REVIEW OF RECENT WORK ON THE RECOVERY OF RARE EARTH ELEMENTS FROM SECONDARY SOURCES

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[Hbet][Tf2N]	bis(trifluorométhylsufonyl)imide
[Hbet-STFSI-PS-DVP]	betainiumsulfonyl (trifluoromethanesulfonylimide) poly(styrene-co-divinylbenzene)
[EMIMHSO4]	1-ethyl-3-methylimidazoliumhydrogensulfate
AMD	Acid mine drainage
AC	Activated carbon
BR	Bauxite residue
CCPs	Coal combustion products
CMD	Coal mine drainage
DAS	Dispersed alkaline substrate
DOE	Department of energy
DVB	Divinylbenzene
EDTA	Ethylenediaminetetraacetic acid
HDEPH	Di-(2-ethylhexyl)phosphoric acid
HRT	Hydraulic retention time
ISL	In-situ leaching
HREEs	Heavy rare earth elements
LREEs	Light rare earth elements
MREEs	Middle rare earth elements
NASC	North American shale composite
NMD	Neutral mine drainage
PG	Phosphogypsum
REE	Rare earth elements
REO	Rare earth oxides
TBP-TOPO	Tributyl phosphate-trioctylphosphine oxide
TENORM	Technically enhanced naturally occurring radioactive material
TREE	Total rare earth elements
WEEE	Waste electrical and electronic equipment

1 INTRODUCTION

Rare earth elements (REEs) are of growing interest and their applications cover many fields. In particular, they are essential in the design of emerging technologies such as wind turbines, hybrid cars and mobile phone speakers (EuRare, 2017). Thus their demand in recent years has continued to increase. China, with nearly half of the world's known reserves, dominates REEs production. Indeed, 94 % of REEs production is held by China (Schlinkert & van den Boogaart, 2015). In view of the growing demand and the desire to emancipate themselves from China, many countries, including Canada, are evaluating the potential to exploit their own resources. Conventionally, REEs are commercially extracted from rare earth deposits that contain REEs-bearing minerals such as bastnaesite, monazite, and xenotime, and among others. However, demand for REEs exceeded supply between 2010 and 2015 (Standing Committee of Natural Resources-Canada, 2014). Thus, since conventional fields cannot meet this demand, the recovery of REEs from secondary sources could become a new source of supply.

Secondary sources of REEs that appear promising and highlighted in this document are: acid mine drainage (AMD), bauxite residue (BR), coal combustion products (CPP), phosphogypsum (PG) and uranium mine tailings. Depending on the type of secondary source, different methods have developed to recover REEs: acid and/or alkaline leaching, bioleaching, pyrometallurgical processes, co-precipitation, sorption, etc. The purpose of this review is, therefore, to gather recent information on this subject. To this end, the studies published over the past five years have been compiled and synthesized. This information will allow the improved knowledge of current research, to better understand the challenges involved in the recovery of REEs from these sources and to better target future research.

2 PRE-CONCENTRATION AND POTENTIAL RECOVERY OF REES FROM ACID MINE DRAINAGE (AMD)

2.1 PRESENCE OF REEs IN AMD

Mine drainage refers to contaminated water resulting from the water flow, which contacts mining residues (tailings, waste rock, ore, mine openings, etc.) containing acidogenic minerals, when exposed to the atmosphere or oxidizing environments and in the absence of sufficient neutralizing minerals (Skousen *et al.*, 1998). Even though it is not the most significant parameter, the classification of contaminated mine drainage is often based on its pH values: acid mine drainage (AMD), neutral mine drainage (NMD), alkaline drainage, etc. (Nordstrom *et al.*, 2015). In principle, all types of mine drainage are contaminated, to a certain extent. AMD is one of the most widespread environmental problems faced by the coal and base/precious metal mining industry worldwide. Resulting from the oxidation of sulfide minerals in mine tailings in the presence of H_2O and O_2 (direct) or Fe^{3+} (indirect), AMD is characterized by low pH and high concentrations of metal(loid)s and sulfates. The pH of NMD ranges from 6 to 9 and the concentrations of dissolved metal(loid)s (e.g., Cd, Cr, Co, Hg, Mo, Ni, Sb, As, Se, Zn) exceed discharge criteria (Stantec, 2004) .

The geochemistry and the behaviour of REEs in mine drainage depends on various factors, including the following: i) the abundance of primary REE-bearing minerals; ii) the extent of dissolution/alteration of REE-bearing minerals; iii) the chemistry of REEs in the transporting water; 4) the capacity of solid particulate materials for REE sorption (Serrano *et al.*, 2000; Sun *et al.*, 2012).

Over the past decades, attention was mainly focused on the monitoring and control of common metal(loid)s (e.g. Fe, As, Cu, Ni, Zn), while the presence of REEs in mine drainage is now getting attention in several countries over the world (e.g. United States, Spain, Portugal, Germany) (Ayora *et al.*, 2016; Chávez & Gissela, 2017; Naidu *et al.*, 2019; Ziemkiewicz *et al.*, 2016). The concentration of REEs in neutral to basic waters are usually low (10^{-6} to 10^{-9} m) and NASC-normalized patterns are often dominated by carbonate complexing, whereas REE concentrations in acidic waters are higher (10^{-4} to 10^{-7} m) and NASC-normalized patterns distinctively different, with Al playing a critical role in determining REE speciation (Serrano *et al.*, 2000).

Table 1 presents typical concentrations of REEs measured in AMD, depending on the type of deposit exploited, with values ranging from 0.43 to 17,920 $\mu g.L^{-1}$. REE contents are several orders of magnitude higher than typical groundwater [mean value of 0.008 $\mu g.L^{-1}$ – n = 619 from 31 studies] or surface water such as lakes [mean value of 0.026 $\mu g.L^{-1}$ – n = 74 from 8 studies] and rivers [mean value of 0.01 $\mu g.L^{-1}$ – n = 259 from 16 studies] (Noack *et al.*, 2014). Recent studies showed that mine drainage coming from coal exploitation in the Appalachian Basin (USA) are enriched in middle rare earth elements (MREE) by one to four orders of magnitude compared to groundwater or surface water (Stewart *et al.*, 2017; Ziemkiewicz *et al.*, 2016). According to these authors, with more than 540 t of REEs dissolved each year in AMD, coal mine drainage (CMD) represents a promising secondary source of MREE, including several elements (e.g. Nd, Eu, Dy and Tb) identified as critical resources. Similar REE patterns were observed in CMD in Europe (Germany, Romania, Sweden) (Grawunder *et al.*, 2014) and in India (Sahoo *et al.*, 2012).

The enrichment of mine drainage in REEs can be due to the weathering of REE-bearing minerals [bastnaesite (carbonates) and monazite (phosphates)] found in sedimentary and igneous rocks under the aggressive acidic action of AMD, humic acid and CO_2, as well as the dissolution of secondary Fe-Mn oxyhydroxide minerals enriched in REEs (Ayora *et al.*, 2015; Gammons *et al.*, 2003).

Contrary to AMD, the presence of REEs in NMD is less documented. A relatively recent study (Shahhosseini *et al.*, 2017) investigated the geochemistry of REEs in NMD (characterized by high sulfate and bicarbonate concentrations) and in a river, both located in the vicinity of a coal washing plant in northern Iran. The results showed NMD was enriched in HREEs, with a similar signature to coal (except for the depletion in LREE and the enrichment of Eu), while the river presented mostly MREEs. Overall, the total concentrations in the NMD were lower (5.1 ± 3.9 $\mu g.L^{-1}$) than in the river water (13.4 ± 1.8 $\mu g.L^{-1}$), where Fe-rich sediments were enriched in La and Ce. A previous study investigated the geochemistry of REEs in near-neutral water (mine drainage) and solids at abandoned mines in Italy (Medas *et al.*, 2013). In this last study, mine tailings showed peak concentrations of REEs as high as 300 $mg.kg^{-1}$, while mine drainage (pH 6.2 to 7) flowing out of the mine tailings heaps showed a mean concentration of 53 $\mu g.L^{-1}$ REE.

Table 1. *Typical concentrations of REEs in AMD.*

Country	Mine Site Localization	Type of resources exploited	pH	Fe (mg/L)	SO_4^{2-} (mg.L^{-1})	REE (µg.L^{-1})	LREE (µg.L^{-1})	HREE (µg.L^{-1})	U (µg.L^{-1})	Th (µg.L^{-1})	References
USA	Appalachian Basin (Pennsylvania, n = 15)	Abandoned and inactive coal mine	n.i.	n.i.	n.i.	70 - 2,070	n.i.	n.i.	n.i.	n.i.	Ziemkiewicz *et al.* (2016)
USA	Appalachian Basin (Pennsylvania, n = 18)	Abandoned and inactive coal mine	2.9-4.4.	9.1-385	276-2,140	0.43-1,130	0.026-391	0.26-742	n.i.	n.i.	Stewart *et al.* (2017)
USA	Abandoned mines in the Anthracite and Bituminous Coalfields (Pennsylvania, n = 140)	Anthracite and bituminous	2.7-7.3	0.046-512	2.7-31	1.069-1,185	n.i.	n.i.	0.006-100	0.003-24	Cravotta III (2008)
USA	Berkeley Pit Lake (Montana, n = 22)	Abandoned copper mine	2.3-2.4	1,000	9,150	3,340-3,520	1,900-2,050	1,420-1,490	826-883	125-132	Gammons *et al.* (2003)
Spain	Monte Romero (Iberian Pyrite Belt - n = 1)	n.i.	2.7	161	3,5	7,900	n.i.	n.i.	n.i.	n.i.	Ayora *et al.* (2016)
Spain	Almagrera (Iberian Pyrite Belt - n = 1)	n.i.	2.6	744	11,7	3,500	n.i.	n.i.	n.i.	n.i.	Ayora *et al.* (2016)
Spain	Iberian Pyrite Belt (n = 35)	n.i.	n.i.	n.i.	n.i.	70 – 13,000	n.i.	n.i.	n.i.	n.i.	Ayora *et al.* (2016)
Spain	La Poderosa Mine (Rio Odiel Basin)	Copper	1.8-2.4	1,330-1,730	n.i.	11,000	7,450	3,550	n.i.	n.i.	Chávez (2017)
Spain	Tinto-Odiel Estuary (n = 5)	Fluvial sector contaminated by industrial water (copper foundries and phosphogypsum deposits)	2.57-2.65	n.i.	n.i.	200-1,099	150-817	50.3-282	12.2-76.7	n.i.	Borrego *et al.* (2012)
Portugal	Jales (Iberian Pyrite Belt - n = 12)	Inactive gold mine	5.6 - 7.4	n.i.	4.0 - 221	0.015 - 70.4	n.i.	n.i.	n.i.	n.i.	Prudêncio *et al.* (2015)
Poland	Wiśniówka mining area (south-central)	Quartzites and quartzitic sandstones	1.4-2.2	13,500-45,700	26,900-91,800	219-17,920	127-12,884	91.2-5,030	n.i.	n.i.	Migaszewski *et al.* (2019)
Iran	Sarcheshmeh mine (n = 10)	Porphyry copper deposit	1.9-3.2	329-8,600	121-12,080	30.5-10,650	n.i.	n.i.	n.i.	n.i.	Sharifi *et al.* (2013)
Germany	Mining district of Lower Lusatia (n = 10, Contaminated Lake Water depth from 0 to 10 m)	Lignite	2.6-5.4	144-538	478-1,950	267-329	248-307	19-22	n.i.	n.i.	Bozau *et al.* (2004)
India	Jaintia Hills coalfield (Meghalaya, n = 12)	Coal mine	1.6-4.8	38.5-290	457-4,.90	714	n.i.	n.i.	n.i.	n.i.	Sahoo *et al.* (2012)
China	Xingren County (southwestern Guizhou Province, n = 10)	Gold and coal mines	2.7 - 4.6	0.87 - 703	372 - 2,794	118 - 926	97.1-659	21.2-267	n.i.	n.i.	Li and Wu (2017)
Cuba	Santa Lucia mine (n = 21)	Inactive Zn-Pb mine	2.5-2.6	up to 4,620	up to 6,750	370-860	n.i.	n.i.	n.i.	n.i.	Romero *et al.* (2010)

Speciation experiments conducted by Serrano *et al.* (2000) showed that REEs predominately occurred as free-ion species and sulfate complexes in AMD, while phosphates, hydroxide and chloride complexes were quite negligible. Comparative REE speciation was observed in samples collected from abandoned Cu mines in Montana (Berkeley Pit Lake, MT, USA), showing that REEs are mainly present in AMD as sulfate complexes (Gammons *et al.*, 2003). These authors also observed a depletion of LREE relative to HREE, which can be explained by their sorption on the surfaces of secondary precipitates. They concluded that the mobility of REEs and U can be influenced by the presence of secondary precipitates (e.g. strengite, jarosite and schwertmannite). Verplanck *et al.* (2004) observed that the mobility of REEs in the environment is strongly dependent on pH. Field studies as well as experiments performed in the laboratory on real AMD (6 samples) showed that REEs remain soluble at a pH below 5.1 in acidic sulfate waters, while their precipitation and/or sorption onto solid phases were observed at pH values between 5.1 and 6.6. Moreover, it appeared that attenuation of REEs is more influenced by the presence of Al colloids than Fe colloids in water streams that received AMD (Verplanck *et al.*, 1999). These results are in accordance with the results obtained by Sun *et al.* (2011), which indicate that REE mobility is strongly influenced by pH. Other factors including redox conditions, salinity, dissolved organic matter and the type of chelating agents present in water streams can affect the mobility of REEs. The geochemical behaviour of REEs in the environment has been reviewed in detail by Migaszewski and Gałuszka (2015).

