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# RECOVERY OF RARE EARTHS FROM INDUSTRIAL WASTE RESIDUES: A CONCISE REVIEW

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## Abstract

*Between 2000 and 2012, China has been producing more than 95% of the annual world supply of the rare-earth elements (REEs). Due to large and increasing domestic demands, China has introduced tight export quota for rare earths. These quota cause rare-earth supply risks outside China, but they also stimulate other countries to look for other rare-earth resources and to develop their own rare-earth industry. The shortage of rare earths stimulates the prospection for new rare-earth deposits, the development of new mines and the re-opening of older mines that had been closed in the past because of economic reasons. The supply risk of rare earths also provides a boost to the research on the recycling of rare earths from End-of-Life consumer goods. Up to now, rare-earth recycling (research) has focused on relatively small volumes of End-of-Life waste with a high REE content. However, rare-earth are also present in lower concentrations in a multitude of industrial residues. This review, therefore, discusses the possibilities to recover rare earths from residues such as pyrometallurgical slags, bauxite residue (red mud), phosphogypsum, mine tailings and waste water. All these waste streams have in common that they only have low REE concentrations, but are available in very large volumes. This implies that these industrial waste streams could provide significant amounts of rare earths, provided efficient recycling flow sheets can be developed.*

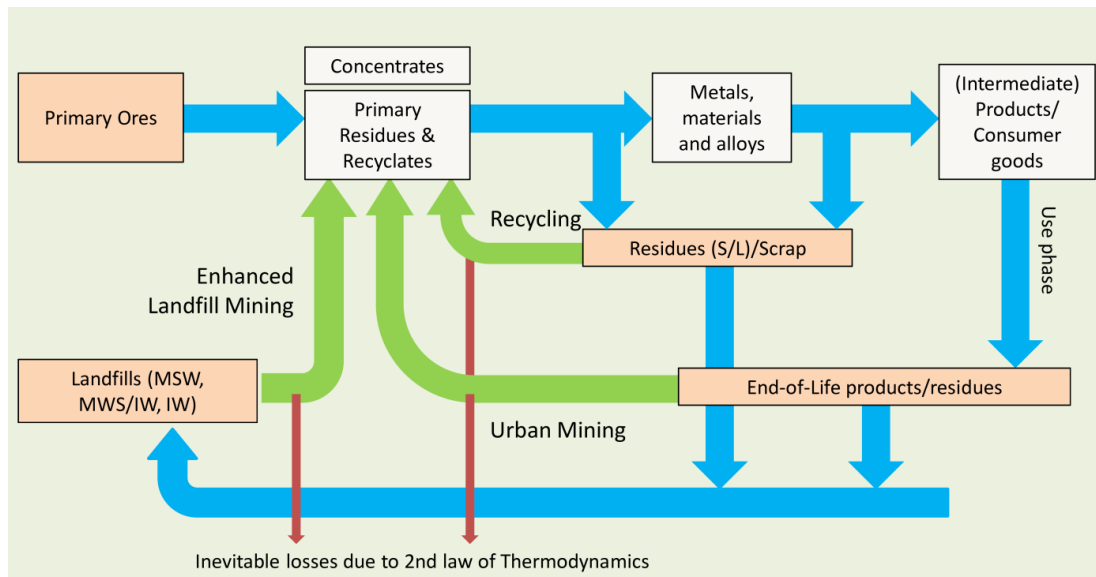
## Introduction

The rare earths or rare-earth elements (REEs) are a group of 17 chemically similar metallic elements (15 lanthanides, plus scandium and yttrium). They are becoming increasingly important in the transition to a low-carbon, circular economy, considering their essential role in permanent magnets, lamp phosphors, rechargeable nickel metal hydride batteries, catalysts and other green economy

applications. The increasing popularity of hybrid and electric cars, wind turbines and compact fluorescent lamps is causing an increase in the demand and price of REEs. The European Commission considers the REEs as the most critical raw materials group, with the highest supply risk.<sup>1</sup> According to the medium-term criticality matrix of the U.S. Department of Energy (DOE), the five *most critical REEs* are neodymium (Nd), europium (Eu), terbium (Tb), dysprosium (Dy) and yttrium (Y).<sup>2</sup> China is presently producing more than 90% of all rare earths, although this country possesses less than 40% of the proven reserves. Due to large and increasing domestic demands, China tightened its REE export quota from 50145 tonnes in 2009 to only 31130 tonnes in 2012. These export quota may cause serious problems for REE users outside of China, and, hence, also for the development of a more sustainable, low-carbon circular economy.

