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Microbial mobilization of rare earth elements (REE) from mineral solids—A mini review

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Abstract: In the light of an expected supply shortage of rare earth elements (REE) measures have to be undertaken for an efficient use in all kinds of technical, medical, and agricultural applications as well as—in particular—in REE recycling from post-use goods and waste materials. Biologically-based methods might offer an alternative and supplement to physico-chemical techniques for REE recovery and recycling. A wide variety of physiologically distinct microbial groups have the potential to be applied for REE bioleaching form solid matrices. This source is largely untapped until today. Depending of the type of organism, the technical process (including a series of influencing factors), the solid to be treated, and the target element, leaching efficiencies of 80 to 90% can be achieved. Bioleaching of REEs can help in reducing the supply risk and market dependency. Additionally, the application of bioleaching techniques for the treatment of solid wastes might contribute to the conversion towards a more sustainable and environmental friendly economy.

1. Rare Earth Elements as Resource

Rare earth elements [REE; lanthanides, atomic numbers 57 to 70 usually excluding promethium (61) due to its instable isotopes, and including also scandium (21) and yttrium (39)] have unique chemical and physical properties and are indispensable for a huge variety of technical application fields. They are often referred to as the "seeds of technology" since they are an important part of many electronic devices such as smartphones, computers, TV sets, and many more [1,2]. Especially in the fast-growing energy sector where REE are used for e.g., catalytic converters,

fluorescent phosphors, rechargeable batteries, and permanent magnet in wind turbines, REEs can contribute in the view of many to a greener economy [3]. However, geogenic REE mineral resources are not infinite and limited as much as fossil resources. This might lead in the future to REE shortages and increased market prices. Therefore, measures have soon to be taken to circumvent these constraints thereby mainly focusing on efficient REE use in technical applications as well as on increased recycling efforts [4].

Even though REE are not "rare" *per se* in the Earth crust, they are very difficult to mine and to purify [2]. Mining also causes environmental problems, because of water pollution, high energy consumption, and radioactive by-products (such as e.g., thorium), which generate radioactive waste [5]. The market of REE gets more and more important and is predicted to increase 8 to 12% per year by 2020 [6]. Furthermore, most operational mines are located in China and the market dependency on China (with 86% of the annual global mining production in 2014) is huge [2,7,8]. Also in the future, China is expected to remain the world's principal rare earth supplier [5]. Worldwide, there is a growing interest to recycle REE from waste to scale down the supply risk. Nevertheless, current rates of recycling REEs by physico-chemical techniques are in many cases below 1% compared to iron and steel which are recycled with rates between 70% to 90%, one of the highest among industrially-used metals [9]. This is mainly due to technological difficulties and, until recently, low prices, and the lack of incentives. The technological issue can be explained by the rather low amounts and different forms of REE in goods. This makes it very difficult to establish a general approach for REE recycling. Rather, the development of product specific recycling schemes is recommended [10]. In addition, due to the small quantities in a wide variety of technical devices and medical applications, REE dissipation after disposal of goods is very critical and REE are irrevocably lost in the environment as e.g., in the case of cerium as additive of diesel or gadolinium used as contrasting agent in magnetic resonance imaging [2,11].

2. Microbe-REE-interactions

In the last decade, several studies have been published addressing the interactions of microorganisms and REE including both REE mobilization from solids through metabolic reactions and REE immobilization from liquids mainly through sorption by biomass as well as the role of REE in bacterial growth. As example, adsorption onto the cell envelope of Gram-positive and Gram negative bacteria were examined, particularly adsorption behavior of europium to *Halobacterium salinarum, Pseudomonas fluorescens*, and *Bacillus subtilis* [12,13]. Recently published work demonstrated sorption of REE (dysprosium in this case) a by the fungal strain *Penidiella* sp. T9 [14]. Dysprosium biosorption took place even at pH values as low as 2.5. When cells of *Roseobacter* sp. AzwK-3b were pre-protonated at this pH with nitric acid, heavy REE such as thulium, ytterbium , and lutetium were adsorbed to a higher degree as compared to light-group REE [15]. Summaries on REE biosorption are given in several recent review articles [16–19].

Microbially mediated mobilization of elements occurs mainly via acidolysis, redoxolysis, and complexolyis [20,21]. Acidolysis (also termed proton-induced solubilization) means the exchange and replacement of elements by from mineral surfaces by protons. Mobilization by reductive or oxidative reactions is described by the term redoxolysis whereas complexolysis is characterized by the reaction of complexing agents with mineral surfaces (also termed ligand-induced solubilization) [20]. These general mechanisms apply for all solid matrices, also those containing

REE. However, it has still to be elaborated why microorganisms mobilize REE and what their ecological advantage from this interaction is. At the moment, only a very limited number of reports is available [22–27] and there is a big lack in studies on the mechanistic interactions between microorganisms and REE since the focus so far has been mainly on microbe-metal-interactions of commodity metals [21]. Microbes might mobilize REE either by pure coincidence through their metabolic reactions or by a true need for these elements. Recent studies demonstrated that some microbes are strictly growth-dependent on the presence of REE, because they act as essential cofactors for some of the microbe's key enzymes. *Methylacidiphilum fumariolicum* cultivated on methane showed positively correlated growth with the different concentrations of cerium [19]. In addition, lanthanum, neodymium, and praseodymium supported growth to a high extent, whereas samarium, europium, and gadolinium were less favorable, but still supportive [19]. It remains to be investigated in future studies, if these findings can be generalized and REE promote growth of other microorganisms as well. Even more as it is discussed in this study that laboratory glassware might contain REE in trace amounts (originating from silicates used in fabrication or additionally supplied during production). REE might be mobilized and released into the medium by cultivation under acidic conditions [19].

