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THE SULFURIC ACID BAKE AND LEACH ROUTE FOR PROCESSING OF RARE EARTH ORES AND CONCENTRATES: A REVIEW

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Abstract

Rare earths are critical to numerous materials and applications underpinning modern civilisation. The majority of the world's rare earth reserves are hosted in the three minerals bastnasite, monazite and xenotime. A key step in the processing of rare earth mineral concentrates is the chemical decomposition of the mineral structure to release the constituent elements. The sulfuric acid bake has historically been, and is also currently, one of the major processes used for this step. Current sulfuric acid bake processes for the Bayan Obo deposit in China and the Mt. Weld deposit in Australia together account for more than half of the world's rare earth production. In the sulfuric acid bake, the rare earth elements are converted to rare earth sulfates which are dissolved in a subsequent water leach. The conditions required to achieve mineral decomposition vary widely for different rare earth minerals. Adjustment of process conditions may often be used to achieve some degree of impurity rejection which is beneficial to downstream processing. This paper reviews the application of the sulfuric acid bake process to ores/concentrates containing mainly monazite, xenotime and bastnasite, and other less common rare earth minerals including euxenite, samarskite, fergusonite, loparite, allanite, eudialyte and pyrochlore. The reported effects of feed mineralogy and process variables such as reaction temperature, bake duration, acid to concentrate ratio and particle size are presented along with a brief review of current understanding of the bake chemistry and water leach results.

Key words: rare earth, sulfation, acid bake, review, roasting, baking, leaching, sulfuric acid, extraction, rare earth processing

1   Introduction

The rare earths are a group of 17 elements comprising the lanthanides, yttrium and scandium (Connelly et al., 2005). These elements may be further grouped, based on atomic mass, into the light rare earth elements (LREE) and heavy rare earth elements (HREE). The elements included in the light and heavy rare earth groups vary, but for this paper light rare earths are defined as La-Gd and heavy rare earths are defined as Tb-Lu and Y (Gupta and Krishnamurthy, 2005). Rare earths are used in a large number of applications underpinning modern civilisation, some of which are summarised in Table 1. The recent increase in importance and price of REE's has been well discussed (Alonso et al., 2012; Humphries, 2012; Simandl, 2014), with a number of studies identifying certain REE's as critical materials necessary to a myriad of important modern technologies (American Physical Society, 2011; Moss et al., 2013; U.S. Department of Energy, 2012).

Table 1   Examples of important technologies utilising rare earths

Application	REE Elements	Products
Nd-Fe-B magnets	- Neodymium - Dysprosium	Electric cars, wind turbines, MRI, laptop hard-drives, mobile phones, headphones, cordless tools, power steering, servo-motors, miniaturization of technology in general
Phosphors	- Europium - Terbium - Yttrium	Fluorescent lighting, plasma TV, computer screens, flat panel FED (Field Emission Displays)
Solid state lasers	- Neodymium - Yttrium	Non-invasive microsurgery, material processing (e.g cutting, welding, heat-treating), dental treatment
Terfenol-D[1]	- Terbium - Dysprosium	High power actuators, naval sonar devices, micropositioners, fluid control valves
Electronics (synthetic garnets)	- Yttrium - Neodymium	Microwave communication devices for defense and satellite industries, frequency and magnetic field meters, tunable transistors
Ceramics	- Yttrium	Yttria-stabilized zirconia refractory, sintering aids, automotive oxygen sensors

[1]Metal alloy exhibiting magnetostriction.
Data from Gupta and Krishnamurthy (2005), Haque et al. (2014), Hurst (2010) and U.S. Department of Energy (2012)

Approximately 200 rare earth bearing minerals have been identified. However, ~95% of the world's known rare earth resources are associated with the three minerals bastnasite, monazite and xenotime (Gupta and Krishnamurthy, 2005). In addition to rare earth bearing ion-adsorption clays, these three have been the principal minerals commercially processed for

extraction of rare earths (Haque et al., 2014). Loparite is also processed for production of rare earths in Russia, but the contribution to global production is small, equal to less than 3% of the total in 2016 (Kosynkin et al., 1993; U.S. Geological Survey, 2017).

The rare earths have ionic radii similar to those of Na^+, Ca^{2+}, Th^{4+}, and U^{4+} in the range of 116-110 pm, and are therefore often found substituting for these elements in minerals (Kanazawa and Kamitani, 2006). The LREEs tend to occupy larger coordination sites with coordination numbers of 8-10, which occur in carbonate and phosphate based minerals, while HREE's tend to concentrate in oxide and some phosphate minerals, with coordination numbers of 6-8 (Kanazawa and Kamitani, 2006). A list of the formulae for the three major rare earth minerals and some of the less common rare earth minerals that have been found amenable to sulfuric acid baking is provided in Table 2 (Castor and Hedrick, 2006, Long et al., 2012). A comparison of the varying rare earth distribution and total rare earth content in monazite, xenotime, bastnasite and ion-adsorption clays is given in Table 3. Monazite is a LREE rich rare earth phosphate incorporating 4-12% ThO_2 (Aplan, 1989) and is usually found in alluvial or placer type deposits. Xenotime is a HREE rich rare earth phosphate usually containing less than ~2.5% ThO_2 (Spears and Pyle, 2002). Xenotime is generally found occurring with monazite in placer type deposits at a xenotime-to-monazite weight ratio of 1:200 to 1:20 (Gupta and Krishnamurthy, 2005). Bastnasite is a LREE rich rare earth fluorocarbonate, with a fluoride content in the range of 6.2-8.5%, and a carbonate content of ~20% as CO_2 (Gupta and Krishnamurthy, 2005).

The presence of the radioactive element thorium in monazite, and to a lesser extent, xenotime and bastnasite, represents one of the major challenges for processing of ores containing these minerals (Long et al., 2010). Thorium must be separated from the rare earths during processing to avoid contamination of the final rare earth products, and thorium-containing radioactive wastes must be properly managed to avoid environmental pollution (Zhu et al., 2015). Long et al. (2010) notes that, due to the tight regulations involved, the handling of radioactivity during processing can significantly impact the economic viability of a rare earth extraction process.

Table 2 A selection of rare earth bearing minerals with recognized or potential economic significance used in sulfuric acid processing studies

Major/Minor	RE mineral	Mineral type	Formula (Long et al., 2012)
Major	Monazite-(Ce)	Phosphate	$(Ce,La,Nd,Th)PO_4$
	Xenotime	Phosphate	YPO_4
	Bastnasite	Carbonate	$(Ce,La,Y)CO_3F$
Minor	Eudialyte	Silicate	$(Na,Ca,REE)_5(Fe^{2+}Mn)(Zr,Ti)[(Si_3O_9)_2](OH,Cl)$
	Allanite (orthite)	Silicate	$Ca(Ce,La,Y,Ca)Al_2(Fe^{2+},Fe^{3+})(SiO_4)(Si_2O_7)O(OH)$
	Euxenite	Oxide	$(Y,Er,Ce,U,Pb,Ca)(Nb,Ta,Ti)_2(O,OH)_6$
	Samarskite	Oxide	$(Y,Er,Fe,Mn,Ca,U,Th,Zr)(Nb,Ta)_2(O,OH)_6$
	Loparite	Oxide	$(Ce,Na,Ca)(Ti,Nb)O_3$
	Fergusonite	Oxide	$YNbO_4$
	Pyrochlore	Oxide	$(Ca,Na,REE)_2Nb_2O_6(OH,F)$

Table 3 Relative rare earth distribution and total rare earth content in monazite, xenotime, bastnasite and ion-adsorption clays

Elements	Rare earth distribution (%)			
	Monazite, Australia	Xenotime, Malaysia	Bastnasite, Mountain Pass, U.S.	Ion-adsorption clay, Longnan, China
LREE (La-Gd)	96.9	14.5	99.7	15.7
HREE (Tb-Lu and Y)	3.9	85.5	0.1	83.1
TREO[a] content (%)	50-70	52-62	70	0.05-0.2

[a]Total Rare Earth Oxide; data from Gupta and Krishnamurthy (2005)

La-Gd includes: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu) and gadolinium (Gd);
Tb-Lu includes: terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu).

Processing of rare earth ores to pure rare earth products is typically a complex and lengthy process, incorporating (a) beneficiation, (b) decomposition of the rare earth mineral concentrate to extract the rare earth elements, and (c) further chemical processing involving impurity removal and separation of individual rare earths to produce purified saleable products.

Sulfuric acid baking, the subject of this review, is one of the major processes used in industry for the mineral decomposition step. The sulfuric acid bake is currently used in the processing of concentrates from two major rare earth deposits, namely Bayan Obo in China and Mt. Weld in Australia (with processing facility in Kuantan, Malaysia) operated by Lynas (Gupta and Krishnamurthy, 2005). Zhu et al. (2015) reported that the sulfuric acid bake process at

Baotou was responsible for more than 60% of China's total rare earth production, which in 2015 accounted for 81% of the world's rare earth production (U.S. Geological Survey, 2017).

The flowsheet for a typical sulfuric acid decomposition process is shown in Figure 1. The rare earths are converted to sulfates by reaction with concentrated sulfuric acid at elevated temperature. The rare earth sulfates are then dissolved during the water leaching step. It is important to note that the rare earth sulfate reaction products are insoluble in concentrated sulfuric acid, and do not dissolve during the digestion stage. Sulfuric acid based decomposition of rare earth minerals was historically carried out as a batch process, in a closed but vented reactor (Eyring, 1964); however, current industrial operations use a rotary kiln, which enables continuous operation (Lynas Corporation Ltd, 2011; Zhang et al., 2015). In this work the decomposition process is referred to as the 'sulfuric acid bake' for consistency; however, the process has been variously described in the literature as a sulfation roast, acid bake or acid digestion.

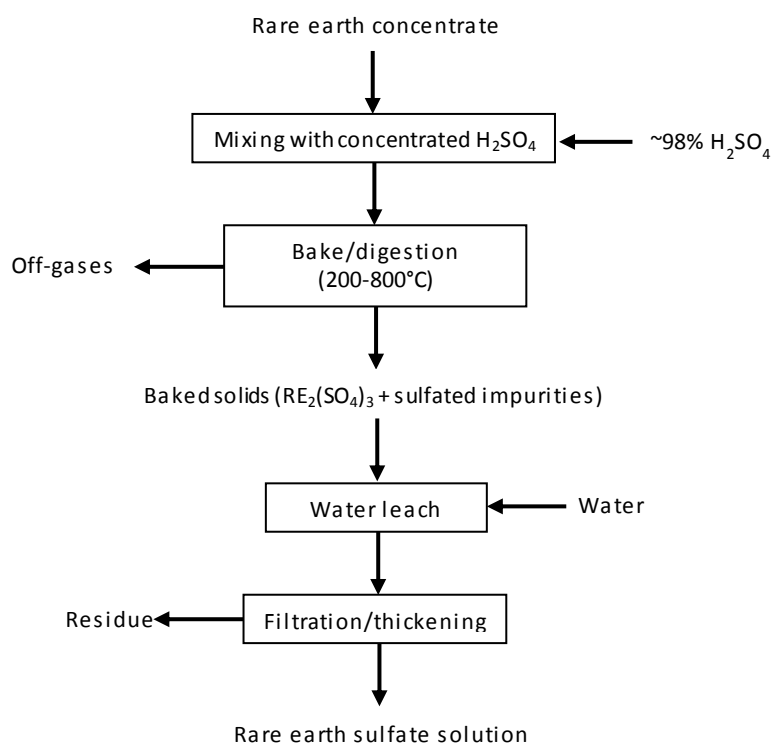Figure 1 Typical process flowsheet for sulfuric acid treatment of a rare earth mineral concentrate (Gupta and Krishnamurthy, 2005; Zhang and Edwards, 2013)

A number of rare earth processing reviews have recently been published, reflecting the current widespread interest in rare earth elements. Jordens et al. (2013) published a review on the beneficiation of rare earth minerals, while Xie et al. (2014) reviewed the separation of

rare earths by solvent extraction. Zhu et al. (2015) reviewed processing technologies used for separation of thorium and uranium from rare earths during rare earth production. General reviews on the hydrometallurgical processing of rare earth concentrates by Sadri et al. (2017a) and Jha et al. (2016) have also recently been published, while the processing of monazite for production of rare earth elements has been reviewed by Kumari et al. (2015). The Sadri et al. (2017a) review provides an overview of some industrial sulfuric acid bake processes, while Jha et al. (2016) and Kumari et al. (2015) only provide brief descriptions of the acid bake process. A review specifically focused on the sulfuric acid bake of rare earth ores/concentrates has thus far been lacking, in spite of the current significance of the acid bake process to global rare earth production.