To tackle the REE supply challenge, a threefold approach can be proposed. A first component of this strategy is to *substitute* critical rare earths by less critical metals. Secondly, the REE supply risk can be mitigated by investing in *sustainable primary mining* from old or new REE deposits. Mining companies are now actively seeking for new exploitable rare-earth deposits and old mines are being reopened.<sup>3</sup> A good example is the Mountain Pass Mine in California, which restarted production in 2012. However, because of the absence of economic and/or operational primary deposits on their territory, many countries will have to invest in *technospheric mining*. Jones and co-workers (Figure 1) distinguish between (1) *direct recycling* of pre-consumer manufacturing REE scrap/residues; (2) *urban mining* of post-consumer (often complex multi-material) End-of-Life products; (3) *landfill mining* of historic (and future) urban and industrial waste residues containing REEs. Direct recycling and urban mining are focusing on resources with a very high content of rare earths, but the total volumes accessible to recycling are relatively low. The most interesting sources of rare earths for recycling are permanent magnets, nickel metal hydride batteries and lamp phosphors. Despite the existence of a vast literature dealing with (mostly lab-scale) research efforts on REE recycling, *less than 1%* of the REEs were being recycled in 2011. This is mainly due to inefficient collection, technological difficulties and a lack of incentives. Compared with the primary extraction of REEs from ores, the recovery of REEs via technospheric mining has the advantage that there are no issues with radioactive thorium and that the composition of the obtained REE concentrate is less complex. For instance, lamp phosphors contain mainly Eu, Tb, Y, Ce, La, but are devoid of Nd, Pr and Dy.

Binnemans *et al.* recently published a comprehensive overview of the state-of-the-art of recycling of rare earths, focusing on End-of-Life material streams.<sup>4</sup> On the other hand, much less attention has been paid to industrial waste residues



**Figure 1:** Different ways to close materials loops in a circular economy: (1) direct recycling of pre-consumer scrap and residues, (2) urban mining of End-of-Life consumer goods and other products, (3) landfill mining of historically landfilled pre-consumer and post-consumer waste streams. Reproduced from Jones *et al.* 2011<sup>5</sup>

containing rare earths (both present in historic landfills and being freshly produced). These industrial waste residues contain much lower concentrations of REEs than the End-of-Life consumer goods that are considered for recycling via urban mining activities. However, the volumes of these residues are enormous so that the total amounts of REEs locked in these residues are also very large. This review paper gives an overview of the possibilities to recover rare earths from important industrial waste streams, i.e. metallurgical slags, bauxite residue (red mud), phosphogypsum, mine tailings, and waste water streams.

## Metallurgical slags

Very efficient pyrometallurgical processes have been developed for the recovery of metal values from electronic scrap, spent automobile exhaust catalysts and spent industrial catalysts. In its Hoboken site near Antwerp (Belgium) Umicore operates an integrated smelter and refining plant for recovering metals from Waste Electrical and Electronic Waste (WEEE). The list of recovered metals includes silver, gold, platinum-group metals (platinum, palladium, ruthenium, rhodium, iridium), indium, bismuth, tin, selenium, tellurium, antimony, arsenic, and the base metals copper, nickel and lead. However, the employed metallurgical flow sheets have not yet been developed for recovery of rare earths. Because of the high affinity of the REEs for oxygen, the REEs end up in diluted (oxidic) form in the slag of the so-called “copper smelter” and finally in the slag of the lead blast furnace. Moreover, the REE content of these slags

consists largely of cerium. Cerium is not a critical metal. In fact, it is expected that mining of rare-earth ores for the production of neodymium (to be used in permanent magnets) will lead to an oversupply of cerium, due to the large natural abundance of cerium and its relatively low demand. This is due to the so-called “balance problem”.<sup>6</sup>

