

# Beneficiation of REE: Prospects for Biotechnology Deployment

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## Abstract

Given the increasing global demand for rare earth elements (REE), prospects for REE recovery from both traditional and non-traditional sources have been a focus of intense interest. Many have noted the need for ecologically sustainable alternatives to conventional pyrometallurgical and hydrometallurgical methods to recover REE. Among the newer approaches that have garnered recent interest are those that rely on microbiological processes or microbiologically produced reagents to recover the rare earths. Biological approaches can often avoid many of the environmental and or safety hazards associated with the corrosive (e.g., strong acids) or toxic chemicals (e.g., organic solvents) often used in hydrometallurgy as well as costs related to the high energy, reagent and capital requirements and potential air emissions associated with pyrometallurgy. Microbial processes are considered environmentally friendly because they are “natural”, although opportunities also exist to improve on native capabilities by the application of synthetic biology. In this chapter we will focus on some important factors that have not been as widely discussed but which should be considered in planning actual deployment of biological approaches for recovery and purification of rare earths, drawing on some of our own experience for examples. In particular we will focus on geochemical and biogeochemical constraints posed by the feedstocks from which REE may be extracted, for both bioleaching and biosorption, and point out the importance of aqueous equilibrium modeling as a tool for interpreting results and supporting design of biological recovery methods. We will also discuss some important cost factors for REE recovery that are specific to biological processes.

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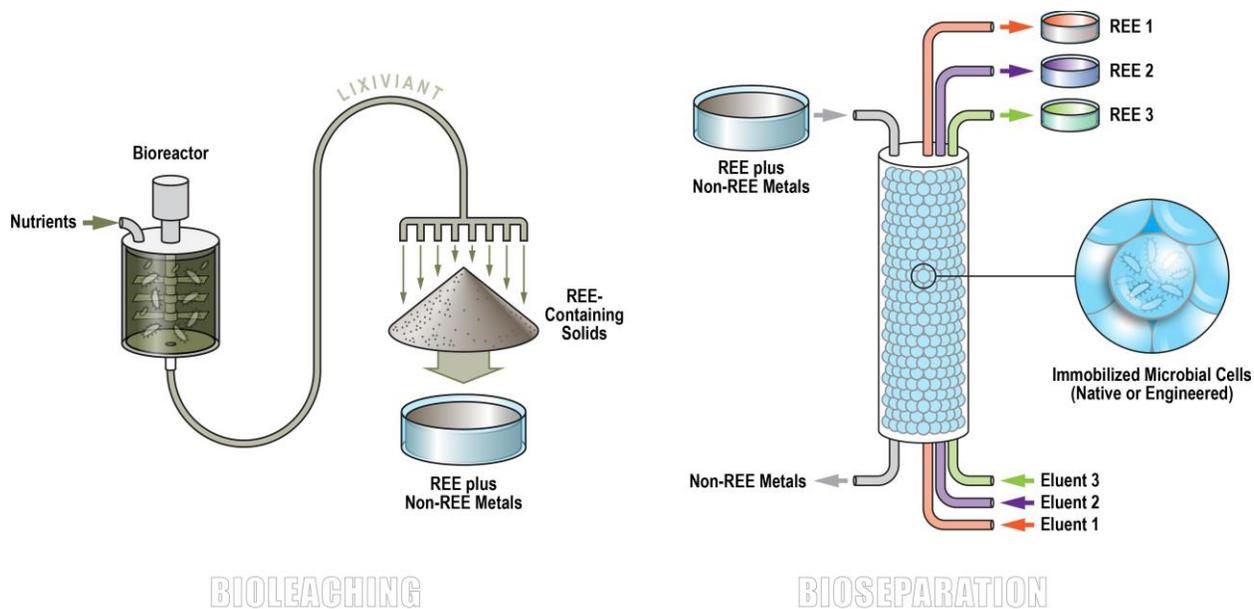
## **Abstract**

Given the increasing global demand for rare earth elements (REE), prospects for REE recovery from both traditional and non-traditional sources have been a focus of intense interest. Many have noted the need for ecologically sustainable alternatives to conventional pyrometallurgical and hydrometallurgical methods to recover REE. Among the newer approaches that have garnered recent interest are those that rely on microbiological processes or microbiologically produced reagents to recover the rare earths. Biological approaches can often avoid many of the environmental and or safety hazards associated with the corrosive (e.g., strong acids) or toxic chemicals (e.g., organic solvents) often used in hydrometallurgy as well as costs related to the high energy, reagent and capital requirements and potential air emissions associated with pyrometallurgy. Microbial processes are considered environmentally friendly because they are “natural”, although opportunities also exist to improve on native capabilities by the application of synthetic biology. In this chapter we will focus on some important factors that have not been as widely discussed but which should be considered in planning actual deployment of biological approaches for recovery and purification of rare earths, drawing on some of our own experience for examples. In particular we will focus on geochemical and biogeochemical constraints posed by the feedstocks from which REE may be extracted, for both bioleaching and biosorption, and point out the importance of aqueous equilibrium modeling as a tool for interpreting results and supporting design of biological recovery methods. We will also discuss some important cost factors for REE recovery that are specific to biological processes.

## 1.0 Introduction

Multiple reviews have been published in recent years on the increasing global demand for rare earth elements (REE) and prospects for REE recovery from both traditional and non-traditional sources (Binnemans, Jones, et al., 2013; Fathollahzadeh et al., 2019; Ganguli & Cook, 2018; Gaustad et al., 2020; Jyothi et al., 2020; Løvik et al., 2018; Nassar et al., 2015; Tunsu et al., 2015; Weber & Reisman, 2012; Zhang et al., 2020). Many have noted the need for ecologically sustainable alternatives to conventional pyrometallurgical and hydrometallurgical methods to recover REE (Jha et al., 2016; Sovacool et al., 2020). Among the newer approaches that have garnered recent interest are those that rely on microbiological processes or microbiologically produced reagents to recover REE (Barmettler et al., 2016; Hennebel et al., 2015; Zhuang et al., 2015). Biological approaches can often avoid many of the environmental and or safety hazards associated with the corrosive (e.g., strong acids) or toxic chemicals (e.g., organic solvents) often used in hydrometallurgy as well as costs related to the high energy, reagent and capital requirements and potential air emissions associated with pyrometallurgy (Adesina et al., 2017; Cui & Zhang, 2008; Pollmann et al., 2016; Rasoulnia et al., 2020; Zhuang et al., 2015). Microbial processes are considered environmentally friendly because they are “natural”, although opportunities also exist to improve on native capabilities by the application of synthetic biology (Adesina et al., 2017).

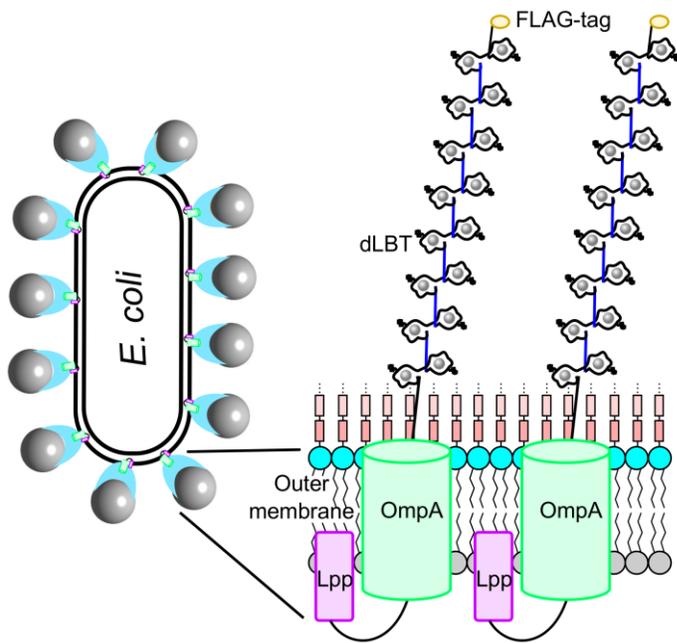
Microbial processes can be harnessed for both solubilization of metals from solid matrices (“bioleaching”)(Bosecker, 1997) and concentration and purification of solubilized metals that occur in mixtures (“biosorption/desorption” or “bioseparation”) (Moriwaki & Yamamoto, 2013). Figure 1 depicts the processes.



**Figure 1.** Schematic representation of bioleaching (left) and bioseparation (right). Graphic prepared by David Combs, INL.

Bioleaching is a long accepted practice for commercial recovery of some metals, in particular copper (Bosecker, 1997) but recently a number of researchers have been evaluating its application for recovery of rare earths, using both bacteria and fungi. REE-containing solids that have been subjected to bioleaching in the laboratory include gibbsite (aluminum ore) (Ibrahim & El-Sheikh, 2011), red mud (waste of aluminum production) (Qu & Lian, 2013), monazite (light-REE phosphate minerals) (Brisson et al., 2015; Corbett et al., 2017; Fathollahzadeh et al., 2018; Hassanien et al., 2014; Maes et al., 2017; Shin et al., 2015), bastnaesite (carbonate-fluoride mineral) (Zhang et al., 2018), ion-adsorption clay (Barnett et al., 2018), shale (Amin et al., 2014), waste electrical and electronic equipment (Di Piazza et al., 2017; Fonti et al., 2015), waste phosphors (lighting) (Hopfe et al., 2017; Reed et al., 2016) and spent petroleum fluid catalytic cracking (FCC) catalyst (Ferreira et al., 2018; Reed et al., 2016). Microbes mediate the release of REE from these materials primarily by acid production, as will be discussed in Section 2 of this chapter.

While bioleaching aims to get the metals into solution, bioseparation or biosorption approaches are aimed primarily at concentrating and enriching (relative to other co-solubilized ions) the target metals once they are in solution. Biosorption relies on the binding of metals to selective ligands produced by and anchored on cell surfaces or extracellular biomaterials; after the metals are partitioned from the leachate solution onto the biological surfaces they are desorbed (stripped) into another solution. Using a smaller volume of stripping solution results in concentration of the metals. Metal selectivity is imposed at the sorption step by the particular binding ligands, which typically incorporate carboxyl, phosphate, and hydroxyl groups (Fein et al., 1997). Numerous researchers have reported REE binding on native bacterial surfaces where such functional groups are common (Andrès et al., 2003; Moriwaki & Yamamoto, 2013; Takahashi et al., 2005; Takahashi et al., 2010; Yoshida et al., 2004). More recently, Park et al. have described bacteria engineered to express “lanthanide binding tags” (LBT) at high density on their surfaces. The LBT have enhanced selectivity for binding of lanthanides compared to other non-REE metals (Figure 2), and they also exhibit preferential binding of heavy rare earth elements (HREE) compared to light rare earth elements (LREE) (Park et al., 2017; Park et al., 2016). For REE, because of their chemical similarity, separation of individual REE is a particularly prized outcome. Selectivity (for REE over non-REE or for particular REE) can also be imposed during the desorption step by the chemistry of the stripping solution. Factors important for optimal application of biosorption and desorption for REE separation will be discussed in Section 3.



**Figure 2.** Surface display of LBT by *E. coli*. A) Cartoon depicting the lpp-ompA mediated display dLBTx8. Blue lines represent the Muclb spacer. Flag<sup>TM</sup> Tag on the N-terminus. Reprinted with permission from Park et al. (2017), Figure 1, p. 13473. Copyright 2017 American Chemical Society.

In practice, leaching as well as sorption can result in some metal separation or enrichment.

Unless the solid is completely dissolved, the relative abundances of metals in a leachate often differ from the original bulk solid phase (Corbett et al., 2017). For example, leaching by an organic acid that has chelating properties (e.g., citric acid) can result in selective solubilization of metals that preferentially complex with the chelator. On the other hand, while solid dissolution by an agent such as hydrochloric acid might generally be considered non-selective leaching, the metal composition in the resulting leachate will still be a function of the stability of the metal-containing phases in the solid and the solubility of the individual metals in the leachate (and the kinetics of dissolution/precipitation). These concepts are expanded upon later in this chapter.

