



A review of the beneficiation of rare earth element bearing minerals

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ABSTRACT

Rare earth elements (REEs) comprise the fifteen elements of the lanthanide series as well as yttrium, and may be found in over 250 different minerals. These elements are required for many different applications such as high-strength permanent magnets, catalysts for petroleum refining, metal and glass additives and phosphors used in electronic displays. The only REE bearing minerals that have been extracted on a commercial scale are bastnäsite, monazite, and xenotime. These minerals may be beneficiated using gravity, magnetic, electrostatic and flotation separation techniques. Increased demand for the different products manufactured from REE has resulted in a constriction of supply from China, which currently produces 97% of the world's rare earths, via export quotas. Many new rare earth deposits are currently being developed to help meet the demand void created by the Chinese export quotas, however most of these developing deposits include rare earth minerals for which there is limited processing knowledge. This paper examines the separation techniques that are currently employed for rare earth mineral beneficiation and identifies areas in need of further research.

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Contents

1. Introduction	98
2. Currently exploited minerals	99
2.1. Bastnäsite	99
2.2. Monazite	100
2.3. Xenotime	102
2.4. Ion-adsorbed clays	102
2.5. Other rare earth minerals	102
3. Beneficiation unit operations	102
3.1. Gravity separation	102
3.2. Desliming	104
3.3. Magnetic separation	104
3.4. Electrostatic separation	104
3.5. Froth flotation	104
3.5.1. Surface chemistry	105
3.5.2. Bastnäsite flotation	105
3.5.3. Monazite flotation	107
3.6. Beneficiation of other rare earth minerals	108
3.6.1. Gravity and magnetic separation of other rare earth minerals	108
3.6.2. Flotation of other rare earth minerals	109
4. The future of REE processing	111
5. Conclusion	111
5.1. Bastnäsite	112
5.2. Monazite/xenotime	112
5.3. Other REE Minerals	112
Acknowledgements	112
References	112

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1. Introduction

The term rare earth elements (REEs) refers to the fifteen metallic elements of the lanthanide series, coupled with the chemically similar yttrium, and occasionally scandium (Gupta and Krishnamurthy, 1992). These elements are typically split into two sub-groups, the cerium sub-group of “Light” rare earth elements (LREEs) which includes La to Eu and the yttrium sub-group of “Heavy” rare earth elements (HREEs) which include the remaining lanthanide elements, Gd to Lu, as well as yttrium (Gupta and Krishnamurthy, 1992; Trifonov, 1963). Scandium, when it is classified as a rare earth element, is not included in either the LREE or HREE classifications (Gupta and Krishnamurthy, 1992). Multiple grouping configurations have been used in the past, typically when classifying these elements based on varying chemical criteria. However, from the standpoint of rare earth element-bearing mineral exploitation, the sub-groupings listed above are sufficient (Schoeller and Powell, 1955).

The ionic radii of elements in the periodic table generally increase with atomic number, however the rare earth elements exhibit a unique reduction of their ionic radii with increasing atomic number, which is termed the lanthanide contraction (Gupta and Krishnamurthy, 2005; Pradip, 1981). The lanthanide contraction may be explained by the fact that as one traverses the lanthanide series, the increasing charge on the nucleus (associated with increasing atomic number) causes the electron shells of these elements to be pulled closer to the atom's nucleus (Spedding, 1975). This increased attraction is not offset by additional electrons being added, as the additional electrons of the lanthanide series occupy an inner 4f sub-shell that is heavily shielded from neighboring sub-shells (Spedding, 1975).

The ionic radii of the lanthanide $[M]^{3+}$ ions is shown in Fig. 1 along with the ionic radius of the trivalent ions of yttrium and scandium (Gupta and Krishnamurthy, 2005). Their similarity in ionic radii means that the rare earth elements are interchangeable in most minerals and are consequently very difficult to separate (Gupta and Krishnamurthy, 2005). Fig. 1 also helps to illustrate why yttrium is considered to be one of the “heavy” rare earths (on the basis of similar ionic radius and chemical properties) and why scandium, with its much smaller ionic radius, is often excluded from rare earth element groupings (Gupta and Krishnamurthy, 2005).

In spite of their name, and aside from promethium, which does not exist naturally in a stable form, the abundance of rare earth elements in the earth's crust is actually significantly higher than other commonly exploited elements, including the platinum group elements and mercury (Gupta and Krishnamurthy, 1992; Trifonov, 1963). The crustal abundance of the individual rare earth elements is shown in Fig. 2. As a comparison, the crustal abundance of gold and silver are 5×10^{-7} wt.% and 1×10^{-5} wt.% respectively (Trifonov, 1963). The difficulty in rare earth mineral exploitation

is that the rare earth minerals are not commonly found in economic concentrations (Gupta and Krishnamurthy, 2005; Vijayan et al., 1989). Rare earth elements are never found as pure metals, instead they are found in a variety of minerals including silicates, oxides, carbonates, phosphates and halides (Levy, 1924; Vijayan et al., 1989). There are more than 250 rare earth minerals that have been discovered to date, many containing very low concentrations of REE varying from 10 to 300 ppm (Chi et al., 2001; Gupta and Krishnamurthy, 2005; Vijayan et al., 1989; Zhang and Edwards, 2012).

The challenge of the REE supply due to the scarcity of mineral deposits is aggravated by the fact that the elements are never found in an equal or even predictable distribution (Gupta and Krishnamurthy, 1992). The REE crustal abundance, as depicted in Fig. 2, also demonstrates the Oddo-Harkins' rule, which states that elements with even atomic numbers are significantly more prevalent in the earth's crust than their neighbors in the periodic table (Parak, 1973; Trifonov, 1963). The availability of HREE is even further impacted by the fact that the rare earth element distributions of the two most commonly extracted rare earth minerals, bastnäsite and monazite, exhibit lower percentages of the elements samarium to lutetium than would be expected based on the abundance data from Fig. 2 (Gupta and Krishnamurthy, 1992).

The demand for rare earth elements has spiked in recent years due to their increasing usage in numerous high-technology applications, including high strength permanent magnets, phosphors for electronic displays, applications in a variety of renewable energy technologies, and as alloying agents in metals (Crow, 2011; Meyer and Bras, 2011; Preinfalk and Morteani, 1986). Each of these applications requires specific rare earth elements (the lanthanides are not all interchangeable) as can be seen in Table 1. Combining the resultant differing levels of demand for each rare earth element with the crustal abundance variations described above, it can be seen that the task of ensuring a stable mineral supply of these elements presents significant challenges (Meyer and Bras, 2011). For example, magnet and phosphor manufacturers require terbium (Tb) and europium (Eu), two of the least abundant REEs, and will therefore be more affected by REE supply issues than a manufacturer of petroleum refining catalysts requiring lanthanum (La) and cerium (Ce), which are an order of magnitude more abundant.

There are approximately one hundred million tons of proven rare earth oxide reserves in the world, scattered across more than 30 countries (Chen, 2011). However, 97% of the world's supply currently originates in China (Pitts, 2011). Increased development in China has prompted the Chinese government to limit yearly export quotas to approximately 35,000 tons of rare-earth oxides, while non-Chinese yearly demand is expected to reach 80,000 tons by the year 2015 (Chen, 2011; Chi et al., 2001). This constriction of supply is being met by the development of many new rare earth

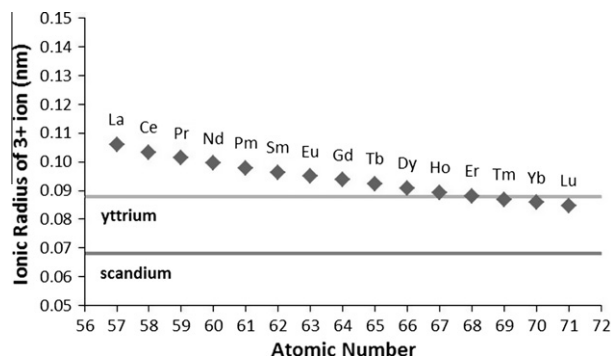


Fig. 1. The Lanthanide Contraction. Adapted from (Gupta and Krishnamurthy, 2005).

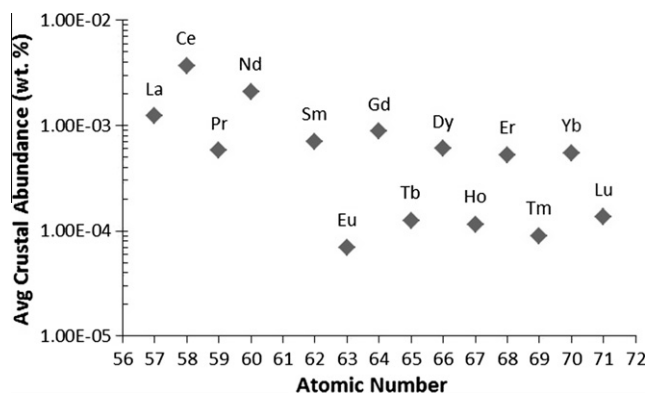


Fig. 2. Crustal abundance of lanthanide elements. Adapted from (Trifonov, 1963).

Table 1

Rare earth element requirements by application. Adapted from (Long et al., 2010).

REE applications	La (%)	Ce (%)	Pr (%)	Nd (%)	Sm (%)	Eu (%)	Gd (%)	Tb (%)	Dy (%)	Y (%)	Other (%)
Magnets			23.4	69.4			2.0	0.2	5.0		
Battery alloys	50.0	33.4	3.3	10.0	3.3						
Metal alloys	26.0	52.0	5.5	16.5							
Auto catalysts	5.0	90.0	2.0	3.0							
Petroleum refining	90.0	10.0									
Polishing compounds	31.5	65.0	3.5								
Glass additives	24.0	66.0	1.0	3.0						2.0	4.0
Phosphors	8.5	11.0				4.9	1.8	4.6		69.2	
Ceramics	17.0	12.0	6.0	12.0						53.0	
Other	19.0	39.0	4.0	15.0	2.0		1.0			19.0	

Percentages are estimates of the total REE content required in a given application.

mining projects which each have their own unique mining and processing challenges (Chen, 2011). The more unique issues facing potential REE producers include (Delaney, 2010):

- A limited availability of technical expertise (outside of China).
- The issues associated with the radioactive wastes produced as by-product of REE extraction.
- The high degree of capital outlay associated with new REE plants (conventional plant costs are close to one billion dollars).
- The lack of a predictable and readily available market price (REE are sold on contract, as per industrial minerals).
- The very short time period during which a new REE mine must start-up to ensure sufficient demand for its products.
- The inconsistent demand levels for individual REE (new production will likely produce an excess supply of cerium and lanthanum, which will have a negative impact on their respective prices unless additional applications for these elements are developed).

The beneficiation of the REE bearing minerals is a subject which requires a great deal of investigation to fill the knowledge gaps surrounding the developing rare earth projects. A number of books exist that present detailed information on the life-cycle of REE from world-wide mineral occurrences through to their numerous end-use applications (Browning, 1908; Eyring, 1964; Ginzburg, 1963; Gupta and Krishnamurthy, 2005; Levy, 1924; Schoeller and Powell, 1955; Trifonov, 1963). Similarly, there are numerous peer-reviewed articles on REE mineralogy as well as the hydrometallurgical processing of REE concentrates (Alex et al., 1998; Bau, 1991; Gromet, 1983; Ring et al., 1993; Schnetzler and Philpotts, 1970; Uda et al., 2000). A common feature amongst these sources is their lack of detailed descriptions of the beneficiation processes required to concentrate REE bearing minerals. The reasons for this gap are most likely threefold (Abeidu, 1972; Cheng et al., 1994; Cuthbertson, 1952; Fuerstenau et al., 1982; Gupta and Krishnamurthy, 1992; Jiake and Xiangyong, 1984; Pavez and Peres, 1994; Pradip, 1981):

- (1) There are only three major REE bearing minerals that are currently exploited commercially (bastnäsite, monazite, and xenotime) excluding ion-adsorbed clays, which currently undergo little or no beneficiation.
- (2) The economically viable occurrences of two of these three minerals (monazite and xenotime) are typically in heavy mineral sand deposits, for which the beneficiation processes are well-developed and require little or no comminution.
- (3) The third REE bearing mineral (bastnäsite) has been economically extracted on a large scale in only two locations worldwide (Mountain Pass, USA and Bayan Obo, China).