2.2 PROCESSES AND MATERIALS FROM AMD TREATMENT AND REE PRE-CONCENTRATION

Based on REE geochemistry and behaviour in AMD and water streams that received AMD, it is expected that the addition of alkaline agents to neutralize the acidity of AMD during both active and passive chemical treatments will lead to the removal of REEs. Various mechanisms such as co-precipitation with oxyhydroxides (mainly Al) and sorption onto Al/Fe oxyhydroxide occurred in the immobilization of REEs from AMD treatment. Additional chemical treatments including the sorption of REEs on modified or unmodified sorbents have also been studied over the last few years to evaluate their efficiency to remove REEs from AMD and eventually to pre-concentrate them on solid phases for their potential subsequent recovery. The following sections will briefly discuss the performances of both (co-)precipitation (Table 2) and sorption (Table 3) to remove REEs from AMD.

2.2.1 (Co-)precipitation

REE precipitation as phosphates

According to the detailed review by Jha *et al.* (2016), a large number of REE-bearing phosphate minerals have been found in nature, indicating that REEs have a strong affinity towards phosphates and a natural tendency to form stable precipitates. Chávez and Gissela (2017) studied the influence of final pH, the nature of acid solutions used to control pH (HCl, H_2SO_4, HNO_3) and the molar ratio of P/REEs on the precipitation of REEs. Results showed that the precipitation of REEs from diluted solutions is quite ineffective (< 15 %), although an increase in the P/REE ratio (from 2/1 to 41/1) slightly improved the recovery of REEs (from 2-10 % to 8-15 %). Despite this slight improvement of REE recovery, the increase in the P/REE ratio should be considered with caution as the amount of transition elements (e.g. Co, Cd, Mg, Al, Ca, Zn) in precipitates also increased, and reduced the purity of the final REE precipitates. A small effect of pH was observed in the different scenarios tested (pH 2.3 and 2.5), while the use of H_2SO_4 to adjust the pH seemed to be slightly more effective than HCl or H_3PO_4. Moreover, the use of NaOH to adjust the pH during the pre-treatment step (Fe removal at pH 3.7-3.8) was recommended over CaO and MgO, as the amount of Al precipitated during this pretreatment step was reduced with the use of NaOH.

Al- and Fe-oxyhydroxides

Barcelos *et al.* (2018) evaluated the potential to immobilize and pre-concentrate Eu and Ho from synthetic AMD ($[Eu]_0$ = 75-380 $mg.L^{-1}$, $[Ho]_0$ = 80-412 $mg.L^{-1}$) through (co-)precipitation and sorption onto Al/Fe oxyhydroxides. Experiments were conducted using various Al/Fe/REE molar ratios in the range of 500:0:5 to 400:100:25, as the presence of Al can influence the stability of REE-bearing precipitates and therefore their recovery potential. Results showed that REE removal efficiencies (> 99.99 %) were not influenced by Al/Fe/REE ratios or hydraulic retention time (from 4 to 90 days). However, the proportion of Eu and Ho in the reducible and oxidizable phases slightly increased with the addition of Al in the structure of Fe-oxyhydroxides, while the amounts of REEs associated with refractory oxides decreased compared to experiments performed without Al addition. These findings are consistent with the results of Pietralonga *et al.* (2017), where a decrease in La-bearing precipitates stability was observed as the proportion of both La and Al introduced during the precipitation increased. No difference in terms of La precipitation or retention on solid phase with Fe/Al ratios was found. They also observed a re-mobilization of La (from 1.4-37 % after 42-49 days to 9-100 % after

90 days) from precipitates formed in the presence of high concentrations of La (Fe/Al/La ratios of 500/125/125 and 500/250/125).

Recent studies evaluated the efficiency of active and passive treatment for REE removal from AMD and their pre-concentration by a factor of 10^3 to 10^4 depending on AMD chemistry and treatment process used (Ayora *et al.*, 2016; Stewart *et al.*, 2017; Ziemkiewicz *et al.*, 2016). Stewart *et al.* (2017) found that most REEs were sorbed onto Si/Al and Ca/Mg precipitates relative to Fe-precipitates, consistent with the observations made by Ayora *et al.* (2016) and Zhang and Honaker (2018). Therefore, REE precipitation as phosphates or Al-precipitates effectively (> 80%) concentrated REEs from AMD or pregnant solutions (pre-treatment by ion exchange) in precipitation sludge (Table 2). More details of studies performed on real AMD are given in Section 2.3.

2.2.2 Sorption

Over the past decades, extensive work has been done to evaluate the performance of various sorbents, including raw and modified materials (e.g. granular grafted hydrogel composites, modified biohydrogels, plant and animal-derived materials, oxidized multiwalled carbon nanotubes), in REE removal from aqueous solutions. A relatively recent detailed review thoroughly discusses the scientific literature on REE sorption, after 2013 (Anastopoulos *et al.*, 2016). Previously, Das and Das (2013) summarized the literature (1995-2011), which was then updated by Gupta *et al.* (2018) on the use of biosorbents for REE removal. Several operating parameters such as solution pH, contact time, adsorbent dose, initial composition of the solution to be treated and temperature are important factors that influence REE sorption and therefore, the potential to concentrate them on the sorbent.

The literature review by Anastopoulos *et al.* (2016) synthesizes the key findings on several REE removal methods by sorption using various materials. Maximum sorption capacities for REE were as following: Ce(III), from 50 $mg.g^{-1}$ (EDTA-β-cyclodextin) to 1,000 $mg.g^{-1}$ (prawn carapace); Dy(III), 78 $mg.g^{-1}$ (oxidized multiwalled carbon nanotubes); Eu(III), from 0.05 $mg.g^{-1}$ (modified cactus fibres) to 156 $mg.g^{-1}$ (malt spent rootlets); La(III), from 0.9 $mg.g^{-1}$ (hydroxyapatite) to 333 $mg.g^{-1}$ (granular grafted hydrogel composites); Gd(III), from 56.2 to 85.4 (surface modified mesoporous silica nanoparticle, one or two steps); Nd(III), from 0.1 $mg.g^{-1}$ (SiO_2) to 323 $mg.g^{-1}$ (magnetic nano-hydroxyapatite); Sm(III), from 90 $mg.g^{-1}$ (activated biochars from cactus fibres, pH 3) to 350 $mg.g^{-1}$ (activated biochars from cactus fibres, pH 6.5); Pr(III), from 58.8 $mg.g^{-1}$ (orange peel) to 146.4 $mg.g^{-1}$ (brown seaweed); Sc(III) and Y(III), 30.5 $mg.g^{-1}$ (lysine-functionalized mesoporous material) vs. 45.5 $mg.g^{-1}$ (NaOH modified *Pleurotus ostreatus*), respectively.

More recent studies using sorption processes for REE removal and pre-concentration from aqueous solutions used kaolin (Yanfei *et al.*, 2016), activated biochar (by low-temperature pyrolysis of sawdust) (Komnitsas *et al.*, 2017), porous amine-epoxy networks (Wilfong *et al.*, 2017), activated carbon with $KMnO_4$ (Kano *et al.*, 2017), geopolymers (Fiket *et al.*, 2018), etc. However, testing with actual effluents over long periods of time or techno-economic studies of the various materials for proper comparison are yet to be performed.

Kaolin used for the removal of La, Nd and Y showed maximum sorption capacities of 1.73, 1.58, and 0.97 mg/g, respectively (Yanfei *et al.*, 2016). Testing was conducted in batch mode, with 10-150 mg.L^{-1} La and Nd, and 10-120 mg.L^{-1} Y. Similarly, geopolymers (prepared from coal ash) were found to be effective for REE sorption from solutions of 1 mg.L^{-1} REEs (Ce, La, Nd, Pm, Dy, Er, Eu, Gd, Ho, Lu, Sc, Sm, Tb, Y, and Yb) (Fiket *et al.*, 2018).

Activated biochar was also effective for the removal of Nd and Sc from aqueous solution, but overall performance was found to be inferior to that of activated carbon. Further research was recommended to optimize the biochar production and performance (Komnitsas *et al.*, 2017). Nonetheless, biochar activation is commonly used to improve its physical properties and adsorptive capacity (Braghiroli *et al.*, 2018). Activation refers to a physical or chemical treatment (using H_3PO_4, KOH, steam or CO_2 gas at various temperatures, etc.) of biochar to maximize its pore density and surface area available for sorption.

Porous amine-epoxy monoliths and particles synthetized via a polymer-induced phase separation process was also effective in REE (La, Nd, Eu, Dy, and Yb) pre-concentration from aqueous solutions (Wilfong *et al.*, 2017). Moreover, consecutive recovery−strip−recovery of > 93 % of REEs from synthetic AMD, at a fouling metal/REEs ratio of 12,000/1, pH of 2.6 was deemed promising for new studies using these materials.

Table 2. *Performance of AMD neutralization and metal(loid)s precipitation for REE pre-concentration from AMD.*

AMD Type	REEs species	Mechanisms involved	Set-up and operating conditions	REEs removal (%)	REE concentration on sludge (mg/kg)	References
Synthetic solution	[Tb]0 = 31.8 mg/L in the presence of Ce, Eu, Dy and Yb	Sorption	Precipitation using synthetized nano-$Mg(OH)_2$ (< 5 nm), t = 30 min	> 97.5	1,830	Li *et al.* (2013)
Synthetic AMD	[La]0 = 0.03-3.47 $mg.L^{-1}$	(Co-)precipitation onto Al/Fe oxyhydroxides and sorption	pH = 11.7, HRT = 0-90 d, Fe/Al/La ratios between 500/125/0 and 500/250/125	90-99.9	n.i.	Pietralonga *et al.* (2017)
Synthetic AMD	[Eu]0 = 75-380 mg/L, [Ho]0 = 80-412 $mg.L^{-1}$	(Co-)precipitation onto Al/Fe oxyhydroxides and sorption	pH = 9, HRT = 60 d	> 99.99	6,050 - 30,830 for Eu and 7,230 - 29,670 for Ho	Barcelos *et al.* (2018)
Real AMD (Cueva de la Mora mine, Spain)	All REEs (including Sc and Y); 3,5-7,9 $mg.L^{-1}$	(Co-)precipitation onto Al oxyhydroxides and sorption	CaO- and MgO-dispersed alkaline substrates (passive treatment), pH > 6 for CaO column and pH > 9 for MgO column	100	300 - 8,000 for TREE and < 17 $mg.kg^{-1}$ for U and < 4 $mg.kg^{-1}$ for Th	Ayora *et al.* (2016); Ayora *et al.* (2015)
Real AMD (La Poderosa mine, Spain)	All REEs (including Sc and Y); < 17 $mg.L^{-1}$	Direct precipitation of REEs as phosphates	Pre-treatment to remove Fe [addition of H_2O_2 and adjustment of pH at 3.7-3.8]	15 % through direct precipitation and 99% if REEs are preconcentrated by ion exchange	n.i.	Chávez and Gissela (2017)
Real AMD (West Kentucky, USA)	All REEs (including Sc and Y); 6.14 $mg.L^{-1}$	(Co-)precipitation onto Al/Fe oxyhydroxides and sorption	Addition of NaOH to adjust pH at 4.8-6.1	> 80	11,000	Zhang and Honaker (2018)
Real AMD (Appalachian Basin, USA)	All REEs (including Sc and Y)	(Co-)precipitation onto Al/Fe oxyhydroxides and sorption	Addition of lime to adjust pH	> 99	152-714	Ziemkiewicz *et al.* (2016)

Activated carbon

Activated carbon (AC) is a well-known material in wastewater treatment due to its unique properties (large pore volume and high surface area) which allow the adsorption and pre-concentration of various elements (e.g. potentially problematic and/or high value-added) initially contained in aqueous solutions. The application of modified or unmodified AC to remove REEs from aqueous solutions has been evaluated. Qing (2010) showed that AC produced from bamboo had a maximum sorption capacity of 120 $mg.g^{-1}$ La, at pH 7.20. Similarly, the study of Awwad *et al.* (2010) used AC prepared from rice husk, a residual low-cost biomass material from agriculture, by chemical activation using H_3PO_4. The parametric study evaluated the influence of several parameters (time, pH, initial concentration and temperature) on the La and Er adsorption capacity of the AC produced. The reported sorption capacities were 175.4 $mg.g^{-1}$ for La(III) and 250 $mg.g^{-1}$ for Er (III).