As noted above, multiple reviews as well as many individual reports have been published recently regarding the potential for biological approaches to offer environmentally sustainable REE recovery. In this chapter we will focus on some important factors that have not been widely discussed

but which should be considered in planning actual deployment of biological approaches for recovery and purification of rare earths, drawing on some of our own experience for examples. In particular we will focus on geochemical and biogeochemical constraints posed by the feedstocks from which REE may be extracted, for both bioleaching and biosorption, and point out the importance of aqueous equilibrium modeling as a tool for interpreting results and supporting design of biological recovery methods. We will also discuss some important cost factors for REE recovery that are specific to biological processes.

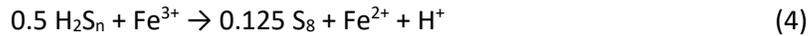
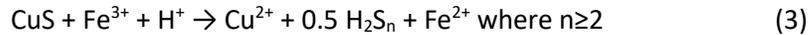
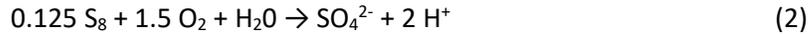
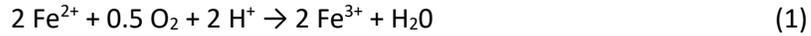
## **2.0 *Technical constraints for bioleaching of REE-containing feedstocks***

The particular characteristics of REE-containing materials will dictate whether and what kind of biological approaches are likely to be attractive for REE leaching. These characteristics can be chemical, physical, or economic (which can include geographic factors). In this section, factors related to the chemical composition of feedstocks are discussed, with respect to the consequences for general bioleaching approach, constraints on leaching yields, and compatibility with microorganisms.

### **2.1 *Reduced vs. oxidized feedstocks***

Biological processes have been widely accepted and practiced for the extraction of copper and gold from ores for decades, or in the case of copper, perhaps centuries (Brierley, 2016). As much as 10-15% of global copper production is currently estimated to result from bioleaching (Roberto, 2017). Other metals which have been commercially recovered by bioleaching include zinc, cobalt, uranium and nickel (Brierley & Brierley, 2013; Kaksonen et al., 2018). These metals have in common that they frequently occur in sulfidic ores, providing conditions suitable for acidophilic iron and sulfur oxidizing microorganisms to produce ferric iron and sulfuric acid that promote solubilization of the target metals (Evangelou & Zhang, 1995; Kaksonen et al., 2018). For example, in copper bioleaching, iron-oxidizing organisms aid in the oxidation of ferrous to ferric iron (Equation 1) (Rawlings, 2005). Elemental sulfur is oxidized to sulfate by acidophilic sulfur oxidizing microbes and acidity is generated (Equation 2). The

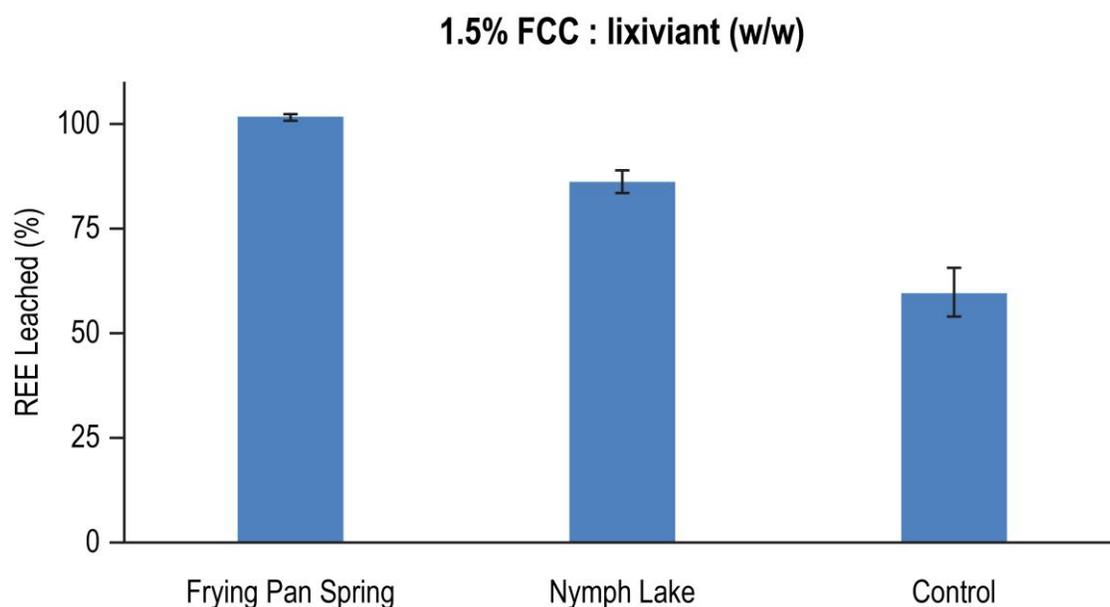
ferric ion and protons can then chemically attack the solid copper sulfides to leach the metal into solution (Equation 3). The ferric ion is also returned to ferrous iron by poly-sulfide oxidation (Equation 4). The leaching microbes are involved in Equations 1 and 2.



For gold, rather than directly leading to the dissolution of the target metal, microbial sulfur oxidizing capabilities are utilized to dissolve the sulfidic mineral matrix that can otherwise shield the gold from chemical treatment. Subsequent gold leaching by non-biological means, typically using cyanide solutions, follows. This gold ore pretreatment process is known as bio-oxidation, rather than bioleaching (Olson et al., 2003). Dissolution of minerals other than those actually containing the targeted metals is also a feature of approaches suggested by Johnson and colleagues, where reductive microbial metabolisms such as ferric iron or manganese oxide reduction that result in dissolution of oxidized minerals promote the release of incorporated or sorbed metals such as nickel or cobalt (Hallberg et al., 2011; Johnson, 2012).

Conventional rare earth ores (e.g., bastnaesite, monazite, xenotime, ion adsorption clays) are typically oxidized and non-sulfidic (Van Gosen et al., 2017) and thus relying on acidophilic S and Fe oxidizers for *in situ* generation of acidic leaching agents for these ores would require external provision of suitable substrates (reduced sulfur compounds). Ibrahim and El-Sheikh added *Acidithiobacillus ferrooxidans*, ferric sulfate and sulfuric acid to low grade gibbsite ore to initiate lixiviant production, and they observed that when sulfur (0.5%) was added the bioleaching efficiency increased 10% (Ibrahim & El-Sheikh, 2011). In our own work we observed REE recovery using biolixiviant generated by mixed

cultures of microorganisms enriched from Yellowstone National Park acidic geothermal features (Figure 3). The organisms were enriched using a medium that was first adjusted to pH 4 with sulfuric acid, and reduced sulfur was added as an electron donor for the microbes. With growth the medium pH decreased further to between 2 and 3. The growing enrichments were incubated with fluid catalytic cracking (FCC) catalyst for 6 weeks at 65°C with shaking at 150 rpm. The lixiviants generated by enrichments from Frying Pan Spring and Nymph Lake resulted in 1.7-fold and 1.4-fold more leaching, respectively, than the abiotic control (uninoculated medium at pH 4) (Figure 3).



**Figure 3.** Total REE leached from FCC catalyst (1.5%, w/w) after 6 weeks with microorganisms grown in situ with *Sulfolobus* medium (Leibniz Institute DSMZ-German Collection of Microorganisms and Cell Cultures), 25 mM K<sub>2</sub>S<sub>4</sub>O<sub>6</sub> and elemental sulfur (0.1% w/v). Error bars indicate standard deviations for three replicate experiments. Water samples for enrichment were collected from Frying Pan Springs (pH 2.0, 82°C), and Nymph Lake (pH 2.8, 74°C) in Yellowstone National Park, WY in October 2013.

Unconventional sources for REE might be more amenable to bioleaching based on such metabolism; for example, coals often contain significant levels of reduced sulfur (Calkins, 1994) and in fact REE have been shown to be present in acid mine drainage from coal mines (Ayora et al., 2016; Stewart et al., 2017; Zhao et al., 2007). In those cases, bioleaching based upon sulfide oxidation would

be attractive; the responsible organisms are likely to already be naturally present, and the primary requirements to promote leaching would be sufficient availability of oxygen and water.

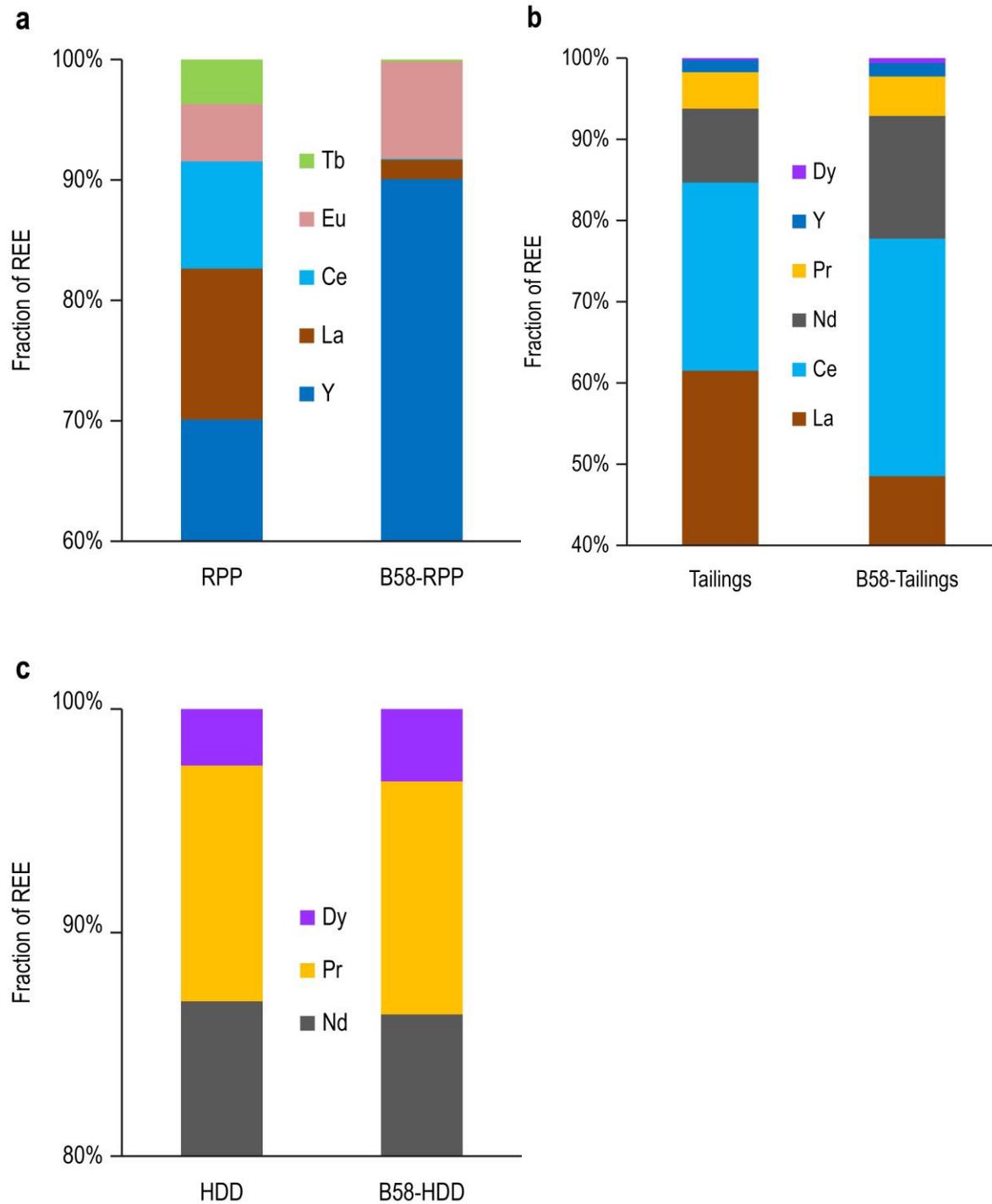
For non-sulfidic feedstocks, the most common biological approach proposed for solubilizing metals relies on microbes that partially oxidize added organic carbon compounds. These organic carbon reliant organisms, known as heterotrophs, do not necessarily gain an advantage by growing in the presence of the ores or REE feedstocks, and indeed can be cultivated separately or in the presence of the solids containing the target metals. Each option has its advantages and disadvantages, as will be discussed in a subsequent section. Organic substrates are converted by the heterotrophs to compounds that promote mineral dissolution, typically organic acids and/or other chelators (the acids may themselves be chelators). Silica mineral dissolution can also be promoted by biological ammonia production from nitrogen containing organic compounds (Jain & Sharma, 2004) but this mechanism is less likely to be useful for REE given the low solubility of REE at the higher pH engendered by ammonia production. In general metal solubilization is generally slower with bioleaching compared to conventional hydrometallurgical approaches using more corrosive agents, but the potentially lower waste disposal costs and environmental benefits, coupled with the fact that the carbon substrates could be derived from municipal, industrial or agricultural wastes, could make heterotrophic bioleaching attractive for some REE containing feedstocks (Jin et al., 2019; Thompson et al., 2018).