A recent review of Chinese REE mineral processing schemes by Zhang and Edwards (2012) demonstrates that even when peer-

reviewed publications from China are added to the literature body on REE beneficiation, opportunities still exist for timely, meaningful research. Recently announced quota restrictions for Chinese REE exports, coupled with increasing demand for these elements, have resulted in REE prices that justify developing a number of new REE deposits (Chen, 2011; Meyer and Bras, 2011). Given the nature of the deposits under development, the existing knowledge base of REE beneficiation must be increased (Chen, 2011).

This paper explores the current physical beneficiation of rare earth element-bearing minerals with regard to the minerals processed, the unit operations employed, some processes currently utilized at the major rare earth mines and processing plants and finally, areas necessitating further research.

2. Currently exploited minerals

Rare-earth bearing minerals can be differentiated into multiple groups based on their rare earth element content. These minerals may be identified as cerium or yttrium type minerals based on whether the distribution of the lanthanides in the mineral is part of the previously described “light” or “heavy” rare earth subgroups (Cesbron, 1986; Trifonov, 1963). Similarly, they may be complex minerals, with a rare earth element distribution that includes all of the lanthanides, or selective minerals, with rare earth element distributions that only include a portion of the lanthanides (Ferron et al., 1991).

A listing of some common rare earth minerals, along with chemical formulas, specific gravities, magnetic characteristics, contents of rare earth oxide (REO), uranium and thorium of these minerals (where this information is known) is shown in Tables 2–6. In these tables bastnäsite, monazite and xenotime are highlighted in bold as they are the three commonly extracted REE bearing minerals.

The trivalent rare earth cations have coordination numbers between 6 and 10 with larger coordination numbers (8–10) corresponding to the larger rare earth cations of the LREE and smaller coordination numbers (6–8) for the smaller HREE cations (Kanazawa and Kamitani, 2006). This is important as the REE with smaller coordination numbers are more likely to be present in oxides such as silicates, resulting in a higher concentration of HREE in these minerals, whereas carbonates are more likely to have increased concentrations of LREE (due to their higher coordination numbers) (Kanazawa and Kamitani, 2006). Table 7 gives examples of the REE distributions found in major deposits of these minerals, as well as the REE distribution of the ion-adsorbed clay deposits of China.

2.1. Bastnäsite

Bastnäsite is a fluorocarbonate mineral with a rare earth content of approximately 70% rare earth oxide that is primarily Ce,

Table 2

Carbonate REE bearing minerals. Adapted from (Anthony et al., 2001; Long et al., 2010; Rosenblum and Brownfield, 1999)

Mineral name	Chemical formula	Density (g/cm ³)	Magnetic properties	Weight percent			Relevant sections
<i>Carbonates</i>			Para/diamagnetic?	REO	ThO ₂	UO ₂	
Ancylite (Ce)	Sr(Ce,La)(CO ₃) ₂ OH·H ₂ O	3.82–4.30	n/a	46–53	0–0.4	0.1	2.1, 3.1, 3.3, 3.5.1, 3.5.2
Ancylite (La)	Sr(La,Ce)(CO ₃) ₂ OH·H ₂ O	3.69	n/a	46–53	0–0.4	0.1	
Bastnäsite (Ce)	(Ce,La)(CO₃)F	4.90–5.20	Paramagnetic	70–74	0–0.3	0.09	
Bastnäsite (La)	(La,Ce)(CO₃)F	n/a	Paramagnetic	70–74	0–0.3	0.09	
Bastnäsite (Y)	Y(CO₃)F	3.90–4.00	Paramagnetic	70–74	0–0.3	0.09	
Calcio-ancylite (Ce)	(Ca,Sr)Ce ₃ (CO ₃) ₄ (OH) ₃ ·H ₂ O	3.95	n/a	60	–	–	3.6.1
Calcio-ancylite (Nd)	Ca(Nd,Ce,Gd,Y) ₃ (CO ₃) ₄ (OH) ₃ ·H ₂ O	4.02	n/a	60	–	–	
Doverite	YCaF(CO ₃) ₂	3.90	n/a	–	–	–	
Parisite (Ce)	Ca(Ce,La) ₂ (CO ₃) ₃ F ₂	4.33	Paramagnetic	59	0–0.5	0–0.3	
Parisite (Nd)	Ca(Nd,Ce) ₂ (CO ₃) ₃ F ₂	4.20–4.50	Paramagnetic	–	–	–	
Synchysite (Ce)	Ca(Ce,La)(CO ₃) ₂ F	3.90	n/a	49–52	1.6	–	3.6.1
Synchysite (Nd)	Ca(Nd,La)(CO ₃) ₂ F	4.14 (calc)	n/a	–	–	–	
Synchysite (Y) (doverite)	Ca(Y,Ce)(CO ₃) ₂ F	3.90	n/a	–	–	–	

Table 3

Halide REE bearing minerals. Adapted from (Anthony et al., 2001; Long et al., 2010; Rosenblum and Brownfield, 1999)

Mineral name	Chemical formula	Density (g/cm ³)	Magnetic properties	Weight percent			Relevant sections
<i>Halides</i>			Para/diamagnetic?	REO	ThO ₂	UO ₂	
Fluocerite (Ce)	(Ce,La)F ₃	5.93	Paramagnetic	–	–	–	3.5.3
Fluocerite (La)	(La,Ce)F ₃	5.93	Paramagnetic	–	–	–	
Fluorite	(Ca,REE)F ₂	3.18–3.56	Diamagnetic	–	–	–	
Gagarinite (Y)	NaCaY(F,Cl) ₆	4.11–4.29	n/a	–	–	–	
Pyrochlore	(Ca,Na,REE) ₂ Nb ₂ O ₆ (OH,F)	4.45–4.90	Paramagnetic	–	–	–	
Yttrifluorite	(Ca,Y)F ₂	n/a	n/a	–	–	–	

Table 4

Oxide REE bearing minerals. Adapted from (Anthony et al., 2001; Long et al., 2010; Rosenblum and Brownfield, 1999)

Mineral name	Chemical formula	Density (g/cm ³)	Magnetic properties	Weight percent			Relevant sections
<i>Oxides</i>			Para/diamagnetic?	REO	ThO ₂	UO ₂	
Anatase	(Ti,REE)O ₂	3.79–3.97	Diamagnetic	–	–	–	3.6.2
Brannerite	(U,Ca,Y,Ce)(Ti,Fe) ₂ O ₆	4.20–5.43	Paramagnetic	–	–	–	
Cerianite (Ce)	(Ce ⁴⁺ ,Th)O ₂	7.20 (syn)	n/a	–	–	–	
Euxenite (Y)	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) ₂ O ₆	5.30–5.90	Paramagnetic	–	–	–	
Fergusonite (Ce)	(Ce,La,Y)NbO ₄	5.45–5.48	Paramagnetic	–	–	–	
Fergusonite (Nd)	(Nd,Ce)(Nb,Ti)O ₄	n/a	Paramagnetic	–	–	–	3.6.1
Fergusonite (Y)	YNbO ₄	5.60–5.80	Paramagnetic	–	–	–	
Loparite (Ce)	(Ce,Na,Ca)(Ti,Nb)O ₃	4.60–4.89	n/a	–	–	–	
Perovskite	(Ca, REE)TiO ₃	3.98–4.26	Diamagnetic	<37	0–2	0–0.05	3.6.1
Samarskite	(REE,Fe ²⁺ ,Fe ³⁺ ,U,Th,Ca)(Nb,Ta,Ti)O ₄	5.00–5.69	Paramagnetic	–	–	–	3.6.1
Uraninite	(U,Th,Ce)O ₂	10.63–10.95	Paramagnetic	–	–	–	

La, Pr and Nd (~97.95% of total REO) (Gupta and Krishnamurthy, 1992, 2005). Bastnäsité would be considered a selective, cerium type mineral although these classifications are not absolute due to the interchangeable nature of the lanthanide elements (Cesbron, 1986; Ferron et al., 1991; Trifonov, 1963). Within the last 50 years bastnäsité has replaced monazite as the chief mineral source of rare earth elements (Ozbayoglu and Umit Atalay, 2000). This is primarily due to the discovery and development of the world's largest REE mine, the Bayan Obo mine in China, and the Mountain Pass mine in the United States (Gupta and Krishnamurthy, 2005). It is interesting to note that Bayan Obo, which accounted for 45% of the world's REE production in 2005, was initially developed as an iron ore mine in 1927 (it is also China's largest iron ore mine with almost 1.5 billion tonnes of reserves) and did not begin REE production until decades later (Gupta and Krishnamurthy, 2005; Wu, 2008). This major source of rare earths is in fact the tailings of the iron ore processing scheme at this mine (Zhang and Edwards, 2012). The separation process for bastnäsité ores may employ numerous operations including gravity and magnetic concentration, however the two deposits mentioned here rely pri-

marily on flotation using a fatty-acid or hydroxamate-based collector system (Chi et al., 2001; Fuerstenau et al., 1982; Jake and Xiangyong, 1984).

2.2. Monazite

Monazite is a phosphate mineral with a rare earth content of approximately 70% rare earth oxide that is, similarly to bastnäsité, primarily Ce, La, Pr and Nd (varies by deposit between 83.55% and 94.5% of total REO) and would consequently be considered a selective, cerium type mineral (Cesbron, 1986; Ferron et al., 1991; Gupta and Krishnamurthy, 1992, 2005; Trifonov, 1963). Unlike bastnäsité, monazite also includes 4–12 wt.% thorium and a variable amount of uranium (values are typically small but have been reported to be as high as 14 wt.%) (Gramaccioli and Segalstad, 1978; Gupta and Krishnamurthy, 2005). Monazite is found throughout the world in placer deposits, beach sands, and is also a component of the Bayan Obo deposit (Gupta and Krishnamurthy, 2005). The most important deposits for monazite extraction are the beach sands, which are typically concentrated via initial

Table 5

Phosphate REE bearing Minerals. Adapted from (Anthony et al., 2001; Long et al., 2010; Rosenblum and Brownfield, 1999).

Mineral name	Chemical formula	Density (g/cm ³)	Magnetic properties	Weight percent			Relevant sections
				REO	ThO ₂	UO ₂	
Phosphates			Para/diamagnetic?	REO	ThO ₂	UO ₂	
Britholite (Ce)	(Ce,Ca) ₅ (SiO ₄ ,PO ₄) ₃ (OH,F)	4.20–4.69	Paramagnetic	56	1.5	–	
Britholite (Y)	(Y,Ca) ₅ (SiO ₄ ,PO ₄) ₃ (OH,F)	4.35	Paramagnetic	56	1.5	–	
Brockite	(Ca,Th,Ce)(PO ₄)·H ₂ O	3.90	n/a	–	–	–	
Chevkinite (Ce)	(Ca,Ce,Th) ₄ (Fe ²⁺ ,Mg) ₂ (Ti,Fe ₃₊) ₃ Si ₄ O ₂₂	4.53–4.67	Paramagnetic	–	–	–	
Churchite (Y)	YPO ₄ ·H ₂ O	3.26	n/a	–	–	–	
Crandallite	CaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	2.78–3.04	n/a	–	–	–	
Florencite (Ce)	CeAl ₃ (PO ₄) ₂ (OH) ₆	3.45–3.54	n/a	–	1.4	–	3.6.2
Florencite (La)	(La,Ce)Al ₃ (PO ₄) ₂ (OH) ₆	3.52	n/a	–	1.4	–	
Florencite (La)	(Nd,Ce)Al ₃ (PO ₄) ₂ (OH) ₆	3.70 (calc)	n/a	–	1.4	–	
Fluorapatite	(Ca,Ce) ₅ (PO ₄) ₃ F	3.10–3.25	n/a	–	–	–	3.6.1, 3.6.2
Gorceixite	(Ba,REE)Al ₃ [(PO ₄) ₂ (OH) ₅]·H ₂ O	3.04–3.19	Diamagnetic	–	–	–	
Goyazite	SrAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O	3.26	Diamagnetic	–	–	–	
Monazite (Ce)	(Ce,La,Nd,Th)PO ₄	4.98–5.43	Paramagnetic	35–71	0–20	0–16	2.2, 3.1, 3.3, 3.4, 3.5.1, 3.5.3, 3.6.2
Monazite (La)	(La,Ce,Nd,Th)PO ₄	5.17–5.27	Paramagnetic	35–71	0–20	0–16	
Monazite (Nd)	(Nd,Ce,La,Th)PO ₄	5.43 (calc)	Paramagnetic	35–71	0–20	0–16	
Rhabdophane (Ce)	(Ce,La)PO ₄ ·H ₂ O	3.77–4.01	n/a	–	–	–	3.6.2
Rhabdophane (La)	(La,Ce)PO ₄ ·H ₂ O	4.40	n/a	–	–	–	
Rhabdophane (Nd)	(Nd,Ce,La)PO ₄ ·H ₂ O	4.79 (calc)	n/a	–	–	–	
Vitusite (Ce)	Na ₃ (Ce,La,Nd)(PO ₄) ₂	3.60–3.70	n/a	–	–	–	
Xenotime (Y)	YPO ₄	4.40–5.10	Paramagnetic	52–67	–	0–5	2.3, 3.1, 3.3, 3.4, 3.6.2

Table 6

Silicate REE bearing Minerals. Adapted from (Anthony et al., 2001; Long et al., 2010; Rosenblum and Brownfield, 1999).

