cost						
(million $/year)	23.8	23.8	20.3	68.6	20.7	0
(% in total cost)	77−83	86−87	78	30	82−86	0
biosorption cost						
(million $/year)	4.2−6.0	3.0−3.3	4.9	139.1	2.7−3.6	14.9−16.5
(% in total cost)	15−19	11−12	19	60	11−14	95−96
postprocessing cost						
(million$/year)	0.8−1.1	0.7	1.0	23.1	0.6−0.8	0.5−0.8
(% in total cost)	3−4	2−3	4	10	3	4−5
unit processing cost ($/(tonne of feedstock))	58−62	55−56	52	461	48−50	0.3
unit production cost ($/(kg of TREO))	136−227	318−410	142	25	256−546	130−574
TREO basket price ($/(kg of TREO))[a]	306−368	65−150	28	13	13	17−22
TREO price increase required for break-even (*x*-times)	0.4−0.7	2.7−4.9	5.1	1.9	20.1−42.6	7.5−26.6
capital cost (in $ million), assumed life of 20 years	5.7−6.4	5.2−5.3	11.1	52.5	6.0−6.8	59.8−60.2

[a]Our product is mixed TREO at 95% or higher purity, with price discounted by 30% from the 99+% pure individual REO prices.

feedstock processing cost ($0.3/(tonne of feedstock)), owing to its low REE concentration as well as economies of scale associated with a larger scale operation.

The production cost per kilogram of TREO is a reflection of both the feedstock processing cost and the REE concentration of the feedstock. The only high-grade feedstock included, Bull Hill ore, showed the most competitive production cost ($15/(kg of TREO)). By contrast, although geothermal brine benefits from a very low feedstock processing cost ($0.3/(tonne of feedstock)), its unit TREO production cost is the highest ($124−553/(kg of TREO)) among all the feedstocks due to its low REE concentration.

It is also desirable to compare biosorption with other REE extraction methods such as hydrometallurgy and magnetic partitioning. The operating cost of a hydrometallurgy plant for the Bear Lodge project (that includes Bull Hill) was estimated to be less than $10.78/(kg of TREO),[26] while our biosorption process for Bull Hill ore requires $15/(kg of TREO) as shown in Table 2, with outputs of a comparable quality (95% versus 97% TREO purity). The higher biosorption cost is primarily due to the use of different rare earth absorbents and different assumptions on material (re)generation and reuse, and waste management that are more favorable for the Bear Lodge project, to be discussed more in the following section. In another report, REEs are extracted from geothermal brine using a metal−organic framework (MOF) sorbent.[32] By assuming the same REE concentration in the feedstock (1.045 ppm) and applying the same cost assumptions with no contingency cost,[32] the material cost of biomass production for our biosorption was estimated to be $6.06/(kg of TREO) (data available in Supporting Information—Excel spreadsheet), similar to the reported $6.02/(kg of TREO) for the MOF sorbent.[32]

TEA for Entire Process. Table 3 summarizes the TEA results for the entire process from ore mining (when applicable) to TREO production. Our product is mixed TREO at 95% or higher purity, while the market price publicly available is 99% or purer individual REO. The Bear Lodge project suggested a discount rate of 20−30% for their 97+% pure TREO relative to the 99+% pure individual REO prices.[26] Similarly, we discounted our TREO price by 30% from the 99+% pure individual REO prices for a conservative estimation.

Major factors that affect process economics include (1) REE composition, (2) REE concentration, (3) preprocessing requirements, and (4) waste management. Each feedstock has its pros and cons, and our TEA results detail the trade-offs between these factors.

REE Composition. The REE composition of the feedstocks is the primary driver of the economic performance. Since individual REE prices differ substantially, the presence of high-value REEs heavily influences the profitability of feedstock processing. Scandium oxide, for example, has a value of $4,200/kg (MineralPrices.com; accessed on Mar. 31, 2017), while cerium oxide is sold at $1.8/kg,[33] making the revenue from selling 1 kg of scandium oxide equivalent to over 2 tonnes of cerium oxide. As a result, coal ash from the Appalachian basin, where 94% of the revenue is derived from scandium, is the most profitable feedstock (profit of $170/(kg of TREO)). The presence of scandium appears to be a general feature of coal ash feedstock, as it is present in elevated concentrations in over 100 coal ash samples from 22 power plants in the United States,[20] and the economic potential of extracting scandium was reported to be enormous through an examination of 11 global coal ash samples.[34] Based on the specific assumptions listed in Supporting Information Table S1, Appalachian coal ash offers a payback period of 1 year and a high internal rate of return (IRR) of 513%. Togo and Lower Radical mine tailings, whose REE values are the second highest ($65−$150/(kg of TREO)), also benefit from scandium that generates 80−91% of the total revenue. Round Top, having the third highest REE value ($28/(kg of TREO)), generates 86% of the revenue from heavy REEs such as dysprosium and erbium. By contrast, the Bull Hill revenue is significantly lower due to the predominance of low-value light REEs that constitute the majority of the revenue (99.5%). As a result, the Bull Hill TREO value ($/kg) is only 4% that of Appalachian coal ash, 20% that of Togo mine tailings, and 47% that of Round Top. Therefore, the presence of high-value REEs is critical to the profitability of a REE recovery process.

