



# A review of hydrometallurgical flowsheets considered in current REE projects

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## Summary

The last 10 years witnessed a sharp increase in the number of REE projects under development because of a surge in REE prices. Seeking to take advantage of escalating metal prices, many junior mining companies focused exploration efforts on REE. Although determining the size and nature of a REE property is a key step in project development, it was quickly discovered that the metallurgical processes required to extract REE from these deposits are dependent on ore mineralogy, which is commonly varied and complex. A wide range of extractive metallurgical processes are known for REE minerals including caustic cracking, acid baking, agitated leaching, heap leaching, and ionic desorption. Furthermore, options for recovering REE from leach liquors are also numerous. In many cases, equipment used in these processes is relatively novel, and operating experience to benchmark against is minimal. Hence extensive testing is required to minimize the risks associated with these projects.

In this paper we review the various metallurgical processes currently under consideration by mining companies pursuing REE deposits, and attempt to identify potential key challenges and risks.

## 1. Introduction

The boom in rare earth element (REE) prices, which peaked in mid-2011, prompted the appearance of many new junior REE mining companies on the Australian and Toronto Stock exchanges (ASX and TSX). Many of these companies claimed easy metallurgy for their projects and presented accelerated paths to production and the phrase 'race to production' was commonly used (Trumbull, 2013). Typical hurdles in the 'race' are defining the resource, developing a metallurgical flowsheet, and gaining environmental permits. REE have been mined and processed for decades, but recent processing experience is predominantly in China, and although information on processing technologies in that country are known, mineralogical differences make this knowledge of limited relevance. In the West, detailed design knowledge for the separation of REE has been largely lost.

Herein we present an overview of the processing routes used by selected REE junior mining companies and by the

two current or recent operating mines in the Western world (Mount Weld mine, Western Australia; Mountain Pass mine, California). Using data from publically available preliminary economic assessments (PEA), preliminary feasibility studies (PFS), feasibility studies (FS), and other NI 43-101 compliant technical documents, as well as environmental impact statements (EIS) and press releases, we review 26 projects, including 12 from North America, 7 from Africa, 4 from Australia, and one from each of South America, Europe, and Asia (Table 1). The Mount Weld mine and concentrator is operated by Lynas Corporation with a hydrometallurgical processing plant in Malaysia (Lynas Advanced Materials Plant; LAMP). The first concentrate was fed to the kiln in November 2012. The Mountain Pass mine is operated by Molycorp Inc. A new plant started its ramp-up in January 2013, but never achieved technical, production, or economic targets, and was recently placed on Care and Maintenance (Molycorp, 2015).

## 2. REE project geology and mineralogy

Adopting the geological classification of REE deposits provided by Simandl (2012, 2014), we consider projects that are related to alkaline rocks and carbonatites, and vein, placers (and paleoplacers), and ionic clay deposits (Table 1).

The alkaline granite-hosted projects are typically relatively low grade (<2% TREO), but display a comparatively high relative HREO (Heavy Rare Earth Oxide; Sm to Lu+Y) distribution (HREO/TREO, %). With the exception of the Kvanefjeld project in Greenland, all alkaline rock associated projects have a HREO distribution of greater than 20%. The mainly xenotime Browns Range project has the highest relative HREO distribution (87%). The HREE-carrying minerals are typically xenotime (YPO<sub>4</sub>), zirconium silicates (eudialyte or zircon), or fergusonite (Y,Ln(NbO<sub>4</sub>)).

Both plants now operating in the Western world were designed to process carbonatite-type mineralization. Ore grades for this type of deposit vary significantly, from a low 0.1% TREO in the Lofdal project (Dodd et al., 2014) to an exceptionally high 54.3% in the Gakara deposit (Rainbow Rare Earths, 2015). The Lofdal mineralization consists predominantly of xenotime, which is highly unusual for a carbonatite-related deposit.