Mineral name	Chemical formula	Density (g/cm ³)	Magnetic properties	Weight percent			Relevant sections
<i>Silicates</i>			Para/diamagnetic?	REO	ThO ₂	UO ₂	
Allanite (Ce)	(Ce,Ca,Y) ₂ (Al,Fe ²⁺ ,Fe ³⁺) ₃ (SiO ₄) ₃ (OH)	3.50–4.20	Paramagnetic	3–51	0–3	–	
Allanite (Y)	(Y,Ce,Ca) ₂ (Al,Fe ³⁺) ₃ (SiO ₄) ₃ (OH)	n/a	Paramagnetic	3–51	0–3	–	
Cerite (Ce)	Ce ₉ Fe ³⁺ (SiO ₂) ₆ [(SiO ₃)(OH)](OH) ₃	4.75	Paramagnetic	–	–	–	
Cheralite (Ce)	(Ca,Ce,Th)(P,Si)O ₄	5.28	n/a	–	<30	–	3.6.2
Eudialyte	Na ₄ (Ca,Ce) ₂ (Fe ²⁺ ,Mn ²⁺ ,Y)ZrSi ₈ O ₂₂ (OH,Cl) ₂	2.74–3.10	n/a	1–10	–	–	3.6.1
Gadolinite (Ce)	(Ce,La,Nd,Y) ₂ Fe ²⁺ Be ₂ Si ₂ O ₁₀	4.20	Paramagnetic	–	–	–	
Gadolinite (Y)	Y ₂ Fe ²⁺ Be ₂ Si ₂ O ₁₀	4.36–4.77	Paramagnetic	–	–	–	
Gerenite (Y)	(Ca,Na) ₂ (Y,REE) ₃ Si ₆ O ₁₈ ·2H ₂ O	n/a	n/a	–	–	–	
Hingganite (Ce)	(Ce,Y) ₂ Be ₂ Si ₂ O ₈ (OH) ₂	4.82 (calc)	n/a	–	–	–	
Hingganite (Y)	(Y,Yb,Er) ₂ Be ₂ Si ₂ O ₈ (OH) ₂	4.42–4.57	n/a	–	–	–	
Hingganite (Yb)	(Yb,Y) ₂ Be ₂ Si ₂ O ₈ (OH) ₂	4.83 (calc)	n/a	–	–	–	
limoriite (Y)	Y ₂ (SiO ₄)(CO ₃)	4.47	n/a	–	–	–	
Kainosite (Y)	Ca ₂ (Y,Ce) ₂ Si ₄ O ₁₂ (CO ₃)·H ₂ O	3.52	n/a	–	–	–	
Rinkite (rinkolite)	(Ca,Ce) ₄ Na(Na,Ca) ₂ Ti(Si ₂ O ₇) ₂ F ₂ (O,F) ₂	3.18–3.44	n/a	–	–	–	
Sphene (titanite)	(Ca,REE)TiSiO ₅	3.48–3.60	Paramagnetic	<3	–	–	
Steenstrupine (Ce)	Na ₁₄ Ce ₆ Mn ₂ Fe ₂ (Zr,Th)(Si ₆ O ₁₈) ₂ (PO ₄) ₇ ·3H ₂ O	3.38–3.47	n/a	–	–	–	3.6.2
Thalenite (Y)	Y ₃ Si ₃ O ₁₀ (F,OH)	4.16–4.41	n/a	–	–	–	
Thorite	(Th,U)SiO ₄	6.63–7.20	Paramagnetic	<3	–	10–16	
Zircon	(Zr,REE)SiO ₄	4.60–470	Diamagnetic	–	0.1–0.8	–	3.1, 3.2, 3.5.3, 3.6.1

Table 7

REE Distributions of major rare earth mineral deposits. Adapted from (Chen, 2011; Long et al., 2010).

Element	Bastnäsit Mountain Pass, USA	Bastnäsit Bayan Obo, China	Monazite Green Cove Spring, USA	Xenotime Lehat, Malaysia	High Y REE clay Longnan, China	Low Y REE clay Xunwu, China
La (%)	33.8	23.0	17.5	1.2	1.8	43.3
Ce (%)	49.6	50.0	43.7	3.1	0.4	2.4
Pr (%)	4.1	6.2	5.0	0.5	0.7	7.1
Nd (%)	11.2	18.5	17.5	1.6	3.0	30.2
Sm (%)	0.9	0.8	4.9	1.1	2.8	3.9
Eu (%)	0.1	0.2	0.2	Trace	0.1	0.5
Gd (%)	0.2	0.7	6.0	3.5	6.9	4.2
Tb (%)	–	0.1	0.3	0.9	1.3	Trace
Dy (%)	–	0.1	0.9	8.3	7.5	Trace
Ho (%)	–	Trace	0.1	2.0	1.6	Trace
Er (%)	–	Trace	Trace	6.4	4.9	Trace
Tm (%)	–	Trace	Trace	1.1	0.7	Trace
Yb (%)	–	Trace	0.1	6.8	2.5	0.3
Lu (%)	Trace	Trace	Trace	1.0	0.4	0.1
Y (%)	0.1	Trace	2.5	61.0	65.0	8.0

Bolded values indicate that a certain mineral deposit is a major source of the given element.

high-capacity gravity separation steps, to take advantage of the high specific gravity (monazite has a specific gravity greater than 5, while the typical gangue minerals in these deposits have specific gravities less than 3.5), followed by additional gravity, magnetic, electrostatic and occasionally flotation separation steps (Bulatovic and Willett, 1991; Ferron et al., 1991; Houot et al., 1991; Neiheisel, 1962; Zhang and Edwards, 2012).

2.3. Xenotime

Xenotime is a yttrium phosphate mineral with a rare earth oxide content of approximately 67% with Ce, La, Pr, Nd contents that are much less than monazite or bastnäsité (~8.4%) (Gupta and Krishnamurthy, 1992, 2005). Xenotime is typically found alongside monazite in concentrations of 0.5–5.0% of that of monazite (Cesbron, 1986; Ferron et al., 1991; Gupta and Krishnamurthy, 2005; Trifonov, 1963). Xenotime is important, in spite of its rarity, as it is a major source of HREE along with the Chinese ion-adsorbed rare earth bearing clays (Cheng et al., 1994; Chi et al., 2001). Xenotime is typically a by-product of monazite processing and as such, its processing follows a similar path to that of monazite (Cheng et al., 1994; Ferron et al., 1991). A limited amount of research into xenotime beneficiation has focused on its extraction from monazite using flotation and magnetic separation (Cheng, 2000; Cheng et al., 1993, 1994; Ito et al., 1991).

2.4. Ion-adsorbed clays

Ion-adsorbed clays are a very important source of heavy rare earth elements (up to 60% of REO content in these clays comes from yttrium group elements) with these elements occurring as rare earth element ions (Zhang and Edwards, 2012). Due to their nature, these clays require little to no physical beneficiation, being processed directly using hydrometallurgical methods. These will not be discussed in this paper, but further information can be found in Chi et al. (2001).

2.5. Other rare earth minerals

As can be seen in Tables 2–6, there are numerous minerals that contain REE, many of which have been exploited to varying degrees of success. However, these are typically small-scale, unique operations for which it is difficult to obtain data, and even more difficult to determine general separation characteristics. A limited discussion of such minerals is included in Section 3.5.

3. Beneficiation unit operations

The principle separation processes employed in the beneficiation of rare earth minerals include gravity separation, magnetic separation, electrostatic separation and froth flotation. These processes will be examined as they have been applied to rare earth minerals.

3.1. Gravity separation

Rare earth minerals are good candidates for gravity separation as they have relatively large specific gravities (4–7) and are typically associated with gangue material (primarily silicates) that is significantly less dense (Ferron et al., 1991). The most commonly utilized application of gravity separation is in monazite beneficiation from heavy mineral sands. Beach sand material is typically initially concentrated using a cone concentrator to produce a heavy mineral pre-concentrate (20–30% heavy minerals) before a more selective gravity separation step, often employing a spiral concen-

trator, is used to achieve concentrations of 80–90% heavy minerals (Gupta and Krishnamurthy, 1992). At this point, a series of magnetic, electrostatic and further gravity separation operations must be applied, according to each individual deposit's mineralogy (Ferron et al., 1991).

An example of a flowsheet designed to concentrate monazite from Egyptian beach sands containing approximately 30 wt.% valuable heavy minerals can be seen in Fig. 3 (Moustafa and Abdelfattah, 2010). In this flowsheet, low specific gravity gangue is discarded via wet gravity concentration (the authors employed a Wifley shaking table for this purpose), then low intensity magnetic separation is used to discard any ferromagnetic minerals without removing paramagnetic monazite (Moustafa and Abdelfattah, 2010). The non-magnetic stream that remains contains most of the valuable monazite, zircon and rutile as well as a portion of the gangue minerals which were not removed in the first two steps. A series of gravity, magnetic and electrostatic separations are then applied to exploit the different properties of the monazite, zircon and rutile minerals and produce the final concentrate streams. Rutile is removed as it reports to the conductor fraction after electrostatic separation (monazite and zircon are non-conductive) and then diamagnetic zircon may be removed from the paramagnetic monazite via further magnetic separation (Moustafa and Abdelfattah, 2010).

In addition to the processing of beach sands, gravity separation, (shaking tables, spiral concentrators, and conical separators) is used in combination with froth flotation at many rare earth mineral processing operations throughout China (Chi et al., 2001). An example of this is at Bayan Obo, where gravity separation has been employed between the rougher and cleaner flotation circuits to efficiently separate monazite and bastnäsité from the iron-bearing and silicate gangue material (Chi et al., 2001; Jake and Xiangyong, 1984). Some challenges associated with gravity separation of the Bayan Obo ore are that gangue minerals (e.g. barite) have similar specific gravities to the desired rare earth minerals and report to the concentrate stream. In addition, gravity separation is ineffective at separating very fine particles resulting in large losses of rare earths (Ming, 1993). Some separation of very fine particles can be achieved for minerals with very large differences in specific gravity, such as gold from silicate gangue, by employing centrifugal gravity separators such as the Knelson, Falcon and Mozley Multi-Gravity Separators (Falconer, 2003; Gee et al., 2005). Most of these fine particle separators are designed for semi-continuous operation where the valuable dense material is present in low concentrations (<0.1 wt.%) which may limit their suitability to REE mineral separation (Fullam and Grewal, 2001). The ongoing development of centrifugal separators capable of continuous operation (e.g. Knelson CVD) may address this issue as the manufacturers claim to be able to process feed materials with valuable heavy mineral contents of up to 50 wt.% (Fullam and Grewal, 2001).