This article reviews both current and historical industrial processes, patents and research studies on sulfuric acid baking for processing of ores/concentrates containing monazite, xenotime and bastnasite as major rare earth minerals and ores/concentrates containing less common rare earth minerals including heavy rare earth tantaloniobates (euxenite, samarskite and fergusonite), loparite, allanite, eudialyte and pyrochlore. A brief review of the chemistry of the acid bake process is also presented along with an examination of the effects of temperature, acid addition, mineralogy and particle size. The water leaching step, following the bake, is also examined, and an analysis of the effects of liquid to solid ratio, temperature and acidity on the solubility and extraction of rare earths and impurities is provided.

2   Sulfuric Acid Baking of Monazite

Only baking with concentrated sulfuric acid or digestion in sodium hydroxide has found industrial application for monazite (Neelameggham et al., 2014). Caustic conversion is the preferred industrial process for processing of high grade monazite sands, while the sulfuric acid bake is typically used for lower grade ores/concentrates. The caustic route has the advantage of inherently achieving separation of phosphorus from the rare earths in the form of trisodium phosphate, a potentially saleable product in the fertilizer industry. However, the higher cost of the reagent makes the caustic route less suitable for lower grade concentrates. A cut-off grade of ~70 wt.% rare earth mineral has been quoted for the caustic conversion process due to the high reagent consumption (Lucas et al., 2014).

The sulfuric acid treatment route was first utilised for processing of monazite concentrates from mineral sands deposits in the United States in the late 1800's and early 1900's

(Hammond, 1947; Kithil, 1915) and is currently used by Lynas Corporation for rare earth production from a monazite concentrate (38% TREO) from the Mt. Weld deposit in Australia (Lynas Corporation Ltd, 2011). A summary of conditions from studies in the literature on sulfuric acid baking/digestion of monazite bearing ores/concentrates is given in Table 4.

Table 4 Published conditions for sulfuric acid bake/digestion of monazite bearing concentrate

Ore/concentrate grade data[a]	Acid: solid ratio (w/w)	Bake temperature (°C)	Time (h)	RE extraction in leach (%)	Leach medium	Reference
	~1.1:1	200 then 300			water	(a)
60 % TREO[b]	2.8:1	210-230	3		water	(b)
70 % monazite	2.9 to 3.2:1	204-215	1.5		water	(c)
	1.56:1	200-230	5		water	(d)
	1.56:1	210	4	99	water	(e)
40 % TREO	1.5:1	200-245	2		water	(f)
90 % monazite	2.76:1	210	4	98	water	(g)
	2:1	250	1	90	water	(h)
	2-3:1	250-300	0.5			(i)
60 % TREE[c]	2:1	160	1	98	water	(j)
	2.9:1	210	4		water	(k)
97 % monazite	2:1	200-220	2		water	(l)
5.1% TREE	0.6:1	220	1	83	water	(m)
	2.5:1	220	2.5		water, then acid	(n)
	1.1 to 1.7:1	180-220	2	>95		(p)
50-60 % TREO	1.4:1	500-900		~92	water	(o,p)
25 % TREO	2.5:1	225	3.5		water	(q)
1.2 % monazite	2.5:1	270	1.8	83-86	water	(r)
93 % monazite	1.7:1	200-800	2	55-99	0.9 M H_2SO_4	(s)
47.9 % TREE	1 to 4:1	180-250	1-4	up to 97	water	(t)
7.1 % TREO	0.43:1	700	2	66	water	(u)

[a] Descriptions of ore/concentrate grade in the literature varied from % TREO to % TREE to % monazite mineral;

[b] TREO = total rare earth oxide; [c]TREE = Total Rare Earth Elements

References: (a) McCoy (1921) (b) Pilkington and Wylie (1947) (c) Urie (1947) (d) Shaw et al. (1954) (e) Barghusen and Smutz (1958) (f) Borrowman and Rosenbaum (1961) (g) Tobia (1963) (h) Kawamura et al. (1966) (i) Takeuchi (1976) (j) Te Riele and Fieberg (1982) (k) AlFulaij and AbdelAziz (1996) (l) Moustafa and Abdelfattah (2010) (m) Notzl et al. (2013) (n) Ahmed et al. (2015) (o) Zhu et al. (2015) (p) Zhang et al. (2015) (q) Sadri et al. (2017b) (r) Soltani et al. (2018) (s) Demol et al. (2018) (t) Berry et al. (2018) (u) da Silva et al. (2018)

2.1   Effect of Temperature

2.1.1   Low Temperature Processes (<300 °C)

Early studies on sulfuric acid based decomposition of monazite quickly identified that minimum temperatures of 200-250°C were required for complete breakdown of the mineral in a relatively short period of time (see data in Table 4). Baking at these temperatures is characterised by complete solubilisation of the rare earths, thorium and phosphate in the subsequent water leach (Eyring, 1964), assuming that the acid to feed ratio and bake duration/kinetics are not limiting factors. Table 5 lists the various chemical reactions which occur during sulfuric acid bake process at various temperatures (Wang et al., 2010; Li et al., 2010; Demol et al., 2018; Schwartz et al., 2000). Temperatures lower than 200°C have generally been insufficient for complete decomposition in a reasonable time due to slow reaction kinetics (Shaw et al., 1954; Takeuchi, 1976). In a study with an Idaho monazite sand, Shaw et al. (1954) found that at 140°C a reaction time of 44 hours was required to achieve complete mineral decomposition. Takeuchi (1976) studied the rate of reaction of a monazite sand sample at temperatures between 200 and 300°C, and found that the decomposition rate steadily increased with increasing temperature over this range. However, some monazites have been found amenable to acid treatment at temperatures lower than 200°C. Tassinari et al. (2001) obtained over 70% rare earth extraction from a Brazilian monazite sample using concentrated sulfuric acid at room temperature. In this case, the unusually high dissolution of the monazite was attributed to its presence as very small crystallites with a high surface area. Monazite concentrate from the Richard's Bay deposit in South Africa has also been found to be unusually amenable to digestion with sulfuric acid. Virtually complete decomposition was achieved by leaching in concentrated sulfuric at 160°C for two hours (Te Riele and Fieberg, 1982).

A low temperature acid bake process, using a bake temperature of less than 300°C, was initially adopted by China in the 1970s for processing the rare earth concentrate produced as a co-product from the Bayan Obo iron ore deposit (Zhang et al., 2015). Advantages cited for China's low temperature bake process included a consistent product quality and ease of operation. However, the downstream flowsheet for purification of the leach solution was long and complex, including precipitation of rare earth double sulfates followed by caustic conversion (Zhang et al., 2015).

2.1.2 *High Temperature Processes (≥300 °C)*

A number of studies established that increasing the bake temperature to 300°C or above could lead to the conversion of thorium sulfate to insoluble thorium phosphate type

compounds. In an early patent by McCoy (1921) a process was described involving a two-stage digestion of an Indian monazite sand (92% monazite), with the second stage carried out at approximately 300°C for 8-10 hours. It was claimed that after this treatment thorium reported to the leach residue as an insoluble thorium phosphate, possibly a metaphosphate (Table 5). A similar process was patented by Berndt (1920) using a slightly higher final bake temperature of 300-350°C for only 1-1.5 hours. Thorium was described as being in an insoluble and concentrated form following this treatment. Both authors described the desired final digestion product becoming a yellow or yellow-green colour. A third patent from this era, filed by the Lindsay Light Company (1921), claimed that a thorium compound with the formula $Th(PO_3)_2SO_4$ was formed when monazite sand was treated with sulfuric acid at an unspecified high temperature for an extended period of time, while the rare earths were not affected. This compound was insoluble in both water and dilute sulfuric acid. Recently, Demol et al. (2018) found that an amorphous thorium phosphate type compound, possibly thorium pyrophosphate, precipitated in the leach stage after baking monazite at 300°C.

Although these proposed processes achieved at least partial separation of thorium from the rare earths during the digestion stage, the high temperature digestion process was not utilised in industry at the time (Eyring, 1964; Wylie, 1959). Reasons cited included: (a) the thorium product thus produced was relatively inert making subsequent chemical processing difficult, (b) the technical problems associated with the higher temperature treatment, and (c) the unwanted oxidation of cerium under these conditions (Wylie, 1959). Note that in these earlier studies thorium, rather than the rare earths, was viewed as the desired product, mainly due to potential use of thorium for generation of nuclear power (Wylie, 1959). However, there is currently very little market for thorium, which has not yet realised its potential in the nuclear industry, and thorium is now viewed as a radiation hazard during processing of rare earth ores (Zhu et al., 2015).

The first reported industrial use of a high temperature (>300°C) sulfuric acid bake process occurred in China for processing of Baotou concentrate (Huang et al., 2015; Zhang et al., 2015). The flowsheet used is shown in Figure 2. Purification via the double sulfate route, used in the earlier low temperature process, was replaced with a neutralisation step followed by solvent extraction of rare earths from the sulfate solution or precipitation of a mixed rare earth carbonate.

Rare earth concentrate

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Drying
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Off-gases ← Roasting with concentrated sulfuric acid (800-900°C) ← ~98% H_2SO_4

Residue ← Leaching

Impurity removal ← Lime
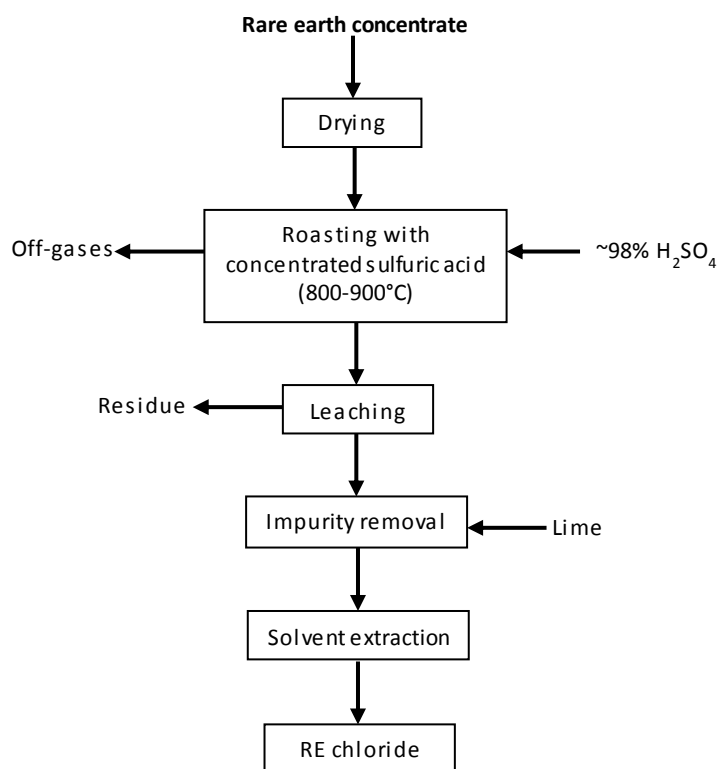
Solvent extraction

RE chloride

Figure 2 High temperature sulfuric acid bake process flowsheet used at Baotou, as described in Zhang et al. (2015)