In comparison to calcium, the addition of lanthanum and cerium increased the activity of methanol dehydrogenase in *Methylobacterium radiotolerans*, *M. fujisawaense*, and *M. zatmanii* by a factor of four to six suggesting the induction of latent genes [24]. Mutant strains of *Methylobacterium extorquens* showed a REE-dependent growth behavior [26]. Concentrations of lanthanum as low as 2.5 nM stimulated growth on methanol in comparison to the addition of only calcium due to the increased activity of a lanthanide-dependent methanol dehydrogenase. Due to this fact, it has been suggested that methylotrophic microorganisms might find an application in REE biomining and recycling [26]. How effective the organisms are in the recovery of REE, however, remains to be investigated. Also the metabolism of non-methylotrophic microorganisms such as *Bradyrhizobium* is influenced by REE [27]. Mainly cerium, lanthanum, and praseodymium stimulated the formation of extracellular polymeric substances, but not bacterial growth.

3. Biological Mobilization of REE from Solids

Biohydrometallurgical technologies offer an alternative to physico-chemically based methods of REE recycling (Table 1). These technologies—termed "bioleaching" —are well-known in the mining industry and especially suited at low elemental concentrations in the materials of interest where conventional techniques for metal recovery cannot be economically performed [20,28]. In this context, bioleaching of REE was investigated regarding the recovery from spent industrial catalysts and luminescent powder originating from cathode ray tubes (CRT). A heterogenic culture of sulfur oxidizing *Acidithiobacilllus ferrooxidans, A. thiooxidans*, and *Leptospirillum ferrooxidans* was grown at 30 ℃ and a pH of 2. The recovery rate after 16 days for yttrium from the CRT powder was 70% [29]. Leaching efficiencies were tested in the presence and absence of ferric iron, since the addition of Fe^{2+} was assumed to enhance bacterial resistance to high levels of metals. Experiments showed that the presence of such elements suppressed bacterial growth, resulting in lower leaching efficiency. As in many bioleaching approaches, there is a negative dose-response relationship regarding pulp density [30]. This negative effect of high powder dose was also observed when treating CRT powder suggesting either a certain toxicity of the dissolved metals [29] and/or a

mechanical stress on the microorganisms.

Early bioleaching experiments to mobilize REE form solid minerals were published in the late 1980 and beginning of 1990ies [31–33]. Zircon containing Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (in total 7.3 g REE per kg) was leached in suspensions of 10 g/l by *Acetobacter methanolicus* and *Acidithiobacillus* (formerly *Thiobacillus*) *ferrooxidans* resulting after experimental optimization in total REE mobilization efficiencies of 62.1% and 79.6%, respectively [31]. Zircon was first ground to a grain size of about 60 μm. Using unground zircon and applying the same experimental conditions resulted in a remarkable decrease of leaching efficiency. Only about 18% of the REE were solubilized. Mainly gluconic acid formed by the microorganisms was responsible for the leaching process [7]. Cell-free assays with gluconic acid as lixiviant showed leaching efficiencies of only 4%, thus indicating that microbial metabolic activity plays an important role in bioleaching. During microbial leaching a differentiation between light and heavy REE took place. There was a preference of mobilizing light REE rather than heavy REE. In contrast, the reaction of zircon with gluconic acid in the absence of the microorganism showed no differentiation [31]. The treatment of phosphorus furnace slag (containing in total 7 g REE per kg) by *Acetobacter methanolicus* gave REE rates of up to 70% [7,34].

A more detailed study on REE extraction from zircon resulted in mobilization efficiencies of approximately 80% with extraction rates of 1.1 mg per hour using *Acidithiobacillus ferrooxidans* and 67% at a rate of 1.4 mg per hour applying *Acetobacter methanolicus*, respectively [33]. However, there were distinct mechanistic differences regarding recovery efficiencies between autotrophic *A. ferrooxidans* and heterotrophic *A. methanolicus*. Most of mobilized REE were adsorbed by the biomass of *A. ferrooxidans* and only a minor portion was present in the cultivation fluid. Using praseodymium as a model compound, it has been demonstrated that sorption onto *Acidithiobacillus* biomass took place within minutes [33]. In contrast, higher amounts of REE were found in the cultivations fluids of *A. methanolicus* indicating that biosorption was less pronounced. For both *A. ferrooxidans* and A. *methanolicus*, leaching efficiencies (sum of REE present in the biomass and the supernatant) decreased with increasing REE atomic numbers resulting in maximum recoveries of 91.6% (for La) and 89.4% (for Pr and Nd), respectively [33].