Outside of China, lab-scale gravity separations have been successfully completed on Turkish and Australian deposits with very fine-grained mineralizations (Guy et al., 2000; Ozbayoglu and Umit Atalay, 2000). In both of these cases, one of the key findings was that the rare-earth minerals were concentrated into the very fine (<5 µm) particle size range (Guy et al., 2000; Ozbayoglu and Umit Atalay, 2000). This was dealt with by either modifying the grinding steps to prevent excess fine generation or by employing a Multi-Gravity Separator, specifically designed to recover ultrafine particles via gravity separation (Guy et al., 2000; Ozbayoglu and Umit Atalay, 2000). The modified grinding procedure employed an attrition scrubbing step prior to further grinding to produce a product that was 100% –300 µm (the size which was identified as the maximum limit for downstream flotation), while reducing the slime losses to the –5 µm size fraction by an average of 7.8% (Guy et al., 2000). The results from Guy et al. (2000) can be seen in

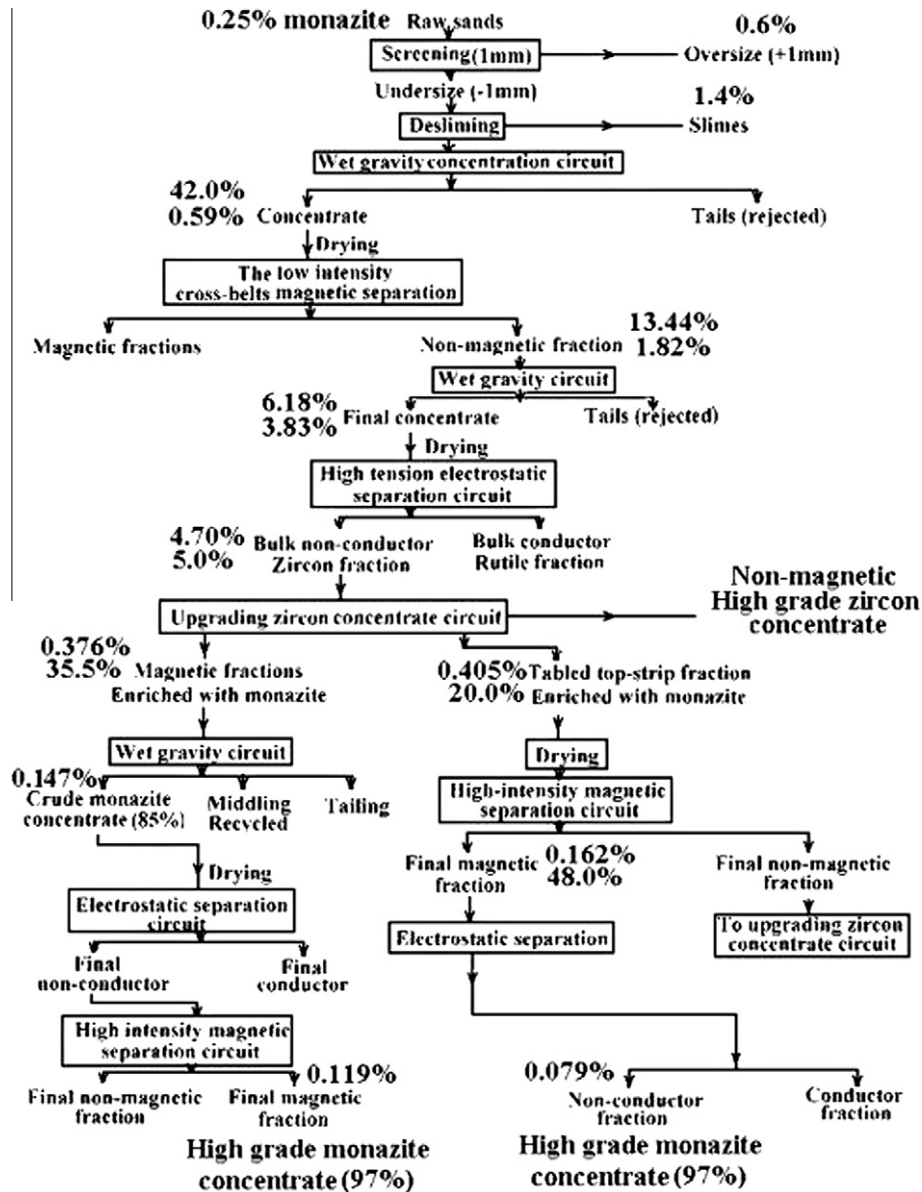


Fig. 3. Flowsheet for concentrating monazite from Egyptian beach sand. For each stream, the first and second percentages represent total weight recovery and monazite grade respectively. Reproduced with permission from (Moustafa and Abdelfattah, 2010).

Fig. 4. The importance of adequately liberating rare earth minerals without excessive fine production has also been shown by Fangji and Xinglan (2003) who employed screening and secondary grinding steps after gravity and magnetic separations at a mine in Maon-iuping, China to produce a bastnäsite flotation concentrate with a grade of 62% REO and a recovery of 80–85%.

A final interesting application of gravity separation to rare earth mineral concentration is the use of roasting operations prior to gravity separation as outlined in a 1956 patent (Kasey, 1956). The idea presented involved roasting a rare earth carbonate ore at temperatures in excess of 1000 °C to convert the carbonates into oxides, thereby increasing the mineral density and susceptibility to gravity separation (Kasey, 1956). The process proposed by Kasey (1956) included an industrial application involving quenching the roasted ore particles from high temperatures; a process that would likely significantly decrease the energy required for crushing and grinding operations as detailed by Fitzgibbon (1990) in their re-

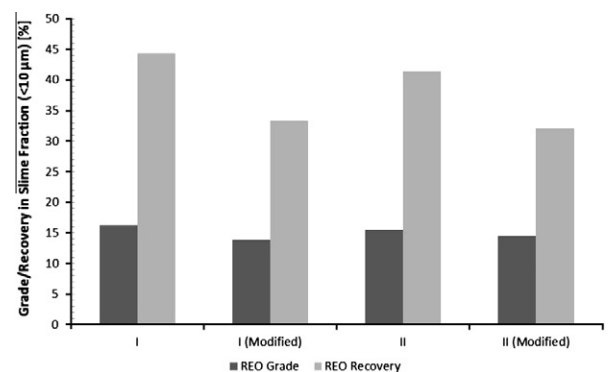


Fig. 4. Changes in REO slime losses with modified grinding procedure. Adapted from (Guy et al., 2000).

search into thermally assisted liberation. To the best of authors' knowledge, this process was never successfully applied on an industrial or pilot scale.

3.2. Desliming

The considerable loss of rare earth minerals in the fine size fractions produced in the comminution of finely-grained rare earth ores has been addressed in an unconventional way using microwave radiation. Chistov et al. (1995) were able to reduce the production of slimes (<5 µm) from 43.0% to 18.9% via a 2.45 GHz, 5 kW microwave treatment that heated the ore to 540 °C (approximate 600 s exposure time) prior to grinding. The authors did not give detailed mineralogy of this ore (it was identified only as a complex niobium/rare metal ore from Tomtor, Russia) however, they did identify structural changes to the ore's iron-bearing minerals as they were exposed to increasing microwave treatment times (Chistov et al., 1995). The authors identified magnetite and hematite as the potential cause for the observed non-linear heating behavior of the ore with increasing microwave exposure time (Chistov et al., 1995). This process, if it could be scaled-up to an industrial operation would likely realize considerable improvements in rare earth recovery simply due to the decreased losses in desliming operations. There is currently a great deal of research into microwave assisted liberation and the effect on downstream processing, which may result in the development of industrially applicable microwave processes that could be applied to rare earth mineral beneficiation (Can and Bayraktar, 2007; Jones et al., 2005; Kingman, 2006; Kumar et al., 2010; Leonelli and Mason, 2010).

3.3. Magnetic separation

Magnetic separation techniques are a common separation step in rare earth mineral beneficiation to eliminate highly magnetic gangue, or to concentrate the desired paramagnetic REE bearing minerals such as monazite or xenotime (Gupta and Krishnamurthy, 1992). As explained previously, rare earth elements generally have a series of electrons occupying a shielded 4f sub-shell and these electrons will typically have magnetic moments which do not cancel out, resulting in a material with some degree of magnetism (Spedding, 1975). The magnetic susceptibilities of individual rare earth elements have been calculated by Ito et al. (1991) and used to predict rare earth minerals magnetic susceptibilities based on their chemical compositions. This work focused on the magnetic susceptibilities of the most common M³⁺ lanthanide ions and did not investigate any changes in magnetic behavior for different oxidation states of these elements. The results of these calculations indicated that the elements from gadolinium to erbium had the highest magnetic susceptibilities of all the lanthanides, and the higher concentrations of Gd, Dy and Er ions present in xenotime explained its threefold increase in magnetic susceptibility when compared with monazite (Ito et al., 1991).

Along with gravity separation, magnetic separators are instrumental to monazite beneficiation from beach sands. They are used to eliminate strongly magnetic minerals such as magnetite prior to more selective separation steps, and are also used to separate paramagnetic monazite from non-magnetic heavy mineral gangue material such as zircon and rutile (Ferron et al., 1991; Tran, 1991; Zhang and Edwards, 2012). Xenotime, a paramagnetic mineral which is more susceptible to magnetic separation than monazite, may be isolated using these techniques, however for fine grain sizes (<100 µm), flotation is the preferred means of separation (Rosenblum and Brownfield, 1999; Zhang and Edwards, 2012).

Magnetic separators are used in the beneficiation of Chinese bastnäsite rare earth ores to eliminate Fe-bearing gangue minerals prior to rare earth-specific separation steps, and as a cleaning step

for flotation feeds and concentrates (Chi et al., 2001; Zhang and Edwards, 2012). In the case of China's second biggest rare earth deposit, the Sichuan Maoniuping Rare Earth Ore, magnetic separation has been combined successfully with gravity separation to achieve a bastnäsite recovery greater than 55% without the need for flotation (Chi et al., 2001).

Test work has been conducted on an Australian rare earth ore to examine the possibility of magnetically separating ground ore after being subjected to a roasting operation (Chan, 1992). Roasting temperatures from 400 °C up to 1000 °C were tested, however no benefit to the response to magnetic separation of the ore was observed (Chan, 1992). In another series of experiments similar to those described in the gravity separation section of this paper (Section 3.1), the effect of feed fineness on the susceptibility of a rare earth ore to a series of magnetic separations was investigated (Gao and Chen, 2010). The results of this work showed that when the feed (with a Sc grade of 48.9 g/t) had a particle size of 80% – 74 µm the recovery and grade of the scandium and rare earth concentrate were optimized, yielding a Sc grade of 314.89 g/t with a recovery of 77.53% (Gao and Chen, 2010).

3.4. Electrostatic separation

Electrostatic separation is a beneficiation technique that exploits the differences in conductivity between different minerals to achieve separation (Higashiyama and Asano, 2007; Kelly and Spottiswood, 1989a,b,c). Electrostatic separation techniques are typically only used when alternative processing techniques will not suffice, as the comminution steps in mineral processing flowsheets are generally wet processes and the energy requirements to drive off all moisture prior to electrostatic separation can be significant (Kelly and Spottiswood, 1989a). In the context of rare earth mineral processing, the typical use of electrostatic separation is in the separation of monazite and xenotime from gangue minerals with similar specific gravity and magnetic properties (Ferron et al., 1991; Zhang and Edwards, 2012). A specific example of this is when xenotime, which is more strongly paramagnetic than monazite, is concentrated with ilmenite after magnetic separation of heavy mineral sands (Gupta and Krishnamurthy, 1992). In this case the only means by which xenotime may be removed from the ilmenite is via electrostatic separation, as ilmenite is conductive but xenotime is not (Gupta and Krishnamurthy, 1992).