Biosorbents

Biosorbents, originating from various sources such as algae, fungi, plants and animals, represent promising low-cost material to sorb REEs from aqueous solutions. The efficiency and operating factors influencing REE sorption are reviewed in detail by Das and Das (2013) and, more recently, by Gupta *et al.* (2018). Several mechanisms including chelation, ion exchange, electrostatic interaction, complexation, intercellular bioaccumulation and precipitation are involved in the pre-concentration of REEs by biosorbents (Gupta *et al.*, 2018). According to these authors, biosorbents seem to effectively recover REEs from aqueous solutions but their applications are restricted due to the difficulty to adequately regenerate biosorbents for subsequent use without damaging the biomass.

Table 3. *Performance of sorption for REE pre-concentration from AMD.*

AMD Type	**REE species**	**Sorbent used**	**pH**	**Optimal time (min)**	**REE removal (%)**	**Adsorption capacity (mg.g^{-1})**	**References**
Synthetic solution	[La]0 = 1,389-27,781 mg.L^{-1}	AC (40 g.L^{-1})	6.0	30	n.i.	76.4	Iannicelli-Zubiani *et al.* (2018)
Synthetic solution	[La]0 = 50-300 mg.L^{-1}	AC (3 g.L^{-1})	3.5	30	n.i.	175	Awwad *et al.* (2010)
Synthetic solution	[La]0 = 100 mg.L^{-1}, in the presence of Lu, Yb, Eu, Y, Sc	AC (0.25 g.L^{-1})	3	480	n.i.	0.048	Kano *et al.* (2017)
Synthetic solution	[Er]0 = 50-300 mg.L^{-1}	AC (3 g.L^{-1})	3.5	60	n.i.	250	Awwad *et al.* (2010)
Synthetic solution	[Eu]0 = 25-800 mg.L^{-1}	AC (1 g.L^{-1})	3.5	60	~ 52.5	86	Anagnostopoulos and Symeopoulos (2013)
Synthetic solution	[Eu]0 = 800 mg.L^{-1}	AC (1 g.L^{-1})	3.5	60	10	86	Anagnostopoulos and Symeopoulos (2013)
Synthetic solution	[Sc]0 = 20 mg.L^{-1}	AC (10 g.L^{-1})	3	1,440	76.8	n.i.	Komnitsas *et al.* (2017)
Synthetic solution	[Nd]0 = 20 mg.L^{-1}	AC (10 g.L^{-1})	3	1,440	87.9	n.i.	Komnitsas *et al.* (2017)
Synthetic solution	[La]0 = 1389-27781 mg.L^{-1}	Modified AC (40 g.L^{-1})	6	90	92.2 - 99.9	107	Iannicelli-Zubiani *et al.* (2018)
Synthetic solution	[La]0 = 25 mg.L^{-1}	AC and silica composite (1 g.L^{-1})	4	30	~ 80	103	Ramasamy *et al.* (2018)
Synthetic solution	[Sc]0 = 25 mg.L^{-1}	AC and silica composite (1 g.L^{-1})	4	1,440	~ 100	113	Ramasamy *et al.* (2018)
Synthetic solution	[Y]0 = 25 mg.L^{-1}	AC and silica composite (1 g.L^{-1})	4	30	~ 100	84.1	Ramasamy *et al.* (2018)
Synthetic solution	[Sc]0 = 20 mg.L^{-1}	Biochar (10 g.L^{-1})	3	1,440	52.3	n.i	Komnitsas *et al.* (2017)
Synthetic solution	[Nd]0 = 20 mg.L^{-1}	Biochar (10 g.L^{-1})	3	1,440	78.6	n.i	Komnitsas *et al.* (2017)
Synthetic solution	[La]0 = 25-500 mg.L^{-1}	Biochar (1 g.L^{-1})	7	1,440	n.i.	275	Wang *et al.* (2016)
Synthetic solution	[Y]0 = [La]0 = [Ce]0 = [Nd]0 = [Sm]0 = 100 mg.L^{-1}	Carbon black (2.4-40 g.L^{-1})	2	1,440	50-82	4.37 (La) 35.0 (Ce) 36.4 (Nd) 19.9 (Sm) 6.09 (Y)	Smith *et al.* (2016)
Synthetic solution	[La]0 = 135-270 mg.L^{-1}	Modified charcoal (670 g.L^{-1})	7.20	480	n.i.	215	Qing (2010)

AMD Type	**REEs species**	**Sorbent used**	**pH**	**Optimal time (min)**	**REEs removal (%)**	**Adsorption capacity (mg/g)**	**Reference**
Synthetic solution	[La]0 = 135-270 mg.L^{-1}	Modified charcoal (670 g.L^{-1})	7.20	480	n.i.	215	Qing (2010)
Synthetic solution	[Sm]0 = 75.2 mg.L^{-1}	Activated biochar (0.33 g.L^{-1})	6.5	1440	~ 100	350	Hadjittofi *et al.* (2016)
Synthetic solution	[La]0 = 25-500 mg.L^{-1}	Modified biochar (1 g.L^{-1})	7	720	> 85	362	Wang *et al.* (2016)
Synthetic solution	[La]0 = 300 mg.L^{-1}	Fish scale (0.3 g.L^{-1})	6.0	240	n.i.	200	Das *et al.* (2014)
Synthetic solution	[La]0 = 250 mg.L^{-1}	Neem Sawdust (0.2 g/L)	6.0	180	n.i.	160	Das *et al.* (2014)
Synthetic solution	[Nd]0 = [Dy]0 = 0.10 mg.L^{-1}	Salmon milt (2 g.L^{-1})	4	60	> 99	n.i.	Takahashi *et al.* (2014)
Synthetic solution	[Eu]0 = 25 mg.L^{-1}	Malt spent rootless (1 g.L^{-1})	4.5	60	~ 70 %	156	Anagnostopoulos and Symeopoulos (2013)
Synthetic solution	[Eu]0 = 800 mg.L^{-1}	Malt spent rootless (1 g.L^{-1})	4.5	60	~ 17.5%	156	Anagnostopoulos and Symeopoulos (2013)
Synthetic solution	[La]0 = 10-200 mg.L^{-1}	Carboxylic acid functionalized diatomite (1 g.L^{-1})	4-7	20-120	>90	139	Zhou *et al.* (2016)
Synthetic solution	[Nd]0 = 288 mg.L^{-1}	Calcium alginate and γ-poly glutamic acid (1.6 g.L^{-1})	3.5	360	n.i.	238	Wang and Liang (2014)
Synthetic solution	[Nd]0 = 100-1, 200 mg.L^{-1}	Salmon milt (20 g.L^{-1})	3.5	180	n.i.	50.1	Takahashi *et al.* (2014)
Synthetic solution	[Nd]0 = 10-500 mg.L^{-1}	Magnetic nanohydroxyapatite (1 g.L^{-1})	5.5	150	98	323	Gok (2014)
Synthetic solution	[La]0 = [Yb]0 =10 mg.L^{-1}	Nanoscale zerovalent iron particles (1 g.L^{-1})	4.7	30	> 99.9	61.0 (La) 409. (Yb)	Crane and Sapsford (2018)
Real mining effluent	[Sc]0 = 5 mg.L^{-1}, in the presence of all REEs	Modified AC (1 g.L^{-1})	4	n.i.	> 90	n.i.	Ramasamy *et al.* (2018)
Industrial effluent (ceramic industry, India)	[La]0 = 250 mg.L^{-1}	Fish scale (Glass column: flow rate: 1 ml/min, bed height: 12 cm and dilution: 50 %)	6	n.i.	89.5	n.i.	Das *et al.* (2014)
Acid mine drainage (Parys Mountain, UK)	[REE] = 36-200 μg.L^{-1}	Nanoscale zerovalent iron particles (4 g.L^{-1})	2.5	30	> 99.9	n.i.	Crane and Sapsford (2018)

2.3 RECOVERY POTENTIAL OF REEs FROM AMD AND TREATMENT SLUDGE/RESIDUE

2.3.1 Case studies

As conventional AMD treatments through the neutralization of acidity and (co-)precipitation of metals/REEs immobilize nearly 100 % of REEs and concentrates them by a factor of 10^3 to 10^4 depending on AMD chemistry and treatment (active versus passive), research has recently focused on the recovery of REEs from AMD sludge. To date, a limited number of studies emphasized the potential for REE recovery from AMD and precipitates formed during passive or active treatment of AMD, although these residual materials represent a promising secondary source of REEs.

This section will present three case studies on the potential to recover REEs from AMD treatment sludge/residue: Case Study I, located in Cueva de la Mora mine (Iberian Pyrite Belt, Spain)(Ayora *et al.*, 2016; Ayora *et al.*, 2015); Case Study II, located in La Poderosa mine (Rio Odel Basin, Spain) (Chávez & Gissela, 2017); and Case Study III, located in the Appalachian Basin (USA) (Stewart *et al.*, 2017; Ziemkiewicz *et al.*, 2016).

Case Study I: Passive treatment of AMD from Cueva de la Mora mine and REEs pre-concentration (Ayora et al., 2016; Ayora et al., 2015)

The first case study, located at the Cueva de la Mora mine site (Spain), evaluated the behaviour of REEs during the passive treatment of AMD using two successive columns of DAS-systems (dispersed alkalinity substrate, consisting of wood shavings, as coarse and highly porous materials, and calcite or caustic magnesia, as neutralizing materials for trivalent and bivalent metals removal, respectively) through laboratory and field scale experiments. Laboratory experiments confirmed that 100 % of REEs were removed from the AMD and that no REEs were retained by the Fe-precipitates (schwertmannite and goethite) formed in the calcite column. Most of the REEs were retained on basaluminite precipitates (15-20 %) and on decantation residues (25-40 %) mainly composed of gypsum, fluorite, epsomite and becherite, while only few amounts (5-10 %) were retained on the MgO column. Results from field experiments showed similar REE patterns even if no exhaustive characterization of calcite- and caustic magnesia-based DAS were conducted. The estimated concentrations of REEs and radioactive elements in the AMD sludge were 0.03-8 % for REEs, but only 17 $mg.kg^{-1}$ for U and 4 $mg.kg^{-1}$ for Th. Based on these results, the authors concluded that even if low concentrations of REEs are retained by passive treatment, AMD represents a modest but suitable secondary source of REEs as AMD is expected to persist in this area for at least another 100 years.

Case Study II: Potential to recover REEs from AMD from La Poderosa Mine through precipitation as phosphates (Chávez & Gissela, 2017)

In the second case study, Chávez and Gissela (2017) evaluated the potential to recover REEs from actual AMD produced from an abandoned mine located in the Odiel and Tinto basins (Spain) after pre-concentration of these elements by ion exchange. Two series of experiments were conducted: i) direct precipitation of REEs from AMD in the presence of phosphate and ii) pre-concentration of REEs through ion exchange followed by acid elution and precipitation in the presence of an excess of phosphate (P/REE ratio of 40/1). Results showed a small loss of REEs (< 8 %) during AMD pretreatment for iron removal by oxidation, in the presence of H_2O_2 and precipitation at pH 3.7-3.8, indicating that the sorption of REEs on Fe-oxyhydroxides is not favourable. This observation is in accordance with the results obtained by Ayora *et al.* (2016). Chávez and Gissela (2017) also observed that only 15 % of REEs can be removed by direct precipitation, while the addition of an ion exchange pretreatment (10-60 % of REEs recovered) allowed for the recovery of more than 90 % of REEs from pre-concentrated solution. Therefore, a pre-concentration step could significantly improve the potential of recovering the REEs initially present in AMD by precipitation as phosphates, while direct precipitation is more efficient on REEs concentrated solutions (Chávez & Gissela, 2017).