Also anaerobic microorganisms have been applied for the mobilization REE from solid materials. Yttrium was mobilized from phosphogypsum (a by-product originating from fertilizer production) in a fixed-bed reactor by sulfate-reducing *Desulfovibrio desulfuricans* with efficiencies of almost 80% [32].

Gibbsite samples (4.9 g of REE per kg) in the shale beds of Um Bogma formation in South-Western Sinai (Egypt) was processed through a bioleaching procedure where cultures of *Acidithiobacillus ferrooxidans* were pumped through a column (1.2 m in height) filled with 1 kg of mineral [35]. Additionally, factors influencing leaching efficiency such as incubation period (1 to7 days), sulfur addition (0.1% to 0.5%), and mineral pre-treatment (sterilized or non-sterilized) was investigated. Mobilization showed a gradual increase with increasing reaction time and reached an optimum after 6 days. Further prolongation of the incubation time did not improve efficiency. Sulfur addition was observed to increase the bacterial acid formation and, therefore, positively influencing the leaching efficiency. On the other hand, pre-sterilization of the mineral decreased the leaching efficiency compared to the non-sterilized material probably due to the elimination of the endogenous microflora during sterilization. By optimization, total REE mobilization resulted in 67.6%.

Table 1. Overview of biological REE mobilization from solid matrices. B=bacteria, F=fungi, Y=yeast; RT=room temperature; nd= not determined.

Matrix	REE	Organism (strain)	Type	Carbon source	Leaching agent (acid)	Process	Time (d)	Temp. (℃)	pH	max. leaching efficiency (%)	Ref.
Ash-slag waste	Sc, Y, La, Nd, Sm, Gd	acidophilic chemolithoautotrophs	B	CO_2	sulfuric	batch	10	45	0.9-2	7.4-59.5	[38]
Ash-slag waste	Sc, Y, La, Nd, Sm, Gd	acidophilic chemolithoautotrophs	B	CO_2	sulfuric	batch	10	45	1.8-2.6	15-30	[42]
Carbonaceous shales	nd	*Aspergillus niger* *Aspergillus flavus* *Aspergillus terreus* *Aspergillus ficuum* *Penicillium aeruginosa* *Penicillium cyclopium* *Penicillium diversum* *Penicillium oxalicum*	F	sucrose	citric, oxalic	batch / cell free	7 / nd	30 / nd	4.2-6.4 / nd	18-86 / 11-45	[40]
Fluorescent powder from CRT	Y	*Acidithiobacillus ferrooxidans* *Acidithiobacillus thiooxidans* *Leptospirillum ferrooxidans* (mixed culture)	B	CO_2	sulfuric	batch	16	30	nd	70	[29]
Gibbsite	nd	*Acidithiobacillus ferrooxidans*	B	CO_2	sulfuric	column	nd	30	1.8	67.6	[35]
Monazite	Ce, La, Nd, Pr	*Aspergillus niger* (ATCC1015)	F	glucose, fructose, sucrose, xylose, starch	citric, gluconic, oxalic, succinic	batch / cell-free	6 / 2	25-28 / 25-28	2.1-2.2 / 2.3-2.5	0.1-0.2 / 0.1-0.2	[41]

Monazite	Ce, La, Nd, Pr	*Aspergillus terreus* (ML3-1)	F	glucose, fructose, sucrose, xylose, starch	itaconic, succinic	batch	6	25-28	2.1-2.2	1.7-2.4	[41]
						cell-free	2	25-28	2.5-2.7	0.8-1.6	
Monazite	Ce, La, Nd, Pr	*Paecilomyces* sp. (WE3-F)	F	glucose, fructose, sucrose, xylose, starch	acetic, gluconic, succinic	batch	6	25-28	2.1-2.5	1.5-3	[41]
						cell-free	2	25-28	2.6-3.1	0.8-1.5	
Monazite	nd	*Aspergillus ficuum*	F	glucose, lactose, maltose, starch, sucrose	citric, oxalic	batch	9	30	3.0	75.4	[43]
						cell free	1		4.4	55.0	
Monazite	nd	*Pseudomonas aeruginosa*	B	glucose, lactose, maltose, starch, sucrose	2-ketogluconic	batch	8	35	6.0	63.5	[43]
						cell free	1		7.7	47.7	
Phosphogypsum	Y	*Desulfovibrio desulfuricans*	B	lactate (in whey)	nd	column	nd	32	6.7-7	77	[32]
Quartz conglomerate	Y, Ce, Pr, La, Nd, Yb, Dy, Sa	endogenous acidophilic chemolithoautotrophs		CO_2	sulfuric	column	365	nd	3.5	16.3-76.1	[45]
Red mud	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc	*Penicillium tricolor* (RM-10)	B	sucrose	oxalic, citric, gluconic	batch (one-step)	50	30	2-2.5	36-78	[36]
						two-step	50	30	3-3.4	18-62	
						cell-free	16	30	3.8-4.2	24-62	