Electrostatic separation is a valuable technique for heavy mineral sand beneficiation, and the successful application of this process to separate ultrafine (<37 µm) coal particles may present an opportunity to treat the fines produced in many currently operating mineral processing circuits that account for significant rare earth losses (Higashiyama and Asano, 2007). Unfortunately, all electrostatic separation techniques (drum-type, belt-type, plate-type etc.) suffer from the requirement that the feed material must be completely dry (Higashiyama and Asano, 2007). Aside from the heavy mineral sand deposits, almost all other discovered rare earth deposits (aside from the ion-adsorbed clays in southern China) require some form of comminution prior to separation and these grinding operations are heavily reliant on slurried feed material. The energy costs associated with completely drying a ground ore prior to an electrostatic separation step are likely to be far too cost-prohibitive for such a process to be applied on an industrial scale.

3.5. Froth flotation

Froth flotation is commonly applied to the beneficiation of rare earth ores due to the fact that it is possible to process a wide range of fine particle sizes and the process can be tailored to the unique mineralogy of a given deposit. An illustration of this is the Bayan

Obo rare earth mineral deposit, with its complex inter-related mineralogy and a grain size of 10–74 μm , which would render it impossible to process were it not for flotation (Zhang and Edwards, 2012).

The area of froth flotation of rare earth minerals has seen a relatively large amount of research compared to other beneficiation techniques. The research has primarily focused on bastnäsité and monazite, in terms of their surface properties as they relate to flotation response, as well as industrial scale flotation experiments in plants such as Mountain Pass and Bayan Obo.

3.5.1. Surface chemistry

In the study of surface characteristics, the electrical double layer governs the adsorption of various flotation reagents, which in turn directly affect the flotation response of a given mineral (Pradip, 1981). For mineral surfaces in flotation, a very important property that can be used to characterize the electrical double layer is the isoelectric point (IEP); which is the pH value at which the zeta potential is zero (Pope and Sutton, 1973). The IEP can be used to predict the sign of the charge on a mineral surface in a given pH region (Pope and Sutton, 1973). Understanding the zeta potential of a mineral, and the IEP, combined with a knowledge of a collector's ionization behavior at various pH levels in aqueous conditions allows one to predict the mechanism of collector adsorption on the mineral surface (Cheng et al., 1993; Pope and Sutton, 1973). The variation of this parameter in the presence of various flotation reagents is important in understanding flotation as the IEP of different minerals in an ore can help select flotation conditions which allow one mineral to be effectively separated from the other minerals present (Cheng, 2000; Cheng et al., 1994; Fuerstenau et al., 1992; Pradip, 1981). The IEP values for bastnäsité and monazite reported in literature vary greatly, with ranges from pH 1.1 to 9.0 for monazite and pH 4.6–9.5 for bastnäsité (Cheng, 2000; Houot et al., 1991). Measurements for other minerals are usually quite repeatable (In_2O_3 and CuO have reported IEP values of 7.0–7.7 and 8.5–9.7 respectively) (Kosmulski, 2001). The discrepancies observed for the rare earth minerals may be due in part to the fact that both these minerals have a limited degree of solubility in water, and, the potential determining ions (those ions that can interact with both mineral surface and aqueous phase in forming the electrical double layer), the composition, and the structure of the mineral surfaces will vary significantly depending on the source of the mineral samples (Cheng, 2000; Houot et al., 1991; Pradip, 1981). Additional explanations for the variability in IEP could include errors in sample storage and the presence of impurities in pure mineral samples or the indifferent electrolytes used in the measurement of IEP. However, a review of the published procedures used during these investigations suggests that the observed variations in IEP are likely due to sample variability and not experimental error (Abeidu, 1972; Cheng, 2000; Cheng et al., 1994; Jiaké and Xiangyong, 1984; Pavez et al., 1996; Pradip, 1981).

3.5.2. Bastnäsité flotation

Flotation is used to beneficiate bastnäsité in many locations, including the two largest rare earth deposits; Mountain Pass and Bayan Obo (Zhang and Edwards, 2012). Common collectors used for bastnäsité flotation include variations of hydroxamates, fatty acids, dicarboxylic acids and organic phosphoric acids (Ferron et al., 1991; Jun et al., 2003). Typical depressants used in these situations include sodium silicate, sodium hexafluorosilicate, lignin sulfonate and sodium carbonate (Houot et al., 1991).

Fatty acids have traditionally been the collector of choice in bastnäsité flotation due to their widespread availability and use in mineral flotation in general. However, they have been shown to be unselective for bastnäsité flotation, requiring elevated temperatures, as shown in Fig. 5, and the addition of large volumes

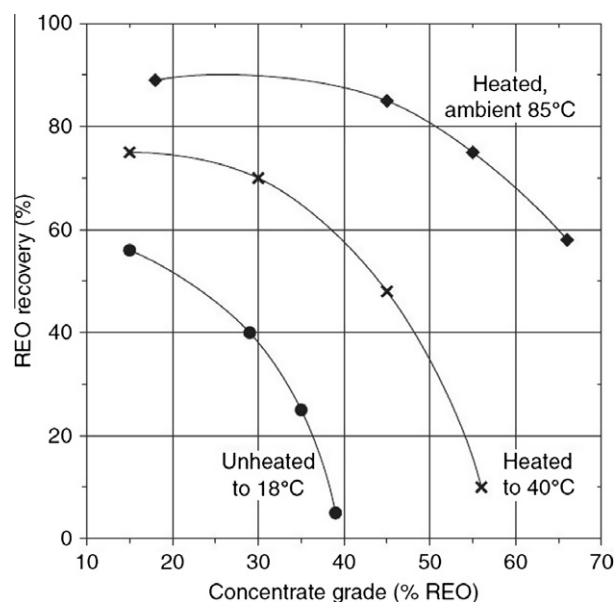


Fig. 5. Effect of temperature on Bastnäsité flotation using a fatty acid collector. Reproduced with permission from (Bulatovic, 2010).

of depressant to achieve a reasonable separation (Bulatovic, 2007, 2010; Jianzhong et al., 2007; Pradip, 1981).

The mechanism behind fatty acid and hydroxamate collector adsorption onto bastnäsité mineral surfaces is believed to be chemisorption, as examples of both anionic collector types (sodium oleate and hydroxamate) have been shown to adsorb onto this mineral at pH values where the zeta potential of the mineral is negative (Houot et al., 1991; Pavez et al., 1996). The improved flotation response through the use of hydroxamates can be explained in part by the fact that the collector molecules are believed to form stable chelates with rare earth cations present on the mineral surface, with the resultant multidentate complexes having a greater stability than that of fatty acids adsorbed onto the same mineral surfaces (Houot et al., 1991; Pavez et al., 1996; Pradip, 1981). Hydroxamic acids may exist in one of two different forms, hydroxyamide or hydroxyoxime, as seen in Fig. 6, but only the hydroxyamide form is able to form chelates with metal cations (Pradip and Fuerstenau, 1983). The adsorption of a chelating collector (N-hydroxyl phthalicimide) at the bastnäsité surface is shown schematically in Fig. 7 (Ren, 1993). An additional benefit of the hydroxamic acids is that they are believed to interact with rare earth cations in solution to form hydroxylated rare earth ions, which then adsorb onto the mineral surface, acting as additional activation sites (Cheng et al., 1993). The enhanced selectivity of a hydroxamic acid (alkyl hydroxamate) in comparison to fatty acids (tall oil) at Mountain Pass has been explained by the fact that alkyl hydroxamate is more likely to form chelates with the rare earth

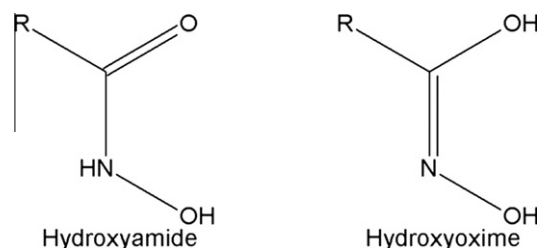


Fig. 6. The two tautomeric forms of hydroxamic acid. Adapted from (Pradip and Fuerstenau, 1983).

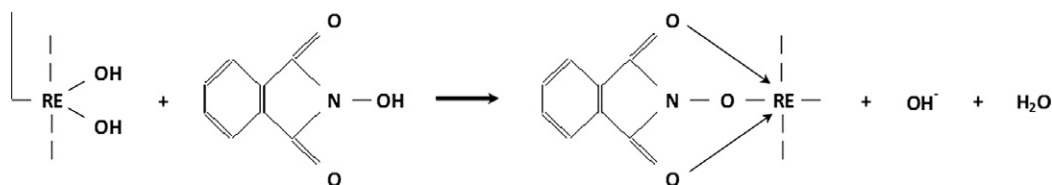


Fig. 7. Schematic of chelation reaction between bastnäsité surface and N-hydroxyl phthalicimide. After (Ren, 1993).

ions in bastnäsité than the calcium and barium ions present on the mineral surfaces of calcite and barite (Jianzhong et al., 2007; Pavez et al., 1996; Pradip, 1981; Pradip and Fuerstenau, 1983). The effectiveness of hydroxamic acids at the Bayan Obo mine has been shown to be affected by water hardness and decreasing pH, as Ca^{2+} and Mg^{2+} ions can consume large amounts of the collector, and excess hydrogen ions prevent the formation of the chelated compounds (Fangji et al., 1989).

The effect of elevated temperatures on flotation has been explained (for the Mountain Pass orebody) by the increased solubility of fatty acids (and other collector molecules) with increasing temperature, increased solubility of cations present on the mineral surface, and preferentially enhanced collector adsorption on the bastnäsité surface relative to gangue minerals (Pradip, 1981). The effect of temperature on bastnäsité flotation selectivity is due to a significant increase in the rate of collector adsorption onto bastnäsité relative to gangue such as calcite and barite (Pradip, 1981). This increase in bastnäsité collector adsorption with temperature may be due to the fact that for the Mountain Pass ore, process conditions (i.e. pH) are such that only bastnäsité is able to make the transition from physical adsorption to chemical adsorption mechanisms (and hence an overall increase in collector adsorption) with increasing temperature, shown in Fig. 8 (Houot et al., 1991; Pavez et al., 1996; Pradip, 1981). It is possible that, in a mechanism slightly different to the one shown in Fig. 8, the interaction of calcite and fatty acid collector molecules at the conditioning temperature used in Mountain Pass would fall into one of the regimes where collector adsorption is actually decreased with increased temperature. Pradip (1981) observed that the grade of the bastnäsité concentrate decreased (without any decrease in the recovery of bastnäsité) as temperature was increased above an optimum temperature of 75 °C. This finding suggests that at temperatures above 75 °C, gangue minerals adsorb greater amounts of collector, thereby reducing the grade of the bastnäsité concentrate (Pradip, 1981). Pradip (1981) did not conduct enough experiments to conclusively determine the exact mechanisms behind the effect of temperature in this flotation system. In a later study Pradip and Fuerstenau (1985) were able to calculate the free energies of adsorption of hydroxamate onto bastnäsité, barite and calcite surfaces as a function of temperature. Their results showed that the adsorption of hydroxamate onto the bastnäsité surface was thermodynamically favored over calcite and barite at all temperatures investigated (Pradip and Fuerstenau, 1985). Interestingly, as the temperature increased from 21 °C to 41 °C the difference between the free energies of adsorption of bastnäsité and calcite and bastnäsité and barite increased (Pradip and Fuerstenau, 1985). While this study examined the effect of temperature on hydroxamate adsorption, it is possible that the improved performance of sodium oleate flotation at Mountain Pass with increased temperature could be explained in a similar manner. With the planned re-opening of the Mountain Pass mine the influence of temperature on the flotation of bastnäsité may warrant further investigation.