Table 1. REE Projects and REE mineralogy overview.

| Property          | Owner                            | Country   | Development Stage | Host Rock                | REE Carrying Minerals   | % TREO Ore | % HREO relative | Reference                 |
|-------------------|----------------------------------|-----------|-------------------|--------------------------|---|------------|-----------------|---------------------------|
| Bokan Mountain    | Ucore Rare Metals Inc.           | USA       | PEA               | Alkaline rock-associated | Thalenite, bastnasite, xenotime, monazite   | 0.65       | 40              | Bentzen et al., 2013      |
| Browns Range      | Northern Minerals Ltd.           | Australia | FS                | Alkaline rock-associated | Xenotime  | 0.66       | 87              | Northern Minerals, 2015   |
| Dubbo             | Alkane Resources                 | Australia | FS                | Alkaline rock-associated | Eudialyte, bastnasite, zircon, natroniobite, columbite  | 0.9        | 25              | Alkane Resources, 2012    |
| Kvanefjeld        | Greenland Minerals               | Greenland | FS                | Alkaline rock-associated | Steenstrupine (complex sodic phospho-silicate)  | 1.2        | 11.8            | Greenland Minerals, 2015a |
| Nechalacho        | Avalon Rare Metals Inc.          | Canada    | FS                | Alkaline rock-associated | LREE in bastnasite, synchisite, monazite and allanite. HREE in zircon, fergusonite and xenotime | 1.72       | 27.3            | Ciulescu et al., 2013     |
| Norra Karr        | Tasman Metals Ltd.               | Sweden    | PFS               | Alkaline rock-associated | Eudialyte   | 0.59       | 52              | Short et al., 2015        |
| Port Hope Simpson | Search Minerals Inc.             | Canada    | PEA               | Alkaline rock-associated | Allanite, fergusonite, chevkinite   | 1.07       | 19.6            | Dreisinger et al., 2014   |
| Round Top         | Texas Rare Earth Resources Corp. | USA       | PEA               | Alkaline rock-associated | Yttrifluorite   | 0.06       | 72              | Hulse et al., 2014        |
| Strange Lake      | Quest Rare Minerals Ltd.         | Canada    | PEA               | Alkaline rock-associated | Complex silicates, phosphates and zircon  | 0.93       | 39              | Gowans et al., 2014       |
| Zeus              | Matamec Explorations Inc.        | Canada    | FS                | Alkaline rock-associated | Eudialyte   | 0.41       | 37              | Saucier et al., 2013      |
| Ashram            | Commerce Resources Corp.         | Canada    | PEA               | Carbonatite              | Monazite, trace bastnasite, xenotime  | 1.81       | 4.7             | Gagnon et al., 2015       |
| Bayan Obo         | CN Northern Rare Earth (Grp)     | China     | Operating         | Carbonatite              | Bastnasite / monazite   | 6          |                 | Zhi Li and Yang, 2014     |
| Bear Lodge        | Rare Element Resources Ltd.      | USA       | PFS               | Carbonatite              | Bastnasite, synchysite, monazite, cerianite, ancylite   | 4.7        | 4.4             | Dahlberg, 2014            |

Table 1. Continued.