Concurrently, pyrometallurgical flow sheets for the recycling of valuable metals from batteries can produce slags rich in rare earths. In 2011, Rhodia (Solvay) and Umicore announced that they had jointly developed a process for recycling of rare earths from nickel metal hydride rechargeable batteries.<sup>7,8</sup> Although the details of the process have not been revealed, it is based on Umicore’s patented Ultra High Temperature (UHT) smelting technology.<sup>9</sup> An industrial-scale pilot plant has been operational in Hoboken since September 2011 and this pilot plant has an initial annual capacity of 7000 tonnes, corresponding to approximately 150000 (hybrid) electric vehicle batteries or 250 million mobile phone batteries.<sup>10,11</sup> Not only nickel metal hydride batteries, but also lithium-ion batteries can be recycled in this facility. At this moment, the process has been optimised for End-of-Life portable nickel metal hydride batteries. The batteries are fed in a vertical shaft furnace, together with a small amount of coke and a slag former.<sup>9</sup> At the bottom of the shaft furnace, oxygen-enriched air is injected into the furnace. The process requires relatively little external energy input, because the combustion of the plastic casing of the batteries and the organic electrolytes releases large amounts of energy. The metals are converted into a Ni-Co-Cu-Fe alloy and a slag. The slag consists mainly of oxides of calcium, aluminium, silicon, and iron, and also contains lithium and rare earths.<sup>12</sup> These oxide slags can be processed to recover lithium and to produce rare-earth concentrates that are subsequently used as a feed in the rare-earth separation plant of Rhodia in La Rochelle, France.

Academic research on the presence of REEs in metallurgical slags, as part of a REE-recovery scheme, has been fairly limited up to now. Müller and Friedrich investigated the recycling of nickel metal hydride batteries and measured the rare-earth content in CaO-SiO<sub>2</sub>-CaF<sub>2</sub> based slag both in laboratory tests and pilot scale trials.<sup>13</sup> As expected, the rare-earth metals collected in the slag phase and for their experimental set-up, high concentrations (50-60% REEs) were obtained. Additionally, some information on the presence of rare-earth oxides in flux powders used in the continuous casting of steels is available, as well as on slags resulting from the smelting of rare-earth-containing iron ores.<sup>14-21</sup> A wealth of information on the formation of rare-earth-containing minerals in magmas is available in the geological community, although geological conditions and time scales may not be very relevant for REE-recovery operations. The available thermodynamic data for rare earths elements in *FactSage*, the most widely used thermodynamic calculation system for

high temperature oxide systems, is fairly limited.<sup>22</sup> In order to make the recovery of rare earths from metallurgical slags more efficient, the problem of dilution of the rare earths in *oxide slags* has to be solved. Once the rare earths have been concentrated into solid REE-rich phases, they can then be removed from these phases by leaching. Apart from metallurgical slags, other residues from thermal processes such as coal combustion ashes, oil shale ashes and ashes of waste incinerators contain significant concentrations of rare earths.<sup>23-25</sup> In general, the concentrations in bottom ashes are higher than in the fly ashes.

## **Bauxite residue (red mud)**

Bauxite is the most important aluminium ore and it is a mixture of impure hydrated aluminium oxides. Depending of the type of deposit, gibbsite, boehmite or diaspore is the principal aluminium component. Bauxite contains only between 30–50% alumina,  $\text{Al}_2\text{O}_3$ , the rest being silica, various iron oxides, titanium dioxide, but also calcium, sodium and small amounts of zinc, gallium, nickel, vanadium, zirconium, niobium, thorium, uranium and rare earths.<sup>26,27</sup> The alumina must be purified before it can be refined to aluminium metal. This is done using the Bayer process, where bauxite is digested in a hot sodium hydroxide solution. This converts the alumina to aluminium hydroxide, which dissolves in the hydroxide liquor. The other components of bauxite do not dissolve. The solution is clarified by filtering off the solid impurities, which forms the so-called *bauxite residue* or red mud. The actual composition of red mud depends on the type of bauxite, the mining location and the process parameters of the Bayer process. The pH of the wet red mud slurry is about 12.