Case Study III: Active and passive treatment of coal mine drainage (CMD) from the Appalachian Basin (USA) (Stewart et al., 2017; Ziemkiewicz et al., 2016)

Recent studies were performed to evaluate the potential of REE recovery from precipitates produced during active or passive treatment of CMD, located in the Appalachian Basin (USA). Stewart *et al.* (2017) sampled precipitates (n = 22) and CMD (n = 18) from inactive and abandoned coal mines to evaluate the potential for REE pre-concentration from CMD sludge. Their results showed that, at pH values above 6.6, REE concentrations from CMD significantly decreased regardless of the treatment applied (passive versus active), while REE concentrations in precipitates were increased by a factor of 10^3-10^4. Nevertheless, the concentrations of REEs measured in Ca-Mg-rich precipitates (from lime neutralization) and Si-Al-rich precipitates (from limestone drains) were higher than for Fe-precipitates. The authors also observed that acidic CMD represents a better secondary REEs source than circumneutral CMD, due to the higher REE concentrations found in CMD and therefore, in precipitates formed during CMD treatment that produce Ca-rich or Si/Al-rich solids. These results confirmed the observations made by Ziemkiewicz *et al.* (2016) indicating the potential of AMD sludge to concentrate REEs. The factor of concentration was as high as 1×10^3 to 4×10^3, depending on AMD composition and treatment used. Experiments performed in the laboratory showed a complete dissolution of AMD sludge in the presence of H_2SO_4 at a pH of 1 and ambient temperature, indicating the potential for REE recovery from AMD (Ziemkiewicz *et al.*, 2017). REE products were then recovered (90-100 %) from the leachate through solvent extraction using D2EHPA and precipitation as oxalate (100 % recovered) (Ziemkiewicz *et al.*, 2018). Based on these promising results related to the potential recovery of REEs from AMD sludge, a pilot scale has been built to confirm the performances observed at laboratory scale and assess capital and operating costs.

2.3.2 Ongoing research

An alternative option to pre-concentrating REEs from AMD is nanofiltration (NF). López *et al.* (2018) evaluated the performance of both fresh and aged (immerged during 1 month in H_2SO_4 solution at 1 M) NF membrane to reject REEs from AMD. Their results showed that NF270 is an efficient technique to reject more than 98 % of REEs from a synthetic AMD at pH 1. However, the authors demonstrated low chemical resistance of this NF membrane at acidic pH and a decrease in the rejection rates of REEs after one month of exposure to a solution of sulfuric acid. Additional experiments highlighted that polymeric membranes can be more resistant to acidic solution, while allowing satisfactory REE rejections (> 95%) from synthetic AMD (after Fe removal by precipitation) (López *et al.*, 2019). These results showed that a polyamide-based membrane (Desal DL) is more suitable than a sulphonated-based membrane (HydraCoRe 70pHT) to pre-concentrate REEs from synthetic AMD, while recovering sulphuric acid as a permeate. Researches are currently funded by the US Department of Energy (DOE) to improve knowledge on the potential to recover REEs from AMD. Among the numerous projects funded, there are the following: i) the use of ceramic membranes to recover REEs from AMD sludge (“Low-Cost Rare Earth Element (REE) Recovery from Acid Mine Drainage Sludge” by Research Triangle Institute) and ii) the development of a hydrometallurgical process to recover REEs from AMD conventional treatment residue (“At-source Recovery of Rare Earth Elements from Coal Mine Drainage” by West Virginia University Research Corporation) (DOE, 2017).

2.4 CONCLUSION AND RESEARCH NEEDS

Due to the depletion of high-grade ore deposits and increasing demands towards high technology metals (e.g. REE, Co, Li), AMD is considered as new promising secondary source of elements including precious or base metals as well as REEs. A limited amount of research is available about the precipitation of REE from AMD in a perspective of value-added elements recoveries. Actual results showed that passive and active treatments are effective at scavenging REEs from Ca-Mg-rich precipitates (from lime neutralization) and Si-Al-rich precipitates (from limestone drains) by a factor of 10^3 to 10^4, while Fe-precipitates showed poor REE retention. Recent studies emphasized that its complete dissolution can be achieved under acidic conditions, allowing 100 % of REE recovery from AMD treatment sludge. However, the main limitation in REE recovery from AMD treatment sludge is the complex separation of REEs from undesirable and more reactive metals such as Fe and Al.

Based on previous studies, research needs should mainly be focused on: i) the identification of AMD containing satisfactory REE concentrations produced from Canadian mine waste; ii) the development of effective and low-cost hydrometallurgical processes to pre-concentrate REEs from AMD, recover these elements from sludge/residue and produce high-purity REEs; iii) evaluate the behaviour of radioactive elements (U and Th) during AMD treatment and in radioactive sludge.

3 RECOVERY OF REES FROM BAUXITE RESIDUE (BR)

3.1 CONTEXT

Bauxite is a lateritic rock characterized by a high alumina content (Al_2O_3). It contains 30 to 50 % of alumina and is the main ore used to produce aluminum (Binnemans *et al.*, 2015). The most common process for the production of aluminum from bauxite is the Bayer process. In this process, bauxite is digested in a concentrated solution of sodium hydroxide at a temperature between 150 and 200 °C in an autoclave at pressures of up to 40 atm (Binnemans *et al.*, 2015). Under these conditions, alumina is transformed into aluminum hydroxide, which is soluble in NaOH solution, due to the amphoteric nature of aluminum, while the other bauxite compounds do not dissolve (Binnemans *et al.*, 2015). The remaining constituents are silica, iron oxides, titanium dioxide, calcium and, in lower amounts, gallium, nickel, vanadium, niobium, thorium, uranium and REEs (Binnemans *et al.*, 2013b). The solution is clarified by filtering solid impurities, i.e. bauxite residue (BR) or red mud (pH~12) (Binnemans *et al.*, 2015).

Every year, about 150 million tonnes of BR are produced worldwide (Evans, 2016). However, less than 2 million tonnes are recycled (Evans, 2016). In addition, the former reserves, with a total estimated inventory of 3 to 4 billion tonnes (Zhang, 2018) are not included in any plan of waste management. All these residues are stored in landfills that occupy large areas. Long-term storage can impact the surrounding area by disturbing the air, soil and groundwater quality. For example, a major environmental event took place on October 4, 2010 at the Ajka alumina plant in Hungary as consequence of inappropriate waste management. Following a breach in a dike at a residues disposal site, approximately 600,000 m^3 of BR was released (Borra *et al.*, 2016a). This incident was responsible for the contamination of 40 km^2 of land. Nine people were killed in the tragedy and 122 were seriously hurt. Contamination was observed in the river closest to the site (Khairul *et al.*, 2019). However, this event is not an isolated case since several places worldwide have suffered similar environmental events (Hammond, 2014). Consequently, the management of the large quantities of residues generated each year has become one of the most important environmental challenges in recent years.

BR is an important potential source of iron (up to 60 % of BR) (Binnemans *et al.*, 2013a). Moreover, REEs are not leached during the Bayer process and are concentrated by a factor of two in the BR, compared to the original bauxite (Ochsenkühn-Petropulu *et al.*, 1994). In some BR, Sc (natural abundance of 22 ppm) can reach concentrations above 50 ppm (Borra *et al.*, 2016a). Due to its high price ($ 4,600/kg Sc_2O_3) (Ober, 2018), this element alone represents 95 % of the economic value of all REEs in BR. Consequently, based on the high price of some REEs and on the growing demand of these elements, BR can represent an interesting alternative source of REEs.

The main processes of REE recovery from BR are purely hydrometallurgical or a combination of pyrometallurgical and hydrometallurgical (Wang *et al.*, 2011).

3.2 HYDROMETALLURGICAL PROCESS

A hydrometallurgical process consists of a succession of chemical operations leading to: i) the leaching of one or several targeted elements from the ore/waste, ii) the purification of the solution (removal of impurities) and iii) the extraction of the targeted element(s) from this solution. In the following section, different leaching techniques applied to the recovery of REEs from BR are presented.

3.2.1 Alkaline leaching

Alkaline leaching has been used for the recovery of REEs, more specifically for scandium. This technique is based on the fact that Sc can form soluble compounds with carbonate ions (Pasechnik *et al.*, 2004). For example, in a solution containing 100 g.L^{-1} of $NaHCO_3$, 16.7 g.L^{-1} of Sc_2O_3 are dissolved at 25 °C. The major advantage of this technique is that large amounts of acid are not needed to acidify the highly alkaline BR (pH~12). The main disadvantage is, however, that Sc is the only element recovered. Indeed, the formation of soluble carbonate complexes for other REEs is less efficient than for Sc (Binnemans *et al.*, 2015). In addition, Sc recovery remained low (< 30 %), which may be due to the presence of scandium in iron oxide matrices (Borra *et al.*, 2016a).

3.2.2 Acid leaching

This technique consists of leaching the REEs contained in BR with acids. These acids can be of different types: inorganic acid or organic acid. The most commonly used inorganic acids in this case are nitric acid (HNO_3), hydrochloric acid (HCl) and finally sulfuric acid (H_2SO_4) (Borra *et al.*, 2016a). The organic acids which can be used in this process are citric acid, acetic acid or EDTA (ethylene diaminetetraacetic acid) (Borra *et al.*, 2016a).

A comparative study using different acids (HCl, HNO_3 and H_2SO_4) characterized the effectiveness of leaching BR with HNO_3 under the following conditions: 0.5 M HNO_3, at ambient pressure and temperature. Recovery rates for Sc and Y were of 80 % and 96 % respectively (Ochsenkühn-Petropulu *et al.*, 1996). For the recovery of Sc from BR using HNO_3, a pilot-scale installation has been developed (Ochsenkühn-Petropoulou *et al.*, 2002). The study showed that the large volume of liquid waste generated was the main limitation of this method. Indeed, nitrate ions were adsorbed on the surface of the BR, and consequently a large volume of water was necessary for their recovery (Petrakova *et al.*, 2014). In order to limit the amount of liquid waste generated, other methods were considered.

The formation of silica gel is another problem potentially encountered during acid leaching. The formation of such silica gel induces problem during filtration and therefore during the recovery of REEs. This gel can form when the acid concentration becomes too high. Indeed, the dissolved concentration of silica increases with the concentration of acid. This implies an increase of the saturation index and thus forms a silica gel in the solution. To limit this effect, Rivera *et al.* (2018) attempted to extract REEs by dry digestion (H_2SO_4 and HCl) followed by leaching using water. This two-stage treatment showed a high extraction of REEs and a reduction of silica gel formation. When the generated acid leaching solution was reintroduced into the circulation system (multistage circulation), REE concentrations increased significantly from 6-8 $mg.L^{-1}$ to 20 $mg.L^{-1}$. When using this multistage circulation method, acid consumption remained unchanged and water consumption was greatly reduced at the end of the leaching cycle. By limiting the amount of water consumption, silica gel formation was avoided. Although promising, this method requires further studies, specifically to improve the recovery of REEs.

As mentioned previously, organic acids can also be used for the leaching of REEs. However, their efficiency is lower than for inorganic acids at a given temperature (Borra *et al.*, 2016b; Lenz *et al.*, 2015). When mixed together, the combination of organic and inorganic acids can, however, improve selectivity during Sc recovery (Zhou *et al.*, 2018). Vind *et al.* (2018) showed that Sc was linked to different mineral phases in BR. Hematite (α-Fe_2O_3) contained 55 ± 20 % of the total Sc, goethite (α-FeOOH) represented about 25 ± 20 % of the total Sc and 10 ± 5 % of the total Sc was zircon-related. Thus, during the leaching of the Sc, a co-dissolution of the iron was observed. To limit this effect, Zhou *et al.* (2018) conducted selective leaching of Sc under the following conditions: 40 mL (HCl + H_2O): 10 g BR: 2 g EDTA. The leaching efficiency of Sc and Fe was 79.6 % and 6.12 %, respectively. This technique implies a reduction of acid consumption and helps to improve the separation of iron and scandium.

3.2.3 Bioleaching

The amount of acid used for REEs recovery processes is a major problem. Thus, bioleaching techniques could help to solve this problem. However, the use of bacteria is less suitable given the high pH of the BR and the lack of nutrients necessary to sustain the bacteria population. Fungi can produce organic acids, amino acids or proteins in the presence of an organic medium. These metabolites then form complexes with the metal ions present in the BR (Borra *et al.*, 2016a). The use of the fungus *Aspergillus niger* has shown its effectiveness in recovering metals from BR (Vakilchap *et al.*, 2016). *Aspergillus niger* secreted organic acids allowing leaching of Al, Ti and Fe with leaching efficiencies of 69.8 %, 60 % and 25.4 %, respectively. The fungus *Penicillium tricolor* RM-10 has also been used in the recovery of REEs and radioactive elements (Qu & Lian, 2013). However, recovery of light rare earth elements (LREEs) remains low and co-dissolution of the main elements is unknown (Borra *et al.*, 2016a).