| Property        | Owner                           | Country      | Development Stage     | Host Rock          | REE Carrying Minerals         | % TREO Ore | % HREO relative  | Reference                   |
|-----------------|---------------------------------|--------------|-----------------------|--------------------|-------------------------------|------------|------------------|-----------------------------|
| Gakara          | Rainbow Rare Earths Limited     | Burundi      | Reserves Development  | Carbonatite        | Monazite, bastnasite          | 54.3       | 1.1              | Rainbow Rare Earths, 2015   |
| Lofdal          | Namibia Rare Earths Inc.        | Namibia      | PEA                   | Carbonatite        | Xenotime                      | 0.1        | 76               | Dodd et al., 2014           |
| Montviel        | GeoMega Resources Inc.          | Canada       | PEA under development | Carbonatite        | Ba-Ce carbonates and monazite | 1.5        | 1.8              | Belzille et al., 2015       |
| Mountain Pass   | Molycorp Inc.                   | USA          | Care and Maintenance  | Carbonatite        | Bastnasite                    | 8          | 1                | Molycorp 2014 a, b, 2015    |
| Mt Weld         | Lynas Corp. Ltd.                | Australia    | Operating             | Carbonatite        | Monazite, apatite             | 15.4       | 3                | Lynas, 2005                 |
| Ngualla         | Peak Resources Ltd.             | Tanzania     | PFS                   | Carbonatite        | Bastnasite, monazite          | 4.54       | 1.9              | Peak Resources, 2014        |
| Songwe Hill     | Mkango Resources Ltd.           | Malawi       | PFS                   | Carbonatite        | Synchysite, apatite           | 1.6        | 6.8              | Croll et al., 2014          |
| St-Honoré       | Magris Resources Inc.           | Canada       | unknown               | Carbonatite        | Bastnasite / monazite         | 1.65       |                  |                             |
| Zandkopsdrift   | Frontier Rare Earths Ltd.       | South Africa | PFS                   | Carbonatite        | Monazite                      | 1.9        | 7.8              | Harper et al., 2015         |
| Serra Verde     | Mineracao Serra Verde           | Brasil       | PFS (not published)   | Ionic clay         | N/A                           | 0.16       | 25 (37 if no Ce) | Rocha et al., 2013 and 2014 |
| Tantalus        | Tantalus Rare Earths AG         | Madagascar   | Reserves Development  | Ionic clay         | N/A                           | 0.09       | 19 (30 if no Ce) | Desharmais et al., 2014     |
| Eco Ridge       | Pele Mountain Resources Inc.    | Canada       | PEA                   | Vein / sedimentary | Monazite + U minerals         | 0.15       | 11.4             | Cox et al., 2012            |
| Nolans Bore     | Arafura Resources Ltd.          | Australia    | FS                    | Vein / sedimentary | Apatite, allanite             | 2.6        | 4                | Arafura Resources, 2014     |
| Steenkampskraal | Great Western Minerals Grp Ltd. | South Africa | FS                    | Vein / sedimentary | Monazite                      | 14.4       | 3.8              | Clay et al., 2014           |

Recent studies indicate that the Lofdal deposit, consisting of narrow veinlets of albitite that have been subjected to late carbonate alteration, is hydrothermal and not carbonatite hosted (Williams-Jones et al., 2015). Mineralization at Gakara is probably carbonatite related; where exposed the mineralization consists of variably oriented veins and veinlets a few cm to tens of cm thick (Rainbow Rare Earths, 2015). No NI 43-101 compliant report is available on the company website.

The two ionic clay projects (Table 1) are a distinct category and are similar to the ionic clay projects in Southern China. Grades are typically very low (<0.2% TREO) and only REE adsorbed onto clay minerals are recovered. REE associated with competent REE-carrying minerals (e.g., monazite, xenotime) are refractory and not typically extracted during the clay desorption process. Cerium and thorium are not sorbed on clay but were precipitated during weathering as the moderately refractory mineral cerianite ( $\text{Ce}^{4+}, \text{Th}$ ) $\text{O}_2$ , and both elements are therefore typically not extracted in the desorption process (Rocha et al., 2013, 2014). It therefore makes sense to report the relative HREO distribution expressed as HREO/(TREO-Ce), which consequently leads to HREO distributions of 30% (Tantalus) and 37% (Serra Verde).

### 3. Generic REE flowsheets

A generic conceptual flowsheet describing most of the processes is shown in Figure 1. The following steps are normally included.

- Mineral beneficiation to produce an upgraded mineral concentrate. Most processing costs are incurred in the hydrometallurgical plant, where REE are chemically extracted using an acid or alkaline reagent or a combination thereof. Operating costs are usually directly related to material throughput, therefore a reduction in mass recovery (or equivalent increase in concentrate grade), even at the expense of some REE recovery, is usually worth considering. Ionic clays cannot be economically upgraded and are therefore treated on a whole ore basis.
- Chemical extraction using acid to dissolve REE into a pregnant leach solution (PLS), commonly after an alkaline process to ‘crack’ the refractory minerals.
- Primary purification. Most flowsheets include a simple acid neutralization step using alkaline reagents such as lime, limestone,  $\text{MgO}$ ,  $\text{MgCO}_3$ , or  $\text{Na}_2\text{CO}_3$ . Care must be taken when using calcium-based reagents in sulphate media because REE co-precipitation with gypsum can lead to significant REE losses. Elements such as Th, Fe, P and Al are usually targeted at this stage.
- Crude (or primary) REE precipitation. Many flowsheets produce a partial purified intermediate REE precipitate, which is subsequently re-leached (with or without selective cerium removal). This allows further purification steps to be conducted on more concentrated solutions and therefore a much smaller plant size (and associated lower capital expenditure).