With a worldwide annual production of 120 millions of tonnes and a total inventory of 2.7 billion of tonnes, stored in huge holding ponds, *red mud* poses a significant and hazardous problem. The latter was revealed recently by the dam failure of the Ajka refinery in Hungary and the resulting loss of human lives and environmental catastrophe. In Europe, besides Hungary, refineries exist in Bosnia Herzegovina, France, Germany, Greece, Ireland, Italy, Romania, Slovakia and Spain.

Unlike other high volume wastes (fly ash, metallurgical slags), red mud finds no industrial application besides minor use in cement and ceramic production. Many researchers have already looked at the valorisation of *red mud*, besides its use in the construction industry. Red mud has a high metal content and extraction of metals from red mud can be economically feasible. Iron is a main constituent of red mud, and it can make up to 60% of the mass of the red mud. In fact, its red colour is caused by the oxidised iron (mostly hematite or  $\text{Fe}_2\text{O}_3$ ). In view of the rather large content of iron oxide, attempts have been made in the past to use red mud as a source of iron.

Iron recovery studies were initiated as early as in the 1950s and may be classified into two major approaches, i.e. smelting and solid state reduction. In the former red mud is treated in a blast furnace in the presence of a reducing agent where the iron oxides are reduced, generating pig iron and a titanium-rich slag (also containing the REE). In the solid-state reduction the red mud is mixed with a reducing agent or contacted with a reducing gas at certain temperature, resulting in the formation of metallic iron or the conversion of ferric iron to magnetite, which could either be used for steelmaking or as a charge to the blast furnace. So far, these iron recovery processes have not been commercially successful, because of specific problems associated with red mud. The large sodium content of red mud prohibits the use of blast furnaces where the high temperatures lead to the evaporation of sodium oxide in the lower (hotter) regions of the blast furnace and its re-deposition in the colder regions, where it attacks the ceramic refractory bricks and also leads to the formation of so-called *sodium nests*, which are hard outgrowths that obstruct the free flow of the charge inside the furnace. Moreover, red mud contains a lot of water, which would have to be removed first, thus representing a high cost if fossil fuels are used for drying.

During the processing of bauxite by the Bayer process, all the rare earths end up in the red mud. The enrichment factor of the rare earths in red mud compared to bauxite is about a factor of two.<sup>28</sup> The average concentration of rare earths in bauxite from Greece is 506 ppm, whereas the average concentration of the resulting red mud is 1040 ppm.<sup>28</sup> Red mud is rich in scandium. Red mud from Greece contains about 130 ppm, whereas red mud produced from Jamaican bauxite has a scandium concentration of up to 390 ppm.<sup>29</sup> However, the red mud produced from bauxites from Moengo in Suriname have the highest rare-earth concentrations, with scandium concentrations as high as 1700 ppm.<sup>30</sup> These scandium concentrations are much higher than the average abundance of 22 ppm of scandium in the Earth's crust, and point to a significant enrichment of scandium in bauxite and in red mud. There exist minerals with a high scandium content (*e.g.* thortveitite and lolbeckite), but they form only very small deposits.<sup>31</sup> The lack of rich scandium deposits hampers the widespread use of scandium, although scandium could find useful applications as an alloying metal for aluminium and as a recyclable Lewis acid catalyst for the production of fine chemicals. For these reasons, the recovery of scandium from red mud could be of high economic interest. Scandium represents more than 95% of the economic value of rare earths in red mud.

There are numerous studies on the extraction of rare earths, and of scandium in particular, from red mud. The two main approaches are either purely hydrometallurgical processes or a combination of pyrometallurgical and hydrometallurgical processes.<sup>31</sup>

The purpose of the hydrometallurgical processes is to selectively leach the minor metals from the red mud, leaving behind the major components such as iron oxides. It has been an important discovery that the rare earths are readily leachable from red mud by diluted mineral acids, whereas these elements cannot be leached from bauxite under the same experimental conditions.<sup>32</sup> After leaching, the rare earths can be recovered from the leachate by selective precipitation as the oxalate, or by solvent extraction. The rare earths can be selectively dissolved by digesting red mud with a dilute acid solution made by dissolving SO<sub>2</sub> in water (sulphurous acid), leaving most of the iron undissolved. Also sodium, aluminium and silicon present under the form of sodalite are brought into solution, but the rare earths can be recovered by solvent extraction. A comparative study of leaching with different acids (HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>3</sub>), has shown that 0.5 M HNO<sub>3</sub> is the best leachant and that the leaching can be performed at ambient temperatures and pressures.<sup>33</sup> 80% of the scandium present and 96% of the yttrium could be recovered, but the leaching procedure was less efficient for the light lanthanides (30 to 50% recovery). The leaching process with dilute HNO<sub>3</sub> has been performed at a pilot scale and optimised for the recovery of scandium from red mud.<sup>34</sup>