A recent study highlights the bioleaching performance of chemoheterotrophic bacteria on BR (Qu *et al.*, 2019). Here, an acid-generating bacterium has been identified in a BR reservoir, *Acetobacter sp.* The behaviour of this bacterium has been studied and it appears that even an environment not specifically adapted to the bacterum, *Acetobacter sp.*, allowed the bioleaching of BR.

3.2.4 Ionic leaching

Davris *et al.* (2014) used the ionic liquid 1-ethyl-3-methylimidazoliumhydrogensulfate [EMIM HSO4] for hot bauxite residue leaching. The recovery rate of REEs at 190 °C was 60 %. However, all of the Fe and Ti and 35 % of Al were in soluble form. In another study, Davris *et al.* (2016) used bis(trifluoromethylsufonyl)imide [Hbet][Tf2N]. The dissolution of the Sc did not exceed 45 %. The dissolution of iron was < 3 % and that of aluminum was about 30 %. Ca and Na were completely dissolved and a negligible dissolution of silica and titanium was observed. As a consequence of their high price, ionic liquid pickling solutions are often applied to purify/strip the metals dissolved and then reused during the process. Although the recovery rate is lower in this case, selectivity was higher (Nockemann *et al.*, 2006).

Ionic liquids are also used for the extraction of REEs from aqueous solution. Avdibegović *et al.* (2018) used betainium sulfonyl (trifluoromethanesulfonylimide) poly(styrene-co-divinylbenzene) [Hbet-STFSI-PS-DVB] to absorb REEs. In this case, the first step consisted of leaching the BR with a high concentration of H_2SO_4. Fe(III) was removed with ammonia as a pre-treatment step. Indeed, a high concentration of Fe(III) decreased the effectiveness of [Hbet-STFSI-PS-DVB] for the absorption of REEs. The results were compared with those from the selective precipitation extraction with a phosphate solution. The study shows that the recovery of Sc is effective after Fe removal. Selective precipitation is less effective than the method with [Hbet-STFSI-PS-DVB]. However, the purity of the Sc (47 %) can be improved by performing additional cycles.

3.2.5 Purification and recovery of REEs

Solvent extraction is a technique based on the non-miscibility of two phases associated to extract a desired element. An aqueous phase is generally brought into contact with an organic phase containing extractants. The structure of the extractant governs separation and selectivity. Liu and Li (2015) present in their review the different types of organic extractants and their efficiency in the recovery process of metals and REEs from BR. The main disadvantage is the volatility of the organic solvents used. This can make their handling difficult and sometimes dangerous (Zhang, 2018).

At the end of the process, dissolved REEs must be converted to pure REE compounds for use in technological applications. The most common method is the selective precipitation of REEs as oxalate (Bandara *et al.*, 2016). By calcination, these compounds are transformed into oxides. Other methods can also be used such as carbonate or sulfate precipitation for REEs recovery (Xie *et al.*, 2014). After the production of pure compounds, metals are produced by molten electrolysis (Zhang *et al.*, 2019).

3.3 PYROMETALLURGICAL PROCESSES

The pyrometallurgical process is a thermal process used to separate and recover targeted elements. This technique is presented as a pre-treatment of the BR or as a step in the recovery of REEs. The energy cost is the main factor to take into account for such process.

Among the pyrometallurgical processes, reductive melting of BR can be used. Reductive melting is a process used in the manufacture of cast iron during the high-temperature processing of coke and Fe. Since BR contains significant proportions of Fe, this process appears pertinent. In this process, the BR is treated in a blast furnace. However, prior sintering with a reducing agent is necessary to reduce iron oxides and generate pig Fe and Ti-rich slag. The different fusion processes for the recovery of iron in BR are presented by Borra *et al.* (2016a). In this article, the different conditions for the following operations are detailed: melting temperature, flows used during melting (limestone, lime, silica, dolomite, etc.), types of reducers (coal, coke, wood, etc.). REEs from the produced slag can be washed with HNO_3 or HCl given good recovery rates (Borra *et al.*, 2015). In addition, Rivera *et al.* (2019) conducted a study on high-pressure acid leaching of slag to recover REEs. The slags were obtained by reductive fusion. The use of mixtures of coke, lime and silica at 1,500 °C allowed for a good separation of Fe from the slag. Ti and Si were not co-dissolved due to the application of high-pressure acid treatment. The tests were carried out with H_2SO_4 and HCl in order to compare extraction efficiency but also selectivity. Leaching with H_2SO_4 at 150 °C allowed for a good recovery of the scandium (90 % vw.t.) but a low recovery of REEs. The likely formation of $CaSO_4$ hindered the dissolution of the other REEs. Leaching with HCl at 120 °C resulted in a Sc recovery of 80 % w.t. and approximately 95 % w.t. of Y, La and Nd were recovered. However, a strong co-dissolution of Al was observed (> 90 % w.t.). This process seems promising for the separation of Fe, the limitation of co-dissolution of Ti and Si, as well as for the recovery of Sc. However the method still needs to be optimized.

Merging as the first step in the treatment of BR is not the only method. The use of heat can be used at different levels during the extraction process. A patented process for the recovery of REEs has been developed by Orbite Aluminae Inc. (Binnemans *et al.*, 2015). By saturating the leachate with HCl, it is possible to induce the crystallisation of $AlCl_2.6H_2O$. The solid is separated from the solution and converted by calcination into Al_2O_3, with the recovery of gaseous HCl. Following this, the iron chloride formed is hydrolyzed to Fe_2O_3 between 155 and 177 °C. After the removal of Fe_2O_3, the REEs are concentrated in the solution and can be recovered by solvent extraction. Most of the elements present are extracted from the BR, although the use of HCl can be dangerous. Especially under gas form, as it can be highly corrosive.

A sulfation, roasting and water leaching process was also used as a method for recovering REEs. This technique is particularly interesting given its low acid consumption and rapid kinetics (Anawati & Azimi, 2018). Sulfation converts most oxides into their respective sulfates. During the roasting stage, some sulfates are unstable, including iron sulfates. REEs sulfates are, however, stable during this stage and can be recovered. The final step consists of leaching the REEs sulfates with water. Borra *et al.* (2016b) showed that by roasting for one hour at 700 °C with an acid: BR ratio of 1:1, 60 % w.t. of Sc and more than 80 % w.t. of other REEs can be extracted after leaching at room temperature (7 days without agitation or 2 days with agitation). Under these conditions, less than 1 % of Fe and Ti and less than 20 % of Al were dissolved. No dissolution of Si was observed and the sodium was completely dissolved. Following this process, a purification and recovery step will be necessary (Anawati & Azimi, 2018). For this purpose, Onghena *et al.* (2017) used an ionic hydrophobic liquid, [Hbet][Tf2N] extractant. Their studies showed that the sulfation, roasting and water leaching process selectively leached scandium. The use of ascorbic acid also improved the separation of iron and scandium by reducing Fe(III) to Fe(II) during leaching. The multistage leaching with water increased the concentration of Sc and decreased acid consumption. In addition, Sc was selectively extracted using [Hbet][Tf2N]. Co-extracted metal ions were removed from the ionic phase with HCl and purified Sc was removed by stripping with H_2SO_4. Apart from the host elements of the precipitate, including sodium, the purity of the scandium was 98 %.

3.4 CHALLENGES OF THE RECOVERY OF REES FROM BR

Developing an effective management strategy for the large volume of BR produced each year is a big environmental challenge. The recovery of REEs from BR could be a good alternative to address these problems. The methods described above have many advantages, but they have their limits. When developing a process for the recovery of REEs, such limits must be taken into account in order to:

- Develop methods with a good recovery rate and selectivity. Some methods are not selective enough, leading to co-dissolution of Fe, Al, Ni, Ca and Ti.
- Limit the formation of silica gel for better subsequent filtration.
- Study the mineralogy of BR in order to develop and choose appropriate techniques of REEs recovery.
- Limit the amount of residual liquid and/or solid waste during the recovery process.
- Take into account the energy costs associated with pyrometallurgical methods and the chemical costs associated with acid or alkaline leaching.

4 RECOVERY OF REES FROM COAL COMBUSTION PRODUCTS (CCPs)

To date, coal remains one of the most important sources of energy in the world. It currently supplies 37 % of the world's electricity needs (Association, 2019). In Canada, 34 Mt of coal was used for electricity generation in 2016 (NRCan, 2018b). However, coal can also be found in many other fields: metallurgical processes, activated carbon manufacturing, chemicals and industrial products, etc. In addition, coal contains a large number of critical elements such as Ge, Ga, U, V, Se, REEs, Sc, Y, Nb, Au, the elements of platinum group and Re. Given the growing demand for many critical elements, it could become a secondary source for the production of these elements (Dai & Finkelman, 2018). Many recent studies have focused on the recovery of REEs from coal and coal co-products (Dai & Finkelman, 2018; Franus *et al.*, 2015; Huang *et al.*, 2019; King *et al.*, 2018; Mondal *et al.*, 2019; Rozelle *et al.*, 2016; Wang *et al.*, 2019). Coal and coal combustion products (CCPs) appear to be a promising source of REEs. While coal is found in many uses, CCPs are rarely used and are considered waste (Franus *et al.*, 2015). Recent studies therefore focus on the recovery of REEs from CCPs. These CCPs are: fly ash, bottom ash, boiler slag, flue gas desulphurization gypsum and other types of materials such as fluidized bed combustion ash, cenospheres and scrubber residues (Association, 2019). Global coal ash contains an average of 485 ppm total rare earth oxides (TREO) (Ketris & Yudovich, 2009). Some coal ashes may contain REE concentrations of up to about 1000 ppm (Seredin & Dai, 2012). This product would therefore be a promising source of REEs. In order to develop effective technologies for the recovery of REEs, it is important to understand the distribution of REEs in CCPs. Kolker *et al.* (2017), using an SHRIMP-RG ion microprobe, confirmed that REEs, present in coal fly ash, were mainly found in aluminosilicate glasses. However, the composition of CCPs varies from one source to another (Seredin & Dai, 2012). For example, the distribution model may change between bottom ash and fly ash (Wang *et al.*, 2019). Thus, the recovery methods will have to be adapted according to the distribution of REEs according to CCP types. Studies on the recovery of REEs from CCPs generally focus on coal fly ash. This fine grain material is easily available in thermal power plants but, rarely used (Lanzerstorfer, 2018). The fineness of the grains induces limiting energy costs since no grinding step is necessary before leaching treatment (Lanzerstorfer, 2018). In the following section, various studies on the recovery of REEs from coal ash are presented.

4.1 PHYSICAL SEPARATION PROCESSES

Physical separation processes are often used as a pre-treatment method. These methods are intended to separate a high REE-containing fraction from a low REE-containing fraction and reduce the amount of material to be transported to the processing plant. Dai *et al.* (2014) observed that the finer fraction (<25 µm) was more enriched in REE. Blissett *et al.* (2014) have therefore developed a method for pre-treating fly ash. This process was done by a flotation, magnetic separation and hydrocyclone classification step. But this wet process is quite complex and requires a separate treatment unit. Lanzerstorfer (2018) then proposed a process for air classification of REE-enriched fractions from fly ash. Unlike other processes for the production of REE-enriched fractions, this process is dry and simple to carry out on an industrial scale. Lanzerstorfer (2018) showed that REEs were enriched in the finest fractions by a factor of 1.05 to 1.65, but also that the degree of enrichment and supply depended on the type of REEs. HREEs were generally concentrated in fine fractions, while LREEs were concentrated in coarse ones.

Suganal (2018) studied coal ash from the Pilimanan pilot plant. The REE content in this material is 77.85 ppm. In this study, the authors attempted to increase the concentration of REEs by using shaking table and magnetic separator methods. The shaking table showed that REE concentrations increased up to twice. However, the results for the magnetic separation technique were not significant. Lin *et al.* (2017) compared different physical separation methods (particle size, magnetic and density separation) to evaluate their effectiveness on different CCP samples. The results highlighted that the density separation method showed the highest REE enrichment rates and REE enrichment varied according to the type of CCP.