To improve upon the performance of fatty acid flotation, researchers have utilized phosphoric acids (Houot et al., 1991; Jun et al., 2003), hydroxamic acids (Fangji et al., 1989; Fuerstenau and Pradip, 1991; Houot et al., 1991; Jianzhong et al., 2007; Jun

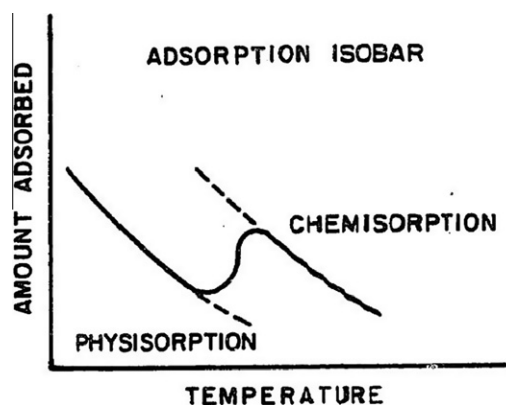


Fig. 8. Adsorption isobar of adsorption amount versus temperature showing transition region between physical adsorption and chemical adsorption. Reproduced with permission from (Pradip, 1981).

et al., 2003), petroleum sulfonate (Morrice and Wong, 1983) and a patented collector emulsion consisting of: secondary amine-modified suphonated fatty acid, high rosin containing tall oil fatty acid, anionic petroleum sulfonate and high molecular weight primary amine (Bulatovic, 1988). These alternative flotation schemes focus on minimizing reagent usage and eliminating costly processing steps including the heating of flotation pulps (such as Mountain Pass) prior to flotation (Bulatovic, 1988; Fuerstenau and Pradip, 1991). Hydroxamic acid collectors have been shown to be preferable to phosphorous-based collectors (phosphoric/phosphonic acids) for carbonate flotation, as maintaining the pH at the acidic levels required for the successful application of phosphorous-based collectors can prove difficult for this type of mineral (Ni et al., 2012). For Chinese bastnäsité ores, a naphthyl hydroxamic acid collector, known as H₂₀₅, has been widely used to produce rare earth oxide concentrates with grades of 50% REO or more (Jianzhong et al., 2007; Zhang and Edwards, 2012). This H₂₀₅ collector is preferable over cycloalkyl hydroxamic acids as it is less costly, requires fewer depressants, and the non-polar naphthyl group present in the H₂₀₅ collector molecule is more stable and has more carbon atoms than the cycloalkyl group (Yan, 1991). The use of H₂₀₅ does have some drawbacks as its frothing abilities are not as good as cycloalkyl hydroxamic acid (in practice the frother used for H₂₀₅ flotation contains 5–6% cycloalkyl hydroxamic acid) and the high dosage of H₂₀₅ required to successfully float rare earth minerals reduces the selectivity of this reagent (Yan, 1991). Similar to fatty acids, the H₂₀₅ flotation process is still quite expensive, and further research into phosphoric acids and modified hydroxamic acids is ongoing to develop collectors that minimize reagent costs whilst achieving acceptable rare earth oxide concentrate grades (Jianzhong et al., 2007; Jun et al., 2003; Ren, 1993; Ren et al., 1997). An example of this is the L₁₀₂ hydroxamic acid collector which is an improvement over H₂₀₅ as it requires a lower dosage, resulting in decreased reagent costs, and can achieve comparable results with only one rougher and one cleaner flotation stage (Fangji et al., 2002).

As explained previously, the key process step in the beneficiation of the Mountain Pass ore is the heated flotation of bastnäsité from calcite and barite using a fatty acid collector system (Fuerstenau and Pradip, 1991; Pradip, 1981). The Bayan Obo rare earth deposit, in contrast, is actually a very large iron ore deposit with a relatively small quantity of rare earth minerals present amongst the iron mineralization (Gupta and Krishnamurthy, 1992). Numerous processing schemes have been described for this deposit; the common elements for many of these flowsheets involve a non-selective flotation of rare-earths and similar gangue minerals from the iron-bearing minerals followed by a more selective flotation step to beneficiate the REO concentrate (Chi et al., 2001; Jiake and Xiangyong, 1984; Zhang and Edwards, 2012). According to Jiake and Xiangyong (1984), the non-selective flotation step can be completed using a fatty acid, but this poses problems downstream. This is because the fatty acid, a portion of which will chemically adsorb to the surface of gangue minerals, must be removed from adsorption sites, to be replaced by a more selective collector such as hydroxamic acid to facilitate the selective flotation of the REO (Jiake and Xiangyong, 1984).

Choices for depressants are invariably influenced by the composition of the ore deposit and the major gangue minerals present in the flotation feed. There are several depressants that have been thoroughly investigated in the established rare earth flotation processes. At Mountain Pass, lignin sulfonate is added as a depressant to suppress the calcite and barite gangue minerals, however it also affects bastnäsité to a certain degree (Houot et al., 1991; Morrice and Wong, 1983). Sodium carbonate is used extensively in bastnäsité flotation to control the supply of carbonate anions which affect both the pH of flotation and the surface properties of bastnäsité and related gangue minerals (CO_3^{2-} is a potential-determining ion for these minerals) (Fuerstenau and Pradip, 1991; Houot et al., 1991). Smith and Shonnard (1986) showed that the addition of sodium carbonate preferentially increased the magnitude of the negative surface charge on both calcite and barite while leaving bastnäsité unaffected. However, other research has shown that with elevated sodium carbonate additions (≥ 1 mM) the surface charge of both calcite and barite are positive at pH 9 while bastnäsité has a negative surface charge (Fuerstenau and Pradip, 1991; Pradip, 1981). This effect helps the negatively charged lignin sulfonate molecule to achieve its depressant effects by adsorbing onto the positively charged surfaces of barite, allowing fatty acid molecules to adsorb in greater quantities to the surface of the bastnäsité mineral (Fuerstenau and Pradip, 1991; Pradip, 1981). The same research also noted that the selective nature of lignin sulfonate is not affected by the elevated temperatures at which flotation takes place in the Mountain Pass plant (Fuerstenau and Pradip, 1991; Pradip, 1981).

Sodium fluoride and sodium hexafluorosilicate have also been used by different researchers as generic depressants for barite and calcite gangue in the Mountain Pass system (Houot et al., 1991; Morrice and Wong, 1983; Pradip, 1981). At Bayan Obo, sodium silicate is used to depress iron-bearing and silicate minerals, which are not present in the Mountain Pass ore (Houot et al., 1991; Jiake and Xiangyong, 1984). Taikang and Yingnan (1980) identified hydroxamic acid and sodium silicate as the two most important reagents for successful flotation of the Bayan Obo ores; the sodium silicate addition was large enough (25 kg/t) to depress the flotation of all minerals, and then a small amount of hydroxamic acid was added to selectively float only the rare earth minerals. This very large requirement for sodium silicate has been addressed by Jun (1992) who showed that a combination of sodium silicate and either alum or carboxymethyl cellulose (CMC) reduced the dosage required to achieve an efficient depression of gangue minerals in Chinese rare earth flotation. Sodium metaphosphate has been shown to be an effective depressant of calcite gangue at slightly

alkaline pH and in the presence of a hydroxamic acid collector (Ni et al., 2012). Sodium hexafluorosilicate has also been used at Bayan Obo to depress fluorite, calcite and barite minerals as well as to act as an activator for rare earth minerals (Jiake and Xiangyong, 1984; Taikang and Yingnan, 1980). Fangji et al. (1989) showed that the popular H_{205} collector does not require the addition of sodium hexafluorosilicate to achieve an effective beneficiation of rare earth oxide minerals at Bayan Obo, which is significant as sodium hexafluorosilicate is an environmental pollutant as well as a hazard for plant workers (Jun, 1989; Yan, 1991). The elimination of sodium hexafluorosilicate in the work of Fangji et al. (1989) was not explained in detail but the authors did state that the RE^{3+} cation was able to form more stable chelates with the H_{205} collector than other metallic cations such as Ca^{2+} , Mg^{2+} , Fe^{3+} and Ba^{2+} ; this property was exploited, in conjunction with long mixing times, to desorb the H_{205} collector from the gangue minerals and increase the REE grade of the concentrate. Recently Cui et al. (2012) investigated the interaction of hydroxamates with bastnäsité and other rare earth oxides and confirmed that hydroxamates will form chelates with calcite and barite gangue minerals when rare earth minerals are not present. However, when rare earth minerals are present, preferential adsorption of hydroxamate collectors onto rare earth minerals surfaces (due to the more highly charged RE^{3+} cations) is still expected (Cui et al., 2012; Pradip and Fuerstenau, 1983).

In the case of the collector emulsion mentioned previously, additional suggested gangue depressants include: citric acid and oxalic acid (for quartz, dolomite, calcite, and barite gangue), and alkali metal hydrogen sulfides (for fluorite, albite and mica gangue) (Bulatovic, 1988). The effective use of metal salts such as aluminum and lead in flotation are heavily dependent upon the collector system, as they have been used in some instances as bastnäsité activators, as depressants for both monazite and bastnäsité at elevated pH, and in one case as a selective depressant of monazite in the presence of bastnäsité (Houot et al., 1991; Ren et al., 2000).

While flotation has proven to be a very useful technique for the separation of bastnäsité, it is important to note that a process employing only flotation will most likely underachieve compared to one that employs multiple (different) unit operations. Fangji and Xinglan (2003) have shown that a properly designed bastnäsité beneficiation process employing sizing, gravity, magnetic and flotation separation steps can outperform alternative bastnäsité separation processes at other plants such as: Mountain Pass (flotation at elevated temperatures), Weishan (flotation using hydroxamic acid) and Dalucao (magnetic and gravity separation). Specifically, their process at the Maoniuping plant was able to achieve similar grades (62–70% REO) to the best performing plants (Weishan produces a concentrate with a grade of 69.55% REO) while achieving recoveries that were significantly higher than the best performer amongst the other plants (85–92% REO recovery at Maoniuping versus 78.11% at Dalucao) (Fangji and Xinglan, 2003).

3.5.3. Monazite flotation

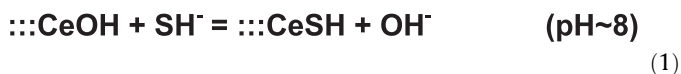
The flotation process of monazite minerals is different to that of bastnäsité due to the different mineralogy of the deposits, as well as the lack of research sources dealing with the same deposit (unlike the Bayan Obo and Mountain Pass processes). Monazite gangue minerals can include ilmenite, rutile, quartz, and zircon and typically require slightly different flotation reagents than bastnäsité ores to achieve a reasonable separation (Pavez and Peres, 1993, 1994).

Monazite behaves in a similar manner to bastnäsité in terms of collectors used (fatty acids and hydroxamates) as the monazite surface will contain many of the same rare earth cations present on the bastnäsité (Jiake and Xiangyong, 1984). The adsorption

mechanism of both fatty acids and hydroxamates onto a monazite mineral surface is believed to be chemical in nature, similar to bastnäsite minerals, and the increased bastnäsite selectivity of these collectors with increasing temperature applies similarly to monazite flotation (Houot et al., 1991; Pavez et al., 1996; Pavez and Peres, 1993).

Two of the typical monazite gangue minerals, zircon and rutile, require a depressant in order for selective flotation to be possible (Pavez and Peres, 1994). Common depressants used for this purpose include sodium silicate (also used in bastnäsite flotation), sodium sulfide and sodium oxalate (Abeidu, 1972; Houot et al., 1991; Pavez and Peres, 1993, 1994). The depressing action of both sodium sulfide and sodium oxalate has been proposed to be in part due to a selective activation of monazite (Abeidu, 1972; Bulatovic, 2010; Zakharov et al., 1967). The available literature on sodium sulfide and sodium oxalate employs reagent nomenclature (gangue activators referred to as depressants) that is not in accordance with generally accepted flotation terminology. To ensure their work is accurately represented, the original authors terminology will be used when describing these two reagents.