## **2.2 *Complex chemical composition of feedstocks leads to complex leachates***

Feedstocks with sufficient REE content to be potentially attractive for recovery include wastes from industrial mineral processing such as red mud (bauxite residue), phosphogypsum from phosphate production, kaolin production wastes, metallurgical slags and mine tailings, and wastes from energy production or waste management such as coal ash or incinerator ash (Abramov et al., 2018; Antonick et al., 2019; Binnemans, Pontikes, et al., 2013; Dehaine & Filippov, 2015; Emsbo et al., 2015; Funari et al.,

2016; Klauber et al., 2011). End of life consumer products (e.g., fluorescent lamps, computer hard disk drives, mobile phones, various motors) and industrial processing materials (e.g., fluid catalytic cracking catalysts, glass polishing powders) have also been identified as possible targets for REE recycling (Binnemans, Jones, et al., 2013; Fonti et al., 2015; Tunsu et al., 2015). These solids are compositionally complex, and other matrix components besides REE will interact with the biolixiviant and be extracted from the solids. The effectiveness of REE leaching will be a function of multiple factors, including pH, temperature, chelating agents, competing stable and metastable solids, and interactions with numerous species that result from the dissolution of the matrix in which the REE were originally contained (Rasoulnia et al., 2020). Kinetics of course also plays a role. This complex situation explains why the relative abundances of metals in a solid feedstock are not always mirrored in the leachate composition. For example, Figure 4a shows the REE metal composition in retorted phosphor powder (RPP) solid compared to the metal composition in the leachate generated after 24 hours of contact with a biologically produced lixiviant. In this case, yttrium accounts for 70% of the REE in the original solid waste and almost 90% of the REE in the leachate (Reed et al., 2016). The leachate is also enriched in europium relative to the original RPP, and cerium and lanthanum are much less abundant. Terbium is almost absent from the leachate. A reasonable explanation for these observations is that the Y and Eu in the RPP occur as oxides, which are likely more soluble than the La, Ce and Tb containing phosphates (Reed et al., 2016).

In another example, leachate from REE ore tailings exhibited relative enrichment in Ce and neodymium and a relative depletion of La compared to the original solids (Figure 4b). However not all materials exhibit bias with respect to leaching; for example, the relative abundances of REE in leachate of hard disk drive (HDD) magnets were similar to those in the starting material (Figures 4c).



**Figure 4.** Relative distributions of REE in solid materials (left bar) and bioleachates (lixiviant generated by *Gluconobacter oxydans* B58, denoted B58) after 1 day leaching (right bar) at 1.5% (w/v) pulp density of (a) retorted phosphor powder (RPP), (b) REE ore tailings, and (c) crushed hard disk drive (HDD) magnets. Y-axis shows the cumulative fraction of individual REE.

The preceding examples illustrate the challenge of predicting leaching results for a given material using a given lixiviant. However, we do not have to rely solely on empirical results. Geochemical modeling, based on thermodynamics, can provide critical aid in designing and optimizing conditions for leaching from complex materials. Equilibrium-based predictions facilitate the understanding of experimental results and can guide the selection of leaching conditions for empirical testing. Thermodynamic modeling of REE geochemistry is briefly reviewed in the next section, followed by examples of applications to bioleaching.

### **2.2.1 Thermodynamic modeling of REE in aqueous solutions**

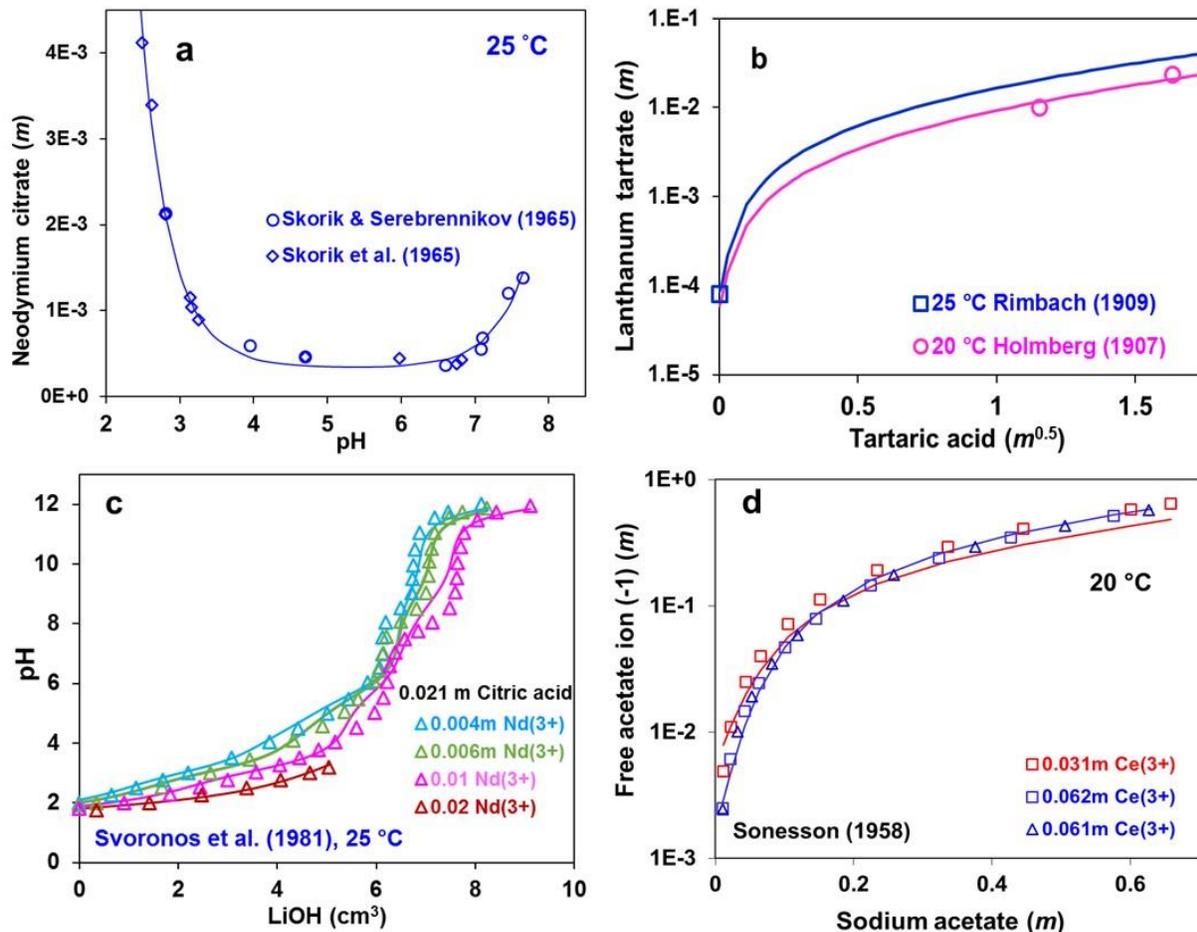
A thermodynamic model is essential for capturing both chemical and phase equilibria in complex, multicomponent systems. Further, the equilibrium behavior can be used as a foundation for a kinetic analysis of leaching. To construct a credible thermodynamic model for aqueous systems containing REE, it is necessary to parameterize and validate it using experimental data such as phase equilibria (i.e., solid-liquid and vapor-liquid equilibria) and solution speciation including acid-base equilibria and complexation equilibria. When necessary, the model should incorporate the effect of organic extractants that form liquid-liquid equilibria with aqueous solutions. An example of a model that satisfies these conditions and has been applied successfully to systems including REE is the Mixed-Solvent Electrolyte (MSE) model (Wang et al., 2006; Wang et al., 2002; Wang et al., 2004). The MSE model combines an equation of state for standard-state properties of individual species, an excess Gibbs energy model, and an algorithm for solving phase and chemical equilibria in multicomponent and potentially multiphase systems. Recently, the MSE model has been applied to simulate phase equilibria, caloric properties and solution speciation in binary and multicomponent aqueous systems containing REE chlorides, sulfates, hydroxides, and various complexing agents (Das et al., 2017; Das et al., 2019; Fujita et al., 2015; Park et al., 2016). These systems have included microbiological media (Fujita et al., 2015).

The most practical way to establish a predictive thermodynamic model is to construct it from the bottom up, i.e., by developing model parameters for the constituent simple subsystems (primarily pure species and binary or ternary mixtures), followed by applying the model to more complex multicomponent systems. To obtain a good set of model parameters that accurately represent complex systems, reliable experimental data for multiple thermodynamic properties are necessary. In general, relatively plentiful experimental data are available for REE in the presence of common inorganic ions. In particular, extensive and critically evaluated foundational data for inorganic REE compounds have been reported in a series of studies by Migdisov and co-workers and Mioduski and co-workers. Migdisov et al. have extensively investigated and established recommended values of standard state properties, solubilities, and complexation constants at room and elevated temperatures (up to 300 °C) for various aqueous rare earth systems, including chlorides (Migdisov et al., 2009; Migdisov & Williams-Jones, 2002; Migdisov & Williams-Jones, 2006; Migdisov et al., 2008), fluorides (Loges et al., 2013; Migdisov & Williams-Jones, 2007; Migdisov et al., 2009), and sulfates (Migdisov et al., 2006; Migdisov & Williams-Jones, 2008). Mioduski and coworkers have compiled and evaluated experimental solubility data for aqueous binary and ternary rare earth chlorides (Mioduski et al., 2008, 2009a, 2009b), fluorides (Mioduski et al., 2014, 2015a, 2015b), iodides (Mioduski et al., 2012), bromides (Mioduski et al., 2013) and selected sulfates (Mioduski, 1999) based on multiple literature sources. These studies are of great importance as they provide a detailed view of thermodynamic properties, phase behavior (i.e., solid-liquid and vapor-liquid equilibria), and complexation behavior within various families of inorganic REE salts. Based on such data sources, detailed thermodynamic models have been established for REE chlorides (Das et al., 2017), sulfates (Das et al., 2019), carbonates (Kim et al., 2020) and phosphates (Fujita et al., 2020) using the MSE framework.

Thermodynamic behavior of rare earths in the presence of organic ligands is of particular importance as it informs the selection of the best lixiviants and, hence, the microbe/metabolic pathways.