- Impurity removal. Undesirable elements such as uranium, radium, residual thorium, and base metals are removed in a secondary impurity removal step.
- Product recovery. A final purified REO product is produced by oxalic acid (followed by calcination) or carbonate precipitation.
- Reagent regeneration. The reagent could be acid ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  or  $\text{HNO}_3$ ), alkaline ( $\text{NaOH}$ ), or  $(\text{NH}_4)_2\text{SO}_4$ . Although this usually leads to a net reduction in reagent consumption (and associated operating expenditures), it is always at the cost of increased operational complexity.

### 4. REE flowsheets: beneficiation and pre-leaching

Typically, metallurgical testwork focuses on the beneficiation and chemical extraction stages. In beneficiation, direct flotation of REE minerals is the main option for the alkaline rock associated and carbonatite ore types due to the finely disseminated nature of the mineralization. Magnetic or gravity separation has also found applications to further upgrade flotation concentrate. Of the 26 projects evaluated (Table 2), 19 included a beneficiation flowsheet. Of these 19 projects, 13 included flotation as a separation technique, including 6 in combination with magnetic separation. Magnetic separation was used as a separation technology in 11 projects, including 2 as a standalone process, 1 combined with dense media separation, and 2 combined with X-ray sorting.

Ideally, low-grade ore is upgraded to a concentrate with minimal losses. In reality mineralogical analyses reveal that the REE-carrying minerals are commonly locked in gangue minerals, leading to reduced concentrate grades. Table 2 summarizes the reported or estimated mineral concentrate grades, as produced. An upgrade factor (concentrate-grade to ore-grade ratio) can be calculated, which typically ranges from 2 to 8, with outliers such as the Browns Range (Northern Minerals, 2015) and Kvanefjeld (Greenland Minerals, 2015a) properties with upgrade factors of 30 and 12.5 respectively.

The design for Ashram deposit stands out due to combined mineral and hydrometallurgical processes to produce feed for chemical cracking (acid bake). Whereas the PEA (Gagnon et al., 2015) reports on a mineral processing route based on froth flotation only, a recent press release of Feb 11, 2015 (Commerce Resources, 2015) indicates that the 10% grade flotation concentrate is pre-leached with  $\text{HCl}$ , and the leach residue further upgraded by wet high-intensity magnetic separation (WHIMS) to produce a final concentrate of 39% TREO.

The Songwe property in Malawi, which produces a 4.7% TREO concentrate, also employs an  $\text{HCl}$ -based pre-leach at moderately low acidity of pH 3 to 3.5 (Croll et al., 2014). The pre-leach (or gangue leach) dissolves the calcite while leaving the REE-carrying minerals apatite and synchysite in the residue. Beer et al. (2014) reported that the pre-leach reduced flotation concentrate mass by 39%, with minimal HREE losses of 1%. The resulting liquor—predominantly  $\text{CaCl}_2$  and  $\text{SrCl}_2$ —is used to regenerate  $\text{HCl}$  by the addition of  $\text{H}_2\text{SO}_4$ , which leads to the formation of gypsum. Similar to the Songwe Hill project,