Sodium sulfide has been reported to have both an activating and depressing effect on zircon, dependent on dosage. For small additions (10 mg/L) Zakharov et al. (1967) showed that sodium sulfide activated zircon, pyrochlore and monazite minerals. However, as the dosage increased (up to 37.5 mg/L) pyrochlore and zircon were depressed, with the monazite flotation unchanged (Zakharov et al., 1967). Sodium sulfide depression of zircon has been explained by the adsorption of SH^- and S^{2-} ions to the mineral surface, and the subsequent unavailability of the metal cations on the mineral surface, reducing the potential sites for collector adsorption (Zakharov et al., 1967). The activation of monazite was explained by the large oxidizing power of rare earth cations on the monazite surface which oxidize the SH^- ions and allow fatty acid collector molecules to adsorb onto the monazite surface (Zakharov et al., 1967). An alternative explanation, for the flotation response of this mineral system in the presence of sodium sulfide is the selective desorption of sodium oleate from zircon and pyrochlore surfaces, with an accompanying incomplete desorption from monazite surfaces (Pol'kin et al., 1967). A third alternative explanation of the mechanism of activation of monazite by sodium sulfide is explained via Eqs. (1)–(5) (Abeidu, 1972):



These equations describe the activation of the rare earth cations (Ce^{3+}) and phosphate anions by sulfide ions and then the subsequent binding of the oleic acid collector (OL). According to Abeidu (1972), the only probable mechanism for monazite activation by sodium sulfide is shown by Eqs. (4) and (5), and the effective depression of zircon minerals by sodium sulfide can then be explained by the inability of silicon ions on the zircon surface to bind

or react with the sulfide ions. While there is no consensus on the mechanism of monazite interaction with sodium sulfide, it is clear that sodium sulfide can be effectively used to float monazite from zircon.

Sodium oxalate has been discussed as both a depressant and activator of monazite flotation, but the prevalent opinion appears to be that sodium oxalate activates monazite when combined with a sulfonate collector (Bulatovic, 2010; Houot et al., 1991). The importance of conditioning time when using sodium oxalate as a depressant agent for monazite gangue can be seen in Fig. 9 (Bulatovic, 2010).

Other important depressants of monazite are starches, which have been used with a variety of collectors including: sulfonates (Houot et al., 1991), cationic amines (Cuthbertson, 1952), phosphoric acid esters (Ferron et al., 1991; Houot et al., 1991) and a unique collector emulsion (different from the patented collector emulsion used for bastnäsite flotation) of a fatty acid, an emulsifier, a phosphonic acid derivative and optional oil/amine additions (Bulatovic and Willett, 1991). Most of these collector systems have not been extensively applied in industrial settings due to the lack of any significant monazite deposits (on the scale of Mountain Pass or Bayan Obo) that require the use of flotation as a separation method.

3.6. Beneficiation of other rare earth minerals

3.6.1. Gravity and magnetic separation of other rare earth minerals

Loparite is an oxide rare earth mineral similar to perovskite, found extensively in Russia's Kola Peninsula where almost 6500 tons of REO are extracted annually (Hedrick et al., 1997). This mineral occurs alongside gangue such as aegirine, feldspar, nepheline and ramsayite and is concentrated via a combination of gravity and magnetic separation techniques (Hedrick et al., 1997). Several other rare earth minerals (including eudialyte, apatite and synchysite (Y)) are extracted in this region; the REE composition of these minerals can be seen in Table 8 (Hedrick et al., 1997).

An interesting study was recently undertaken by Raslan (2009) in which a heavy mineral occurrence with a significant (approximately 1.5 wt.%) occurrence of samarskite (Y) was subjected to lab-scale separations. This work used sieving, desliming, gravity separation (using a shaking table) and magnetic separation to pro-

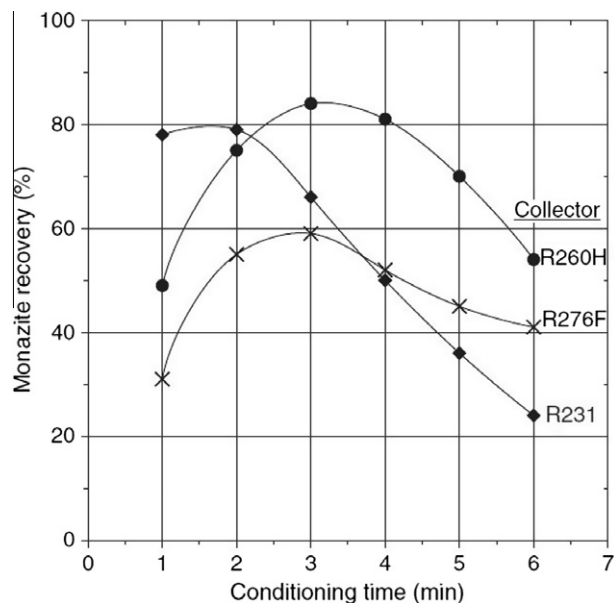


Fig. 9. Effect of conditioning time with sodium oxalate on lab-scale monazite recovery using various sulfonate collectors. Reproduced with permission from (Bulatovic, 2010).

Table 8

REE Distribution in rare earth minerals from Eastern Europe. Adapted from (Hedrick et al., 1997).

Element	Loparite Revda, Russia	Eudialyte Revda, Russia	Apatite Khibiny, Russia	Synchysite (Y) Kutessaisk, Kazakhstan
La (%)	25.0	15.2	24.0	14.0
Ce (%)	50.5	29.7	52.0	26.0
Pr (%)	5.0	2.9	5.5	2.7
Nd (%)	15.0	12.7	14.0	9.8
Sm (%)	0.7	3.4	2.5	3.5
Eu (%)	0.1	1.3	0.5	0.1
Gd (%)	0.6	3.0	1.4	3.5
Tb (%)	–	2.8	0.2	0.7
Dy (%)	0.6	4.3	0.3	4.3
Ho (%)	0.7	2.9	0.1	0.8
Er (%)	0.8	2.1	0.2	3.8
Tm (%)	0.1	–	0.1	0.3
Yb (%)	0.2	1.6	0.1	1.2
Lu (%)	0.2	0.3	0.1	0.3
Y (%)	1.3	21.4	1.5	29.0

Bolded values indicate that a certain mineral deposit contains a significant concentration of the given element.

duce a samarskite (Y) concentrate according to the following procedure (Raslan, 2009):

- A feed consisting of samarskite (Y), columbite, zircon, magnetite, garnet, goethite, ilmenite, hematite and mica was deslimed and then sieved to 100% passing 1 mm.
- The sieved material was sized and the resultant size fractions were individually fed to a gravity shaking table.
- The heavy fractions were then subjected to two magnetic separation steps; the first to remove magnetite and the second high intensity step to produce a non-magnetic concentrate containing predominantly samarskite (Y) and zircon.

On a lab-scale, these researchers were able to produce a non-magnetic samarskite (Y) concentrate comprised of 73.8 wt.% samarskite (Raslan, 2009).

3.6.2. Flotation of other rare earth minerals

Apart from monazite and bastnäsite, there is very little research available on the flotation of rare earth minerals such as xenotime and even less for some of the newer complex ore deposits such as Mount Weld in Australia.

The surface characteristics of xenotime have been studied by Cheng (2000), with the reviewed literature values of the point of zero charge (the point at which the concentration of positively charged ionic species is equal to the concentration of negatively charged ionic species on the mineral surface) for this mineral exhibiting a wide range of values, similar to the point of zero charge (PZC) results obtained for bastnäsite and monazite. This work also confirmed the variation in chemical composition of both monazite and xenotime minerals from surface to bulk, and concluded that this is a likely cause for the wide variation in reported values for the PZC and IEP values of these minerals (Cheng, 2000). Another study of monazite and xenotime mineral flotation, with a sodium oleate collector, concluded that sodium fluoride additions altered the bubble attachment times as a function of temperature (Cross and Miller, 1989). With sodium fluoride additions in excess of the concentration needed for surface precipitation, bubble attachment times decreased with increasing temperature, but with insufficient sodium fluoride additions, bubble attachment times were actually shown to increase (Cross and Miller, 1989). This finding illustrates the importance of determining the optimum concen-

tration of flotation reagents, in addition to the correct type of reagents, for the recovery of a rare earth mineral.

Another novel rare earth flotation process involved completely depressing monazite and an unspecified yttrium-bearing mineral using phosphoric acid at acidic pH, and an organic depressant to achieve a separation through reverse flotation. The naturally hydrophobic gangue (albite, chlorites and aegirine) floated without the need for collector addition (Feron et al., 1991).

Disregarding Bayan Obo and Mountain Pass, the published literature on flotation as a means of REE concentration is limited. In the 1960s a process for flotation of monazite and steenstrupine was investigated for the large Kvanefjeld rare earth deposit in Greenland (which is only now in 2012 beginning to move towards full-scale development) using sodium oleate as a collector and sodium silicate as a depressant (Sorensen and Lundgaard, 1966). This study also explored the use of lanthanum ions as an activator for the rare earth minerals, with limited success. Lanthanum ion uptake was correlated directly with flotation recovery of monazite and steenstrupine, however excess lanthanum ion additions were found to increase the flotation recoveries of the gangue (arfvedsonite and aegirine) (Sorensen and Lundgaard, 1966).

Apatite, as can be seen in Tables 5 and 8, can occur in forms that make it another potential source of REE. Some examples of REE-rich apatite deposits include: Kola and Kovdor in Russia, Palfos in South Africa as well as sedimentary deposits in Jordan and Morocco (Jorjani and Bagherieh, 2007). A study by Jorjani and Bagherieh (2007) has recently identified a significant source of REEs in the apatite-containing tailings of the Chadormalu iron ore concentrator in Iran. Apatites are an important mineral for the phosphate industry, and the flotation of this class of mineral is well-established using fatty acid collector systems (Lu et al., 1998). Due to the similar chemical nature of common gangue minerals such as calcite and fluorite, fatty acids such as sodium oleate will preferentially adsorb onto these gangue minerals instead of apatite (Lu et al., 1998). Apatite from the Kola Peninsula in Russia has been successfully recovered via flotation using a tall oil collector and sodium silicate as a gangue depressant (Houot, 1982). After six flotation stages (one rougher, two scavenger and three cleaner stages), the resultant concentrate grade was 94.8% apatite with a 94% phosphate recovery (Houot, 1982).

The other major rare earth deposit that is actively being developed is in Mount Weld in Australia where the complex mineralogy of the deposit is distinct from currently operating rare earth mines (Chan, 1992). Some of the rare earth minerals comprising the Mount Weld ore body include: monazite, cheralite, cerianite, florencite, and small quantities of rhabdophane (Chan, 1992). Goethite, apatite, crandalite, dolomite, cryptomelane and jacobsonite are present as gangue (Chan, 1992). Two flotation schemes have been proposed for this ore body. The first, by Chan (1992), describes a blended collector emulsion (separate from previously mentioned collector emulsions) of fatty acid, with an emulsifier such as a secondary amino modified sulfonated fatty acid and an oil as froth stabilizer, with sodium sulfide, sodium silicate and a starch as depressants. This work also mentions the possibility of utilizing an amine collector, provided suitable depressants could be developed, as being advantageous due to the ease with which an amine could be removed from mineral surfaces after flotation (Chan, 1992). The second method, by Guy et al. (2000), employs a fatty acid collector with sodium sulfide, starch and sodium silicate as the depressants. As the Mount Weld deposit has only recently been brought to full-scale production, there is currently no available data to determine which flotation scheme has been adopted and how it is performing. A comparison between these two reagent schemes shows that the primary path of innovation for new flotation processes for rare earth ores has thus far involved

Table 9
Current and potential non-Chinese REE producers. Adapted from (Chen, 2011; Cox et al., 2011; Colorado Rare Earths Inc., 2012; Johansson and Pooley, 2012; Lafleur and Ayad, 2012; Nestour, 2011; Swinden and Siegfried, 2011).