Primary experimental data for REE – organic ligand systems are available to a lesser extent and cannot be, at present, as satisfactorily systematized as those for inorganic systems as discussed above. Nevertheless, the MSE model has been applied to elucidate the leaching of REE from phosphogypsum using gluconic acid (Antonick et al., 2019), the effects of citrate and acetate complexation on the recovery of REE from bacterial surfaces (Park et al., 2016) and the effect of diethylenetriaminepentaacetic acid (DTPA) chelation on REE in wastewater environments (Fujita et al., 2020). Here, we analyze representative examples of thermodynamic modeling of organic REE systems and compare the simulations with experimental data. The key requirement for the thermodynamic modeling of such systems is the simultaneous representation of speciation data (typically available from titration curves and/or spectroscopic measurements) and solubility measurements (typically as a function of both pH and ligand concentration). For this purpose, Figure 5 shows the behavior of rare earth systems in the presence of organic (citric, tartaric, and acetic) acids and illustrates the accuracy of the MSE model for capturing the complexation effects. Figure 5a presents the solubility of neodymium citrate in aqueous solutions containing 0.1 M NaClO<sub>4</sub> and sodium citrate as a function of pH, adjusted using HClO<sub>4</sub> and NaOH, at 25 °C and compares the calculations with experimental data (Skorik et al., 1965; Skorik & Serebrennikov, 1965). The solubility diagram shows a strong dependence of the solubility of the neodymium citrate phase, NdC<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·3.5H<sub>2</sub>O, on pH, which is a consequence of the stability of citrate complexes. Remarkably, the solubility increases at pH values above neutral, which would not have been the case in the absence of complexation because the precipitation of neodymium hydroxide would have interfered. Figure 5b shows the changes in lanthanum tartrate solubility with increasing tartaric acid concentration, which is in good agreement with experimental results (Holmberg, 1907; Rimbach & Schubert, 1909). Initially, the solubility increases significantly with the addition of a trace amount of tartaric acid due to the complexation effect. However, solubility starts to level off at concentrations above 1 *m* tartaric acid. Figure 5c presents the titration curves in the Nd(ClO<sub>4</sub>)<sub>3</sub>-citric acid-LiClO<sub>4</sub>-LiOH-H<sub>2</sub>O system. The MSE model accurately reproduces the experimentally

observed (Svoronos et al., 1981) characteristic titration curve patterns that are due to the changes in speciation while the pH is varied by adding LiOH at different initial  $\text{Nd}(\text{ClO}_4)_3$  concentrations (0.004 m - blue curve, 0.006 m - green curve, 0.010 m - pink curve, and 0.020 m - red curve). Depending on Nd and LiOH concentration, a transition to a relatively high pH may be observed without hydroxide precipitation due to strong complexation. Figure 5d illustrates the complexation effect of acetate ligands in the  $\text{Ce}(\text{ClO}_4)_3\text{-NaClO}_4\text{-HClO}_4\text{-CH}_3\text{COOH-Na}(\text{CH}_3\text{COO})$  system.  $\text{NaClO}_4\text{-HClO}_4$  was used to set the ionic strength of the solution to 2.0 M; the concentration of  $\text{Na}(\text{CH}_3\text{COO})$  was varied while the  $\text{CH}_3\text{COOH}$  concentration was kept constant at 2.5 M. In this case, acetate ions form considerably weaker complexes than citrates or tartrate ions. The concentration of free acetate ions directly quantifies the extent of cerium acetate complexation, which goes down with an increase in cerium concentration. Eventually, with excess  $\text{Na}(\text{CH}_3\text{COO})$  added to the system, the predicted concentration of free acetate ions plateaus in agreement with experimental data (Sonesson, 1958).



**Figure 5.** Calculated and experimental phase behavior and thermodynamic properties of rare earth-containing systems in the presence of complex-forming organic ligands (i.e., citrate, tartrate, and acetate): (a) Solubility of Nd citrate ( $NdC_6H_5O_7 \cdot 3.5H_2O$ ) in aqueous solutions as a function of pH at 25 oC; pH was varied using  $HClO_4$  and  $NaOH$ , while  $NaClO_4$  (0.1 M) was used as a background electrolyte; (b) solubility of lanthanum tartrate in tartaric acid solution around room temperature; (c) titration curves for the  $Nd(ClO_4)_3$ -citric acid- $LiClO_4$ - $LiOH$ - $H_2O$  system at 25 oC; pH of solutions containing different amounts of Nd perchlorate ( $Nd(ClO_4)_3$ ) (0.004-0.02 m) was varied by adding  $LiOH$ ; (d) free acetate ion concentration as a function of sodium acetate concentration in the  $Ce(ClO_4)_3$ -  $NaClO_4$ - $HClO_4$ - $CH_3COOH$ - $Na(CH_3COO)$  solution at 20 °C. The symbols represent experimental data (Holmberg, 1907; Rimbach & Schubert, 1909; Skorik et al., 1965; Skorik & Serebrennikov, 1965; Sonesson, 1958; Svoronos et al., 1981) whereas the curves represent calculated results.

Calibration of the model against experimental solubility, titration and speciation data makes it possible to make predictions of the effect of complexation on solubility in cases when direct solubility data in ligand-bearing solutions are not available. This is illustrated in Figure 6 for Nd in the absence and

presence of complexing ligands. First, the solubility of Nd (as a representative REE) is calculated as a function of pH and compared with experimental data (Rao et al., 1996; Silva, 1982) at 25 °C in the presence of 0.1 m NaCl. The results indicate a strong pH dependence of the solubility, which is generally controlled by the precipitation of crystalline Nd hydroxide. This pH dependence is similar across the lanthanide series. Then, Figure 6 illustrates the effects of two organic chelating agents, i.e., acetic and gluconic acids, on the availability of Nd in solution. To isolate the effect of complexation from the effect of pH, the concentrations of acetic and gluconic acids were fixed at 0.1 m and the pH was varied by adjusting the concentrations of HCl and NaOH. Thus, the increase in solubility at a fixed pH is due to the complexation of Nd with the organic ligands. Gluconic acid is a stronger complexing agent than acetic acid due to the presence of hydroxyl groups in addition to the carboxylic group. Figure 7 shows the speciation of Nd in the presence of gluconic acid as a function of pH. At 25 °C, gluconic acid forms four stronger (more stable, and therefore more abundant) and two weaker (less stable, and therefore less abundant) complexes with Nd as a function of pH. The sum of the concentrations of the complexes and uncomplexed neodymium is equal to the total Nd solubility. Such understanding of equilibrium solubility is a necessary foundation for understanding REE behavior, although kinetics can of course affect experimental observations. For example, the slow precipitation kinetics of REE phosphate phase(s), either in an amorphous or crystalline form, were postulated to have resulted in exposures of microbes to higher REE concentrations in laboratory experiments than expected from equilibrium predictions (Fujita et al., 2015).

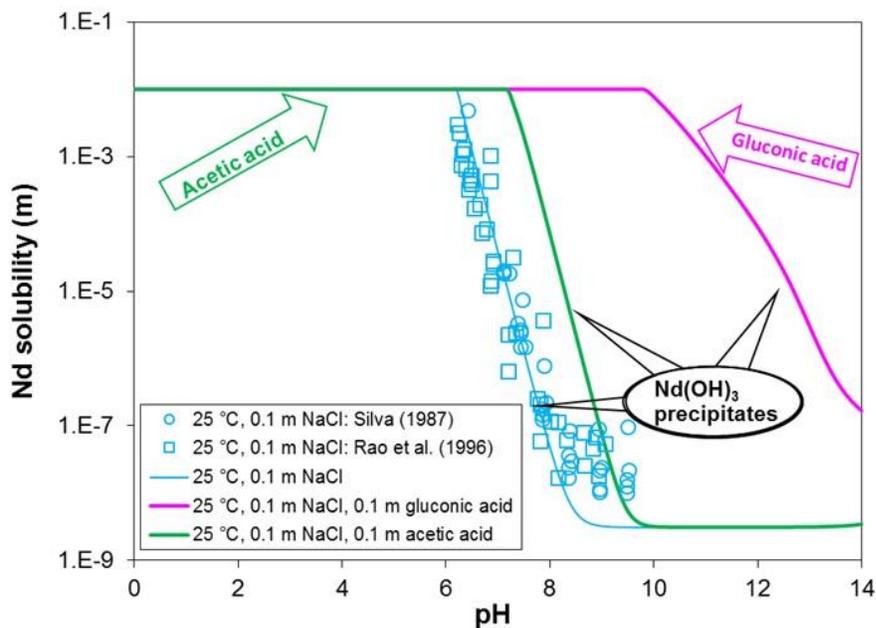
### **2.2.2 Thermodynamic modeling of REE leaching from industrial feedstocks**

Based on the parameterization for simpler, well-defined subsystems, the model can be applied to study the recovery of REE from compositionally complex industrial wastes. Here we present the example of a coal fly ash derived from an Appalachian Basin coal. In the fly ash, REE occur in a matrix containing elements such as Si, Al, Fe, Ca, Mg, Na, K, Ti, Ba, Sr, and P. The behavior of the matrix elements is practically important and can also be simulated using the MSE model. In the simulation, the mixture of amorphous

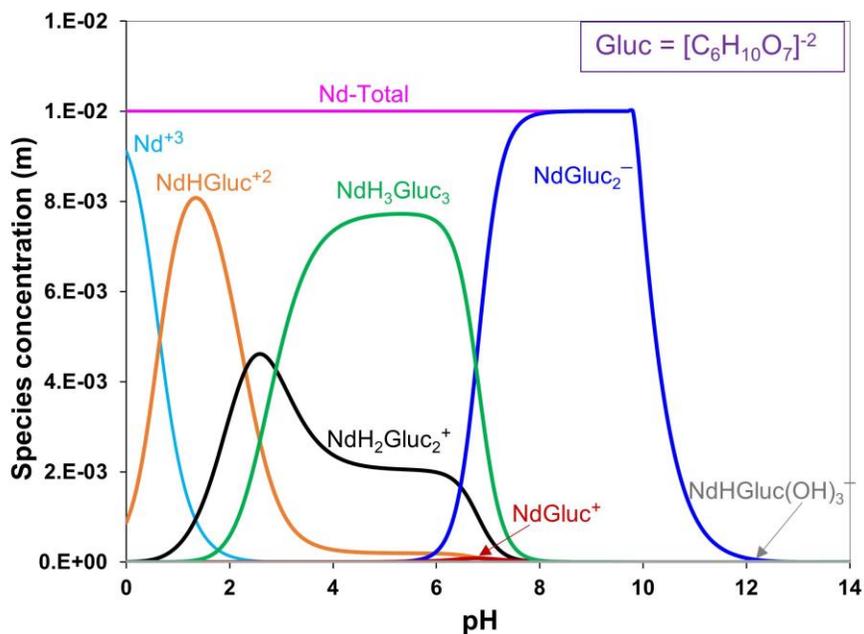
oxides of the matrix elements has been allowed to equilibrate with hydrochloric, acetic or gluconic acid at varying concentrations. Nd was used as a representative REE; the dissolution and complexation behavior of other REE is expected to be qualitatively similar. Figure 8 shows the predicted total concentration of Nd dissolved from the fly ash sample as a function of either pH ranging from 0 to 6 (Figure 8a) or the concentration of the added acid (Figure 8b). For each acid system, the pH was adjusted by changing the acid concentration. At low pH values, all Nd is predicted to dissolve (cf. the horizontal line in Figure 8a) whereas the solubility of Nd at higher pH values is controlled by the formation of  $\text{NdPO}_4$ .  $\text{NdPO}_4$  starts to form at a pH of about 1.6 for HCl and about 3.6 for both acetic and gluconic acids. Gluconic and acetic acids are more effective than HCl for the dissolution of Nd at pH values between 1.6 and 3.8 because of the formation of complexes between Nd and the organic acids. Due to the differences in complexation strength discussed earlier, gluconic acid is more effective than acetic acid in solubilizing Nd at pH above  $\sim 3.8$ . While the solubility plot as a function of pH (Figure 8a) illustrates the effect of complexation at a fixed pH, it is also of interest to simulate the concentration of the acid that is necessary to dissolve Nd. The latter simulation reflects the interplay of the effect of acid strength (which increases in the order acetic acid < gluconic acid < HCl) with the effect of complexation, which is the strongest for gluconic acid. As shown in Figure 8b, gluconic acid dissolves more Nd at low acid concentrations, which is primarily due to complexation. However, HCl is more efficient to obtain a complete solubilization of Nd from the sample (cf. the flat lines in Figure 8b).