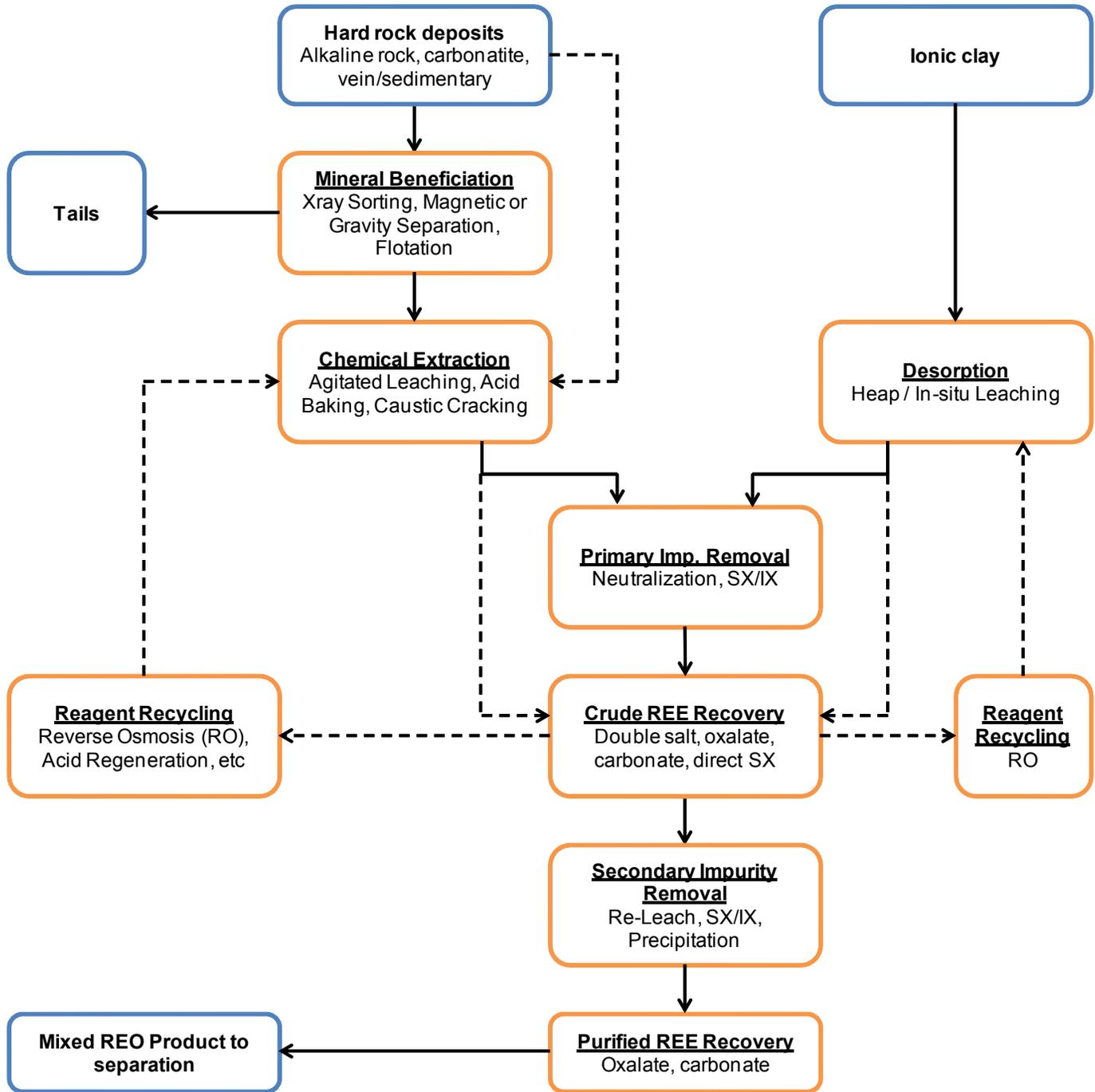


Fig. 1. Generic conceptual REE flowsheet.

the Lofdal property also uses an HCl based pre-leach to remove gangue minerals (Dodd et al., 2014).

### 5. Chemical treatment of concentrate

All projects require the use of hydrometallurgy (e.g., leaching, cracking, baking, sulphation) to dissolve the REE from the carrier minerals and subsequent separation of impurities (Fe, Al, PO<sub>4</sub>, Th, U, base metals, radionuclides) from the REE.

A significant range of technologies and reagents is used in concentrate leach processes (Table 3). Of the 18 concentrate leach processes reviewed, 11 use sulphuric acid as primary lixiviant, 3 use hydrochloric acid and 1 uses nitric acid (Bokan Mountain). In addition, three projects (Songwe Hill, Mountain Pass and Lofdal) use an intermediate caustic crack step to metathesize or crack phosphate minerals into REE hydroxides, which are subsequently leached in hydrochloric acid.