Separation processes can also be useful in the recovery of other elements during the REE recovery process. Indian fly ashes showed high concentrations of iron oxides, the presence of which poses a problem in the hydrometallurgical processes used for the recovery of REEs. Thus Nugroho *et al.* (2019) attempted to recover iron from an optimized physical separation process. The increase in magnetic field intensity and the decrease in grain size of coal fly ash in a wet separation increased the recovery of magnetic iron (25.89 %). Finally, Phuoc and Wang (2017) worked on a new method for separating and physically recovering REEs from coal ash using a laser beam. This technique reduced the consumption of acid or toxic solvents during leaching (Dai & Finkelman, 2018).

To summarize, these processes helped to: i) concentrate the REEs in a specific fraction, thus limiting the quantity of material to be treated; ii) limit the problems related to the presence of iron oxides in hydrometallurgical processes for the recovery of REEs, and iii) reduce the quantity of acid used during the recovery of REEs. Although the physical separation and/or recovery techniques presented here are promising, they are generally only one step in the recovery of REEs.

4.2 LEACHING PROCESSES

4.2.1 Acid and alkaline leaching

Acid leaching is often used in the extraction of REEs from ores (Jha *et al.*, 2016; Sinha *et al.*, 2016). In addition, this technique is also used for the recovery of elements from coal ash (Kashiwakura *et al.*, 2013; Meawad *et al.*, 2010). However, the significant presence of impurities such as Al and Si may limit the effectiveness of the method (Hood *et al.*, 2017; King *et al.*, 2018). Fly ash and bottom ash are mainly amorphous glass (aluminosilicate glass) (Dai & Finkelman, 2018; Hood *et al.*, 2017; Wang *et al.*, 2019) and the REEs present in these ashes are mainly associated with this amorphous glass (Wang *et al.*, 2019). Thus, a simple leaching with HCl does not completely dissolve the REEs. In view of this, alternative methods have been found. Wang *et al.* (2019) noted that 70 % of the REEs contained in these fly ashes were found in amorphous glass. In order to allow the dissolution of the REEs and to facilitate their extraction, a successive leaching with NaOH and HCl was applied. NaOH precipitated the REE hydroxides and made the silica soluble. The following two equations explain these mechanisms:

$6\ NaOH + REEs_2O_3 \rightarrow 2\ REEs(OH)_3 \downarrow + 3Na_2O$ *Eq.1*

$NaOH + SiO_2 \rightarrow NaHSiO_3$ *Eq.2*

As a result, the ashes were leached with HCl. This acid leaching dissolved the REE hydroxides and generated soluble REE chlorides via the following reaction:

$3\ HCl + REEs(OH)_3 \rightarrow ReCl_3 + 3\ H_2O$ *Eq.3*

Under the optimal conditions determined by Wang *et al.* (2019), leaching with NaOH removed 41.10 % of the silica and after acid leaching, 88.15% of the REEs were recovered, thus demonstrating the effectiveness of the combination of alkaline and acid leaching. In view of the presence of other critical elements in fly ash, Wang *et al.* (2019) developed a process for the recovery of REEs, Al and Ga. The following figure shows the process diagram.

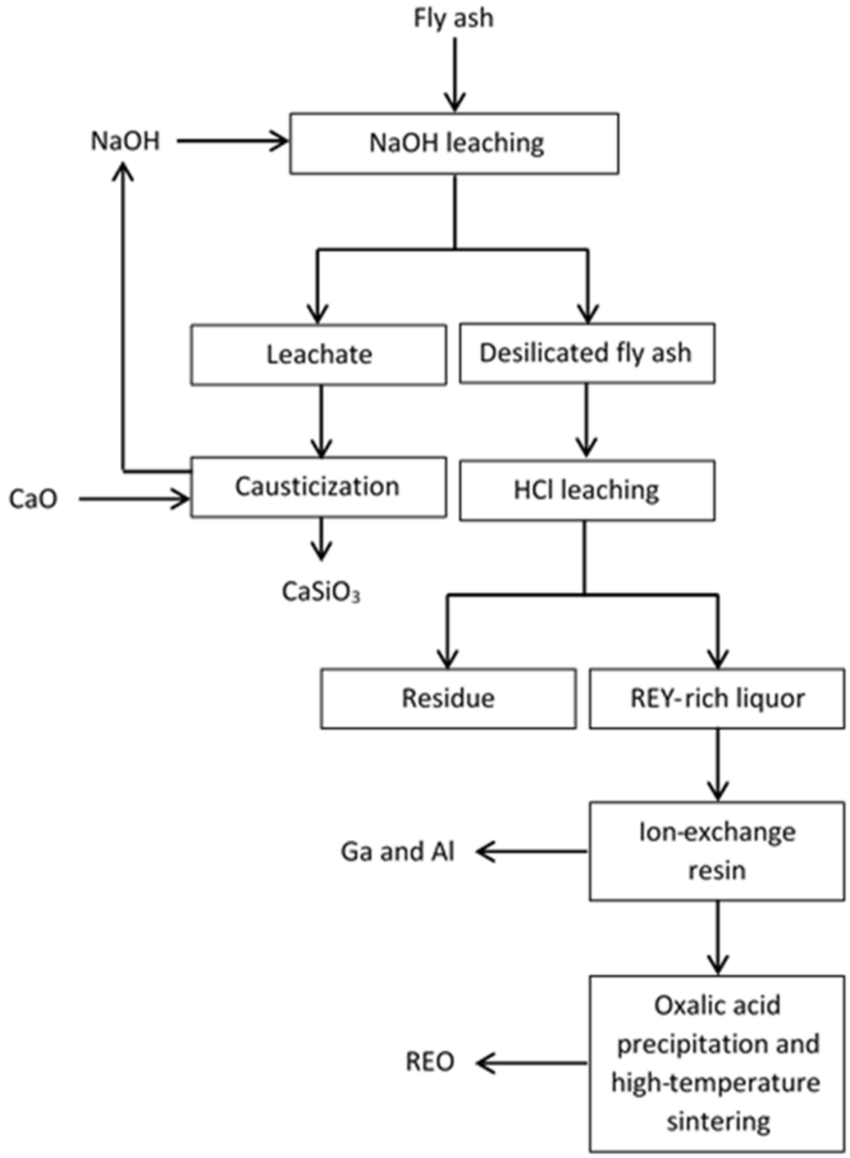

Figure 1. *Flow diagram of REY (REEs+Y) extraction from fly ash by Wang et al. (2019).*

The same processing method may be more or less effective depending on the type of CCP studied. King *et al.* (2018) worked on three CCPs from the Appalachians, Illinois and Powder River Basin (USA). The authors applied the alkaline and acid leaching (NaOH-HCl) method to these three samples. They observed that for the sample from the Powder River Basin, a high amount of calcium was present compared to the other two samples. During HCl leaching of samples from the Powder River Basin, the recovery rate of REEs was high (nearly 100 % of the TREE content). In contrast, for samples from Illinois and Appalachia, REEs recovery rates were less than 40 %. For the latter, the alkaline leaching step before acid leaching is necessary to improve the recovery rate of REEs. The recovery of REEs from Appalachian CCPs after NaOH-HCl leaching resulted in the recovery of 85 % of REEs. During the optimization of the method, King *et al.* (2018) tested different NaOH concentrations. They concluded that the positive variation in NaOH concentration improved the recovery of REEs but that it could also affect the dissolution of glass.

Although, the combination of alkaline and acid leaching effectively recovered the REEs present in CCPs, this method is not necessary appropriate if the CCPs have a high alkali metal content. A simple acid leaching method would recover the majority of REEs. A recovery of REEs, Al and Ge would increase the profitability of the method. However, this method requires large quantities of reagents which seriously impact the cost and consequently the potential of the method.

4.2.2 Bioleaching

Bioleaching is based on the microbial dissolution of compounds. Bioleaching has low chemical and energy costs and reduces the amount of waste generated, making it a very valuable technique. The use of *Aspergillus ficuum* at 30 °C and *Pseudomonas aeruginosa* at 35 °C on Egyptian monazite leached 75.4 % and 63.5 % of REEs (Muravyov *et al.*, 2015). The use of *Aspergillus niger* has resulted in the leaching of Cr, Ni, As and Pb from Chinese fly ash (Jadhav & Hocheng, 2015). In Russia, the incubation of coal ash with an acidophilic *chemilithrophic* microbial community recovered 52.0 %, 52.6 % and 59.5 % of Se, Y and La, respectively (Muravyov *et al.*, 2015). A more recent study by Park and Liang (2019) on the bioleaching of trace elements and REEs from coal fly ash using three strains; *Phanerochaete chrysosporium*, *Candida bombicola*, and *Cryptococcus curvatus*. The advantage of these microorganisms is that they tolerate low pH values between 3 and 4. *Candida bombicola* had the best leaching rates: 80.9 % for As, 79.5 % for Mo, 67.7 % for Yb and 64.6 % for Er. Thus the bioleaching of coal ashes is feasible using these strains and *Candida bombicola* is of particular interest.

Studies on bioleaching for the recovery of REEs from fly ash remain limited. In view of the advantages of this technique, additional work is needed.

4.2.3 Ionic extraction

In view of the energy demand of separation processes and the technical challenges they generate when recovering REEs from CCPs, ionic extraction is a potential solution. Rozelle *et al.* (2016) compared ammonium sulfate, an ionic liquid and a eutectic solvent in order to evaluate their effectiveness in extracting REEs from CCPs. Ammonium sulfate has been studied for the production of REEs, while 1-butyl-

3-methylimidazolium chloride, an ionic liquid, has been used with coal products (Painter *et al.*, 2010). Deep eutectic liquid is a mixture of urea and choline chloride and has the advantage of limiting the solubility of silicon and aluminum oxides, thus allowing for the potentially selective recovery of REEs (Nockemann *et al.*, 2006; Rozelle *et al.*, 2016). Recovery rates of up to 89 % REEs have been achieved using ammonium sulfate (Rozelle *et al.*, 2016). However, the use of an ionic liquids or eutectic solvents did not indicate an advantage over ammonium sulfate in the recovery of REEs.

Huang *et al.* (2019) worked on the recovery of REEs from CCPs (China) using various ionic liquids. The REE content from these CCPs was 1350 ppm. The ionic liquids used were: $[N_{1888}]Cl$, $[P_{6,6,6,6,14}]Cl$, $[P_{6,6,6,6,14}]$[SOPAA] and $[P_{6,6,6,6,14}]$. 4 g of CCPs was mixed with different diluted acids (12 mol.L^{-1} HCl, 16 mol.L^{-1} HNO_3, 23 mol.L^{-1} HF). The mixtures were then heated to 200 °C for 9 hours, cooled with air and filtered. The leachate was then put into contact with the ionic liquids for recovery and purification. The recovery rate for REEs was 37.4 %. Once the solution was purified, the REEs were precipitated using oxalic acid. La, Ce, Y, Er, Tm, Yb, and Lu could be detected in the precipitates, which showed the effectiveness of this method. As few studies have been carried out using this method of recovery of REEs from CCPs, further work is still needed to improve extraction efficiency.

4.3 PYROMETALLURGICAL PROCESSES

A heating step during leaching processes could improve REE recovery rates. As mentioned above, REEs are mainly found in aluminosilicate glass. Thus, a simple acid leaching may not be very effective in this case. To improve the extraction of REEs from coal ash, Taggart *et al.* (2018) tested a roasting method. This method consists of adding an additive with the coal ashes and roasting the mixture. Here, different chemical additives were tested: Na_2O_2, NaOH, CaO, Na_2CO_3, $CaSO_4$ and $(NH_4)_2SO_4$. The ashes studied were from American, Illinois, Appalachian and Powder River basins. The use of NaOH in the roasting process has shown good extraction of REEs (about 90 % of the TREE content). However, a too large increase in pH reduced the recovery rate of REEs. For ash from the Powder River Basin, the REEs recovery rate was approximately 100 % regardless of the type of additive added and the ratio of additive to ash used. Ash from this basin contains high concentrations of calcium, so a simple acid leaching is sufficient to extract REEs. However, for the other samples from the Illinois and Appalachian basins, the optimal conditions are: alkaline roasting with a NaOH:ash ratio of 1:1 followed by acid leaching with 1-2 mol.L^{-1} of HNO_3. Alkaline roasting would therefore increase the recovery efficiency of REEs from these ashes.

Another recent study highlights the leaching of REEs in a coal-bearing strata-hosted rare metal deposit in southwest China. Zou *et al.* (2017) used an alkaline water immersion sintering leaching technique (ASAWAL process) and developed the following optimal conditions:

- Calcination of the samples at 860 °C for 30 minutes with a sample:sintering agent ratio of 1:1.5;
- Immersion of the sintered sample at 90 °C for 2 hours with 150 mL of hot water;
- Leaching with 4 mol. L^{-1} of HCl at 40 °C for 2 hours at a ratio L:S of 20: 1 (mL:g).