The effectiveness of REE leaching depends not only on the solubility of the REE but also on the stability of other phases which may scavenge REE, by mechanisms such as sorption or co-precipitation. In the case of coal fly ash leachates, some have been observed to form gels over time. To gain insight into this phenomenon, thermodynamic simulations were performed to investigate whether certain solids might form with a delay after the initial leaching. This was simulated by allowing the formation of various additional crystalline silicate phases, which may form after a prolonged equilibration time. Although the

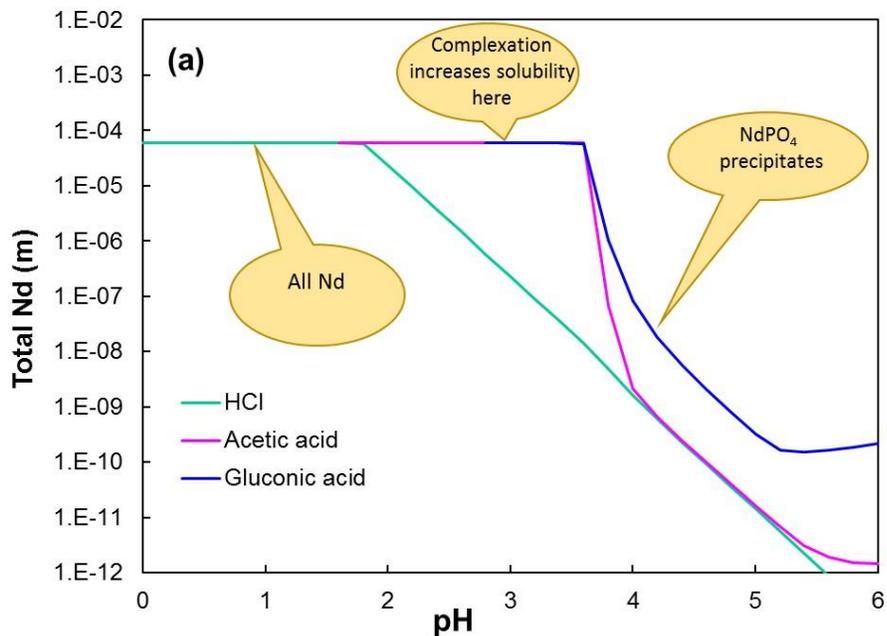
kinetics of such phenomena cannot be predicted using thermodynamic analysis alone, the simulation makes it possible to indicate under what conditions gelation phenomena are possible. The results of the two simulations – without and with certain kinetically controlled crystalline silicate phases – are illustrated in Figure 9 for HCl leachates of the coal fly ash. The figure shows the molality of dissolved Si as a function of pH, which results from varying HCl concentration. These kinetically controlled solid phases start forming at pH above ~2, which leads to a drop in dissolved Si concentration due to the precipitation of additional crystalline silicates (i.e.,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ ,  $\text{KAlSi}_3\text{O}_8$ ,  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ , and  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ) in addition to amorphous  $\text{SiO}_2$ . The formation of such phases may impair the separation of REE due to adsorption phenomena.

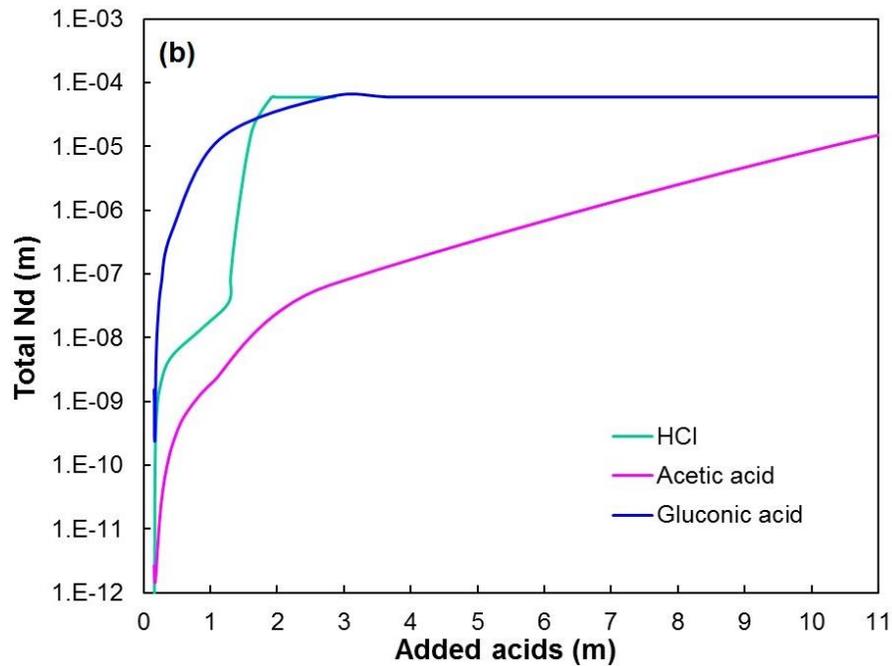


**Figure 6.** Solubility of neodymium hydroxide as a function of pH at 25°C in a 0.1 m NaCl aqueous solution (teal) and in the presence of 0.1 m acetic acid (green) or 0.1 m gluconic acid (purple). The pH was adjusted by varying HCl and NaOH concentrations. The symbols represent experimental solubility data of  $\text{Nd}(\text{OH})_3$  and the curves represent the calculated results.

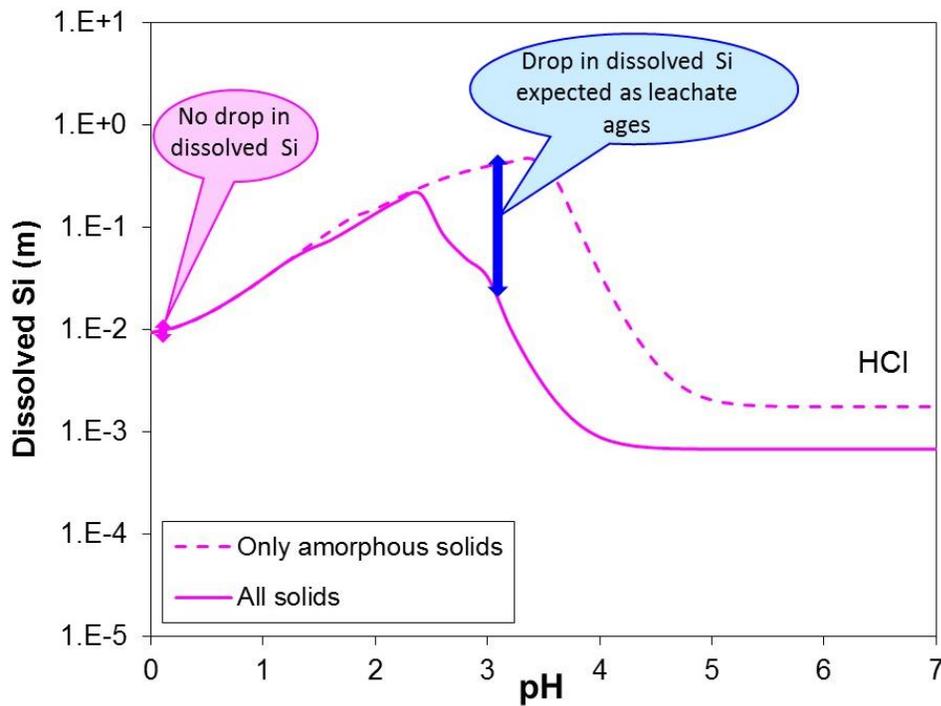


**Figure 7.** Calculated speciation for the system studied in Figure 1 in the presence of 0.1 m gluconic acid. The curves show the concentrations of various complexes between neodymium and gluconic acid as a function of pH.





**Figure 8.** Total dissolved molality of Nd after equilibrating a coal fly ash sample with hydrochloric, acetic, or gluconic acid as a function of (a) pH or (b) molality of added acid.



**Figure 9.** Total dissolved Si concentration predicted by excluding (dashed lines) or including (solid lines) the possible formation of crystalline silicate phases whose formation is kinetically controlled. The

difference between the two lines at a given pH indicates the possibility of formation of solids as the leachate sample ages.

As illustrated by the above examples, geochemical equilibrium modeling provides a powerful tool for understanding the complexities of the solution chemistry of leaching processes. However, care must be taken in the parameterization of the models to ensure that the predictions are accurate. This usually requires a critical analysis of the underlying phase equilibrium and speciation data, followed by a careful analysis of trends within the REE series. Furthermore, application of the models requires an understanding of the behavior of solid phases, some of which may form over the time scale of laboratory experiments, while others may appear long afterward.

### **2.3 Feedstock compatibility with bioleaching microbes**

In addition to limiting REE recovery through equilibrium or kinetic effects, a feedstock or leachate's chemical composition may limit REE recovery through inhibition of microbial activity. REE themselves have generally been considered to have a low environmental impact in natural environments due in part to their typically very low concentrations and the perception that they are less likely to pose a problem than more common heavy metals (Gonzalez et al., 2014; Haque et al., 2014; Kurvet et al., 2017). However, in an industrial leachate, higher REE loads will be present, and some studies have suggested that high REE concentrations can inhibit microbial growth. Some early studies reported inhibition of bacteria and fungi provided with REE at concentrations >10 mM (Talbert & Johnson, 1967; Wurm, 1951). More recently, other researchers have reported that high concentrations of REE can disrupt membrane integrity of *Escherichia coli*, as observed by electron microscopy for Ce<sup>3+</sup> at concentrations  $\geq 0.25$  mM (Chen et al., 2010; Chen et al., 2012) or by atomic force microscopy for Pr<sup>3+</sup> at 1 mM (Peng et al., 2007) and La<sup>3+</sup> at  $\sim 3$  mM (Peng et al., 2004). High concentrations of Gd ( $\geq 0.3$  mM) have also been reported to be toxic to the flagellate algae *Euglena gracilis*, protozoan *Tetrahymena thermophile* and the bacterium *E. coli* in microcosms (Fuma et al., 2001). Additionally, Eu was shown to be inhibitory at  $\geq 10$   $\mu$ M to

Clostridium but a cytoplasmic reduction mechanism for the REE may have helped increase tolerance (Maleke et al., 2019).