Soil	nd	*Streptomyces* sp.	B	sucrose	nd	batch	2	30	nd	12-37	[37]
Th-U-concentrate	Y, La, Ce	*Aspergillus ficuum*	F	nd	citric, oxalic	cell free	1	RT	3.0	2.5-33	[44]
Th-U-concentrate	Y, La, Ce	*Pseudomonas aeruginosa*	B	nd	siderophores	cell free	1	RT	5.3	1.2-5.4	[44]
Zircon	Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	*Acidithiobacillus* sp.	B	CO_2	sulfuric	batch	10	32	1.6	79.6	[31]
Zircon	Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	*Acetobacter methanolicus* (MB 58)	B	glucose	gluconic	batch	10	32	4.0	67.0	[34]
Zircon	Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	*Acidithiobacillus ferrooxidans*	B	CO_2	sulfuric	batch	10	32	nd	45-92	[33]
Zircon	Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	*Acetobacter methanolicus* (IMET B 346)	B	glucose	gluconic	batch	10	32	nd	59-89	[33]

Microbial REE mobilization from solid matrices can also be achieved by fungi. Red mud, a waste material from bauxite processing in aluminum mining operations, was treated with *Penicillium tricolor* [36]. In the study, three different bioleaching processes were performed: One-step bioleaching (fungal growth in the presence of sterilized red mud), two-step bioleaching (pre-cultivation of the microorganisms and in biomass production followed by the addition of sterilized red mud), and finally, cell-free spent medium (cultivation of the microorganisms followed by filtration to obtain cell-free medium, which was then added to sterilized red mud). As part of the study, the effect of red mud pulp density (20, 50, and 100 g/l) was determined. In general, with increasing pulp density, there was an observable decrease in REE leaching efficiencies in all leaching approaches. In the one-step process at a pulp density of 20 g/l, the highest bioleaching efficiency was achieved, whereas at 100 g/l, the two-step bioleaching method exhibits maximum leaching efficiency indicating that the two-step bioleaching process is more suitable for leaching red mud at high pulp densities. Looking at individual REE, leaching efficiency was clearly higher for heavy REE than for the light REE. Overall efficiency generally increased with increasing REE atomic numbers.

Several species of actinomycetes (among them *Streptomyces fungicidicus, S. aureofaciens, S. chibaensis*) have been used to mobilize REE from sandy and silty soil samples [37]. In suspensions of 10 g soil per liter (cultivated for 48 hours at 30 ℃) REE leaching efficiencies of up to 37% were obtained depending on the strain applied.

Instead of pure cultures also mixed microbial cultures have been applied recently for REE mobilization. Acidophilic chemolithotrophic microbial communities leached coal-derived ash-slag waste (ASW; containing per ton: 46 g La, 39 g Nd, 31 g Y, 9.4 g Sc, 7.2 g Sm, 6.5 g Gd) collected from heaps of a heat power station [38]. Experiments were carried out in 300 ml airlift percolators which were loaded with ASW, elemental sulfur, and inoculated with 100mL of a mixed bacterial culture *of A. ferrooxidans, A. thiooxidans, A. caldus, and Sulfobacillus thermosulfidooxidans*. As already shown in earlier experiments [36], a high pulp density resulted in a drastic decrease of REE bioleaching efficiency. Increasing the density from 100 to 330 g per liter, bioleaching efficiency was more than halved [30]. Furthermore, other process parameters such as temperature (25, 28, and 40℃), adjustment of initial pH (pH 3, pH 2.6, pH 2), and different ratios of ASW to elemental sulfur (1:10, 1:100) were evaluated. Rising the cultivation temperature enhanced the leaching efficiency, especially for Sc, Y, and La, whereas a temperature rise from 28 ℃ to 45 ℃ effected the increase 2.2-, 1.7-, and 2.1-fold, respectively. Reducing the amount of sulfur added turned out to have negative effect on the leaching efficiency since the energy substrate was limited and resulted in insufficient amounts of sulfuric acid formation that mainly mediates the bioleaching process. Based on all findings (45 ℃ cultivating temperature, initial pH 2, ASW/sulfur ratio 1:10) a recovery of scandium, yttrium, and lanthanum of 52.0, 52.6, and 59.5%, respectively, was achieved after ten days of bioleaching. Besides coal ASW also slag from municipal waste incineration has been considered as resource for REE recovery although amounts in the slag are rather low [39].

Either contact or non-contact bioleaching (termed earlier as direct and indirect bioleaching) might be the underlying leaching mechanism of metal mobilization. Contact leaching describes the direct physical contact between microorganisms and a solid whereas in non-contact leaching the biomass is physically separated from the solid to be treated. Leaching efficiencies of REE from carbonaceous shale powder were tested with several species of *Aspergillus* and *Penicillium* [40]. Results showed that contact bioleaching noticeably generated higher REE leaching efficiencies of up to 86% after 7 days than non-contact bioleaching, independent from the fungi tested. Overall,

Aspergillus sp. reached higher bioleaching rates than *Penicillium sp.*, thereof *A. flavus* and *A. niger* were the most effective ones. In accordance to previous studies [36,38] findings confirm that the amount of REEs mobilized decreases with increasing sample concentrations, because best leaching efficiency was found in suspension of 10 g/l.