Most combined pyro/hydrometallurgical treatments of red mud use a pyrometallurgical step to first recover iron from red mud and to subsequently concentrate the rare earths in an oxide slag.<sup>35-37</sup> The efforts made to extract iron from bauxite have been described above. The hydrometallurgical step consists of leaching the rare earths from the slag with a diluted mineral acid.<sup>38</sup>

## Phosphogypsum

Phosphogypsum is the main by-product of the production of phosphoric acid and it is formed by the acidic digestion of phosphate rock.<sup>39</sup> The main mineralogical component of phosphate rock (also known as phosphorite) is apatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH,F,Cl). The digestion is mainly done by sulphuric acid, although also nitric acid can be used. Depending on the production method, the phosphogypsum formed consists primarily of either calcium sulphate dihydrate, CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) or calcium sulphate hemihydrate, CaSO<sub>4</sub>·½H<sub>2</sub>O, and with small amounts of silica, fluoride and unreacted phosphate rock. The amount of phosphogypsum produced during phosphoric acid production exceeds the mass of the product, i.e. 4.5 to 5.5 tonnes of phosphogypsum are generated per tonne of P<sub>2</sub>O<sub>5</sub>.<sup>40</sup>

The phosphogypsum stored in waste piles consists in general of calcium sulphate dihydrate. It contains also trace amounts of many other elements, including thorium, uranium and rare earths, which were originally present in the phosphate rock. The concentration of rare earths in phosphate rock is in general only between 0.01 and



0.1 wt%, although phosphate rock of the Kola peninsula in Russia can contain up to 1.0 wt% of rare earths.<sup>41-43</sup> Cerium, lanthanum and neodymium compose about 80% of the total rare-earth content. The rare earths are concentrated in phosphogypsum during the production of phosphoric acid. About 70 to 85% of the rare earths originally present in the phosphate rock end up in the phosphogypsum. The rest remains dissolved in the leaching solution, which also contains the phosphoric acid. Less rare earths are incorporated in the phosphogypsum if the leaching is performed at lower temperatures or with less concentrated sulphuric acid.<sup>41</sup> The average concentration of rare earths in phosphogypsum is 0.4 wt%.<sup>41</sup> This seems to be a very low concentration in comparison with other rare-earth ores. The rare-earth deposits that are currently mined have a rare-earth oxide (REO) content between 3 and 15%. However, given the enormous amounts of phosphate rock processed every year and the fact that rare earths are just a by-product of the phosphoric acid production, phosphogypsum presents a valuable source of rare earths. The potential of phosphogypsum as a source of rare earths has already been recognised in the 1960s. In comparison with red mud, phosphogypsum contains lower concentrations of scandium.

About half of the rare earths present in phosphogypsum can be recovered by leaching the phosphogypsum at ambient temperature with a 0.1 to 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in a solid-to-liquid ratio of 1:10.<sup>41</sup> It is impossible to quantitatively recover the rare earths without destruction of the phosphogypsum lattice. The leaching efficiencies can be increased by a gravity flow of the H<sub>2</sub>SO<sub>4</sub> solution through a column packed with phosphogypsum.<sup>44</sup> Another method for enhanced H<sub>2</sub>SO<sub>4</sub> leaching is the mechanical activation of phosphogypsum by ball-milling.<sup>45</sup> The rare earths can be recovered from the leaching solution by precipitation, for instances as sodium rare-earth double sulphates,<sup>46</sup> or by solvent extraction.<sup>41</sup> Higher leaching efficiencies are obtained by leaching with a HNO<sub>3</sub> solution instead of a H<sub>2</sub>SO<sub>4</sub> solution.<sup>47</sup> Jarosinski and co-authors described a wasteless process for the recovery of rare earths from phosphogypsum.<sup>48</sup> The basic steps are: (1) leaching of the rare earths with dilute sulphuric acid from the phosphogypsum; (2) concentration of the leachate by evaporation, followed by recovery of the rare earths by solvent extraction with nonyl-phenyl phosphoric acid (NPPA) or by selective precipitation with hydrofluoric acid; (3) production of anhydrite (anhydrous calcium sulphate) from the purified phosphogypsum by recrystallisation in concentrated sulphuric acid. Different process parameters had to be used, depending on whether the starting materials were calcium sulphate hemihydrate or dihydrate. The purified anhydrite can be used for production of plaster. Not all rare earths present in phosphate rock end up in phosphogypsum. The process was tested on a pilot scale, but it is too complicated and uneconomical to be industrialised.<sup>49</sup> El-Didamony and co-workers investigated the possibility to leach metals from phosphogypsum with organic