In our own work, we observed inhibition of the ammonia oxidizing bacterium *Nitrosomonas europaea* at nominal Y concentrations  $\geq 0.56$  mM and Eu concentrations  $\geq 0.33$  mM, and of the nitrifying bacterium *Nitrobacter winogradskyi* at  $\geq 0.11$  mM Y and  $\geq 0.07$  mM Eu (Fujita et al., 2015). Note that these concentrations are nominal, given that we observed significant precipitation of the REE following addition to the media. Others have also pointed out that actual aqueous concentrations encountered by organisms are typically lower than the nominal concentrations provided under the testing conditions due to the limited solubility of lanthanides in many aqueous media (Gonzalez et al., 2014; González et al., 2015; Herrmann et al., 2016; Sneller et al., 2000). Gonzalez et al. conducted a comprehensive study of the ecotoxicity of lanthanides to a number of aquatic organisms, and for the bacterium *Aliivibrio fischeri* reported nominal (based on metal added to test cultures) EC<sub>50</sub> values of 18  $\mu$ M for Lu,  $>46$   $\mu$ M for Ce and  $>41$   $\mu$ M for Gd (González et al., 2015). However, for the same *A. fischerii* organism, Weltje reported an EC<sub>50</sub> value of 1.57  $\mu$ M for the free Lu<sup>3+</sup> ion (Weltje et al., 2004). Because of the sensitivity of REE speciation to geochemical conditions, as was discussed in the section on modeling, and the apparent differing sensitivity of particular microbes to different REE (Fujita et al., 2015), it is difficult to determine general threshold concentrations of concern for REE to bioleaching organisms. However, in a leachate, the REE will be soluble, by definition, and therefore it is safe to assume that microbes present will be exposed to elevated soluble concentrations of REE. Whether they are bioavailable however is a different question. Depending on the leachate composition, REE may be present as complexes; for example, Figure 6 in the previous section shows the predicted speciation of Nd in a system with gluconic acid, an organic acid identified as important in a number of REE bioleaching studies (Corbett et al., 2017; Glombitza & Reichel, 2014; Hopfe et al., 2017; Reed et al., 2016; Thompson et al., 2018). In this particular modeled system, Nd solubility is controlled largely by complexation with gluconate. According to the generally accepted model

that biological responses to trace metals are best predicted by the free metal ion activity (Campbell, 1995; Morel & Hering, 1993), the vast majority of the Nd in the system would not be bioavailable at typical environmental pH. However, in the aforementioned studies with *N. europaea* in the absence of a known complexant, inhibition of ammonia oxidation was observed even when measured and modeled soluble concentrations of Eu were  $\leq 2$  ppb, representing  $<1\%$  of the originally added Eu (nominally up to  $660 \mu\text{M}$ , or 100 ppm) (Fujita et al., 2015). In contrast, more recent studies with *N. europaea* and Gd conducted under similar conditions average measured soluble Gd concentrations as high as 90 ppb were not associated with observable inhibition, although high concentrations of Gd (up to  $500 \mu\text{M}$ ; equivalent to 79,000 ppb) complexed with diethylenetriaminepentaacetic acid (DTPA) seemed to cause at least temporary inhibition (Fujita et al., 2020). In the latter case, we hypothesized that DTPA complexation of other essential metals may have played a role. These observations illustrate that much remains to be elucidated with respect to interactions of REE and microbes, and therefore the potential for inhibition of bioleaching organisms, whether directly by the free ion or by other REE species or associated ligands, should not be discounted.

REE-containing materials also often contain heavy metals and or radionuclides that can be solubilized along with the REE (Cánovas et al., 2017; Nassar et al., 2015) and these may also pose a concern for bioleaching organisms (Qu & Lian, 2013; Xu et al., 2014). In end of life consumer products, plastic components or composites and organic glues may be present, and leached organic compounds could also affect the microorganisms, and or bioleaching efficiency. Potential toxicity of leachates to the organisms confers an advantage for bioleaching strategies that separate biological lixiviant production from the actual leaching of the metal-containing feedstock. Such strategies are referred to as “two step bioleaching,” as opposed to “one step bioleaching” where the cells are grown in contact with the solids to be leached (Bosshard et al., 1996; Qu & Lian, 2013). In two step bioleaching, organisms can be cultivated under optimal conditions with respect to lixiviant production, and then the culture medium

would be applied to the REE-containing feedstocks. In an industrial scale deployment, cells would generally not be removed from the medium since that would require a costly processing step (e.g., filtration or centrifugation). As the cells would presumably have already produced an optimal amount of lixiviant, cell inhibition or toxicity is no longer a concern. Two step bioleaching would be a good option for microorganisms that grow rapidly on inexpensive carbon sources where the cost of an extra unit operation to grow cells can be offset. For microorganisms that are difficult to cultivate, require expensive nutrients or grow slowly, an alternative strategy would be cultivation of immobilized cells (note that possible approaches for immobilization are discussed in the section on bioseparation) in a reactor separate from the REE solids, where the cell-free lixiviant fluid can be drawn off to a separate unit for leaching. This allows cell cultivation to be maintained throughout the process and avoids the need for new batch cultivation for each leach cycle. This format would also be amenable to development of a continuous lixiviant production/bioleaching process.

In “one step bioleaching” microbes are cultivated and produce the leaching agents in the presence of the solid feedstock. Separate unit operations for lixiviant production and bioleaching are not required, simplifying the system and reducing costs. In the case of bioleaching by sulfide oxidizers, direct contact between the cells and the sulfidic solids is believed to facilitate electron transfer, resulting in more efficient acid production (Vera et al., 2013). One step bioleaching may also provide better leaching conditions if the cells adhere to the surface of the feedstock, since lixiviant would be produced directly proximate to the solid surface. Fathollahzadeh et al. reported that monazite dissolution and REE leaching increased in the presence of *Enterobacter aerogenes*, and microscopic imaging showed microbial attachment to the monazite surface suggesting that cell contact improved the bioleaching (Fathollahzadeh et al., 2018). However, toxins that are released during leaching can inhibit the desired lixiviant production. Qu and Lian suggested this as one reason that greater REE leaching was observed

with two-step leaching of red mud compared to one-step leaching at pulp densities greater than 5% (w/w), although at < 2% (w/w) the one-step process was more effective (Qu & Lian, 2013).

An additional consideration for one step bioleaching is the effective mass transfer of nutrients for the microbes in the presence of the solid feedstocks. For aerobic organisms, provision of oxygen can be particularly challenging, because oxygen's limited solubility in water generally leads to the requirement for stirring and or sparging with air. This may limit the amount of REE feedstock that can be leached at one time due to the difficulty of aerating large volumes of saturated or suspended solids. In addition, biomass growth can also lead to clogging, between REE feedstock particles as well as inside particles (intra-porosity) if the particles are porous.

The choice of one-step or two-step bioleaching will depend on all of the factors mentioned and the downstream processing steps required. The additional unit operation required for a two-step process compared to a one-step imposes an additional cost factor. On the other hand, the size of unit operations for a single-step process may be prohibitively large to leach the quantity of REE feedstocks required to be processed for profitability. Following bioleaching by either approach, downstream separations will be necessary since the leachate will be a complex mixture of REE and other metals, as well as microbial products. If the presence of cells interferes with downstream operations, it may be necessary to remove cells prior to REE concentration and purification.

Another consideration for one step bioleaching is the presence of other microorganisms in the solid feedstock, aside from those desired for leaching. Recycled feedstocks will not be sterile, and consequently microorganisms "carried along" with the solids may compete with organisms added expressly for bioleaching. If indigenous organisms use the growth substrates provided to the bioleaching organisms, and they do not produce compounds useful for bioleaching, this would reduce the efficiency of the process. However, heterotrophs are common in the environment, and indigenous mixed cultures

can be effective for REE leaching (Barnett et al., 2018). Indeed, use of mixed cultures may in fact be advantageous compared to use of single strains (Hopfe et al., 2017). In order to evaluate the potential for biological contamination and impacts on leaching, tests with real solid feedstocks and under representative conditions will be necessary.

### **3.0 *Technical considerations for bioseparation***

The chemical and physical characteristics of the solid feedstock bound the bioleaching mechanism and together with the lixiviant constituents bound the composition of the leachate. In bioseparation, the chemistry of the immobilized biological ligands together with the chemical composition of the leachate as well as the stripping agent chemistry define the degree of target metal recovery and product purity. These factors are discussed in the following sections.

#### **3.1 *Biological ligand chemistry***

Microbially mediated surface adsorption (biosorption) represents a potentially cost-effective and ecofriendly approach for metal recovery (Fein et al., 2001; Mejáre & Bülow, 2001; Zhuang et al., 2015). Microorganisms have a high surface area per unit weight and exhibit high metal adsorption capacities owing to an abundance of cell surface functional groups with metal coordination functionality (Moriwaki & Yamamoto, 2013). The organic functional groups generally considered most likely to play a role in chelation of metal ions are carboxylic, amino, hydroxyl, phosphoryl, and sulfhydryl groups (Beveridge & Murray, 1980; Cox et al., 1999; Yu & Fein, 2016). Microorganisms produce these moieties naturally as parts of proteins, nucleic acids, and lipids, and therefore the genetic coding for biosynthesis is already present in the organisms.

Owing to the chemical properties of the surface functional groups, a number of reports suggest that biosorption could be particularly amenable to REE extraction (Das & Das, 2013; Gupta et al., 2018).

In particular, the selective extraction of REE over non-REE by microbial cell surfaces has been reported. For example,  $Tm^{3+}$  sorption was favored over  $Fe^{2+}$  sorption on the surface of *Bacillus subtilis* (Moriwaki et al., 2013), while  $Sm^{3+}$  adsorbed more tightly than  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ , and  $Cd^{2+}$  onto *Arthrobacter nicotianae* (Tsuruta, 2006). Additionally, the stability constant (log K) for the interaction of *B. subtilis* with Nd was stronger than for all tested metal cations, except the uranyl oxyanion (Fein et al., 2001). In contrast, the difference in stability constants among individual REEs for cell surface sites is quite small with the exception of a strong preference for scandium (Sc) over lanthanides (Hosomomi et al., 2013; Karavaiko et al., 1996; Moriwaki et al., 2016; Ngwenya et al., 2010). Thus, while a moderate biosorption preference for middle/heavy REE over light REE has been observed (Park et al., 2017; Takahashi et al., 2005), native microbial surfaces are better suited for grouped lanthanide extraction rather than individual REE separation. Nevertheless, a recent study reported a scheme for preprotonation of cell surface functional groups followed by pH-dependent desorption that achieved separation factors for certain REE pairs that exceeded solvent extraction standards (Bonificio & Clarke, 2016). As such, pH modulation during the adsorption and desorption steps may prove an effective strategy for the selective enrichment of specific REEs from feedstock leachates.

In addition to moieties that are synthesized and expressed naturally, organisms may be genetically engineered to produce selective metal-binding peptides or proteins and express them at high density on the cell surface (Hennebel et al., 2015; Park et al., 2016; Wei et al., 2014; Z. Xu et al., 2010; Zhuang et al., 2015). As noted earlier, Park et al. reported the construction of recombinant strains of *Caulobacter crescentus* and *E. coli* with lanthanide binding tags (LBT) inserted at permissive sites of surface proteins, anchoring the LBT to the cell surface (Park et al., 2017; Park et al., 2016). LBT are short peptides optimized to bind lanthanide ions with high affinity and specificity and were originally developed as fusion proteins for biological applications such as X-ray crystallography, nuclear magnetic resonance, and various luminescent visualization techniques (Allen & Imperiali, 2010; Daughtry et al.,

2012; Nitz et al., 2003). The short peptide-based nature of LBTs and high REE binding affinity make them ideal for cell surface display to increase specific REE adsorption. Indeed, REE recovery performance with the LBT-displayed strains revealed improved adsorption capacity and selectivity, and enabled effective REE recovery from a variety of feedstocks (Park et al., 2017; Park et al., 2016). In addition to LBT, the recently discovered lanmodulin protein from *Methylobacterium Exorquens* also shows great promise as a selective binding agent for lanthanides (Cotruvo et al., 2018; Deblonde et al., 2020; Mattocks et al., 2019), and it is possible that microbes could be genetically engineered to express lanmodulin on the cell surface.