Besides a series of solid REE containing waste materials (as described above), native REE bearing minerals such as monazite have also been studied as a substrate for bioleaching operations [41]. Three fungal species (*Aspergillus niger*, *Aspergillus terreus,* and *Paecilomyces* sp.) were cultivated in differently composed growth media and on various carbon sources. As consequence, a mixture of different organic acids such as acetic, citric, gluconic, itaconic, lactic, oxalic, and succinic acid accumulated in the cultivation fluid. Their presence and concentration depended on the fungal strain used. However, REE leaching rates of approximately 3% were rather low, probably due to the nature and type of the solid material. By comparing original REE content in monazite sand it was be concluded that neodymium, cerium, praseodymium, and lanthanum were all mobilized by the three fungal strains in the same ratio and no preferential bioleaching of a particular REE was observed [41]. However, there are indications that REE might be mobilized from solids such as e.g., ash-slag-waste at different degrees by acidophilic sulfur oxidizers. Scandium, lanthanum, cerium, and praseodymium were mobilized from the original matrix by 15 to 20%, whereas neodymium, yttrium, samarium, gadolinium, dysprosium, erbium, and europium showed mobilization rates of 25 to 30% [42]. It remains to be investigated whether this is due to the chemical characteristics of the solid material or due to the metabolic preferences of the microorganisms applied. Interestingly, REE sorption by microbial biomass was not observed under the conditions applied.

Besides *Aspergillus ficuum*, monazite has also been biologically treated with a heterotrophic bacterial strain, *Pseudomonas aeruginosa* [43]. After 9 days at a pulp density of 6 g/l, over 53% of REE were released to the medium. *A. ficuum* was able to mobilize approximately 75%. Also in this study, it was proven that contact bioleaching yielded in significantly higher leaching rates indicating that the presence of microorganisms is necessary to obtain recoveries as high as possible. In an earlier approach using the same microbial strains lanthanum, cerium, and yttrium were released from a thorium-uranium concentrate [44]. Cell-free supernatants obtained as filtrates after cultivation were amended with REE containing concentrates and left to react for 24 hours. *A. ficuum* mobilized 2.5, 20, and 33% of yttrium, lanthanum, and cerium, respectively, whereas *P. aeruginosa* released only 1.2, 4.3, and 5.4%.

In an effort to simulate heap leaching, a long-term study was carried out over a period of 52 months [45]. In the course of the experiments several factors such as e.g., nutrient addition, ferric iron addition, weekly or monthly flushing were tested for their influence on REE release from conglomerate ore containing approximately 400 mg of REE per kg. Endogenous acidophiles were stimulated by the addition of ferric sulfate at pH 3.5. A maximum of 45% of total REE was released.

4. Patents on REE Bioleaching

An overview on a selection of patents covering microbial REE mobilization is presented in Table 2. Interestingly, most of the patents include ashes and slags as well as mining waste in their claims. Other REE containing solids are not considered yet, except luminescent powder originating from fluorescent lamps (DE 102013226042 in Table 2).

Table 2. Selection of patents covering microbial REE mobilization from different solids.

Year	Title	Publication No.	Claims
1987	Microbial leaching rare earth metal-containing phosphate minerals and wastes [original in German]	DD 249156	Low cost and low tech process of REE leaching through gluconic acid formed by *Acetobacter methanolicus* using glucose or glucose-containing waste as carbon source
1988	Separation of rare earth elements from calcium-containing microbial leaching solutions [original in German]	DD 259212	REE leaching through gluconic acid formed by *Acetobcater methanolicus* using glucose as carbon source
2012	Method of processing of phospho-gypsum [original in Russian]	RU 2456358	Cost effective REE extraction by several types of acidophilic microorganisms
2012	Method of processing phosphogypsum with recovery of rare-earth elements and phosphorus [original in Russian]	RU 2457267	Simplified low-cost leaching of REE in vats mediated by a mixed culture of acidophilic sulfur oxidizing micro-organisms
2014	A microorganism capable of leaching rare earth elements, a method for leaching rare earth elements, a micro-organism capable of solidifying rare earth elements, and a method for [original in Japanese]	WO 2014178360 (see also CA 2911097)	Application of mainly *Acidithiobacillus albertienis* in tank leaching to mobilize rare earths from minerals and wastes, particularly scandium
2014	Leaching processes for the extraction of rare earths from phosphate-containing rare earth minerals [original in German]	DE 102012210941 (see also WO2014000972)	REE mobilization from ores in fixed bed reactor using *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferroxidans*
2015	Method of leaching of valuable com-ponents and rare-earth elements from cinder material [original in Russian]	RU 2560627	REE leaching from fly ash slag material by a community of mesophilic chemolitho-trophic acidophilic microorganisms through the formation of sulfuric acid when elemental sulfur was supplied
2015	Activated ionized water and microbial acid improved ionic rare earth *in-situ* leaching mining method [original in Chinese]	CN 105063383	REE leaching from precipitates based on lactic acid bacteria
2015	Device and method for obtaining 2-and 3-valent metal ions from primary and secondary raw materials with the aid of microbial metabolites [original in German]	DE 102013226042 (see also WO2015091256)	REE mobilization from phosphors applying *Schizophyllum commune* in a two- compartment system separated by a dialysis membrane