To the best of our knowledge, scandium is not currently extracted from major mines such as Bayan Obo or Mountain Pass.[35,36] Because the cutoff grade of ore is 1−2%,[37] high-value REEs, such as scandium, may be lost during the screening stage

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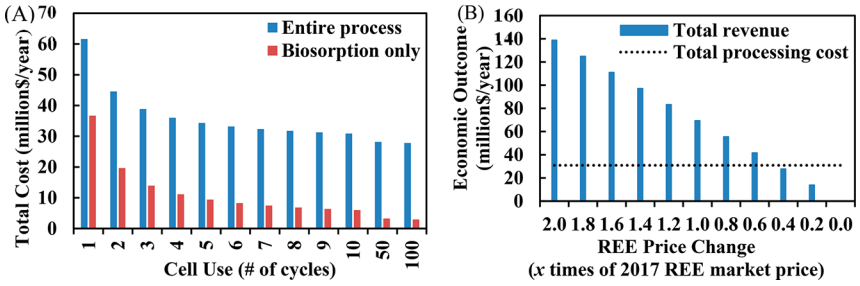

Figure 3. (A) Sensitivity analysis of biomass reuse depicted by the cost as a function of the number of times biomass is used with the Appalachian coal ash. (B) Sensitivity analysis on the effect of REE pricing on revenue with the Appalachian coal ash. The horizontal dotted line represents the total processing cost (million $/year).

or may not be processed due to low techno-economic feasibility. Biosorption could make use of abandoned low-grade feedstocks and efficiently recover high-value REEs.

REE Concentration. REE concentration in the feedstock could either positively or negatively influence the overall profit, depending on the interaction between increased revenue and the biosorption cost. For the unprofitable feedstocks to reach break-even, REE concentration would need to increase by 17 times for Round Top (from 633 to 10,768 ppm) and by 128−149 times for geothermal brine (from 0.6 to 3.2 ppm to 83−474 ppm). While high REE concentrations generate more TREOs and hence, more revenue, the increased revenue and overall profit can be negated by higher biosorption and post-processing costs. Therefore, REE concentration should be considered in combination with REE composition to assess the economic potential.

Preprocessing Cost. The preprocessing requirement for solid feedstocks in categories 1 and 2 constitutes 30−87% of the total cost. Unlike category 1 feedstocks that require sulfuric acid leaching, ion exchange clays could be solubilized using ammonium sulfate, which offers a lower material cost. Additionally, the pH adjustment cost is eliminated as the solution pH of the salt leachate of the ion exchange clays is generally near neutral pH, and thus compatible with biosorption. Therefore, compared to feedstocks from category 1, ion exchange clays in category 2 have a lower operating cost (e.g., $29−31 million/year for coal ash versus $24−25 million/year for the ion-adsorption clays of coal partings). Bull Hill ore requires a relatively high mining and beneficiation cost ($40 million/year) that results in a higher preprocessing cost than other feedstocks. Category 3 feedstocks receive a significant financial boost by not requiring mining, beneficiation, or leaching.

Waste Management. In contrast to category 1 and 2 feedstocks, which generate a large volume of waste solution with high total dissolved solids (TDS), geothermal brine is normally injected back into the ground upon electricity generation to minimize waste. Given that our biosorption process introduces no acids or harmful chemicals, direct injection following mineral extraction is a viable option. It should be noted that coal ash usually contains hazardous materials such as arsenic, mercury, and lead,[38] but we assumed no credits or liabilities for collecting, processing, and disposing coal ash (except the nonhazardous solid waste disposal cost), which may offset one another. Further studies are required to investigate the specific implication of this assumption.

As the technology development effort continues, we will gain more knowledge on the behavior of various cations and anions present in the feedstocks. While U/Th were able to adsorb to the cells surface along with REEs,[16] they are expected to be removed and separated from REEs during the oxalic acid precipitation step.[39] Iron and aluminum are expected to have very low solubility at circumneutral pH and thus will precipitate out in the pH-adjusted (pH, 6) leachate solutions prior to biosorption. Toxic arsenate and mercury form hydrated oxyanions in aquatic solutions and are not expected to adsorb on the cell surface, and thus will remain in the leachate solution. Further studies are needed to investigate the removal of potential co-contaminants of biosorption and to further increase REE purity.