### **3.2 Effect of leachate chemical composition on biosorption**

Biosorption performance depends on several factors, including the identity of the adsorbents, the solution chemistry of the leachate, and conditions such as temperature and the amount of sorbent relative to the target solutes. Among all of the factors, the pH of the leachate is perhaps the most critical driver of REE biosorption efficacy, here defined as the ability both to recover a high percentage of the total REE content and to do so preferentially over non-REE metals. The primary native cell surface functional groups involved in REE adsorption are carboxyl (pKa, 4.3 and 5.5) and phosphoryl (pKa, 2.2 and 6.9) groups (Markai et al., 2003; Martinez et al., 2014; Ngwenya et al., 2010; Texier et al., 2000). Given the protonation of these cell surface functional groups under acid conditions, adsorption efficacy at pH lower than 4 is generally poor for most REE with the exception of Sc (Hosomomi et al., 2013; Moriwaki et al., 2016), which benefits from its smaller ionic radius and stronger Lewis acid characteristics compared to the lanthanides (Giret et al., 2018; Moriwaki et al., 2016). Since the REE feedstock is usually acidic following the (bio)-leaching process, a pH adjustment step (e.g., NaOH addition) is necessary prior to sorption. REE adsorption capacity generally increases with increasing pH (Das & Das, 2013; Kucuker et al., 2017; Park et al., 2016). However, REE solubility, a necessary condition

for sorption, is highly pH dependent and generally decreases with increasing pH, as presented in section 2.2. To avoid the formation of REE hydroxide and or other REE mineral precipitates (depending on solution chemistry), REE biosorption studies are generally limited to  $\text{pH} \leq 6$ . Consequently, the effective pH range for biosorption is largely constrained to between pH 4 and 6. For the coal fly ash leachates described in section 2.2, poor REE solubility at pH 6 constrains the biosorption process to a pH range of 4-5. Given the reduction in adsorption capacity with decreasing pH, a higher biomass to REE ratio may be necessary to achieve high REE extraction efficiency. In addition, efforts to improve biosorption performance under low pH conditions using genetic engineering to produce binding motifs with higher REE affinity or by identifying organisms or macromolecules, such as lanmodulin (Deblonde et al., 2020), that are naturally efficient at REE sorption under acidic conditions may be warranted. For example, in simple synthetic solutions the gram-positive bacterium *Bacillus subtilis* was found to maintain high REE adsorption capacity (relative to *E. coli*) down to a pH of 3 (Martinez et al., 2014; Takahashi et al., 2005). Testing with solutions more representative of real-world feedstock leachates will provide additional insight into the utility of *B. subtilis* and related bacteria for REE recovery via biosorption.

Within the permissible pH range, the identity and concentration of non-REE is another critical factor determining REE biorecovery. Although cell surface functional groups exhibit a general selectivity for REE, many relevant feedstock leachates contain significant concentrations of non-REE metal cations and usually at concentrations much higher than that of REE. High concentrations of the major elements (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ) are found in many REE feedstock leachates, but generally have little impact on REE extraction efficacy (Moriwaki & Yamamoto, 2013; Ngwenya et al., 2009; Park et al., 2017; Texier et al., 1999). For example, in our laboratories' studies with LBT-engineered *E. coli*,  $95.1 \pm 5.6\%$  Tb adsorption was achieved with a synthetic solution mimicking the Great Salt Lake that contained 165,000 ppm major elements and 100 ppb Tb. Less than 1% of the major elements were adsorbed (Brewer, Chang, et al., 2019). Minimal adsorption of major elements was also observed in leachates of REE ore

and low-grade mine tailings (Park et al., 2017). One notable exception is the elevated  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  recovery observed for native *Arthrobacter nicotianae* and LBT-displayed *E. coli* (Park et al., 2020) in Powder River Basin fly ash leachate, which contains  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  at concentrations that are three orders of magnitude higher than total REEs. Similar to major elements, most transition metals such as Zn, Mn, and Ni also pose minimal impediments to REE adsorption efficacy (Park et al., 2017; Park et al., 2020), particularly when the biomass concentration is properly tailored to the feedstock (see below). In contrast, studies with several bacteria have revealed that Cu, Al, Fe(III), Pb, and uranyl cations are the most effective competitors for REE binding to cell surface sites (Fein et al., 2001; Park et al., 2017; Park et al., 2020; Texier et al., 1999), and will be coextracted with REE if present at elevated concentrations. For example,  $\text{Al}^{3+}$  was found to be a strong inhibitor for REE binding to *Pseudomonas aeruginosa* (Texier et al., 1999). In addition, two-element competition experiments in our laboratories using LBT-displayed *E. coli* indicated that  $\text{UO}_2^{2+}$  and  $\text{Al}^{3+}$  were the most competitive non-REE cations, decreasing Tb adsorption efficiency by 25% when present at concentrations 4-fold higher than Tb (Brewer, Chang, et al., 2019). Lead and Cu reduced Tb adsorption efficiency to a similar degree when present at concentrations 10 and 60-fold higher than Tb, respectively. For comparison, 1400 and 33,000-fold higher Mg and Na concentrations, respectively, were required to similarly impact Tb adsorption.

The impact of non-REEs on REE adsorption efficacy can be partially alleviated through solution conditioning and experimental optimization steps. For example, functionalization of the *E. coli* cell surface with LBTs enhanced the cell surface selectivity relative to native *E. coli* cells for Nd over all non-REEs except Cu (Park et al., 2017). Further genetic engineering efforts to increase the ratio of LBT to non-LBT sites or through the use of ligands that are even more selective, e.g., lanmodulin (Cotruvo et al., 2018), may be employed to achieve even greater REE selectivity. In addition, the soluble concentration of many competing metals can be reduced through pH modulation. We have found that soluble Al, Pb, U, and Fe concentrations are significantly reduced in feedstock leachates upon pH adjustment to the 5-6

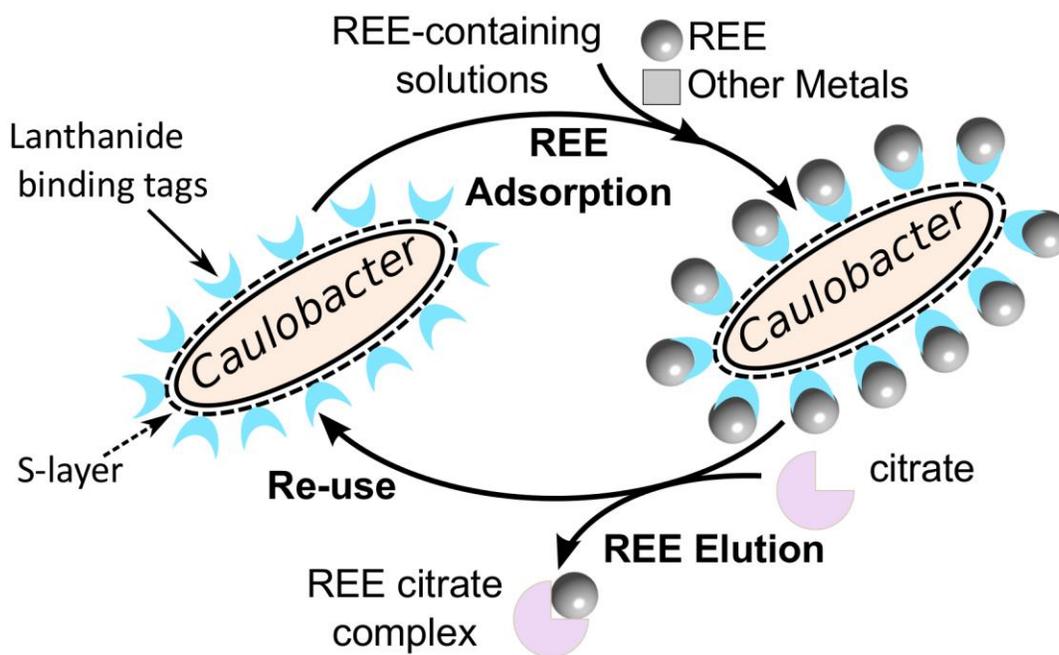
range, which is critical for high purity extraction of REEs from mine tailings and coal byproducts (Park et al., 2017; Park et al., 2020). Lastly, optimizing the adsorbent to REE ratio for a given leachate can also minimize the effect of non-REE sorption on REE recovery. For example, biosorption experiments in our laboratories with synthetic geothermal fluids containing high Al content relative to REE revealed that high REE extraction efficiency and REE purity can be obtained by adjusting adsorbent concentration relative to the REE concentrations in the leachate (Brewer, Chang, et al., 2019).

Compared to the cation composition, there has been less experimental investigation of how the anion content of leachates affects REE adsorption efficacy by biosorbents. Many REE containing leachates contain high concentrations of chloride, sulfate, or nitrate anions as a result of a mineral acid leaching step. However, these anions are weak REE complexants compared to biological ligands and thus their effects on REE adsorption efficacy should be minimal. Although carbonate forms stronger REE complexes, conducting the biosorption step at below circumneutral pH limits the free carbonate concentration. In contrast, phosphate is a strong complexant and REE-phosphates exhibit extremely low solubility across the pH range relevant for biosorption. Therefore, prior to the application of biosorption to leachates that may contain significant quantities of phosphate, geochemical modeling as described in section 2.2 is advised to guide selection of leaching conditions.

### **3.3 Stripping agent chemistry**

After REE are selectively adsorbed, the residual leachate solution is removed, and then a stripping agent is applied to release the captured metals and regenerate the binding sites. The stripping solution should be free of the non-target components of the original leachate, and by using a smaller volume than used for sorption, increased concentration of the REE as well as enrichment relative to the other ions in the original solution can be achieved. Use of a stripping agent that outcompetes the biological ligand but does not harm the structural architecture (cell structure) of the biosorbent allows

the latter to be reused multiple times (Figure 10). Techno-economic analyses of biosorption for recovery of REE determined that biomass recycling, or regeneration and reuse of the sorbent with minimal loss of sorption capacity, can have a significant beneficial impact on cost (Alipanah et al., 2020; Jin et al., 2017). In most reported examples, stripping is performed in a non-selective manner, resulting in desorption of all adsorbed metals (Arunraj et al., 2019; Park et al., 2017; Park et al., 2016; Texier et al., 2002). The selectivity of the extraction process is therefore driven almost exclusively by the biosorption step. Commonly employed stripping agents include organic and mineral acids. Citrate and ethylenediaminetetraacetic acid (EDTA) have been shown to be particularly effective for quantitative desorption given their strong REE complexation and minimal impact on subsequent biosorption capacity (Arunraj et al., 2019; Park et al., 2017; Park et al., 2016; Texier et al., 2002).



**Figure 10.** Process for REE recovery based on biosorption and desorption. REE bound to the *Caulobacter* cell surface can be stripped with citrate. Cells are reused for multiple cycles of sorption/desorption. Reprinted with permission from Park et al. (2016), p. 2735. Copyright 2016 American Chemical Society.

Coupling the adsorption step with a selective desorption process may further improve the REE vs non-REE selectivity of the biorecovery process and potentially enable separation of certain REE. For example, Bonificio and Clarke (2016) examined REE binding onto preprotonated non-engineered (native) bacterial cells, and reported that using different concentrations of nitric acid (pH manipulation) for desorption achieved separation factors for certain REE pairs that exceeded solvent extraction standards (Bonificio & Clarke, 2016). Ultimately, the possibilities to tune the selectivity of sorption and desorption, coupled with the fast kinetics of sorption and desorption, make bioseparation based on biosorption/desorption a promising platform for efficient REE recovery (Hennebel et al., 2015; Park et al., 2016; Takahashi et al., 2005; Texier et al., 1999).