The high temperature acid bake is still currently used for processing 90% of the concentrates produced at Baotou (Zhu et al., 2015). Some variation exists in the literature regarding the actual bake temperature used. Zhang et al. (2015) quotes a temperature range of up to 800-900°C, while other authors indicate a minimum bake temperature of 500°C (Yong et al., 2014; Zhu et al., 2015). The main reported advantage of the high temperature bake process was the rejection of impurities such as iron, thorium, calcium and phosphate, which were rendered insoluble (Yong et al., 2014; Zhang et al., 2015). Other advantages cited included shorter processing times, a single solid-liquid separation step, less damage to equipment, improved rare earth recoveries, strong process continuity and adaptability to different rare earth concentrate grades (Zhang et al., 2015). Figure 3a shows the effect of temperature on the concentrations of iron, phosphorus and thorium in the leach solution for bake temperatures from 450 to 650°C. Less of the impurities leached as the bake temperature increased, while the extent of what was termed in the paper "decomposition rate", presumably a measure of the rare earth extraction (%), only slightly decreased. Demol et al. (2018) also studied the effect of bake temperature on leaching of rare earths and impurities from a high grade monazite concentrate, over a wider temperature range from 200 to 800°C,

and results are shown in Figure 3b. The leach dissolution of all elements was greater than 90% after baking at 250°C. At higher temperatures the dissolution of phosphorus and thorium decreased sharply, similarly to results from acid baking of Baotou concentrate shown in Figure 3a (Zhang et al., 2015). However, the rare earth dissolution also decreased significantly for bake temperatures of 400°C and above (Figure 3b), which differed from the results in Figure 3a.
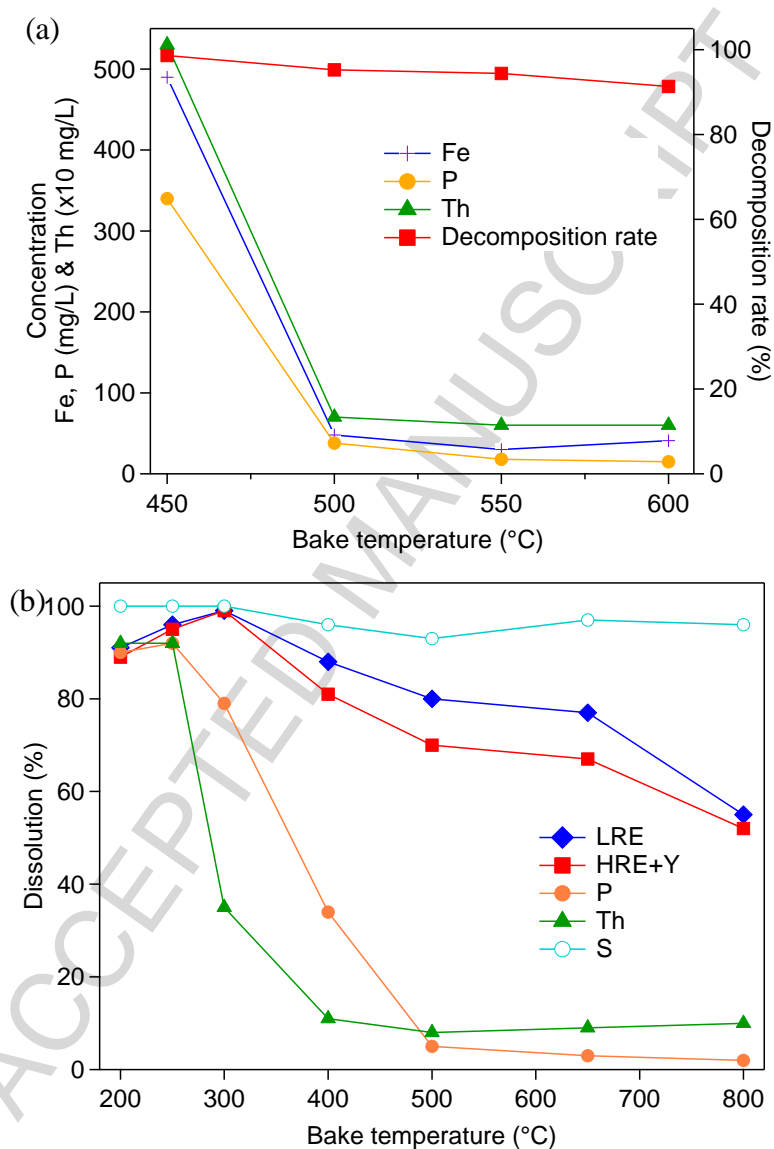

Figure 3 Effect of bake temperature on the leaching of rare earths and impurities for (a) Baotou concentrate between 450°C and 600°C, data from Zhang et al. (2015), and for (b) high grade monazite concentrate between 200°C and 800°C, data from Demol et al. (2018)

The development of the high temperature bake process in China addressed many of the problems of the earlier low temperature process, but also created additional concerns. These were mainly of an environmental nature, relating to an increased amount of toxic off-gases such as sulfur dioxide, hydrogen fluoride and fluorosilicic acid, which require treatment, and the generation of a large quantity of solid radioactive waste residue (Zhang et al., 2015). As a result, a number of recent Chinese studies have focused on developing 'clean' low temperature acid bake processes, similar to the early low temperature bake process but combined with improved technologies for recovery/separation of impurities (Huang et al., 2015; Yong et al., 2014; Zhang et al., 2015).

A patent by Li et al. (2010) also describes a high temperature sulfuric acid bake process, in this case for decomposing an iron-rich monazite ore where iron is finely intergrown with monazite making separation by beneficiation difficult. The patented process involves baking with sulfuric acid in the temperature range of 231-600°C. As with the high temperature Baotou process, the main advantage appeared to be the conversion of impurities, in this case iron, to insoluble phases during the bake while maintaining high rare earth recoveries. Berni et al. (2013) and Teixeira et al. (2018) describe a high temperature acid bake for the selective extraction of rare earths over iron and thorium from an iron-rich monazite ore. The optimum bake temperature was 700°C, giving a rare earth extraction of 73% and iron and thorium extractions of <5% and <10%, respectively. Iron rejection was attributed to thermal decomposition of iron sulfate to hematite.
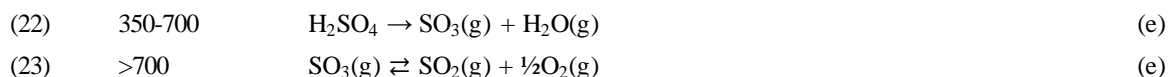
There are some reports in the literature of high temperature acid baking leading to decreased dissolution of rare earths during leaching. In the McCoy (1921) patent, it was stated that the insoluble thorium compound resulting from a bake at 300°C also contained a portion of the rare earths. Nazari and Krysa (2013) also suggested a decrease in solubility of the rare earth sulfates formed at higher baking temperatures. In the Baotou high temperature bake process, there was only a slight decrease in rare earth extraction after baking at 600°C (Figure 3), where a rare earth extraction of 92% was obtained compared to 93-95% for a low temperature bake (Zhang et al., 2015). However, Teixeira et al. (2018) found that rare earth extractions from an iron-rich monazite ore decreased sharply for acid bake temperatures of 750°C and above. Demol et al. (2018) found that rare earth extractions decreased after baking monazite at temperatures of 400°C-800°C (Figure 3b).

2.2 Bake Chemistry

For monazite, the reactions with sulfuric acid are generally assumed to proceed via reactions (1) and (2) in Table 5 (Fernelius et al., 1946; Wang et al., 2010). Very little information is available in the literature on the thermodynamics of the reaction of monazite with sulfuric acid. Jamrack (1963) reported that the reaction of monazite with sulfuric acid is an exothermic process. Using differential thermal analysis (DTA), Takeuchi (1976) estimated the enthalpy of reaction of monazite with sulfuric acid to be approximately -171 kJ/mol (presumably a high grade monazite concentrate, but not stated). Based on the reaction rates from the initial monazite decomposition curves (approximated by proportion of 'unreacted thorium'), Takeuchi (1976) obtained a low activation energy of ~4.2 kJ/mol for the reaction of monazite with sulfuric acid in the temperature range of 200-300°C. The low activation energy generally indicates that the rate controlling step involves the diffusion of acid through an insoluble reaction product layer that coats the rare earth mineral particles in the bake temperature range of 200 to 300°C (Takeuchi, 1976).

Table 5 Reactions reported in the literature for the sulfuric acid bake process

Eq. no.	Bake temperature (°C)	Reactions	Reference(s)
(1)	148-250	$2REPO_4 + 3H_2SO_4 \rightarrow RE_2(SO_4)_3 + 2H_3PO_4$	(a)
(2)	148-250	$Th_3(PO_4)_4 + 6H_2SO_4 \rightarrow 3Th(SO_4)_2 + 4H_3PO_4$	(a)
(3)	148-250	$2RECO_3F + 3H_2SO_4 \rightarrow RE_2(SO_4)_3 + 2HF(g) + 2CO_2(g) + 2H_2O$	(a)
(4)	unspecified	$2YPO_4(s) + 3H_2SO_4(l) \rightarrow Y_2(SO_4)_3(s) + 2H_3PO_4(l)$	(b)
(5)	148-250	$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O(g)$	(a)
(6)	148-250	$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF(g)$	(a)
(7)	148-250	$SiO_2 + 2HF(g) \rightarrow SiF_4(g) + H_2O(g)$	(a)
(8)	unspecified	$Ca_5(PO_4)_3F(s) + 5H_2SO_4(l) \rightarrow 5CaSO_4(s) + 3H_3PO_4(l) + HF(g)$	(b)
(9)	unspecified	$CaCO_3(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(g)$	(b)
(10)	unspecified	$Fe_3O_4(s) + 4H_2SO_4(l) \rightarrow Fe_2(SO_4)_3(s) + FeSO_4(s) + 4H_2O(g)$	(b)
(11)	285-367	$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O(g)$	(a)
(12)	285-367	$Th(SO_4)_2 + H_4P_2O_7 \rightarrow ThP_2O_7 + 2H_2SO_4$	(a)
(13)	300	$CaSO_4 + H_4P_2O_7 \rightarrow Ca_2P_2O_7$	(c)
(14)	285-367	$H_4P_2O_7 \rightarrow 2HPO_3 + H_2O(g)$	(a)
(15)	285-367	$Th(SO_4)_2 + 4HPO_3 \rightarrow Th(PO_3)_4 + 2H_2SO_4$	(a)
(16)	407-435	$Fe_2(SO_4)_3 \rightleftarrows Fe_2O_3 + 3SO_3(g)$	(a)
(17)	400	$2Fe_2(SO_4)_3 + 3H_4P_2O_7 \rightarrow Fe_4(P_2O_7)_3 + 6H_2SO_4$	(c)
(18)	400	$Fe_2(SO_4)_3 \rightarrow Fe_2O(SO_4)_2 + SO_3(g)$	(c)
(19)	800	$3Th(PO_3)_4 + 4La_2(SO_4)_3 \rightarrow 8LaPO_4 + Th_3(PO_4)_4 + 12SO_3(g)$	(d)
(20)	800	$La(PO_3)_3 + La_2(SO_4)_3 \rightarrow 3LaPO_4 + 3SO_3(g)$	(d)
(21)	330	$H_2SO_4 \rightarrow H_2SO_4(g)$	(e)

| (22) | 350-700 | $H_2SO_4 \rightarrow SO_3(g) + H_2O(g)$ | (e) |
| (23) | >700 | $SO_3(g) \rightleftarrows SO_2(g) + \frac{1}{2}O_2(g)$ | (e) |

(a) Wang et al. (2010) (b) Soltani et al. (2018) (c) Li et al. (2010) (d) Demol et al. (2018) (e) Schwartz et al. (2000)

Much of the current knowledge of acid bake reactions listed in Table 5 stems from studies of the reaction of Baotou concentrate with acid. The composition of Baotou concentrate is shown in Table 6. In addition to bastnasite and monazite, the concentrate also contains hematite, fluorite, silica and barite (Gupta and Krishnamurthy, 2005; Wang et al., 2010). In the sulfuric acid bake these minerals are reported to react with acid via reactions (5) to (7) in Table 5 (Wang et al., 2010).

Table 6 Composition of Baotou concentrate from Bayan Obo in China

	TREO	ThO_2	Fe	F	P_2O_5	SiO_2	CaO	BaO
wt.%	59.9	0.24	2.47	8.37	5.31	1.14	9.31	0.60

Data from Wang et al. (2010)

Wang et al. (2010) carried out a thermogravimetric and differential thermal (TG/DTA) study of the decomposition of Baotou concentrate with sulfuric acid at temperatures up to 500°C. An endothermic thermal event observed at 330°C was attributed to a series of reactions initiated by decomposition of phosphoric acid, produced from the initial sulfation of monazite, to pyrophosphoric ($H_4P_2O_7$) and polyphosphoric acids (e.g. $(HPO_3)_n$). As claimed in the earlier patents from the 1920's (Berndt, 1920; McCoy, 1921), this was reported to lead to reaction with thorium to form insoluble thorium pyro- and polyphosphates via reactions (11) to (15) in Table 5 (Wang et al., 2010).