extraction agents dissolved in kerosene.<sup>40</sup> Although the main aim of this study was the removal of radionuclides from phosphogypsum, it also indicates that this method is feasible to recover the rare earths. Phosphogypsum can be decomposed by reaction with ammonium carbonate, so that ammonium sulphate fertiliser and calcium carbonate are formed.<sup>41</sup> The rare earths report to  $\text{CaCO}_3$  and can be recovered by dissolution of  $\text{CaCO}_3$  in  $\text{HNO}_3$ , followed by removal of the rare earths by solvent extraction. Alternatively,  $\text{CaCO}_3$  can be calcined to  $\text{CaO}$  and calcium can be dissolved by leaching with an  $\text{NH}_4\text{Cl}$  solution. This results in a rare-earth rich residue. When phosphate rock is leached with a  $\text{HNO}_3$  solution, all the rare earths are solubilised as nitrates.<sup>41</sup> The  $\text{HNO}_3$  leaching is more favourable than  $\text{H}_2\text{SO}_4$  leaching for the recovery of rare earths from phosphate rock, but  $\text{H}_2\text{SO}_4$  leaching is preferred in industry because of economical reasons. It is evident that  $\text{HNO}_3$  leaching does not produce phosphogypsum.

Phosphoric acid produced by  $\text{H}_2\text{SO}_4$  leaching contains about  $1 \text{ g L}^{-1}$  of rare earths. Different methods have been used to recover the rare earths from crude phosphoric acid.<sup>41</sup> Many researchers have investigated the possibility to recover rare earths and uranium from these phosphoric acid leaching solutions, and most of these methods were based on solvent extraction or ion-exchange.<sup>50-58</sup> Lower temperatures, higher concentrations of phosphoric acid and larger liquid/solid ratios increase the rare-earth concentration in the phosphoric acid leach solution.<sup>49</sup> Addition of surfactants enhances the growth of gypsum crystals and improves the leaching of rare earths.<sup>49</sup> Non-equilibrium extraction via centrifugal contacting was able to increase the separation factor between REEs and iron more than 250 times.<sup>59</sup> The best process for the recovery of rare earths during phosphoric acid production is via the two-stage hemihydrate-dihydrate process.<sup>42</sup> In the first stage, calcium sulphate hemihydrate is precipitated and separated from phosphoric acid by filtration. In the second stage, the calcium sulphate hemihydrate is hydrated in a dilute sulphuric acid solution to the calcium sulphate dihydrate (gypsum). The hydration takes place via dissolution of the hemihydrate, followed by the crystallisation of the dihydrate. This dissolution step brings all the rare earths into solution. On the other hand, rare-earth ions in solution inhibit the crystallisation of the dihydrate, so that the rare earths have to be removed from the solution, which allows their recovery.