### **3.4 Cell immobilization for biosorption**

For an industrial scale biosorption application, the biosorbent should be amenable to high-throughput contact with the REE-containing feedstock leachate, as well as with the subsequent stripping solution. Separation of the aqueous phase from the cells must be simple and robust. One approach that has been utilized for metal biosorption applications is encapsulation of planktonic cells within polymer matrices (Dodson et al., 2015). The goal is to provide a stable, permeable material that permits REE-specific adsorption by the immobilized microbes in a continuous flow extraction system. To maintain the high selectivity of the adsorbent, the use of minimally adsorptive carrier materials is preferable given the high concentrations of non-REE metal contaminants present in most feedstocks. Although most biosorption applications that have utilized encapsulation have focused on bioremediation of heavy metals (e.g., Pb, Cu, Zn, etc), promising initial examples for REE extraction include the encapsulation of *Pseudomonas aeruginosa* in polyacrylamide cubes for REE extraction from synthetic solutions (Texier et al., 2002) and the use of cellulose-embedded yeast for REE extraction from phosphor powder leachates (Arunraj et al., 2019). In our own work, we have pursued another promising approach, the encapsulation

of LBT-displayed cells within polyethylene glycol diacrylate (PEGDA) hydrogel beads, for use in packed bed columns (Brewer, Dohnalkova, et al., 2019). In each case, REE extraction and stripping were performed in a continuous flow packed bed column and multiple reuse cycles were demonstrated. Additional work to improve the biomass loading capacity and mass transfer kinetics will be required to increase feedstock throughput. However, mass transfer kinetics and cell surface accessibility will likely be diminished above a certain cell loading threshold. Indeed, we have found that REE adsorption capacity is no longer proportional to cell loading when immobilizing dense cell slurries (2 g wet weight cells/ml) using a Si sol gel molding process. Coupled with appropriate cell immobilization strategies, a variety of continuous bioreactor configurations can be used for applying various REE-adsorbing microbes for REE recovery. The bioreactors should maximize contact between the biological agents and REE-containing fluids. In addition to the packed bed configurations described in the previously cited literature, fluidized bed bioreactors have also been proposed for various metal adsorption applications (Ilamathi et al., 2014; Monge-Amaya et al., 2015). Efficient extraction of high-purity REE will require establishing a cost-effective bioreactor design, an efficient workflow, and optimized operational conditions. The experimental burden of such optimization steps can be reduced by the development and implementation of reactive transport models that predict the optimal chemical and operational parameters for bioseparation operations.

#### **4.0 General techno-economics of biorecovery**

Promising bench-scale technologies often falter during scale-up because the economics simply do not work at higher scales (Dunbar, 2017; Kappes, 2002). Techno-economic analysis (TEA) is a tool used to project promising concepts to larger scale and identify areas where the technology needs improvement in order to be economically feasible. Below we discuss economic factors relevant to bioleaching and bioseparation of REE.

#### 4.1 REE bioleaching economics

Bioleaching in the mining industry has been considered a low cost option compared to more intensive metal recovery processes such as hydro-, pyro- or electrometallurgical approaches since in principle it only requires construction of an ore or tailings heap, stimulation of microbial activity and time (Brierley & Brierley, 2013). It should be noted that bioleaching processes are inherently slower than other metallurgical processes occurring on the scale of months instead of hours to days and this could potentially impact the economics as well. However, this consideration can be mitigated by developing continuous bioleaching processes that would have a steady output after an initial start-up time. We recently conducted a TEA of our REE bioleaching process using fluidized catalytic cracking (FCC) catalysts as the REE waste stream (Thompson et al., 2018).

In the analysis, we assumed that we would construct a plant to bioleach 10% of the available FCC catalyst in the United States (19,000 tons/year), that the plant would be located next to a petroleum refinery to minimize transportation costs, and that leaching and biolixiviant production efficiencies would be the same as measured experimentally in our laboratory. The TEA identified the significant impact of the pulp density (mass of solid leached/mass of lixiviant applied) on the economics. Our laboratory research showed that lower pulp densities can provide better leaching efficiencies; approximately 50% of REE was recovered following leaching at 1.5% pulp density, versus about 28% recovery at 50% pulp density, in batch leaching studies of FCC catalyst (Reed et al., 2016). It would seem logical to assume that the more efficient recovery of REE would be preferred. However, this assumption does not take into account the cost of the bioreactor required to produce the lixiviant. To leach 1000 kg of FCC catalyst at 1.5% pulp density requires more than 65,000 kg of lixiviant, while at 50% pulp density only 2,000 kg is needed. The fixed capital costs (bioreactor, air compressor, sterilizer, heat exchanger, etc.) for leaching at 1.5% pulp density are 7 times higher than the capital costs for 50% pulp density, and

the operating costs (nutrients, electricity, steam, water and labor) are 27 times higher for 1.5% compared to 50% pulp density (Thompson et al., 2018). Consequently, constructing a plant for 50% pulp density leaching was more economical than the 1.5% pulp density case despite the lower leaching efficiency.

Costs were also sensitive to the amount of REE in the leached feedstocks and the type of REE present. REE content in FCC can range between 1.5 and 5% (Goonan, 2011) and leaching FCC with 5% REE content versus 1.5% REE content in our study would increase profits by 10-fold. The REE present in FCC catalyst are primarily La and Ce, and each was worth about \$2/kg in 2016 (Shanghai Metals market). Sourcing REE feedstocks with higher values would improve economics. Among the most valuable REE are Eu at \$150/kg, Tb at \$400/kg, Pr at \$52/kg and Nd at \$42/kg. The analysis revealed that the bioleaching process by itself was profitable at REE prices in 2011 (a high point due to Chinese restrictions on exports) but was not profitable at REE prices in 2016. However, the process could be made profitable by including a tipping fee for acceptance of the FCC catalyst. Currently, in the petroleum industry, FCC catalyst is considered a hazardous waste and must be disposed in hazardous waste landfills. This costs petroleum refineries as much as \$200/ton for disposal (Marafi & Stanislaus, 2008). If a bioleaching company employing our process could recover this fee and render the waste non-hazardous (or reduce the volume of waste classified as hazardous), bioleaching of REE became economical.

Another opportunity for improvement identified during the TEA was nutrient costs, in particular the glucose cost. Of the total costs for the plant, glucose was responsible for 44% of the overall costs. This finding has led us to focus on alternative carbon sources such as large volume agricultural and food processing wastes for bacterial growth and production of biolixiviant (Jin et al., 2019). Experiments indicated that total REE leaching efficiency remained largely unchanged when corn stover or potato

wastewater were used as carbon sources for microbial bioleaching production. Although new costs would be associated with transport and processing of the complex alternative carbon to simple sugars for microbial growth, analyses suggested that the overall processing costs and environmental impacts would be greatly reduced. Indeed compared to a glucose-based bioleaching plant, even with different REE recovery income and process expenses the predicted net profits quadrupled for the corn stover-based plant and doubled for the potato wastewater-based plant.

#### **4.2 REE bioseparation economics**

Many of the same economic drivers apply to bioseparation processes. An assessment of the techno-economics for integrating a bioseparation approach using LBT-displayed cells into a large-scale process for producing salable total rare earth oxides (TREOs) from 11 diverse REE feedstocks was recently conducted (Jin et al., 2017). For this study, the TEA assumed that the cells were immobilized onto biofilm carrier discs and biosorption was performed in an airlift bioreactor. Elution was performed in a separate column to which the loaded discs were transferred. Pre-processing steps for feedstocks (i.e., beneficiation and leaching) represented 70-80% of the total cost of the REE recovery operation. Thus, using feedstocks that require minimal preprocessing (e.g, geothermal brines, acid mine drainage) can provide a significant economic advantage. As with bioleaching, the feedstock REE loading and composition heavily influences the profitability of the operation. For example, Appalachian basin coal ash, which contains a significant amount of Sc (\$4,200/kg; MineralPrices.com; accessed on Mar. 31, 2017), was the only profitable feedstock at the 2017 REE prices. Feedstocks with higher total REE concentrations, but predominantly comprised of low-value light rare earths, were not profitable for recovery schemes including biosorption. Geothermal brine, despite not needing beneficiation or leaching, had such low REE concentrations that it was not profitable either. For the economics of the bioseparation module itself, a sensitivity analysis highlighted the importance of biomass reusability; 10

reuse cycles were sufficient to reduce the cost of the bioseparation steps by 4-fold. Additional economic considerations for scaling a biosorption process include the costs associated with the specific immobilization platform and the adsorption capacity of the immobilized biosorbent. Maximizing cell adsorption capacity and immobilized biomass density are critical to the economic viability of bioseparation technologies for REE.

## **5.0 Conclusions and directions for future research**

The evaluation of biologically based approaches for recovery of REE is still in its infancy, but research to date indicates their potential to play a role in the development of a more environmentally sustainable and robust supply chain for these metals so critical to modern society. Most likely, new bioleaching or bioseparation approaches for REE recovery will be applied initially to non-traditional REE sources, given the high bar to entry of new technologies into established industries. Potential such sources from which REE might be recovered include ore tailings, bauxite mine residues, phosphogypsum wastes, incinerator ash, metallurgy slags, acid mine drainage, and industrial and municipal wastewaters and sludges (Binnemans, Jones, et al., 2013; Hennebel et al., 2015; Mulchandani & Westerhoff, 2016; Zhuang et al., 2015). These types of materials have the advantage of already being accessible and collected in large quantities, and in fact further processing to recover valuable components could mitigate some of the environmental liabilities that they pose. In addition, mine tailings and ash are already present in particle sizes that are amenable to leaching (Johnson, 2013) while mine drainage and wastewaters could potentially be directly processed by biosorption/desorption. Post-consumer electronics wastes and industrial wastes such as the FCC catalysts and lighting phosphors also represent potential REE feedstocks, although barriers to using these types of wastes may include the high costs (or absence) of systems to collect sufficient volumes for cost effective recycling (Binnemans, Jones, et al., 2013).

Once a potentially viable feedstock is identified, rigorous characterization of its chemical composition is necessary for application of both bioleaching and biosorption, in order to ascertain compatibility with microbial cultures and to predict the effectiveness of the biohydrometallurgical processes. Empirical testing will inevitably be necessary, but the scope of such testing can be greatly narrowed by judicious use of geochemical equilibrium modeling. Such modeling is indispensable for interpreting experimental results and for guiding the selection of optimal leaching and sorption/desorption conditions. Availability of appropriate data for parameterization of the models is however still a challenge; robust thermodynamic data for complexation of REE as well as other potentially competing metals by biologically produced organic ligands is a particular need. Understanding whether constituents in the REE feedstock (and leachate) pose a toxicity concern to bioleaching microbes is also critical, since the selection of a two-step vs one-step bioleaching approach can have a significant impact on costs. In this case, given the diversity of microbial species, testing of the specific feedstocks with the particular microbial culture is likely to be necessary at least for the near future. A better fundamental understanding of microbial interactions with REE and metals in general is critical to accelerate the advancement of biotechnological approaches to REE recovery (Hennebel et al., 2015).

Of course there are also substantial opportunities to “improve” upon nature, for example by increasing microbial tolerance to potential inhibitors, optimizing production of leaching compounds (acids, or chelators), or designing biological ligands with higher affinity for targeted metals, by using synthetic biology techniques (Adesina et al., 2017; Dunbar, 2017). These opportunities are tremendously exciting, but use of genetically engineered organisms in large scale REE or other metal biorecovery operations will require additional studies on their interactions with indigenous microorganisms and native ecosystems, to develop deployment approaches that ensure both the survival of the desired species or traits as well as the mitigation of unwanted and unforeseen negative consequences.

Progress in the development of biotechnological approaches for REE recovery will require concerted effort on the part of microbiologists, molecular biologists, ecologists, geochemists, and engineers. Demonstrating performance at pilot scale will be critical to eliciting commercial interest, although the long and successful history of biotechnology in other industrial applications (e.g., food processing, pharmaceuticals) as well as in biomining should bolster confidence with respect to technical feasibility. Of course, economic factors must also be favorable for biotechnology integration into the REE supply chain. If REE demand continues to rise and the opportunity space for new approaches grows, the environmental benefits of biotechnology may become an increasingly important differentiating factor.

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