Yong et al. (2014) stated that calcium sulfate, formed from reaction of acid with fluorite in the Baotou concentrate, is also attacked by pyrophosphoric acid resulting in the formation of calcium pyrophosphate. However, no experimental evidence was provided for the presence of these species as reaction products.

In the TG/DTA study by Wang et al. (2010) a further thermal event occurred at 425°C which was attributed to decomposition of ferric sulfate to form hematite and sulfur trioxide (Reaction (16) in Table 5). In contrast, results from thermal decomposition studies of pure ferric sulfate indicate that the decomposition occurs in a single stage at a higher temperature, between 600°C and 700°C (Siriwardane et al., 1999; Tagawa, 1984). It is possible that in the

Baotou concentrate reaction mixture the decomposition temperature is lowered by about 200°C.

Li et al. (2010) quoted similar reactions for dehydration of phosphoric acid above 300°C leading to the formation of insoluble thorium and calcium pyrophosphates as described in reactions (11) - (13), but claimed that for an iron-rich ore, iron pyrophosphate is also formed at 400°C, via reaction (17) (Table 5). Ferric sulfate was also said to decompose at 400°C, forming basic iron sulfate via reaction (18) rather than the hematite via reaction (16) reported by Wang et al. (2010) for baking of Baotou concentrate. Both forms of iron were insoluble during water leaching (Li et al., 2010).

Demol et al. (2018) investigated the reaction products formed during acid baking of a high grade monazite concentrate between 200°C and 800°C. In agreement with Wang et al. (2010), insoluble and amorphous thorium polyphosphates were formed at bake temperatures ≥400°C. However, Demol et al. (2018) found that rare earth elements were also partially incorporated into these polyphosphate species, leading to a decrease in rare earth extraction for bake temperatures of 400°C and above. After baking at 800°C, monazite was re-formed leading to a further decrease in rare earth extraction to only 55%, compared to 99% extraction after baking at 300°C. The re-formed monazite was suggested to be the product of a reaction between the thorium and rare earth polyphosphates and rare earth sulfate, as shown in reactions (19) and (20) (Table 5).

An important aspect of acid bake chemistry is the decomposition and volatilisation of sulfuric acid. Both Schwartz et al. (2000) and Soltani et al. (2018) have calculated equilibrium concentrations for the decomposition of pure sulfuric acid based on thermodynamic data and showed that both direct evaporation, and decomposition to sulfur trioxide and water via reactions (21) and (22) respectively are expected to occur at temperatures above ~200°C (Table 5). The indicated extent of direct evaporation of sulfuric acid differed significantly between the two papers, with Soltani et al. (2018) showing direct evaporation to be the predominant process at ~330°C (close to the 337°C boiling point of sulfuric acid), while in Schwartz et al. (2000) the decomposition to sulfur trioxide and water predominated. At temperatures above 350°C, the decomposition via reaction (22) was the major process, in both sources.

As the temperature was further increased, the computed equilibria showed that a second process occurs, involving the decomposition of SO_3 to SO_2 and O_2 via reaction (23) in Table 5, which predominates over reaction (22) as the temperature reaches ~700°C. Higher bake temperatures therefore increase the overall acid requirement due to an increased rate of acid loss to the gas phase. For baking of Baotou concentrate, Zhang et al. (2015) reported that if relatively low temperatures of 150-220°C were used, the decomposition of sulfuric acid could be largely suppressed resulting in tail gases that were more easily treated and recovered. These findings are consistent with the thermodynamic data published by Soltani et al. (2018) and Schwartz et al. (2000), discussed above.

2.3   Effect of Sulfuric Acid to Concentrate Ratio

Concentrated sulfuric acid is required to crack the mineral structure of monazite. Working with a monazite sand, Blickwedel (1949) found that for sulfuric acid concentrations lower than 93% the reaction rate decreased rapidly. However, it was suggested that the use of slightly diluted sulfuric acid (i.e. ~93%) can improve reaction kinetics by allowing better agitation during the digestion, thereby assisting mass transfer of the acid (as cited in Shaw et al. (1954)). This reasoning only applies to a digestion carried out in an enclosed reactor, and is not applicable to conventional acid baking, where any additional water is quickly volatilized.

For a high grade monazite concentrate, an acid to concentrate ratio in the range of 1:1 to 2.5:1 (w/w) is typically used (see Table 4). This is equivalent to 2-3 times the stoichiometric requirement (Zelikman et al., 1966), showing that an excess of acid is needed. Sadri et al. (2017b) found that increasing the acid to concentrate ratio from 1:1 to 2.5:1 (w/w) increased rare earth extraction during acid baking of a 69% monazite concentrate. The increased extraction was at least partially attributed to an increased time required for complete decomposition of acid resulting in a longer effective reaction time. Soltani et al. (2018) similarly found an improvement in rare earth extraction when increasing the acid to concentrate ratio from 2:1 to 3:1 (w/w), for acid baking of a fluorapatite rich monazite concentrate. Similar results were obtained by Takeuchi (1976) for the acid bake of a monazite sand. Berry et al. (2018) found that both thorium and uranium extraction from a monazite concentrate increased as the acid to concentrate ratio increased from 1:1 to 4:1.

2.4 Effect of Particle Size

The reaction kinetics of the ore/concentrate with acid are partially determined by the particle size distribution of the feed material. Reducing the particle size increases surface area per unit mass leading to an increased reaction rate. There is very little information in the literature on the kinetics of the reaction of monazite with sulfuric acid. In one of the few studies available, Takeuchi (1976) showed that the rate of reaction increased dramatically when the particle size decreased from >300 μm to 100-150 μm. A further sharp increase in reaction rate was obtained for a particle size range of 53-74 μm.

A particle size range of 100-150 μm has been reported to be sufficient for decomposition of high grade monazite concentrates within 1-4 hours (Fernelius et al., 1946; Zelikman et al., 1966). Mineral concentrates produced from placer deposits are often treated without grinding (Ahmed et al., 2015; Jamrack, 1963; Urie, 1947), although the size distribution of unground monazite sand can span from 50 to 600 μm (Jamrack, 1963).

3 Sulfuric Acid Baking of Xenotime

Commercial processing of xenotime concentrates has been via the sulfuric acid bake process. The Malaysian Rare Earth Corporation (MAREC) plant in Malaysia processed a xenotime sand concentrate by a sulfuric acid bake process during the 1990's (Meor Yusoff and Latifah, 2002; Sulaiman, 1991). An acid bake process, followed by solvent extraction, was also used by the Megon Company in Norway, founded in 1969, for production of high purity yttrium oxide (99.995%) from xenotime (Gupta and Krishnamurthy, 2005).

Compared to monazite, there has been less work published on the acid baking of xenotime, probably related to it being a much less common rare earth mineral, despite its economic relevance as noted in Table 2 (Gupta and Krishnamurthy, 2005). The acid baking proceeds according to reaction (4) in Table 5 (Vijayalakshmi et al., 2001).

Table 7 summarises the experimental conditions from the published acid baking studies of xenotime. In an early study, Banks et al. (1959) adapted acid bake conditions previously developed at the Ames Laboratory for monazite, to decompose xenotime. They noted that a slightly higher bake temperature and slightly longer bake duration was required for complete decomposition of the xenotime. A bake duration of 10-12 hours was used with a bake temperature of 240-250°C (Banks et al., 1959). This was a much longer bake time than used

in a previous Ames process for monazite, which involved only 4 hours at 210°C and resulted in 99% digestion (Barghusen and Smutz, 1958). Vijayalakshmi et al. (2001) also baked a xenotime concentrate for a relatively long duration of 6 hours at 250°C, and obtained 99% yttrium extraction. In acid baking tests on xenotime concentrate from the Brown's Range deposit in Australia, Hadley and Catovic (2014) reported that temperatures below 275°C were insufficient for complete breakdown of the mineral in 3 hours, and recommended baking at 300°C for >95% rare earth extraction after 1 hour.

Table 7 Published conditions for H_2SO_4 bake/digestion of xenotime concentrate

TREO grade (%)	Y_2O_3 (%)	Acid:solid ratio (w/w)	Bake/digest temperature (°C)	Time (h)	RE extraction in leach (%)	Leach medium	Reference
60	36	1.5:1	240-250	10-12		water	(a)
-	27-40	~2.5:1	250	6	>98	water	(b)
20	-	1:1	275-300	1	~95	water	(c)

References: (a) Banks et al. (1959) (b) Vijayalakshmi et al. (2001) (c) Hadley and Catovic (2014)

Soltani et al. (2018) studied the acid baking of a fluorapatite rich concentrate containing both monazite and xenotime in the temperature range of 190-270°C, allowing a direct comparison of the reactivity of the two rare earth minerals. The leach dissolution of cerium peaked at a bake temperature of 250°C, while that of yttrium, which was mainly hosted in the xenotime, increased up to the highest temperature of 270°C.

When compared with the conditions generally used for acid baking of monazite these observations suggest that xenotime is more refractory than monazite toward digestion with acid. The crystal structure of xenotime differs from that of monazite, being in the tetragonal system (space group $I4_1/amd$) while monazite is monoclinic (space group $P2_1/n$) (Ni et al., 1995). Crystal structure diagrams for monazite and xenotime are compared in Figure 4. The difference in reactivity with sulfuric acid may be related to the different crystal structures.
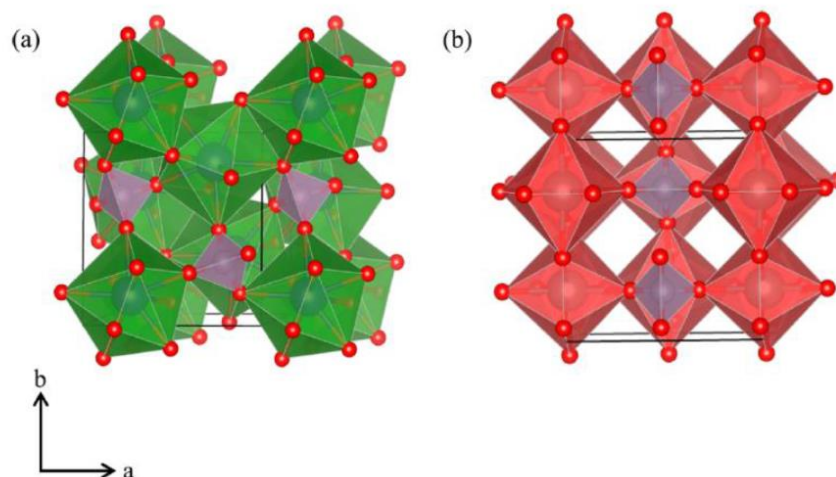
Figure 4 Comparison of (a) monazite ($P12_1/n$) and (b) xenotime ($I4_1/amd$) structures viewed with the c-axis pointing into the page. The CeO_9, YO_8 and PO_4 polyhedra are shown in green, red and grey, respectively. Image from Rafiuddin et al. (2014)

4 Sulfuric Acid Baking of Bastnasite

A larger variety of methods have been used in industry for the processing of bastnasite ores/concentrates compared to monazite and xenotime. These include oxidative roasting followed by acid leaching, sulfuric acid baking, caustic conversion, and chlorination (Gupta and Krishnamurthy, 2005). The oxidative roast followed by acid leach process was developed by Molycorp for production of rare earths at Mountain Pass, before shutdown of the mine in 2002 (Gupta and Krishnamurthy, 2005; Long et al., 2012). This was replaced with a caustic conversion process when the mine was restarted in 2012 (Lucas et al., 2014). An oxidative roast/acid leach process is also used to treat bastnasite concentrates in China (Huang et al., 2015). Approximately 10% of the Bayan Obo concentrate is reportedly processed by caustic conversion (Zhu et al., 2015). A chlorination process has been used in Germany to process a bastnasite flotation concentrate for production of anhydrous rare earth chlorides (Brugger and Greinacher, 1967). Sulfuric acid baking is the primary process used to decompose the Baotou mixed bastnasite and monazite concentrate (with bastnasite to monazite ratios up to 1:0.5) from the Bayan Obo deposit (Zhang et al., 2015; Zhu et al., 2015).