## Mine tailings

The older processing methods of rare-earth ores were not very efficient. Especially during the flotation process of ground rare-earth ores large losses occurred. This has led to the generation of large volumes of solid waste with significant concentrations of rare earths. This solid waste is often dumped in tailing ponds close to the mine or close to the processing plant. The concentrations in these residues are so high that

these tailings can be considered as genuine rare-earth deposits. For instance, the tailings of the Mountain Pass mine in California are considered as the second largest rare-earth deposit in the United States (the largest is the Mountain Pass mine itself). The Mountain Pass mine tailings still contain between 3 to 5% of rare-earth oxides. The processing of monazite in the past has generated large volumes of rare-earth-rich tailings at Rhodia's rare-earth processing plant at La Rochelle (France). Large volumes of mine tailings rich in rare earths are found near the Chinese rare-earth deposits or processing units.<sup>60</sup> The tailings in Baotou received wide attention because they were polluting the environment with radioactive thorium-containing dust.

Mine tailings with economically interesting concentrations of rare earths are not only found near rare-earth mines, but also tailings of uranium mines often contain large concentrations of rare earths. For instance, tailings of uranium mines in Queensland (Australia), Kazakhstan and Kyrgyzstan are presently under investigation as possible new rare-earth deposits. Tailings of titanium mines could also offer possibilities for extraction of rare earths.<sup>62</sup> More efficient extraction of rare earths from old mine tailings would not only give an easy access to significant amounts of rare earths without the need of primary mining activities, but it is also beneficial from an environmental point of view as this could be integrated in remediating mine sites.

## **Wastewater**

Wastewater could also be a source for rare earths, but the potential of this waste stream for the recovery of rare earths remains largely unexplored. In the first instance, rare earths could be recovered from wastewater produced during the extraction and separation of rare earths. Acid mine drainage (AMD) often contains considerable concentrations of rare earths.<sup>63</sup> AMD is the outflow of acidic water from (old) metal mines or coal mines, and it is often heavily contaminated by metals. Some studies report on the possibility to recover uranium and other metals from AMD by ion-exchange resins or by biosorption, but limited information is available on the possibility to recover rare earths.<sup>64-66</sup> One could think that recycling of gadolinium from MRI contrast agents after clinical use does not make sense from an economic point of view, but it has been found that anthropogenic gadolinium contaminates surface and ground water.<sup>67,68</sup> This justifies research activities towards recycling of gadolinium.<sup>69</sup> Yantasee and co-workers have investigated the possibility to bind rare-earth ions by functional groups on the surface of a mesoporous silica support.<sup>70</sup> It has been proposed to use these materials for recovery of rare earths from acidic industrial waste water streams and mining effluents. Whereas solvent extraction is the preferred method for recovery of rare-earth ions from concentrated aqueous waste streams and pregnant leaching solutions, this method is not recommended for removal of rare-earth ions from diluted aqueous waste streams,

because of the unavoidable contamination of the aqueous phase by organic solvents. Therefore, ion-exchange resins and chelating resins are to be preferred. Finally, it has to be mentioned that also bio-based adsorbents such as (chemically modified) chitosan can be of interest.<sup>71-73</sup> Although the biosorption of precious metals and uranium by algae, fungi, bacteria and yeast has been widely explored,<sup>74-82</sup> up to now relatively little attention has been paid to the biosorption of rare earths.<sup>83-86</sup>

## Conclusions

This review has provided an overview of different industrial waste residues that show some potential for recovery of rare earths: slags produced by pyrometallurgical metal recycling processes, bauxite residue (red mud), phosphogypsum, mine tailings and industrial wastewater. These waste streams have in common that they contain relatively low concentrations of rare earths (typically well below 1% of REOs, whereas the present cut-off for extraction from primary ores is about 3%), but large volumes are available and the rare earths are often just by-products. As a consequence, in absolute terms these waste streams contain large amounts of rare earths and they could become economically attractive secondary sources of rare earths. Red mud is a very interesting waste stream for the recovery of scandium, while phosphogypsum is a valuable source of the other rare earths. The joint venture between Umicore and Rhodia to develop the recovery of rare earths from metallurgical slags produced during pyrometallurgical recycling processes of nickel metal hydride batteries shows the potential value of slags as a secondary source of rare earths. However, the high dilution of rare earths in most types of slags still remains a problem and further research is required. The recovery of rare earths from old mine tailings or from industrial water waste streams is still in its infancy. Due to the fact that the concentrations of rare earths in industrial waste residues are low compared to primary rare-earth ores and reclaimed End-of-Life consumer goods (WEEE), special processes dedicated to the recovery of rare earths from these dilute waste streams need to be developed.

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