Sensitivity Analyses of Biomass Recycling and REE Pricing. An important feature of the biosorption process is that the biomass used for REE adsorption can be recycled and reused. Batch-scale tests showed that biomass could be reused three times with no loss of adsorption capacity.[11] Given that costs of cell regeneration and growth nutrients constitute a significant portion of the total expense in biotechnology applications, sensitivity analysis was performed to understand the effect of biomass reuse on cost reduction. With Appalachian coal ash as an example, sensitivity analysis indicated that cell recycling beyond 5 times has limited benefits to reducing the overall process cost (Figure 3A). As is evident, the cost of the biosorption step is the most sensitive to the cell recycling; the cost decreases significantly as the biomass is reused more times.

Another major parameter that significantly affects the profitability is REE price. The historical price of REEs has been volatile, and the individual REEs may exhibit different price trends. The demand for certain REEs such as Nd, Pr, and Dy is projected to increase due to their applications in neodymium−iron−boron (NdFeB) magnets, which are in growing demand for clean energy products such as electric vehicles and wind turbines.[40] On the other hand, the global supply of scandium (Sc) is projected to increase, which may lower the price in the future.[41] To examine the effect of changing REE price on the overall profit, we performed a sensitivity analysis based on the Appalachian coal ash. As shown in Figure 3B, our extraction process would be profitable even if the REE price decreases by half.

Future Improvement Opportunities. Based on the TEA results, a few future scenarios that can further increase the profitability include (1) material recycling and reuse, (2) mineral co-extraction, and (3) a price increase in REEs. These factors may enable opportunities that are not presently economically viable to be pursued.

Material Recycle and Reuse. Our analysis assumed all materials and utilities were purchased at market price and only used once. However, chemicals such as sulfuric acid for leaching and glucose for bacterial growth can be generated for a large-

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scale operation, thereby reducing material costs. Depending on specific location and situation, self-processing and recycling of the waste salt solution could be feasible as well, which would also reduce material and waste management costs. The Bear Lodge project, for example, designed an acid regeneration unit to recover and reuse water, hydrochloric and oxalic acid, and ammonium nitrate.[26] Mountain Pass, on the other hand, planned to construct a chloralkali facility for salt recycling and production of HCl, NaOH, and NaCl.[36] Considering the material, water, and wastewater treatment costs constitute 23−51% of the total cost for solid feedstocks, material reuse and recycling could significantly reduce the overall cost.

Co-extraction. The economic prospect of REE extraction from geothermal brine can be improved by integrating a biosorption process into other mineral recovery systems.[27] Currently, zinc is recovered from geothermal brines, while other minerals such as lithium, boron, manganese, silica, and other metals are under investigation for co-extraction.[27] Togo and Lower Radical are legacy mines that contain leftover metals such as copper, silver, and gold, which can potentially be co-extracted with REEs. If resources and facilities are shared with other metal production operations, profitable REE extraction may be feasible.

REE Market Price. The global REE market has experienced an excess supply in recent years that resulted in a significant decline in REE prices.[18,42,43] As the Chinese government plans to implement more stringent environmental regulations on REE production, REE market prices are expected to increase.[44] Currently, low prices limit the economic viability of our proposed process for several feedstocks; however, the peak prices of several REEs were 5−89 times higher than the current REE prices (http://www.metal-pages.com/). If our analysis was based on peak REE prices in 2011, Bull Hill, Round Top, and one geothermal brine would also become profitable.

The current REE market faces an increasing production cost due to escalating labor and environmental regulations, where it is to be noted that the REE grade decreases over time for existing mines. Biosorption's capability of extracting high-value REEs from nontraditional low-grade feedstock may have a significant impact on the future supply of REEs. Besides significant economic potential, biosorption process encompasses several environmental advantages. First, in contrast to traditional hydrometallurgy,[45] biosorption involves no solvents or harsh chemicals such as strong acid or base. Second, adsorption and desorption are both passive processes, with little energy input required.[17] Third, recycle and reuse of biomass, which can grow with renewable sources such as food scraps, further reduces the carbon footprint. Fourth, co-adsorption of U/Th along with REEs can potentially facilitate removal of radioactive/toxic metals. These advantages highlight the environmental sustainability aspect of the biosorption technology. Overall, value recovery from low-grade waste feedstock enhances the economic and environmental sustainability by alleviating REE supply risk and creating business opportunities in an environmentally friendly manner.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b02147.

Excel spreadsheet listing mass balance analysis by processing step, cost breakdown by processing step and cost components, REE prices, sensitivity analysis, cash flow, data sources, and assumptions (ZIP)

Feedstock preprocessing methods; mass balance analyses of selected feedstocks; TEA assumptions (PDF)

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Notes

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