A mixture of chemolithotrophic sulfur-oxidizing microorganisms (termed VUR-9 and not described in detail) was applied to mobilize 55 to 70% of REE from phosphogypsum after incubation times of up to 30 days at low pH values of 1.5 to 1.8. (RU 2457267 and RU 2457267 in Table2). Also a mixed bacterial culture ("S20 bacterial group") containing mainly *Acidithiobacillus albertiensis* (99.72%), but also *A. thiooxidans* (0.02%), other *Acidithiobacillus* species (0.15%), and unspecified proteobacteria (0.02%) has been used to recover scandium, dysprosium, neodymium, and praseodymium from low-grade mine waste (WO 2014178360 in Table 2). However, the role and function of the different organisms in REE mobilization remains to be investigated.

Sulfuric acid generated by *A. ferrooxidans* and *A. thiooxidans* is the main mobilization agent for biological treatment of REE-containing phosphate minerals through a heap or column leaching process (DE 102012210991 in Table 2). A moderately thermophilic mixed microbial population community of acidophilic chemolithotrophs mobilized scandium, yttrium, and lanthanum from fly ash-slag at 45 ℃ (RU 2560627 in Table 2). Alternatively to sulfur-oxidizing autotrophic microorganisms, heterotrophs such as *Acetobacter methanolicus*, lactic acid bacteria, and fungi (*Schizophyllum commune*) have also been considered for REE mobilization (DD 249156, CN 105063383, DE 10213266042 in Table 2). *Acetobacter methanolicus* has been grown on glucose in the presence of waste slag (derived from the processing of phosphate minerals) bringing 80% of REE in solution (DD 249156 in Table 2). Gluconic acid was the main leaching agent DD 259121 in Table 2).

5.   Perspectives of REE Recovery and Recycling

A promising solid matrix as starting material for a REE recycling is fluorescent powder from spent lamps. It mainly contains three of the five most critical rare earth elements, namely yttrium, europium, and terbium, often in gram quantities per kg of powder [29]. Since the separation and collection of the lamps is already mandatory in many different countries, mainly to remove toxic mercury form the waste, further recycling processes would be applicable. The state of art for REE leaching from lamp phosphors is covered so far mainly through chemical approaches [46]. To be able to recover REEs from lamp phosphors, the phosphor mixture has to be attacked chemically to bring the REEs into solution from where they can be separated by precipitation or solvent extraction. To close product life cycles, REE mobilization following recovery from spent fluorescent lamps seems to have big potential and might contribute to a more sustainable world. Doing so with the aid of microbes makes it a relatively inexpensive approach for industrial waste treatment which is, in addition, flexible enough to be applied for different leachable waste materials. Recent studies of REE mobilization from fluorescent phosphors included besides well-known *A. ferrooxidans and A. thiooxidans* other bacteria (*Komatogateibacter xylinus, Lactobacillus casei, Corynebaterium collunae*), yeasts (*Yarrowia lipolytica*) as well as the tea fungus Kombucha [47–49].

In contrast to chemical leaching which has often a high energy demand to generate high temperatures and produces chemical wastes, bioleaching is supposed to be a much cleaner, efficient, and low cost process to mobilize metals. Although bioleaching of REEs cannot solve all the objectives, it can help to reduce the supply risk and market dependency. In addition, the development of bioleaching methods in general, can contribute to the conversion towards a more sustainable and environmental friendly economy.

The awareness of potential upcoming supply shortage of REE is also affecting current politics.

The European Union (EU) recently launched the European Innovation Partnership (EIP), a program aiming on the reduction of import dependency by improving supply conditions from EU and other sources and by providing resource efficiency and alternative supply [50]. Although bioleaching cannot solve the main objectives of the EIP on its own, it can certainly contribute to the future challenges of the EIP by improving extraction, processing and recycling of critical raw materials [8].

Overall, biological leaching is a relatively inexpensive approach for industrial waste treatment and quite flexible in relation to different growth conditions and different leachable wastes. Compared to traditional chemical processes, bioleaching is supposed to be a "green" technology for the recovery of valuable metals from industrial waste to close element cycles. Its applicability for an industrial REE recovery and recycling remains to be accurately evaluated in detail in the near future.

6. Conclusions

Natural microbial mechanisms that enable the mobilization of elements or metals from solids are the basis of industrial processes mimicking element cycles in nature. New evolving bioleaching and biorecovery processes involving REE can open new doors for "green" recycling strategies which might contribute to a more sustainable world and can help to reduce supply risks and market dependencies.

Conflict of Interest

All authors declare no conflict of interest.