The unit operations for acid baking and water leaching of bastnasite mineral concentrates and ores are much the same as for monazite or xenotime mineral concentrates (see Figure 1). The optimum conditions for sulfuric acid baking of bastnasite mineral concentrates are not as well-defined as for monazite or xenotime mineral concentrates. A summary of published acid bake/cure conditions for bastnasite is given in Table 8.

In the reaction of sulfuric acid with bastnasite, the rare earth fluorocarbonates are converted to sulfates, carbon dioxide and hydrogen fluoride via reaction (3) in Table 5. Hydrogen fluoride can be captured as a by-product by treatment of the off-gases (Neelameggham et al., 2014). The proportion recoverable as hydrogen fluoride depends on the amount of silica present, with hydrofluosilicic acid (H_2SiF_6) being formed if silica is available (Shaw, 1959a). Reaction with acid is reported to be fast and exothermic, with hard, dry agglomerates formed shortly after addition of acid (Merker et al., 1991; Topkaya and Akkurt, 1999). The reaction mixture is naturally agitated by evolution of carbon dioxide. This can lead to frothing, which must be monitored through controlled acid addition (Shaw, 1959a).

Table 8 Published conditions for sulfuric acid bake/digestion of bastnasite concentrate

Deposit	Ore grade (% TREO)	Concentrate grade (% TREO)	Acid: concentrate ratio (w/w)	Bake temperature (°C)	Time (h)	RE extraction in leach (%)	Leach medium	Reference
Mountain Pass[1], U.S.	~10	60	1.3:1	200→650	3-4		water	(a)
Mountain Pass[1], U.S.	7.1	12.4		150→650	2	97	water	(b)
Dong Pao, Vietnam	5-14	32.8		200-300			water	(c)
Beylikahır, Turkey	3.14	23.5	0.91:1	200	2	85-90	water	(d)
Bayan Obo, China		50-60	1.4:1	500-900		~92	water	(e)
Beylikahır, Turkey	3.42	23.0	0.59:1	25 (cure)	1	75-90	water	(f)

[1]These conditions are from an acid baking study using concentrate from Mountain Pass, and do not represent the actual process used commercially at the time.

References: (a) Shaw (1959a) (b) Eisele and Bauer (1974) (c) Merker et al. (1991) (d) Kul et al. (2008) (e) Zhu et al. (2015) and Zhang et al. (2015) (f) Topkaya and Akkurt (1999)

Shaw (1959a) carried out an early investigation into sulfuric acid baking of a Mountain Pass bastnasite concentrate sample containing 60% REO. Direct leaching in dilute mineral acids was initially trialled, but was rejected on the basis of excessive leaching of impurities in addition to rare earths. The sulfuric acid bake process was developed and the effects of temperature, bake duration and acid addition were examined and optimised. A temperature of 200°C for 3 hours with an acid to concentrate ratio of 1.3:1 was required for complete recovery of the rare earths. Obtaining complete removal of fluoride as HF, according to reaction (3) in Table 5, was the primary factor in determining the minimum bake temperature,

as removal of carbon dioxide could be achieved at 65°C. Merker et al. (1991) similarly stated that heating to 200-300°C was necessary for complete removal of fluoride. A further significant discovery by Shaw (1959a) was that a second stage of heat treatment at 650°C could render calcium insoluble, by forming an insoluble calcium sulfate anhydride, with minimal effect on rare earth recovery. This high temperature treatment is somewhat analogous to the high temperature bake processes described above for monazite treatment (Section 2.1.2). In a later study by Eisele and Bauer (1974), a 12% REO Mountain Pass concentrate was similarly treated at 650°C following an initial digestion at 150°C.

Achieving complete removal of fluoride in the bake step during acid baking of bastnasite ores or concentrates is important for preventing rare earth losses due to incomplete dissolution in the water leach. Goode et al. (2013) attributed the low to moderate rare earth extractions obtained during acid baking of a mixed bastnasite and monazite concentrate from the Sarfartoq deposit in Greenland, to formation of insoluble rare earth fluorides. It was not identified whether the proposed rare earth fluorides were formed during the bake or water leach. Goode et al. (2013) found that the insoluble rare earths could be recovered by caustic digestion of the leach residue, which presumably converted the rare earth fluorides to soluble hydroxides.

5   Sulfuric Acid Baking/Digestion of Other Rare Earth Minerals

New rare earth projects are increasingly looking to develop processes for resources with more complex rare earth mineralogy, and often with multiple rare earth hosting minerals. Acid baking studies of rare earth minerals other than monazite, xenotime and bastnasite have been very limited. In particular, there is a lack of studies examining reaction mechanisms, kinetics or thermodynamics of the reaction with sulfuric acid. A summary of published acid bake or leach conditions for some of the less common, yet potentially significant rare earth minerals is given in Table 9. The rare earth distribution and content for these minerals (where available) is given in Table 10.

Table 9 Conditions for H_2SO_4 bake/digestion of euxenite, loparite, allanite, eudialyte and pyrochlore concentrates

RE mineral	TREO grade (%))	Acid:solid ratio (w/w)	Bake/digest temperature (°C)	Time (h)	RE extraction (%)	Origin of ore/concentrate	Reference
Euxenite	29.4	3:1	204→650	4		Arizona, United States	(a)
Euxenite	16.4	3:1 to 3.5:1	336→650	4, 3.5	98	Idaho, United States	(b)
Loparite	30*		200			Kola peninsula, Russia	(c)
Allanite	4.4	0.4:1	200→650	4	75	Mary Kathleen tailings, Australia	(d)
Allanite	2.45	0.75:1 to 1:1	200-250	2-4	90-95	Foxtrot deposit, Canada	(e)
Eudialyte	2.4	150-200 (% stoichiometric)			80-88	Lovozero deposit, Kola peninsula, Russia	(f)
Eudialyte	1.65	4:1 (as 2 M H_2SO_4)	110	0.5	91-97	Norra Karr deposit, Sweden	(g)
Eudialyte	1.0	3.2:1	320	3		Australia	(h)
Pyrochlore	2		165	1			(i)
Pyrochlore	~1.5		250-300		90	Mabounie deposit, Gabon	(j)
Pyrochlore	~1.5	1.6:1	300	3		Mabounie deposit, Gabon	(k)
Samarskite, euxenite, fergusonite		2.5:1	200	2	65-70	Kab Amiri ore, Egypt	(l)

*Equivalent to 95% loparite.

References: (a) Shaw (1959b) (b) Shaw and Bauer (1965) (c) Kosynkin et al. (1993) (d) Baillie and Hayton (1970) (e) Dreisinger et al. (2012) (f) Lebedev (2003) (g) Davris et al. (2016) (h) Lim et al. (2016) (i) Charlot (1976) (j) Donati et al. (2014) (k) Ribagnac et al. (2017) (l) El-Hussaini and Mahdy (2002)

Table 10 Rare earth distribution/content for selected less common rare earth-bearing minerals

REE	REE content/distribution (%)					
	Loparite[a]	Allanite[a]	Eudialyte[b]	Gadolinite[a]	Samarskite[c,*]	Fergusonite[d,*]
La	27.8	20	15.2	1.0		<0.1
Ce	57.1	40	29.7	2.0	1.28	0.76
Pr	3.7	10	2.9	2.0	0.76	0.39
Nd	8.7	20	12.7	5.0	3.46	1.9
Sm	0.91	2.0	3.4	5.0	6.97	2.28
Eu	0.13	0.03	1.3	trace		
Gd	0.21	1.0	3	5.0	12.8	5.5
LREE	98.6	93.0	68.2	20.0	25.3	10.8
Tb	0.07	0.1	2.8	0.5	3.4	1.27
Dy	0.09	0.3	4.3	6.0	13.6	8.65
Ho	0.03	0.1	2.9	1.0		
Er	0.07	0.3	2.1	4.0	4.82	7.94
Tm	0.07	0.1		0.6	0.52	1.0
Yb	0.29	0.3	1.6	4.0	2.81	6.83
Lu		<0.1	0.3	0.6	0.46	0.82
Y	0.14	3	21.4	60	49.2	59.9
HREE+Y	0.8	4.2	35.4	76.7	74.8	86.4
REO content (%)	~30	~5 (3-51)	1-10	~40	~12-25	~30-43

*Values for Eu and Ho not given in source reference.

References: (a) Gupta and Krishnamurthy (2005) (b) Jordens et al. (2013) (c) Butler (1957) (d) Butler (1960)

5.1 Heavy Rare Earth Tantaloniobate Minerals - Euxenite, Samarskite, Fergusonite

The three tantaloniobate minerals, euxenite, samarskite and fergusonite noted in Table 2, are attractive for processing as they host multiple value metals such as rare earths, tantalum, niobium and titanium (Gupta and Krishnamurthy, 2005) Rare earth tantaloniobates are also often highly enriched in the more valuable heavy rare earths (Table 10). The United States, Egypt and Norway have significant deposits of the rare earth tantaloniobate euxenite (El-Hussaini and Mahdy, 2002; Shaw, 1959b; Shaw and Bauer, 1965). The composition of an Idaho euxenite concentrate is given in Table 11 together with a typical composition of the pure mineral. Euxenite has been utilised as a primary source of tantalum and niobium (Ayanda and Adekola, 2011; May et al., 1959), but has not been commercially processed for rare earths to date.

Table 11 Proportions of euxenite constituents and composition of an Idaho euxenite concentrate

	TREO	LREO	HREO+Y	Nb_2O_5	Ta_2O_5	TiO_2	UO_2	ThO_2	Fe_2O_3
Euxenite mineral (%)		16-30	18-28	4-47	1-23	16-30	0.4-12	1-5	
Euxenite concentrate (%)	15			27	3.0	19	3.2	5.0	3.0

Data from May et al. (1959)

The hydrometallurgical processing of euxenite for rare earths has been considered difficult due to the formation of bulky precipitates of niobium, tantalum and titanium during leaching (Kawamura et al., 1966). Decomposition of euxenite by caustic fusion, chlorination and sulfuric acid treatment, both leaching and baking, has been tested (Gruzensky, 1960; May et al., 1959; Shaw and Bauer, 1965). In a sulfuric acid baking study of Idaho euxenite concentrate, Shaw and Bauer (1965) achieved 98% RE extraction by digesting at the boiling point of the reaction mixture (336°C), for 4 hours with an acid to concentrate ratio of 3:1 and a particle size of <74 μm. Using the same procedure previously developed at Ames Laboratory for processing of bastnasite (Shaw, 1959a), the baked product was calcined at 650°C, rendering the majority of the impurities insoluble during subsequent water leaching. The main impurities were iron, silicon, uranium, calcium and thorium. Niobium, tantalum and titanium also remained in the leach residue. Initial tests indicated that the niobium, tantalum, titanium and uranium could be extracted from the residue by leaching in a mineral acid, followed by fractional precipitation (Shaw and Bauer, 1965).

El-Hussaini and Mahdy (2002) investigated sulfuric acid digestion of an Egyptian ore containing euxenite, samarskite and fergusonite. The maximum extraction of rare earths was ~65% after digestion at 200°C for 2 hours, with an acid:ore ratio of 2.5:1, and a particle size of <74 μm. The rare earth extraction could be slightly increased to ~70% by addition of some nitric acid. Extraction of niobium and tantalum was virtually complete, while uranium and titanium were only partially dissolved (~60%) (El-Hussaini and Mahdy, 2002).

Fergusonite has been identified as one of the rare earth hosting minerals in the Nechalacho ore in Canada. Mineralogical studies of the concentrate before and after sulfuric acid digestion at 200°C for 1 hour showed that fergusonite was not broken down during the acid treatment, indicating it may be more resistant to acid digestion than bastnasite and monazite (Notzl et al., 2013).