Company	Deposit location	Countries involved	Capacities (tpy REO)		
			2010	2011–2013	Target post-2015
Molycorp Minerals	Mountain Pass, CA	USA	3000		40,000
Lovozersky Mining Company	Kamasurt Mine, Kola Peninsula	Russia	3000–4400		15,000
Solikamsk Magnesium works	Solikamsk Processing Plant, Urals	Russia			
Indian rare earths	Orissa, Tamil Nadu and Kerala	India	100		10,000
Toyota/Sojitz/Government of Vietnam		Vietnam	1800–2000		>2000
Neo		Thailand			
Lynas/Malaysia	Gebeng, Malaysia	Malaysia			
Industrias Nucleares do Brasil S/A (INB)	Buena Norte	Brazil	1500		>1500
Lynas Corp.	Mount Weld, Western Australia-processing plant in Gebeng, Malaysia	Australia		10,500	21,000
Rareco/Great Western Minerals Group	Steenkramskaal, South Africa	South Africa/Canada		3000	5000
Sumitomo/Kazatomprom/SARECO JV	Kazakhstan	Kazakhstan/Japan		3000	15,000
Toyota/Sojitz/Government of Vietnam	Dong Pao, Vietnam	Vietnam/Japan		300	5000
Toyota/Indian Rare Earths JV	Orissa, India	India/Japan		5000	10,000
Mitsubishi/Neo Material Technologies	Pitinga, Brazil	Japan/USA/Canada/Brazil		500	1000
Alkane Resources	Dubbo, NSW, Australia	Australia		2600	6000
Avalon Rare Metals Inc.	Nechalacho deposit rich in HREEs in NWT, Canada	Canada		0	5000
Quest Rare Metals	Strange Lake and others in Quebec & Labrador, Canada	Canada		0	0
Ucore	Bokan–Dotson Ridge project, Alaska	USA		0	0
Matamec	Kipawa deposit in Quebec, Canada	Canada		0	0
Arafura	Nolan's project, Australia	Australia		10,000	20,000
Great Western Minerals Group	Hoidas Lake, Canada	Canada		3000	5000
Rare Element Resources	Bear Lodge, Wyoming, USA	USA		0	0
Stans Energy Corp.	Kiutessay II Mine, Orlovka, Kyrgyz Republic	Kyrgyz Republic		0	0
Greenland Minerals and Energy	Kvaneffjeld, Greenland	Greenland		0	10,000
Pele Mountain Resources	Elliott Lake, Canada	Canada		0	0
Colorado Rare Earths Inc. (was US Rare Earths)	Wet Mountain/Iron Hill, USA	USA		0	0
Namibia Rare Earths Inc. (was Etruscan Resources)	Lofdal Rare Earths Project, Namibia	Namibia, Canada		0	0
Montero Mining	Wigu Hill, Tanzania	Tanzania, Canada		0	0
Tasman Metals	Norra Karr, Sweden	Sweden		0	0
IAMGOLD	Niobec Mine, Canada	Canada		0	0
Japan–Mongolia JV	Mongolia	Mongolia		0	0
Totals			9500–11,000	37,900	>171,500
Total Projected 2015 Production from Non-Chinese Producers					168,000
Projected Demand for REEs (excluding China)					80,000

Note that projects lacking established production timelines were estimated to not be producing any REO in 2015.

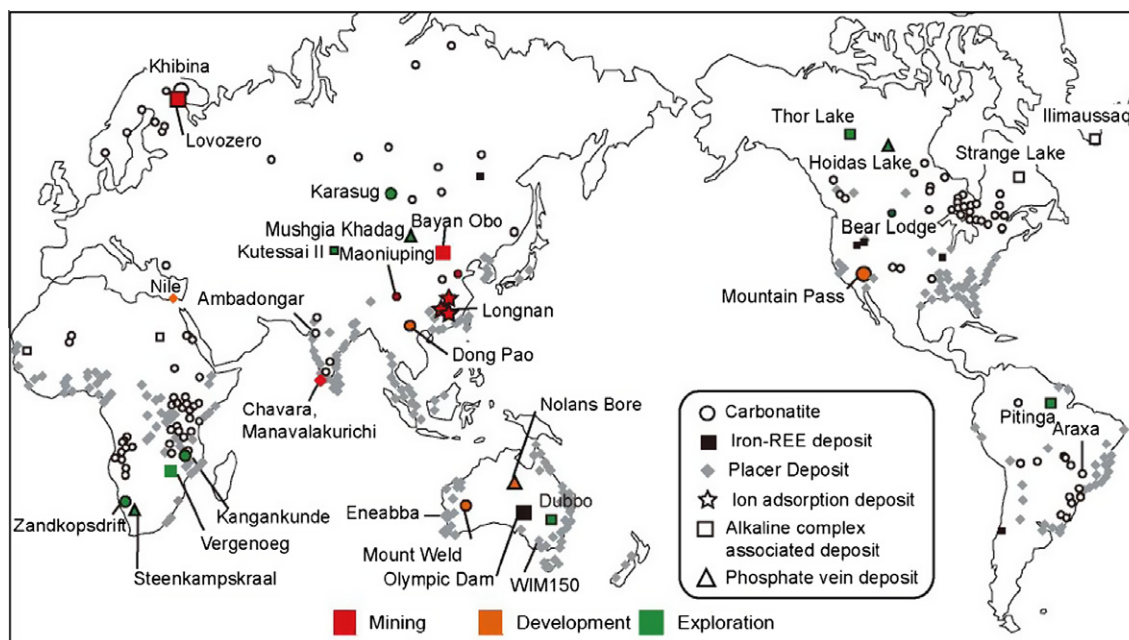


Fig. 10. Worldwide distribution of REE deposits, reserves and operating mines. Reproduced with permission from (Okuya, 2011).

developing new collectors, whilst depressant schemes remain relatively untouched.

4. The future of REE processing

Rare earth mine development is expanding at a rapid pace in light of increasing global demand for these elements in high-technology applications and the quotas being placed on Chinese exports of rare earths (Chen, 2011). In 1989, the annual production capacity of world rare earth mines was approximately 50,000 tonnes, but by 2015 the annual production capacity from non-Chinese sources alone is expected to be close to 170,000 tonnes as detailed in Table 9 (Chen, 2011; O'Driscoll, 1991). This increase in production outside of China is being welcomed by the Chinese government as serious challenges in the mature Chinese rare earth industry have recently come to light (China, 2012). China supplies the majority of the global rare earth demand, however this supply comes from a reserve base that is only 23% of the known global reserves (Chen, 2011; China, 2012). Note that the 23% figure for China's proportion of the world REE reserve base is significantly lower than those reported (50.0% of 2012 world REE reserves) in the widely cited USGS Mineral Commodity Surveys ((Cordier, 2011, 2012; Hedrick, 2009, 2010). The values reported by Chinese sources are reported here as the USGS data does not appear to include a large number of developing Canadian and Australian deposits that have been delineated as REE resources (Simandl, 2012). Since NI 43–101 and JORC reporting requirements are quite stringent in Canada and Australia many of these resources may be classifiable as reserves in other jurisdictions (Simandl, 2012). These resources would then be expected to increase the worldwide total REE reserve base and therefore decrease the Chinese proportion of world reserves (Simandl, 2012). The inevitable depletion of this resource base (the ratio of Chinese ion-absorbed clay reserves, a major source of HREE, to the amount of this material extracted each year has reportedly fallen from 50:1 to 15:1 in the last 20 years), combined with new environmental regulations have led to the creation of a quota system to limit rare earth exports (China, 2012). A rapid expansion of non-Chinese capacity is currently proceeding in response to these quotas. This new growth in global rare earth

capacity may outstrip demand (see Table 9), but it will surely result in multiple new rare earth producers being established. Some of the major deposits scheduled to commence production by 2015 such as the Nechalacho deposit in the Northwest Territories (Canada) and Kvanefjeld (Greenland) will involve minerals and ore compositions that have never been successfully processed and a great deal of industrial and academic research will be required to quickly bridge this knowledge gap. Common minerals, such as sulfides, have been investigated extensively and there are numerous published works on aspects such as interaction with collectors, effects of depressants, and magnetic properties. This knowledge base does not exist for many of the REE minerals and is essential for the successful processing of these minerals. All of the separation techniques described above should be investigated in this context, with a dual focus on the behavior of individual rare earth minerals as well as overall rare earth oxide concentration from ores. The most important of these techniques will likely prove to be flotation as additional reagents and processing conditions are developed and explored.

Fig. 10 shows a worldwide view of rare earth reserves, deposits under development, and currently operating mines; Table 9 displays much of the same data in tabular form. It should be noted that the list of mines and deposits in Table 9 does not match up exactly with the map shown in Fig. 10 as there is no general consensus between authors as to which developing projects have a legitimate chance to develop a full-scale mining operation (and should therefore be included in a discussion of potential REE producers).

5. Conclusion

The separation of rare earth minerals may be fully described using only a handful of mineral developments worldwide, though growing commercial demand for the elements of the lanthanide series has greatly increased the opportunities for the development of new rare earth mineral deposits with novel mineralogy, as well as the research required to effectively separate these minerals. The existing literature on the physical beneficiation of rare earth minerals is mainly focused on the two major REE mineral deposits,

Bayan Obo and Mountain Pass, with a small amount of research material available on other minor rare earth minerals. A considerable amount of rare earth research has been reported in Chinese journals, however, efforts at translating this information have revealed that many of these articles lack the requisite background information (proper chemical names of collector molecules, detailed descriptions of processes etc.) to provide any significant insights into the development of separation processes for alternative rare earth minerals. Each rare earth mineral, no matter how widely investigated, presents significant opportunities for future research.

5.1. Bastnäsite

Bastnäsite processing is accomplished using gravity and magnetic separation steps prior to flotation. Some post-flotation processing may occur in the form of additional gravity and magnetic separations steps but the most important separation process for this mineral is froth flotation. The two most widely explored collector systems are fatty acids and hydroxamates. Reviewing the literature on bastnäsite separation leads to the conclusion that a great deal of research is still required in the separation of these minerals.

- Basic research findings for this mineral such as reported IEP values do not generally agree with one another. Further studies may be able to achieve more reproducible results or propose explanations for the reported differences.
- Chinese researchers have developed a series of alternate reagents to be used in the flotation of the various Chinese bastnäsite deposits yet it seems likely that a great many of the existing processes could benefit greatly from additional work to optimize the flotation process and maximize the utilization of these resources.
- At Mountain Pass, fatty acid and hydroxamate flotation are the principle techniques that have been explored, but with the advances in flotation research, as well as the development of many new flotation reagents since the mine was closed, this deposit will certainly require more research into beneficiation techniques to successfully restart production.
- Many developing REE deposits are finding that their REE mineralogy includes bastnäsite in addition to other REE minerals. These new bastnäsite deposits will require a great deal of future studies to develop beneficiation processes tailored to their varied deposit characteristics.

5.2. Monazite/xenotime

Monazite and xenotime processing is well established from beach sands via a combination of gravity, magnetic and electrostatic separations tailored to the composition of an individual deposit. The flotation of monazite however has not been widely explored. This subject area will become increasingly important as alternate sources of monazite are found in new REE deposits. These deposits may require significantly different beneficiation processes and these needs will drive future research work regarding this mineral. Monazite's physico-chemical characteristics will need to be confirmed and the flotation knowledge base for monazite should also be expanded.

5.3. Other REE Minerals

This paper has presented data on a wide variety of REE bearing minerals, however only some are found in deposits of economic significance. Some examples of these include eudialyte, synchysite, samarskite, allanite, zircon, steenstrupine, cheralite, rhabdophane,

apatite, florencite, fergusonite, loparite, perovskite, cerianite, and pyrochlore. A few of these minerals, such as zircon, apatite and pyrochlore, are extracted for other constituent elements like Zr, P and Nb. As such, the beneficiation of these minerals for REE extraction may be able to borrow extensively from the established processes for these minerals. For the rest, there is essentially no published research available. These minerals present the most attractive opportunity for research into REE bearing minerals as any investigation into the characteristics and behaviors of these minerals, in the context of mineral beneficiation, will present a significant advance in rare earth mineral processing knowledge.

For many of the rare earth-bearing minerals that are present in newly developing deposits there is effectively no peer-reviewed knowledge base to rely on when designing a new rare earth mineral beneficiation process. As the rare earth mineral processing industry grows to accommodate expanding demand, this knowledge deficit will have to be addressed.

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