References

1. Nuwer R (2014) What is the world's scarcest material? BBC, London. Available from: www.bbc.com/future/story/20140314-the-worlds-scarcest-material.
2. Zepf V, Simmons J, Reller A, et al. (2014) Materials critical to the energy sector - An introduction. 2nd ed. BP p.l.c., London.
3. Gibson M, Parkinson I (2011) CIBC report: A rare earth element industry overview. Toronto, Canada. Available from http://de.slideshare.net/RareEarthsRareMetals/cibc-report.
4. Matlin SA, Mehta G, Hopf H, et al. (2015) The role of chemistry in inventing a sustainable future. *Nature Chem* 7: 941–943.
5. Castor SB, Hedrick JB (2001) Rare earth elements. *J Environ Radioactiv* 102: 769–792.
6. Kingsnorth DJ (2014) Der globale Markt der Seltenen Erden - Ein Balanceakt. In: Kausch P, Bertau M, Gutzmer J, Matschullat J. (eds.) *Strategische Rohstoffe - Risikovorsorge*. Springer, Berlin, Heidelberg, 97–121 [in German].
7. Glombitza F, Reichel S (2014) Metal-containing residues from industry and in the environment: Geobiotechnological urban mining. *Adv Biochem Eng Biotechnol* 141: 49–107.
8. Hennebel T, Boon B, Maes S, et al. (2015) Biotechnologies for critical raw material recovery from primary and secondary sources: R&D priorities and future perspectives. *New Biotechnol* 32: 121–127.
9. Graedel TE, Allwood J, Birat JP, et al. (2011) Recycling rates of metals – A status report. UNEP, Nairobi, Kenya.

10. Binnemans K, Jones PT (2014) Perspectives for the recovery of rare earths from end-of-life fluorescent lamps. *J Rare Earths* 32: 195–200.

11. Hatje V, Bruland KW, Flegal AR (2016) Increases in anthropogenic gadolinium anomalies and rare earth element concentrations in San Francisco Bay over a 20 year record. *Environ Sci Technol* 50: 4159–4168.

12. Ozaki T, Gillow J, Francis A, et al. (2002) Association of Eu (III) and Cm (III) with *Bacillus subtilis* and *Halobacterium salinarum*. *J Nucl Sci Technol* 39(sup 3): 950–953.

13. Ozaki T, Suzuki Y, Nankawa T, et al. (2006) Interactions of rare earth elements with bacteria and organic ligands. *J Alloys Compd* 408-412: 1334–1338.

14. Horiike T, Yamashita M (2015) A new fungal isolate, *Penidiella* sp. strain T9, accumulates the rare earth element dysprosium. *Appl Environ Microbiol* 81: 3062–3068.

15. Bonificio WD, Clarke DR (2016) Rare-earth separation using bacteria. *Environ Sci Technol Lett* 3: 180–184.

16. Moriwaki H, Yamamoto H (2013) Interactions of microorganisms with rare earth ions and their utilization for separation and environmental technology. *Appl Microbiol Biotechnol* 97: 1–8.

17. Das N, Das D (2013) Recovery of rare earth metals through biosorption: An overview. *J Rare Earths* 31: 933–943.

18. Ilyas S, Lee JC (2014) Biometallurgical recovery of metals from waste electrical and electronical equipment: a review. *ChemBioEng Rev* 1: 148–169.

19. Nancharaiah YV, Venkata Mohan S, Lens PNL (2016) Biological and bioelectrochemical recovery of critical and scarce elements. *Trends Biotechnol* 34: 137–155.

20. Brandl H, Faramarzi MA (2006) Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste. *China Particuol* 4:93–97.

21. Brandl H (2001) Microbial leaching of metals. In: Rehm HJ (ed.) *Biotechnology*, Vol. 10. Wiley-VCH, Weinheim, 191–224.

22. Pol A, Barends TRM, Dietl A, et al. (2014) Rare earth metals are essential for methanotrophic life in volcanic mudpots. *Environ Microbiol* 16: 255–264.

23. Skovran E, Martinez-Gomez NC (2015) Just add lanthanides. *Science* 348: 862–863.

24. Hibi Y, Asai K, Arafuka H, et al. (2011) Molecular structure of La^{3+}-induced methanol dehydrogenase-like protein in *Methylobacterium radiotolerans*. *J Biosci Bioeng* 111: 547–549.

25. Nakagawa T, Mitsui R, Tani A, et al. (2012) A catalytic role of xoxF1 as La^{3+}-dependent methanol dehydrogenase in *Methylobacterium extorquens* strain AM1. *PLOS ONE* 7: e50480

26. Vu HN, Subuyuj GA, Vijayakumar S, et al. (2016) Lanthanide-dependent regulation of methanol oxidation systems in *Methylobacterium extorquens* AM1 and their contribution to methanol growth. *J Bacteriol* 198: 1250–1259.

27. Fitriyanto NA, Nakamura M, Muto S, et al. (2011) Ce^{3+}-induced exopolysaccharide production by *Bradyrhizobium* sp. MAFF211645. *J Biosci Bioeng* 111: 146–152.

28. Zhuang WQ, Fitts JP, Ajo-Franklin CM, et al. (2015) Recovery of critical metals using biometallurgy. *Curr Opin Biotechnol* 33: 327–335.