5.2 Loparite – Light Rare Earth Tantaloniobate

Loparite (Table 2), another tantaloniobate rare earth mineral, differs from euxenite, samarskite and fergusonite in that it is LREE dominated, while the latter are HREE dominated (see Table 10). The most significant deposits of loparite occur at the Lovozero deposit on the Kola peninsula in Russia, which supplies the bulk of Russia's rare earths, as well as tantalum, niobium and titanium (Kosynkin et al., 1993). Loparite ores are readily upgraded to 80-90% mineral concentrates by beneficiation (Zelikman et al., 1966). The Industrial processing of loparite in Russia is by chlorination (Gupta and Krishnamurthy, 2005). However, loparite is also amenable to digestion in concentrated sulfuric acid (Hedrick et al., 1997; Zelikman et al., 1966). In the acid digestion process, a loparite concentrate is mixed with 85% sulfuric acid and heated to 200°C in the presence of ammonium sulfate. During water leaching of the digestion product, the soluble sulfates of titanium, niobium and tantalum dissolve, while the rare earths are present as insoluble double sulfates. After solid-liquid separation, the rare earth double sulfates are converted to carbonates and are dissolved in nitric acid before further purification and separation steps (Hedrick et al., 1997).

5.3 Allanite

Allanite (Table 2), is an LREE dominated rare earth-bearing mineral of the epidote group (Gieré and Sorensen, 2004). Allanite can be decomposed by hydrochloric acid of moderate concentrations or by treatment with concentrated sulfuric acid (Baillie and Hayton, 1970; Nazari and Krysa, 2013). Deposits containing allanite include the Foxtrot deposit in Canada (Dreisinger et al., 2012) and uranium tailings at Mary Kathleen, Australia (Baillie and Hayton, 1970). Process development work has focused on the sulfuric acid baking route (Baillie and Hayton, 1970; Dreisinger et al., 2012).

Baillie and Hayton (1970) tested sulfuric acid leaching and sulfuric acid baking for recovery of rare earths from the allanite bearing Mary Kathleen uranium tailings. Approximately 65% of the rare earths dissolved in sulfuric acid (of unspecified concentration) at 60% solids density and boiling temperature. Dreisinger et al. (2012) similarly tested sulfuric acid leaching of the Foxtrot allanite-bearing concentrate. It was not clear what acid concentration was used but the leach temperature was 95°C and the leach slurry had a free acidity of 91 g/L H_2SO_4 (0.93 M). More than 95% LREE was extracted, indicating that the allanite in this deposit may be more reactive than the Mary Kathleen allanite. The HREE extractions were

much lower, in the range of 40-70%. In both processes significant amounts of iron, silica and aluminium also dissolved. Baillie and Hayton (1970) avoided excessive dissolution of silica during water leaching by baking at 200°C for 2 hours prior to water leaching, resulting in improved solid-liquid separation. Rare earth extraction was unchanged. Baking at 650°C resulted in the formation of insoluble iron oxide, further improving the purity of the leach solution. This also increased rare earth extraction to 75% (Baillie and Hayton, 1970).

5.4 Eudialyte

Eudialyte is a sodium calcium zirconosilicate mineral as shown in Table 2. Large variations in composition occur between minerals grouped under this name (Zakharov et al., 2011). Eudialyte can incorporate up to 3 wt.% rare earths (Gupta and Krishnamurthy, 2005) and often has a rare earth distribution relatively high in the heavy rare earths and yttrium content as shown in Table 10 (Zakharov et al., 2011). The presence of multiple value metals (i.e. Zr, Nb, REE) makes it an attractive potential resource. Examples of significant eudialyte deposits include the Lovozero deposit on the Kola peninsula in Russia (Lebedev et al., 2003), the Toongi deposit in Australia (Spandler and Morris, 2016), the Ilímaussaq complex in South Greenland (Gupta and Krishnamurthy, 2005) and the Norra Kärr alkaline complex in Sweden (Davris et al., 2016).

Recently, there has been an enhanced interest in eudialyte for production of rare earths (Davris et al.; Lim et al., 2016; Voßenkaul et al., 2017). Treatment with sulfuric acid is generally preferred to treatment with other acids (Lebedev, 2003), although hydrochloric acid has also been used effectively (Ma et al., 2017; Voßenkaul et al., 2017). The name 'eudialyte' means 'easily decomposable' in Greek, referring to its generally ready dissolution in mineral acids (Zakharov et al., 2011). In spite of this, achieving complete dissolution of certain eudialytes has proven difficult due to (a) formation of gelatinous silica phases that prevent filtration (Davris et al., 2016; Lebedev et al., 2003; Voßenkaul et al., 2017), (b) passivation of partially decomposed grains by an acid-impermeable silica layer (Lebedev et al., 2003; Zakharov et al., 2011), and (c) formation of secondary precipitates of zirconium(IV) (Lebedev et al., 2003). Difficulty in leaching can also be related to challenges specific to the eudialyte ore/concentrate being treated, such as: (a) the presence of a highly refractory 'altered' eudialyte mineral phase (Zakharov et al., 2011), or (b) the presence of niobium and titanium within the crystal structure, which reportedly has a negative effect on its leachability (Lebedev et al., 2003).

The Lovozero eudialyte is a good example of a partially refractory eudialyte type mineral of the composition given in Table 12. Lebedev (2003) summarised a number of studies focused on developing an effective process for treatment of this eudialyte concentrate. Leaching in 50% sulfuric acid resulted in 70-80% decomposition of the mineral. Zirconium could be selectively dissolved by adding sodium sulfate to the leach, which ensured rare earth precipitation as rare earth sodium double sulfates. Rare earths were later recovered by further leaching and re-precipitation as hydroxides (Lebedev, 2003), but ~20% of the mineral remained unreacted, and needed more aggressive conditions for complete decomposition. The aggressive leaching could include a large excess of sulfuric acid and/or addition of fluoride ions (Lebedev et al., 2003), which assist cracking of the mineral lattice while also helping to prevent silica gelling (Davris et al., 2016; Lebedev et al., 2003). In a study by Zakharov et al. (2011), it was identified that highly refractory 'altered' eudialyte was present in the Lovozero concentrate, which limited the extent of decomposition. It was suggested that the 'altered' eudialyte would have been formed as a natural hydrothermal transformation product of 'normal' eudialyte (Zakharov et al., 2011).

Table 12 Composition of a eudialyte concentrate from Lovozero, Russia

Oxide	ZrO_2	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	MnO	CaO	Na_2O	Nb_2O_5	TREO
Composition (wt.%)	10.5	51.4	4.4	4.7	1.1	2.0	5.7	12.4	0.6	2.4

Data from Lebedev (2003)

Working with a 1.65% TREO concentrate from the Norra Kärr deposit, Davris et al. (2016) developed a two-stage acid leaching process to avoid formation of a silica gel, using either hydrochloric or sulfuric acid as lixiviant. In the first stage a relatively small volume of 2 M acid was used at 110°C to form a paste that gradually dried as water evaporated. It was demonstrated that in this stage the eudialyte was transformed to a mixture of soluble metal salts and an insoluble siliceous precipitate. Water leaching extracted 91-97% of rare earth elements from the first stage residue, along with only ~60% of the zirconium. The change of acid from sulfuric to hydrochloric decreased the zirconium extraction to a lower value of <20%. Voßenkaul et al. (2017) developed a similar two-stage process. It included a leach solution of low volume and high ionic strength to prevent gelling/polymerisation by forming many silica nuclei which aggregate into insoluble and filterable clusters (Voßenkaul et al., 2017). In another study, sulfuric acid baking of an Australian zirconosilicate ore at 320°C

caused dehydration of silica at the high temperature and acid concentration in the bake which decreased silica leaching (Lim et al., 2016).

The Toongi deposit at Dubbo, Australia, contains a eudialyte-group mineral (Spandler and Morris, 2016) and is currently under development by Alkane Resources. The process flowsheet utilizes whole-of-ore sulfuric acid baking for decomposition of the mineral to achieve the recovery of all value metal components (Lucas et al., 2014). Silica contamination of product streams is avoided, but the chemistry involved has not been made publicly available.

5.5 Pyrochlore

Pyrochlore is a rare earth bearing alkaline earth niobate (Table 2) and a primary source of niobium (Cordeiro et al., 2011). Major deposits of pyrochlore occur in Brazil, Canada, Greenland, the Commonwealth of Independent States (CIS) and Australia (Gupta and Suri, 1993). The composition of pure pyrochlore mineral from Araxá, Brazil is given in Table 13.

Table 13 Composition of pyrochlore from Araxa, Brazil

Oxide	Nb_2O_5	Ta_2O_5	BaO	CaO	ThO_2	MnO	FeO	TiO_2	PbO	SnO_2	H_2O	TREO
Composition (wt.%)	63.4	0.15	16.5	0.44	2.3	0.16	2.4	2.3	0.42	0.10	8.5	3.3

Data from Lucas et al. (2014)

Pyrochlore is amenable to decomposition by sulfuric acid baking (Donati et al., 2014) and sulfuric acid leaching (Charlot, 1976; Walter and Verner, 1963). Charlot (1976) patented a process involving digestion in 15 M sulfuric acid at room temperature, followed by dilution with water. Niobium dissolution was complete, but a portion of the rare earths remained in the residue as sulfates. One of the key elements of the patented process was the addition of a reductant to reduce titanium(IV) to its trivalent state, thereby avoiding loss of niobium through co-precipitation with titanium. After filtration, niobium and the dissolved rare earths were precipitated either by further dilution with hot water, or by addition of oxalic acid. The rare earths could be leached from the niobium precipitate using hydrochloric acid (Charlot, 1976).

Donati et al. (2014) described a process for extraction of niobium, tantalum, rare earths and uranium from a Gabonese pyrochlore concentrate from the Mabounié deposit. The pyrochlore

is intergrown with goethite and crandallite $(CaAl_3(PO_4)_2(OH)_5.H_2O)$. These gangue minerals were removed in a pre-leach with sulfuric acid (of unspecified concentration) and sulfur dioxide, leaving a pyrochlore-rich solid residue. The benefit of sulfuric acid pre-leaching of niobium bearing ores or concentrates was described in a patent by Walter and Verner (1963), where it was claimed to reduce acid consumption and improve the extraction efficiency of niobium in the subsequent more concentrated acid leaching step. However, while Walter and Verner (1963) used a concentrated acid leach following pre-leaching, Donati et al. (2014) used a sulfuric acid bake at 250-300°C followed by water leaching. Approximately 85% of the niobium, 75% of the tantalum, 90% of the rare earth elements and 99% of the uranium dissolved during the acid bake/leach process. Niobium and tantalum were separated from the rare earths by selective precipitation, while the leach solution containing the rare earths and uranium was recycled for use in the pre-leaching step. The process was demonstrated at pilot scale.

6 Factors Affecting Water Leaching and Solubilities of Rare Earths

6.1 Type of Salt

The baked material consists of sulfated rare earths, impurity metals and other reaction products, as well as unreacted minerals and residual acid. The aim of leaching is typically to generate a solution containing the maximum amount of dissolved rare earths at a sufficiently high concentration for subsequent unit operations. Thus, the solids from the sulfuric acid bake process are mixed with water to dissolve the rare earth sulfates. Depending on the feed mineralogy, the resultant rare earth sulfate solution may contain phosphoric acid and/or hydrofluoric acid, in addition to the dissolved cations in the form of various complex species. The Eh-pH diagrams for the system Th-RE-(PO_4)-(SO_4)-H_2O at $25°C$ and different concentrations of metal ions (10^{-3}, 10^{-1} mol/L), phosphate (10^{-3} mol/L) and sulfate (10^{-2}, 10^{-1} and 1 mol/L) published by Kim and Osseo-Asare (2012) predict the stability regions for a variety of species relevant to the hydrometallurgical processing of monazite via sulfuric acid baking and leaching. The solution composition and measured solubility of rare earths, thorium and uranium in sulfuric-phosphoric solutions produced after acid baking/leaching or pre-leaching of rare-earth concentrates provide useful information on solid phases and complex species of these metal ions relevant to baking, leaching and precipitation (Bandara and Senanayake, 2015; Bandara and Senanayake, 2019; Bandara et al., 2018; Demol et al., 2018; Senanayake et al., 2016; Stone et al., 2016).