Under these conditions, the total leaching of Ga and REEs reached 93.37 % and 85.81 %, respectively. However, Nd was barely extracted (< 1 %). This technique allowed most of the REEs to be recovered, but further extraction would potentially allow more REEs to be recovered.

4.4 OTHER METHODS

Another method to recover REEs from CCPs is called Chelok® (Laurino, 2016). In 2009, Periodic Products developed and patented nontoxic, water-insoluble polymers to recover REEs. The Chelok® method is followed in several steps: extraction, polymerization and filtration. The challenges encountered when extracting REEs from CCPs are: 1) the extraction efficiency depends on the concentration of other elements such as calcium, silicon and aluminum oxides; 2) depending on the type of CCPs, extraction techniques will be more or less efficient; 3) the distribution of REEs, in fact REEs can be found in a glass matrix and a simple leaching may not be sufficient; and finally 4) the concentration of REEs may limit the extraction and profitability of the method. By using the Chelok® method, some of these challenges can be addressed. Indeed, the method has already been used for the recovery of REEs from phosphate waste. The semi-optimized yields of this method were equal to or higher than those obtained when extracting REEs from raw ore. The advantages of this technique are:

- The polymers used have a fast reaction kinetics and can bind up to their metal weights;
- The polymers have a binding capacity comparable to more expensive homogeneous water-soluble absorbents;
- The polymers can be adapted to a wide variety of metal species;
- The separation of polymers from the aqueous medium can be done by simple gravity filtration;
- The adsorption reaction can be performed over a wide pH range, between 1.5 and 14;
- High concentrations of sodium, calcium or silicon potentially present do not alter the adsorption reaction.

This technique is still in the experimental stage and further optimization of the following parameters could improve the efficiency of this technology: particle size, composition of the pregnant leach solution, contact time between the material and the extraction solution, etc. However, this technique remains promising both in terms of its effectiveness and profitability (Laurino, 2016).

4.5 CHALLENGES OF RECOVERY REEs FROM CCPs

Coal combustion products have proven to be an interesting source of REEs and many studies have been carried out on this subject. The techniques for recovering REEs depended on the type of CCPs studied but also on the mineralogy of each CCPs. Thus, understanding the distribution of critical elements in CCPs is necessary to develop an appropriate recovery technique. Even if some CCPs contain high levels of REEs, this is not the case for all CCPs. Thus, co-recovery techniques may be interesting to make this process more economically profitable. In order to improve the recovery rate of REEs, preliminary steps may also be required, such as alkaline leaching, heating, physical separation, etc. However, for these types of methods, significant energy and chemical costs may be associated. From an environmental point of view, chemical spills, generation of toxic secondary waste, dust generation during the transport of CCPs, etc., may be linked to this type of pre-treatment. In order to obtain an efficient and cost-effective method, some authors focused on bioleaching or the use of polymers. However, these promising techniques need to be optimized. At present, neither of these methods has been commercially established to recover REEs from CCPs yet. However, in light of recent studies and the growing need for REEs, we have every reason to believe that future work will provide an efficient and cost-effective method.

5 RECOVERY OF REEs FROM PHOSPHOGYPSUM

5.1 CONTEXT

Phosphogypsum (PG) is a byproduct generated from the production of phosphoric acid from phosphate ore and is mainly used to produce phosphate fertilizers for agriculture. Phosphate ore originates from either sedimentary phosphate rock (85-90 %) containing mainly amorphous forms of apatite, such as francolite or from igneous phosphate rock (10-15 %) containing mainly crystalline fluorapatite (Binnemans *et al.*, 2015). Depending on the type of phosphate rock, various amounts of other trace elements, including cadmium, nickel, thorium, uranium and REEs are also present. Sedimentary phosphate rock contains 0.01-0.1 wt % REE, whereas igneous phosphate rock contains 1-2 wt % REE (Binnemans *et al.*, 2015; Habashi, 1985; Wu *et al.*, 2018), with cerium, lanthanum and neodymium accounting for up to 80 % of the TREE content of phosphate rock.

Phosphate rock can be decomposed using various mineral acids, such as H_2SO_4, HNO_3, HCl and H_3PO_4, but here we will focus on the H_2SO_4 process which is the process the most widely used (Wu *et al.*, 2018). The digestion of phosphate rock (fluorapatite, $Ca_5(PO_4)_3F$) with sulfuric acid (H_2SO_4) generates phosphoric acid (H_3PO_4), large amounts of PG ($CaSO_4{\cdot}2H_2O$) and small amounts of silica, fluoride compounds and unreacted phosphate rock according to the following exothermic reaction (Binnemans *et al.*, 2015; Cánovas *et al.*, 2019; Wu *et al.*, 2018):

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF + heat$$

The morphology and composition of PG generated varies depending on the nature and origin of the phosphate rock, the type of phosphoric acid production process used and plant operation parameters, but generally consists of silt-sized gypsum crystals which are softly aggregated (Canovas *et al.*, 2018). The main components of PG are calcium and sulfate (>90 %), in addition to minor elements including Si, Na, Mg, Al, K, P and other trace elements. Most of REEs originally present in the phosphate rock (70-85 %) are transferred to the PG (Binnemans *et al.*, 2015; Habashi, 1985), resulting in a PG REE content of 0.01 to 0.40 wt % (Habashi, 1985; Walawalkar *et al.*, 2016a; Wu *et al.*, 2018). See Figure 2 for an example of a production flow sheet presented by Wu et al. (2018) for the production of phosphoric acid and the partitioning of REEs. Some of the REEs present in PG are thought to replace Ca ions in the gypsum crystals, whereas the majority are thought to be contained in phosphate and fluoride minerals which are easily extracted without the need to destroy the gypsum crystal lattice (Cánovas *et al.*, 2019; Canovas *et al.*, 2018; Rychkov *et al.*, 2018).

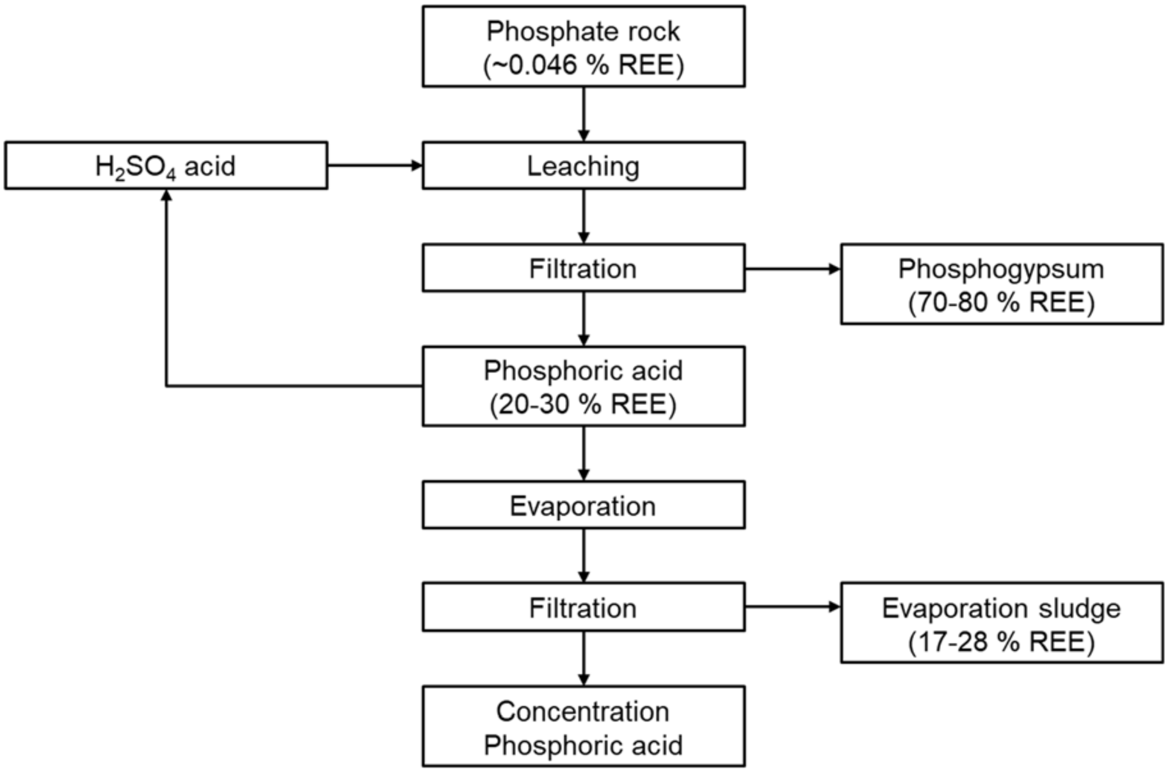

Figure 2. *Phosphoric acid production flowsheet with REE distribution. Modified from (Wu et al., 2018).*

Although the REE content in PG is relatively low, it represents a huge pool of potentially available REEs. According to the US Geological survey's 2019 Mineral Commodity Summary for phosphate rock, 270 million tonnes of phosphate rock was mined globally in 2018 (Jasinski, 2019). Assuming that approximately five tonnes of PG are generated for every tonne of phosphoric acid (expressed as P_2O_5) (El-Didamony *et al.*, 2012; Habashi, 1985) and that more than 95 % of phosphate rock mined is used to manufacture phosphoric acid (Jasinski, 2019), 1.3 billion tonnes of PG was produced globally in 2018 (Canovas *et al.*, 2018). Furthermore, the world consumption of P_2O_5 (contained in products such as phosphoric acid and fertilizers) is expected to increase from 47.0 million tons in 2018 to 50.5 million tons in 2022 (Jasinski, 2019). The feasibility of extracting valuable REEs from these large stockpiles of PG depends on the availability and effectiveness of recovery technologies suited to this type of waste. Such technologies usually involve a leaching step, whereby inorganic acids or organic liquids are used to solubilize the REEs, followed by an extraction step using precipitation, solvent extraction or ion exchange to isolate the REE compounds from the solution.

5.2 LEACHING OF REEs

Three review papers have been published recently describing developments in the leaching of REEs from PG (Binnemans *et al.*, 2015; Canovas *et al.*, 2018; Wu *et al.*, 2018). Most commonly, the leaching of REEs from PG is performed by exposure to inorganic acid solutions or organic liquids (Table 4), where the type and concentration of the leaching solution, the solid to liquid ratio, temperature and reaction time impact the extraction efficiency.

5.2.1 Acid leaching

The most recent example of studies on the H_2SO_4 leaching of REEs from PG is that presented by Rychkov *et al.* (2018). Here PG waste from Russian Kola Peninsula apatite transformation with a REE content of 0.44 wt % was grinded to a particle size of about 8-10 μm to increase its surface area. Leaching experiments using 10-30 % sulfuric acid in combination with ultrasonic impact, to prevent aggregation of the fine PG particles and the addition of a cation-exchange resin directly to leaching solution, to sorb the REE ions in solution and inhibit the formation of REE oxides and double sulfates. The REEs sorbed to the resin were then eluted using an ammonium nitrate solution and precipitated using a solution of ammonium hydrocarbonate as carbonates containing approximately 50 % REEs, for a maximum recovery of 72 % of the REEs initially present in the PG. Work by Lambert et al. (2018) also focused on pretreatment. In this case, microwave irradiation was optimized to enhance the leaching efficiency of REEs from PG derived from sedimentary phosphate rock with a particle size of 71 μm and a REE content of 0.0317 wt %. The optimal process conditions of microwave irradiation at 1,200 W for 15 min and leaching in 1.5 M HCl at a S/L ratio of 1/15 $g.mL^{-1}$ at 85 °C for 60 min, resulted in an extraction efficiency of 99 % for Y, 80 % for Nd (representing LREEs), and 99 % for Dy (representing HREEs). Cánovas *et al.* (2019) compared the use of H_2SO_4 or HNO_3 for the leaching of REEs from samples of PG derived from sedimentary phosphate rock taken from the significant stockpiles (100 Mt covering 1,200 ha) found near the city of Huelva in Spain. Although the highest leaching efficiency (above 80 %) was found when using a 3M HNO_3 solution and reaction time between 4 and 8 hours, this effective leaching also solubilized much of the gypsum and other minor minerals, such as iron oxides, clays, fledspars, halides and phosphates, resulting in high concentrations of impurities in the leachate.