29. Beolchini F, Fonti V, Dell'Anno A, et al. (2012) Assessment of biotechnological strategies for the valorization of metal bearing wastes. *Waste Manage* 32: 949–956.

30. Bossard PP, Bachofen R, Brandl H. (1996) Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. *Environ Sci Technol* 30: 3066–3070.

31. Becker S, Bullmann M, Dietze HJ, et al. (1986) Mass spectrographic determination of selected chemical elements by microbial leaching of zircon. *Fresenius Z Anal Chem* 324:37-42 [in German].

32. Dudeney AWL, Sbai ML (1993) Bioleaching of rare-earth-bearing phosphogypsum. In: Torma AE, Wey JE, Lakshmanan VL (eds.) *Biohydrometallurgical Technologies*. The Minerals, Metals, & Materials Society. Jackson Hole, 39–47.

33. Glombitza F, Iske U, Bullmann M, et al. (1988) Bacterial leaching of zircon mineral for obtaining trace and Rare Earth Elements (REE). In: Norris PR, Kelly DP (eds.) *Biohydrometallurgy*. Proceedings of the International Symposium Warwick 1987. Science and Technology Letters, Kew Surrey, UK, 407–418.

34. Iske U, Bullmann M, Glombitza F (1987) Organoheterotrophic leaching of resistant materials. *Acta Biotechnol* 7: 401–407 [in German].

35. Ibrahim HA, El-Sheikh EM (2011) Bioleaching treatment of Abu Zeneima uraniferous gibbsite ore material for recovering U, REEs, Al and Zn. *Res J Chem Sci* 1: 55–66.

36. Qu Y, Lian B (2013) Bioleaching of rare earth and radioactive elements from red mud using *Penicillium tricolor* RM-10. *Bioresour Technol* 136: 16–23.

37. Hewedy MA, Rushdy AA, Kamal NM (2013) Bioleaching of rare earth elements and uranium from Sinai soil, Egypt using actinomycetes. *Egypt J Hosp Med* 53: 909–917.

38. Muravyov MI, Bulaev AG, Melamud VS, et al. (2015) Leaching of rare earth elements from coal ashes using acidophilic chemolithotrophic microbial communities. *Mikrobiologiya* 84: 216–224.

39. Muehe EM, Schmidt C, He J, et al. (2015) Microbially supported recovery of precious metals and rare earth elements from urban household waste incineration slag. *Adv Mat Res* 1130: 652–655.

40. Amin MM, El-Aassy IE, El-Feky MG, et al. (2014) Fungal leaching of rare earth elements from lower carboniferous shales, southwestern Sinai, Egypt. *Roman J Biophys* 24: 25–41.

41. Brisson VL, Zhuang WQ, Alvarez-Cohen L (2015) Bioleaching of rare earths elements from monazite sands. *Biotechnol Bioeng* 113: 339–348.

42. Tsaplina IA, Panyushkina AE, Grigoreva NV, et al. (2015) Growth of acidophilic chemolithotrophic microbial communities and sulfur oxidation in the presence of coal ashes. *Microbiology* 84: 177–189.

43. Hassanien WAG, Desouky OAN, Hussien SSA (2014) Bioleaching of some rare earth elements from Egyptian monazite using *Aspergillus ficuum* and *Pseudomonas aeruginosa*. *Walailak J Sci Technol* 11: 809–823.

44. Desouky OA, El-Mougith AA, Hassanien WA, et al. (2011) Extraction of some strategic elements from thorium-uranium concentrate using bioproducts of *Aspergillus ficuum* and *Pseudomonas aeruginosa*. *Arab J Chem* [in press].

45. Sapsford DJ, Bowell RJ, Geroni JN, et al. (2012) Factors influencing the release rate of uranium, thorium, yttrium, and rare earth elements from low grade ore. *Miner Eng* 39: 165–172

46. Peelman S, Sun ZHI, Sietsma J, et al. (2014) Leaching of rare earth elements: Past and present. Proceedings of the 1st ERES 2014 – International Conference on European Rare Earth Resources (ERES 2014), Milos, Greece, Sept 4–7, 446–456.

47. Mey S, Kutschke S, Pollmann K (2015) Microbial leaching of rare earth elements from fluorescent phosphor. Abstracts of the VAAM-Jahrestagung 2014, Dresden, Germany, Oct 5–8, 2014, 78–79.

48. Hopfe S, Kutschke S, Möckel R, et al. (2015a) Bioleaching of rare earth elements from fluorescent phosphor with the tea fungus Kombucha. Goldschmidt Abstracts 2015:1307.

49. Hopfe S, Kutschke S, Pollmann K, et al. (2015b) Screening of different microorganisms for the biological leaching of rare earth elements from fluorescent phosphor. Proceedings of the World Congress on New Technologies (Newtech 2015), Barcelona, Spain, July 15–17, 2015, 120-1 to 120-2.

50. European Commission (2013) Reducing the EU's dependency on raw materials: European Innovation Partnership launched. Press Release Database, Brussels, Belgium. Available from: http://europa.eu/rapid/press-release_MEMO-13-92_en.htm.