The composition of a typical leach solution after acid baking and leaching of a monazite concentrate is given in Table 14. The solubilities and/or solubility products for rare earth sulfates/phosphates/fluorides, and some of the common impurity metal salts are given in Table 15. The data show that rare earth phosphates and fluorides have a much lower solubility than the rare earth sulfates, and that thorium phosphate has a much lower solubility than the rare earth phosphates. The solubility of thorium sulfate at 20°C is slightly lower than that of lanthanum, at 1.38 g/100 g (Dean, 1999). A summary of published conditions for the water leach from acid baking studies of monazite, xenotime and bastnasite based ores is given in Table 16.

Table 14 Composition of leach solution from acid baking and leaching of a monazite concentrate

Dissolved species	Th	U	PO_4^{3-}	SO_4^{2-}	Ce	La	Pr	Nd	Sm
Concentration (g/L)	5.3	0.2	26.0	128.0	6.83	3.62	0.73	5.25	0.56

Data from Habashi (2013)

Table 15 Solubilities or solubility products (K_{sp}) for sulfates, phosphates and fluorides of selected rare earths and impurities

Sulfates				Phosphates		Fluorides	
Formula	pK_{sp}	g/100g water	mol/L	Formula	pK_{sp}	Formula	pK_{sp}
$Ce_2(SO_4)_3$		7.6[e]	0.13	$CePO_4$	23.0[b]	CeF_3	19.6[f]
$Nd_2(SO_4)_3$		7.1[b]	0.12	$NdPO_4$	26.0[d]	NdF_3	20[f]
$Y_2(SO_4)_3$		7.3[b]	0.16	YPO_4	24.8[d]	YF_3	20.1[b]
$BaSO_4$	10[c]	0.0003[a]	1.3×10^{-5}	$Ba_3(PO_4)_2$	22.5[b]	BaF_2	6.7[b]
$CaSO_4$	4.6[c]	0.21[a]	0.015	$Ca_3(PO_4)_2$	28.7[b]	CaF_2	10.4[c]
$Fe_2(SO_4)_3$		440[a]	11.0	$FePO_4$	15.0[b]		
$Al_2(SO_4)_3$		38.5[a]	1.13	$AlPO_4$	9.0[c]		
$Th(SO_4)_2$		4.2[a]	0.10	$Th_3(PO_4)_4$	78.6[b]		

Note: All data is between 18-25°C; $pK_{sp} = -Log K_{sp}$

References: (a) Lide (2005) (b) Dean (1999) (c) Patnaik (2003) (d) Firsching and Brune (1991) (e) Linke and Seidell (1965) (f) Mioduski et al. (2015)

Table 16 Published conditions for water leaching following sulfuric acid baking of monazite and bastnasite concentrates and ores (leach medium was water in all cases)

Major RE mineral	TREO (% w/w)	Liquid:solid ratio	Temperature (°C)	Duration (h)	TREO concentration (g/L)	Reference
Monazite	47	10:1 (1st stage)		$1 \rightarrow 3^a$		(a)
Monazite		10:1	cold		$50\text{-}60^b$	(b)
Monazite	40.4	5:1	ice-cold	1		(c)
Monazite		6.6:1	cold	1		(d)
Monazite		2:1 to 3:1		0.08		(e)
Monazite	$\sim\!70^c$		<30		55	(f)
Monazite	5.6		90	2.2		(g)
Monazite	60	10:1	<15		51	(h)
Monazite	60		boiling	1		(i)
Monazite	25	7.5:1	75	15		(j)
Monazite	60	15:1	ambient	1.5		(k)
Bastnasite	23.5	3-8:1	25	0.5		(l)
Bastnasite	60	10:1	ambient	0.5	51	(m)
Bastnasite	23.5	4:1	ambient	3		(n)
Bastnasite	10-13	4:1	ambient	3		(o)

[a]1 hour for first stage, 3 hours for second stage [b]TREO+Th; [c]Reported as 97% monazite; [d]Two-stage leach

References: (a) Ahmed et al. (2015) (b) Barghusen and Smutz (1958) (c) Borrowman and Rosenbaum (1961) (d) McCoy (1921) (patent) (e) Kawamura et al. (1966) (f) Moustafa and Abdelfattah (2010) (g) Notzl et al. (2013) (h) Pilkington and Wylie (1947) (i) Te Riele and Fieberg (1982) (j) Sadri et al. (2017b) (k) Soltani et al. (2018) (l) Kul et al. (2008) (m) Shaw (1959a) (n) Topkaya and Akkurt (1999) (o) Yong et al. (2014)

The Eh-pH diagrams for the Nd-(PO_4)-(SO_4)-H_2O system (Kim and Osseo-Asare, 2012) are provided in Figure 5a,b. The diagrams predict the formation of neodymium sulfate-octahydrate at lower pH, and neodymium hydroxide at higher pH. At the lower sulfate concentration (0.01 mol/L), solid neodymium phosphate is predicted to form at pH 8-10, while at the higher sulfate concentration (1.0 mol/L) the stability region of the sulfate-octahydrate increases and the solid phosphate is not formed. These diagrams highlight how the residual acid or sulfate concentration in the leach can influence the species formed in the water leach. Likewise, diagrams for the Ce–SO_4–H_2O system in Figure 6a,b show that high concentrations of Ce(III) and sulfate ions cause a decrease in the area of stability of $CeSO_4^+$ (Figure 6a) and facilitates the formation of $Ce_2(SO_4)_3 \cdot 8H_2O$ (Figure 6b). Formation of hydrated rare-earth sulfate salts during baking of monazite concentrates and saturation of leach liquors have been confirmed by XRD scans (Bandara et al., 2018; Demol et al., 2018).
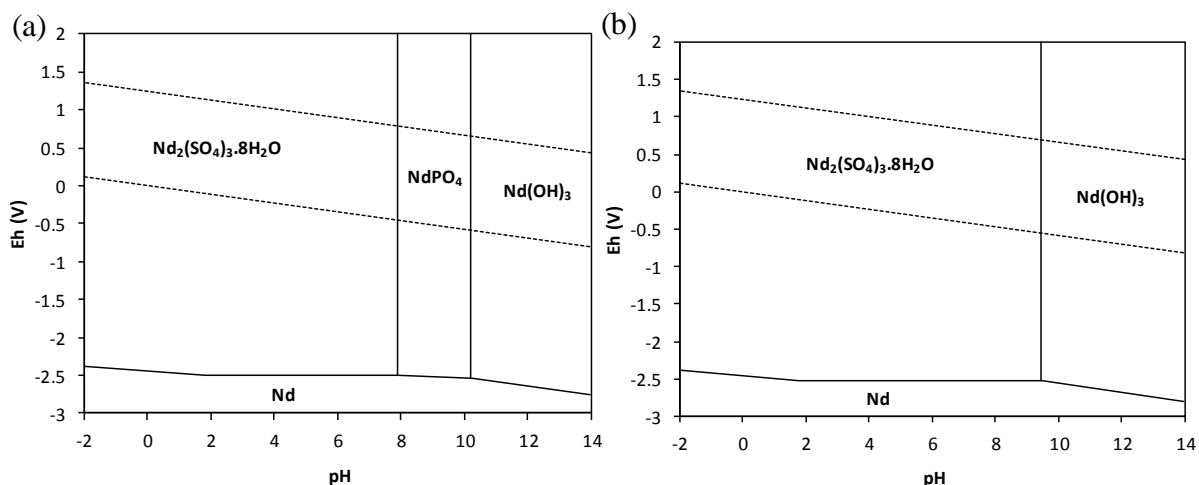
Figure 5 Eh-pH diagrams for the Nd-(PO_4)-(SO_4)-H_2O system at 25°C, [Nd] = 10^{-3} M, $[PO_4]$ = 10^{-3} M, (a) $[SO_4]$ = 10^{-2} M, (b) $[SO_4]$ = 1.0 M; Adopted from Kim and Osseo-Asare (2012).
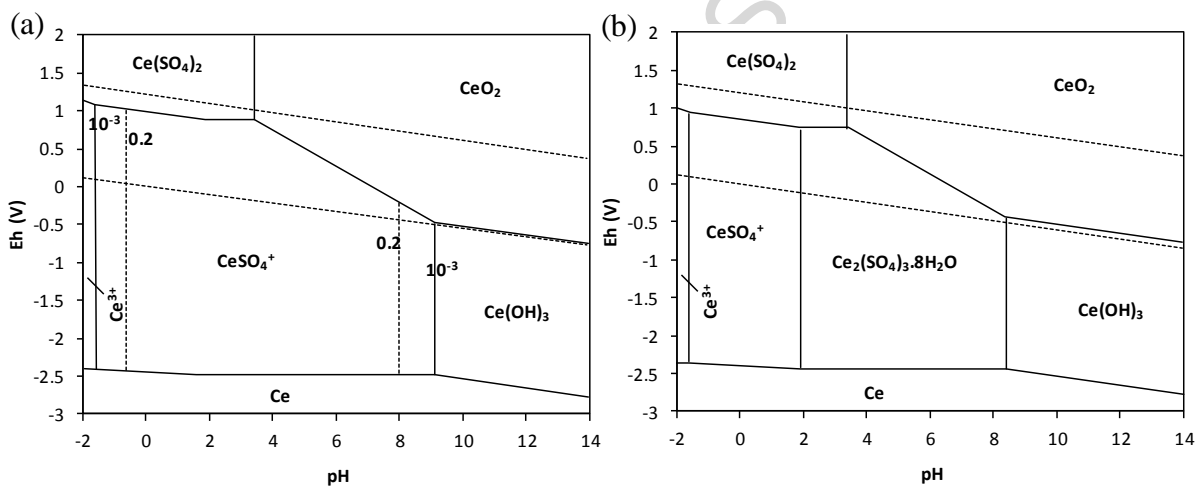

Figure 6 Eh-pH diagrams for the Ce–SO_4–H_2O system at 25 °C, (a) [Ce] = 0.2, 10^{-3} M, $[SO_4]$ = 0.1 M, (b) [Ce] = 0.2 M, $[SO_4]$ = 1.0 M; Adopted from Kim and Osseo-Asare (2012).

6.2 Liquid to Solid Ratio

The liquid:solid ratio needed at the leaching stage of the baked product is thought to be determined by the limited solubility of the rare earth sulfates. Standard solubilities in water range from 2.33 g/100 g for lanthanum sulfate, to more than 22 g/100 g for ytterbium sulfate at room temperature (Dean, 1999). Solubility products (pK_{sp}) are in the range of 2.0-2.5 for $Y_2(SO_4)_3$ and $Nd_2(SO_4)_3$, respectively (Table 15). The effective rare earth solubility in a sulfate based leach solution is highly dependent on the speciation of the complexes formed in solution and the solids precipitated upon saturation, and their solubility (Bandara et al., 2018; Senanayake et al., 2016).

Excessive free acid remaining in the baked material increases the sulfate concentration in solution, thereby reducing the solubility of the rare earth sulfates.

Figure 7 shows the detrimental effect of the increase of sulfuric acid concentration on the solubility of $Ce_2(SO_4)_3$, based on solubility values from Linke and Seidell (1965). At ~7 M H_2SO_4 the solubility of $Ce_2(SO_4)_3$ is close to zero (Linke and Seidell, 1965). A lower grade feed concentrate can also tend to limit the attainable rare earth concentration, due to an elevated sulfate concentration resulting from dissolution of sulfated impurities (i.e. due to the common ion effect as shown in Figure 6).
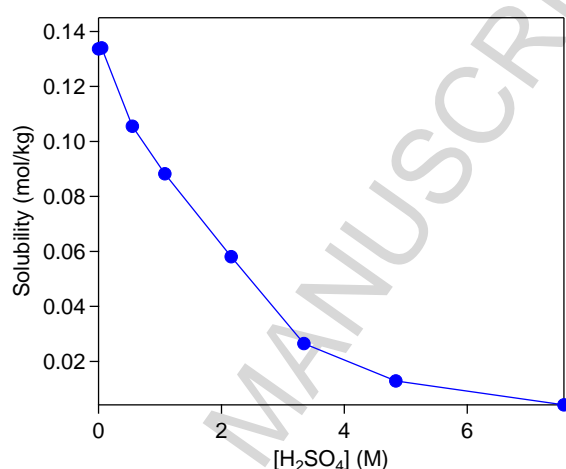

Figure 7 Effect of H_2SO_4 concentration on the solubility of $Ce_2(SO_4)_3$. Data from Linke and Seidell (1965)

For high grade concentrates of both monazite and bastnasite a water to solid ratio of 10:1 has been widely used (see Table 16), and gives a stable leach solution containing approximately 45 g/L TREE in approximately 150 g/L H_2SO_4 (Pilkington and Wylie, 1947; Shaw, 1959a). For concentrates with a significant proportion of soluble silicate minerals, sufficient dilution is necessary to prevent solidification or 'gelling' of the solution through silica polymerisation (Shaw et al., 1954). Whilst the formation of various sulfate/phosphate complex species of rare earth metal ions with sulfate/phosphate ions can enhance the solubility, the presence of other cations in solution originating from the feed/host minerals (Table 2) or additives used in baking/leaching can significantly affect the solubility of REEs due to the formation of other salts of variable solubility depending upon the pH, acid concentration and temperature (Senanayake et al., 2016; Bandara et al., 2018).