Table 4. *Recent literature on leaching of REE from phosphogypsom. Modified from (Lambert et al., 2018).*

		Operating Conditions					
	Lixiviant	**T (°C)**	**Time (h)**	**L:S ratio**	**REE in PG (wt %)**	**Leaching efficiency (%)**	**References**
Acid leaching	1.5 M HNO_3	80	0.33	8	0.020	57	Walawalkar *et al.* (2016b)
	1.5 M HCl	80	0.33	8	0.020	51	
	1.5 M H_2SO_4	80	0.33	8	0.020	23	
	36 % HNO_3	72	1	4	0.042	58	Al-Thyabat and Zhang (2015)
	90 % H_2SO_4 + 10 % H_3PO_4	72	1	6.7	0.034	49	
	10 % H_2SO_4	60	1-2	1.3	0.022	50	Hammas-Nasri *et al.* (2016)
	5 % H_2SO_4	50	2	7	0.022	52	Liang *et al.* (2017)
	10-30 % H_2SO_4 + Grinding, Ultrasonic Activation and Resin Sorption	50	2	7.5	0.44	72	Rychkov *et al.* (2018)
	3 M HNO_3	25	8	30	0.035	85	Cánovas *et al.* (2019)
	1.5 M HCl + microwave irradiation	85	1	15	0.032	Y: 99% Nd: 80% Dy: 99%	Lambert *et al.* (2018)
Organic leaching	0.7-0.9 M TBP-TOPO	55	2	1	0.040	70	El-Didamony *et al.* (2013)
	0.5 M Na_2CO_3 (hot) followed by (0.7-0.9 M) TBP-TOPO	55	2	1	0.040	80	
Bioleaching	Spent medium from *Gluconobacter oxydans* (220 mM gluconic acid)	25	24	50	1.3	61	Antonick *et al.* (2019)

5.2.2 *Organic leaching*

Phosphogypsum is also identified as a technologically enhanced naturally occurring radioactive material (TENORM) containing radionuclides from the ^{238}U and ^{232}Th decay series (El-Didamony *et al.*, 2012). Methods developed by El-Didamony *et al.* (2012; 2013) for the removal of radionuclides (^{226}Ra, ^{210}Pb, ^{238}U, ^{40}K) from PG derived from Sebaiya phosphate rock by leaching with organic extractants were also found to remove REEs. The authors removed 80 % of the REEs from the PG using a tributyl phosphate-trioctylphosphine (0.7-0.9 TBP-TOPO) mixture in kerosene following a hot wash with Na_2CO_3 to first decompose any insoluble compounds that are not extracted by the organic solution. The leaching of REEs from PG with organic solvents is referred to as "solvometallurigal processing" by Binnemans *et al.* (2015) as opposed to hydrometallurgical processing. The advantages of such solvometallurgical processing is a high selectivity for metal recovery, a reduced consumption of acids, a reduction in the volumes of the leaching solutions (Binnemans *et al.*, 2015; Canovas *et al.*, 2018). The recycling of process solutions may provide an energy-efficient, cost-effective and environmentally friendly solution to the use of large volumes of costly and sometimes harmful organic solvents and extractants.

5.2.3 *Bioleaching*

Another alternative leaching method involves direct bioleaching and the use of a biologically produced lixiviant. Although these processes are relatively slow, they occur at lower temperatures and pressures and do not require the use of aggressive reagents, compared to hydrometallurgical processes (Fathollahzadeh *et al.*, 2019). Bioleaching has been used to extract REEs from other types of secondary sources (e.g. bauxite residue, waste electrical and electronic equipment (WEEE) and cracking catalyst (Fathollahzadeh *et al.*, 2019). However, little information is available in the literature on the bioleaching of PG waste specifically. A study by Antonick *et al.* (2019), examined the ability of a gluconic acid dominated biolixiviant to extract REEs from synthetic PG. They found that although the biolixiviant was more effective at leaching REEs than a commercial gluconic acid, it did not perform as well as H_2SO_4 acid. The authors suggest that further tests on industrially sourced PG, in addition to studies of the costs and environmental impacts associated, is needed to decide if the biolixiviant is indeed a better choice for leaching REEs from PG waste.

5.3 RECOVERY METHODS

Most of the available literature on the recovery of REEs from PG focuses on the leaching of REEs. The subsequent recovery of REEs from the leachate is generally achieved using the same separation and purification methods developed for primary sources. Because a mixture of REEs is leached into solution along with many other elements, additional separation and purification, such as precipitation, solvent extraction, ion exchange methods and solid phase extraction are needed to produce REEs in a suitable form and purity for market. Ion exchange involves the adsorption of REE ions from the solution onto an exchanger, which is often selective for specific REEs, followed by a desorption of the REE ions during an elution step (Krishnamurthy & Gupta, 2016). Ion exchange methods are highly selective, but costly and therefore, generally reserved for the production of extremely pure materials. Solvent extraction is also highly selective, but has the advantage of being fast, continuous and cost-effective for large volumes of leachate. For these reasons, it is the most commonly used commercial method to separate and purify REEs from industrial acidic solutions (Krishnamurthy & Gupta, 2016). First, REEs are separated from impurities in the leachate, often using the organophosphorus acid HDEPH, followed by precipitation or further solvent separation into groups of REEs. A new area of study appears to be the development of solid-phase extraction. Hu *et al.* (2018) present recent advances in the use of solid phase extraction and, in particular, the use of nanoporous materials such as mesoporous silica and carbon-based sorbents. They highlight the high enrichment factor, rapid adsorption kinetics, reduced solvent consumption and minimized waste generation when using solid-phase extraction to separate and purify REEs in the context of recovery from secondary sources.

6 RECOVERY OF REES FROM URANIUM MINING ACTIVITIES

6.1 CANADIAN CONTEXT

Canada is one of the world's largest producers of uranium, where all the current operating mines and mills can be found in the province of Saskatchewan (NRCan, 2018a). Uranium mining and milling waste is generally stored in tailings management facilities near mines and mills. Figure 3 below shows the locations of operating, closed and decommissioned waste sites in Canada. The total amount of uranium mine and mill tailings in Canada as of the end of 2016 is 218 million tonnes, including 17 million tonnes from currently operating sites and 201 million tonnes from closed or decommissioned sites (NRCan, 2018a).

Figure 3. *Locations of operating, closed and decommissioned uranium mining and milling waste sites in Canada. Modified from (NRCan, 2018a).*

Canadian uranium deposits are also enriched in REEs, with an average rare earth oxide (REO) content of 0.26±0.20 % (NRCan, 2017). The uranium deposits of the Athabasca Basin in Saskatchewan have a higher REO content of 0.41±0.21 % and are particularly enriched in the high-value HREE, with a relative proportion of HREEs to total REEs of 0.73±0.145. The tailings generated from the Athabasca Basin were therefore identified as the best prospect for the recovery of REEs in Canada from a secondary source (NRCan, 2017).

6.2 RECOVERY OF REES FROM URANIUM MINING AND MILLING

Despite the large amount of tailings generated, uranium mine tailings as a secondary source of REEs has been little studied. However, a few studies have investigated the recovery of REEs from uranium mining and leaching process solutions.

Researchers at the Saskatchewan Research Council have recently been working on recovering REEs from the uranium solvent extraction raffinate generated from the milling process (Lopez-Pacheco, 2017). Using a pre-removal of Al and Fe via neutralization, they use solvent extraction to recover up to 90 % of the REEs present in the initial raffinate. Next, the REEs are separated into heavy and light rare earths and finally into individual high-purity (> 90 %) REEs using subsequent solvent extraction stages. The developed technology is to be tested at the full-pilot scale in the future.

The recovery of REEs as a by-product of the extraction of uranium ore at Denison Mines, Elliot Lake in Ontario, Canada is referenced by Jackson and Christiansen (1993), Edwards and Oliver (2000) and Krishnamurthy and Gupta (2016). First, uranium is removed from the sulfuric acid leachate by ion exchange, leaving a solution containing a considerable amount of REEs. The pH of the uranium-free solution is then increased by the addition of lime, filtered, and acidified with H_2SO_4 to redissolve the REEs. Fe, Al and Th are filtered off as solids and the remaining REEs in solution are precipitated with ammonia gas to produce a 12-30 % total REO concentrate.

REEs have also been recovered from the process solutions at Denison Mine at Elliot Lake by solvent extraction using HDEHP (Krishnamurthy & Gupta, 2016). Following the recovery of uranium, the solution is oxidized and neutralized to precipitate and remove iron. The solution is then acidified with sulfuric acid and 10-20 % of the commonly used organophosphoric acid, HDEHP, in kerosene is added to extract the REEs into the organic phase. The solvent is then stripped with nitric acid to remove thorium and any remaining uranium. The REEs are then precipitated with ammonia gas to produce a concentrate containing 60-70 % REO.

The separation of REEs from uranium mining solutions by ion-exchange appears to give the best recoveries. For example, Shokobayev *et al.* (2015) describe the recovery of REE from in-situ leaching (ISL) of uranium process solutions in Kazakhstan by ion-exchange. The authors reported a recovery of 75-90 % TREE when ammonium nitrate was used for desorption. High concentrations of Al and Fe pose a challenge to the effective separation of REEs from the uranium barren process solutions. Rychkov *et al.* (2016) were able to successfully separate REEs, Al and Fe using a strongly acidic sulfonated polystyrene cation exchange resin (Purolite C-100) with various percentages of divinylbenzene (DVB) linkages. Using a similar strongly acidic sulfonated cationic exchange resin with DVB, concentrates with 90-99 % REO with less than 1 % total impurities were produced by Mashkovtsev *et al.* (2016).

7 CONCLUSIONS

Due to the increasing demand for REEs and the depletion of high-grade REE ore deposits, AMD, BR, CCPs, as well as phosphorus and uranium mine tailings seem promising secondary sources. These wastes are generated in large quantities and management strategies have to be developed to optimize their re-use for the sustainable exploitation of REEs. This bibliographic study highlights the recent methods used for the recovery of REEs from secondary sources, challenges and future work. AMD is one of the major problems encountered in the mining industry. Although AMD can contain non-negligible concentrations of REEs, only a few studies using co-precipitation and sorption methods have been conducted to recovery of REEs from this potential secondary source. Further studies are therefore needed to target mining wastes containing valuable concentrations of REEs in order to reduce the costs of extraction, to increase the effectiveness of methods and to limit the environmental impacts linked to the presence of harmful elements.

For the recovery of REEs from BR, hydrometallurgical and/or pyrometallurgical processes are generally employed, but the selectivity and efficiency of these methods, however, remain significant challenges. To determine the most suitable method for the particular material, a detailed mineralogical study must first be carried out as Fe, Al, Ni, Ca and Ti may co-dissolve with the REEs during the direct leaching of BR. This effect reduces the purity of the REE solution and increases the processing steps, thus increasing energetic, chemical and operational costs. While a bioleaching process may be a better option to recover REEs from BR in terms of environmental impacts, techno-economic conditions must be evaluated.

Much interest has been focused on the recovery of REEs from CCPs in recent years. Large volumes of CCPs are generated every year and despite the low levels of REEs found in some CCPs, the co-recovery of other elements of interest, such as Al and Ga, could improve the potential profitability of the process. Preliminary steps (magnetic separation, alkaline leaching, heating, etc.) can also be applied to concentrate the REEs and improve their recovery. However, an additional step in the REE recovery protocol would increase the cost. To date, there are no existing commercial methods for the recovery of REEs from CCPs. Consequently, more research is needed to develop valuable and sustainable methods to recover REEs from this abundant waste.

Although the REE content in PG is relatively low, it represents a huge pool of potentially available REEs. The feasibility of extracting valuable REEs from these large stockpiles of PG depends on the availability and effectiveness of recovery technologies suited to this type of waste. Most commonly, the leaching of REEs from PG is performed by exposure to inorganic acid solutions and most recent studies demonstrate the importance of a pre-treatment step, such grinding and microwave activation. Organic extractants are also effective in leaching REEs from PG, but the challenge, however, remains in finding the balance between leaching the maximum amount of REEs from the PG while minimizing the co-leaching of impurities such as Al and Fe. Accounting for the cost, energy efficiency and environmental impacts of acidic and organic extraction methods is also of concern. A potential alternative is the direct bioleaching or use of a biologically produced lixiviant to extract REEs from PG waste. Although these processes are relatively slow, they occur at lower temperatures and pressures and do not require the use of aggressive reagents, compared to hydrometallurgical processes.

Despite the large amount of uranium mining and milling tailings produced in Canada and the relatively high proportion of the more valuable HREEs in some Canadian deposits, very little literature on the recovery of REEs from this secondary source is available. From the available information, highly selective ion exchange and solvent extraction methods appear to be preferred and produce a high purity REE product. More research is, however, needed to develop methods for effectively removing the high concentrations of Al and Fe found in the uranium barren process solutions.

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