The limited solubility of rare earth sulfates has been exploited to achieve some degree of separation from impurities by adjustment of the water leach conditions. Powell (1939)

patented a process applicable to monazite, xenotime, thorite and cerite involving a two-stage leach, with a solid-liquid separation step between the stages. The sulfuric acid digestion mixture was initially added to a minimum volume of water to selectively dissolve phosphoric acid, if present, and other soluble impurities while avoiding dissolution of the rare earth sulfates. After filtration, the rare earth sulfates were water leached from the residue at the usual solid to liquid ratio. Kawamura et al. (1966) described a similar process for a Korean monazite to separate thorium and rare earths from other more soluble digestion products, and obtained 90% extraction of thorium and rare earths. Ahmed et al. (2015) also used a two-stage leaching process during processing of an Egyptian monazite sand (47% TREO). The first stage of leaching, using water at 45°C with a water to feed ore ratio of 10:1, dissolved most of the uranium and thorium together with one-third of the rare earths. The second stage of leaching, using a liquid ratio of 3.5 times the slurry volume and additional concentrated sulfuric acid, dissolved the remaining rare earths.

6.3 Temperature

The solubility of rare earth sulfates is inversely proportional to temperature, while the solubility of thorium sulfate increases with increasing temperature up to 40°C where it crystallises as the 9-hydrate salt (Dean, 1999). Above 40°C thorium sulfate crystallises as a tetrahydrate salt, which has an inverse solubility with increasing temperature. Figure 8 shows the effect of temperature on solubility of lanthanum sulfate and thorium sulfate. Because of the inverse relationship of solubility with temperature for the rare earth sulfates, water leaching is generally carried out at ambient or colder temperatures to maximise rare earth solubility (Pilkington and Wylie, 1947). The effect of increasing temperature was investigated by Kul et al. (2008) during water leaching of Beylikahır bastnasite pre-concentrate. At a liquid:solid ratio of 4:1, the recovery of lanthanum dropped from 88% at 5°C, to 78% at 50°C and 59% at 90°C.

In some cases, however, elevated leach temperatures have been used, as shown by the studies summarised in Table 16. Te Riele and Fieberg (1982) leached the baked product at boiling temperature to improve the filtration characteristics of the slurry. The liquid:solid ratio was not specified; however, these results show that virtually complete dissolution of rare earths can occur at high leach temperatures, presumably dependent on a sufficiently high dilution ratio being used such that the solubility limits of the rare earths are not exceeded.
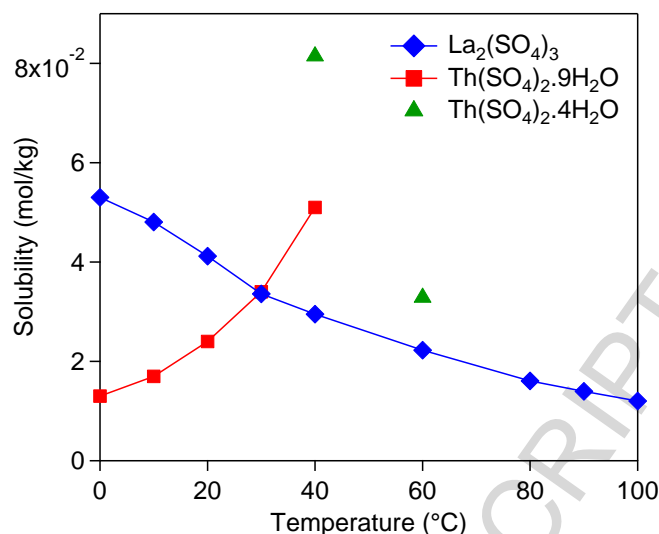
Figure 8 Influence of temperature on the solubility of lanthanum sulfate and thorium sulfate in water. Data from Dean (1999)

6.4 Acid Concentration

As noted above, high acid concentrations in the leach can reduce the solubility of the rare earth sulfates (Figure 7). Conversely, at low acid concentrations the precipitation of thorium phosphate or rare earth phosphates can occur (Shaw et al., 1954). Phosphate may be present in the leach as a product of the sulfation reaction of either rare earth phosphate minerals or phosphate gangue minerals in the feed material. Precipitation occurs at a sufficiently high leach pH, as the concentrations exceed the solubility limit of the rare earth phosphates. Shaw et al. (1954) found that during neutralisation of a leach solution obtained from a high grade monazite concentrate, precipitation of rare earths as phosphates started to occur at pH ~1.2, as shown in Figure 9, while thorium phosphate precipitation occurred at lower pH. These observations made by Shaw et al. (1954) are consistent with the published Eh-pH diagrams (Kim and Osseo-Asare, 2012) for Th(IV)-PO_4 (10^{-3} mol/L) which also show the precipitation of Th(IV) at pH ~1 as $Th(HPO_4)_2 \cdot 4H_2O(s)$ in solutions containing 0.01 mol/L sulfate. However, according to the Eh-pH diagrams a higher pH above 2-3 is required to precipitate $Th(HPO_4)_2 \cdot 4H_2O(s)$ from solutions containing higher sulfate concentrations in the range of 0.1-1.0 mol/L sulfate, due to the higher stability of $Th(SO_4)_2(aq)$, supported by the thermodynamic data (Kim and Osseo-Asare, 2012). However, significant uranium precipitation occurred only at pH values higher than 3.5 (Figure 9).
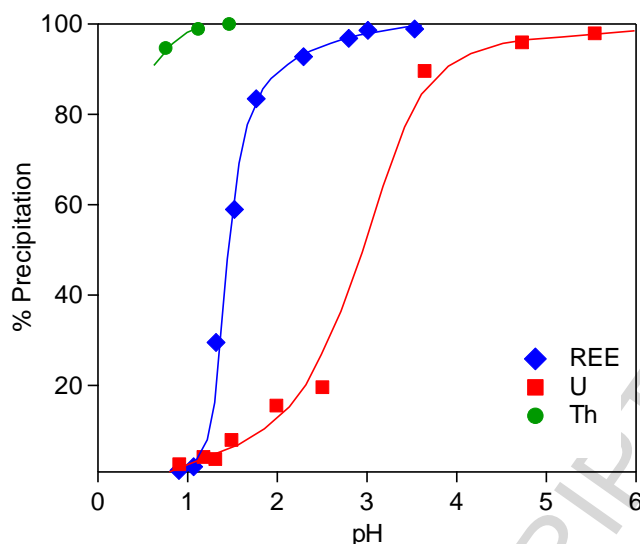
Figure 9 Effect of leach pH on precipitation of thorium, rare earths and uranium from solution containing phosphorus at approximately 0.16 M. Data from Shaw et al. (1954)

Hydrolysis of the rare earths can occur if the leach pH is close to 7. The rare earths react with water to form rare earth hydroxides species, potentially leading to precipitation depending on speciation (Bentouhami et al., 2004):

$$[RE + (H_2O)_n]^{3+} + H_2O \rightleftarrows [M(OH)(H_2O)_{n-1}]^{2+} + H_3O^+ \tag{24}$$
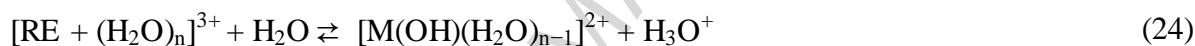
The tendency for hydrolysis increases with increasing atomic weight and the accompanying contraction of ionic radius within the rare earth series (Bentouhami et al., 2004; Katz and James, 1914). Rare earth hydroxide precipitation occurs between pH 6 and 8 (Bentouhami et al., 2004). Actinides generally hydrolyse more readily than the lanthanide elements. For Th(IV), hydrolysis can be initiated in solutions of pH above 3 (Bentouhami et al., 2004), although the precipitation of $RE(OH)_3$ occurs only in alkaline solutions (Kim and Osseo-Asare, 2012) as shown in Figure 5 and Figure 6.

7   Summary and Conclusions

The primary aim of sulfuric acid baking of rare earth ores or concentrates is the decomposition of the rare earth mineral structure, with concomitant conversion of the rare earths into soluble sulfates. A review of the literature has shown that the conditions used to achieve this vary widely for different rare earth minerals.

For monazite, sulfuric acid baking at temperatures above 200℃ with an acid to solid ratio in the range of 1:1 to 2.5:1 is generally required for complete decomposition of the mineral.

Acid baking at 200-300°C results in solubilisation of rare earths as well as impurities. Baking at temperatures above 300°C improves rejection of impurities such as thorium and iron to the leach residue, sometimes at the cost of reduced rare earth extraction. Reactions involving formation of insoluble thorium, iron and calcium phosphates at temperatures above 300°C have been proposed, but with little experimental evidence for reaction mechanisms.

Acid baking is the only process that has been applied in industry for processing of xenotime concentrate. There has been much less investigative work carried out for acid baking of xenotime compared to monazite. The few studies conducted to date indicate that xenotime may be slightly more refractory than monazite, requiring slightly higher bake temperatures and longer residence times. Acid bake temperatures in the range of 250-300°C have been used to obtain rare earth extractions of 95-99%.

Commercial processes for production of rare earths from bastnasite ores/concentrates differ from those for monazite and xenotime, indicating that bastnasite is more amenable to a variety of decomposition methods. Sulfuric acid baking of a bastnasite ore/concentrate has only been applied in industry for processing of Baotou concentrate, which contains both bastnasite and monazite. The bake temperature used is high (500-900°C); however, studies have shown that temperatures as low as 65°C can also be sufficient for complete reaction of bastnasite. A minimum temperature of 200-300°C has been quoted to achieve complete removal of fluorine in the bake stage.

The conditions required for sulfuric acid processing of other rare earth minerals vary widely for the different mineral types. For eudialytes, generally a sulfuric acid leach is sufficient, although eudialytes that are more refractory or contain a refractory portion also exist which needs stronger conditions. Some allanites and pyrochlores can be leached in sulfuric acid while others require acid baking at elevated temperature. Euxenite and loparite appear to be more refractory, requiring an acid bake for complete decomposition of the mineral structure. Fergusonite may be particularly refractory, as it has been reported to be unreactive in an acid bake at 220°C. For most of these rare earth minerals, very few studies have been carried out. Because of the complexity of many of these rare earth minerals, which often carry multiple valuable elements in addition to impurities, subsequent processing to produce pure products is typically complex, particularly if recovery of multiple value metals is desirable. There is a need for improving current understanding of the amenability of these and other less common rare earth minerals to processing via sulfuric acid based treatments.

The bake conditions as well as the leach conditions affect the solubility and therefore the recovery of the rare earth elements. Leaching is usually carried out at ambient or colder temperatures as rare earth sulfates are only moderately soluble in water and have an inverse relationship between solubility and temperature. If the leach solution contains phosphate, then rare earth phosphates may precipitate if the leach pH is too high. The presence of fluoride in the leach can lead to precipitation of rare earth fluorides. In some studies a two-stage leach, involving a concentrated initial leach followed by a more dilute leach, has been used to achieve partial separation of rare earths from impurities such as thorium and phosphate.

8   Acknowledgements

9   Reference List

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Highlights
- Compares bake conditions for monazite, xenotime, bastnasite and other minerals

- Examines chemistry and history of high temperature vs low temperature baking

- Compilation of acid bake reactions found in literature

- Reviews baking of tantaloniobates, loparite, allanite, eudialyte and pyrochlore

- Overview of RE solubility data for water leaching and effect of leach conditions