**Table 2.** Beneficiation processes.

| Property          | % TREO Ore | Beneficiation Process                             | % TREO Concentrate      | Upgrade Factor |
|-------------------|------------|---|-------------------------|----------------|
| Bokan Mountain    | 0.65       | X-ray sorting and magnetic separation             | ~2                      | 3.1            |
| Browns Range      | 0.66       | Magnetic separation and flotation                 | 20                      | 30.3           |
| Dubbo             | 0.9        | none - whole ore leach                            | N/A                     | N/A            |
| Kvanefjeld        | 1.2        | Flotation   | 15                      | 12.5           |
| Nechalacho        | 1.72       | Magnetic separation and flotation                 | 6-8                     | 4.1            |
| Norra Karr        | 0.59       | Magnetic separation                               | 1.6                     | 2.8            |
| Port Hope Simpson | 1.07       | none - whole ore leach                            | N/A                     | N/A            |
| Round Top         | 0.06       | none - whole ore leach                            | N/A                     | N/A            |
| Strange Lake      | 0.93       | Flotation   | 1.5-2                   | 1.9            |
| Zeus              | 0.41       | Magnetic separation                               | 0.75                    | 1.8            |
| Ashram            | 1.81       | Flotation   | 10                      | 5.5            |
| Bayan Obo         | 6          | Magnetic separation and flotation                 | 50                      | 8.3            |
| Bear Lodge        | 4.7        | Size and gravity separation                       | ~10                     | 2.1            |
| Gakara            | 54.3       | unknown   |                         |                |
| Lofdal            | 0.1        | X-ray sorting and magnetic separation             | 17-20 (after pre-leach) |                |
| Montviel          | 1.5        | Flotation   | 3                       | 2.0            |
| Mountain Pass     | 8          | Flotation   | 65                      | 8.1            |
| Mt Weld           | 15.4       | Flotation   | 40                      | 2.6            |
| Ngualla           | 4.54       | Magnetic separation and flotation                 | 17                      | 3.7            |
| Songwe Hill       | 1.6        | Flotation   | 4.7                     | 2.9            |
| St-Honoré         | 1.65       | unknown   |                         |                |
| Zandkopsdrift     | 1.9        | none - whole ore leach                            | N/A                     | N/A            |
| Serra Verde       | 0.16       | none - whole ore leach (desorption of ionic clay) | N/A                     | N/A            |
| Tantalus          | 0.09       | none - whole ore leach (desorption of ionic clay) | N/A                     | N/A            |
| Eco Ridge         | 0.15       | Magnetic separation and flotation                 | 0.6                     | 4.0            |
| Nolans Bore       | 2.6        | Magnetic separation and flotation                 | 8                       | 3.1            |
| Steenkampskraal   | 14.4       | Magnetic separation and dense media separation    | 30                      | 2.1            |

In terms of process simplicity, one could envisage the following ranking from simple to complex: straight agitated leaching; counter current agitated leaching; acid baking; integrated caustic crack; and agitated leaching. Five projects employ straight agitated/atmospheric acid leaching: Montviel (HCl), Norra Kärr ( $H_2SO_4$ ), Zeus ( $H_2SO_4$ ), Ngualla ( $H_2SO_4$ ), and Bear Lodge (HCl). Except for the Norra Kärr and Zeus eudialyte projects, the others are carbonatite hosted. Short et al. (2015) reported that the Norra Kärr project suffers from high silicon dissolution, which could lead to challenging liquid solid separation (LSS) properties and challenging performance in its direct solvent extraction (SX) process route to recover REE.

Due to the high cost of hydrochloric acid, projects involving HCl need to include acid recycling and/or regeneration strategies to remain economically viable. Of the technologies available (for review, see Bedrossian and Connell, 2014), the choice depends on the effluent stream composition and local site conditions. For example, at Mountain Pass a chlor-alkali plant converts NaCl from a separation plant into HCl and NaOH (Molycorp, 2014a), Montviel and Lofdal use low-

temperature reaction of soluble  $CaCl_2$  with  $H_2SO_4$  to form HCl and  $CaSO_4 \cdot 2H_2O$  (Yu et al., 2013), and Bear Lodge uses evaporation and distillation of excess free HCl to form 20.2% HCl for re-use (Dahlberg, 2014).

Integrating the acid regeneration circuit adds a degree of complexity and should be thoroughly tested to determine the effect of impurities on the acid regeneration circuit and, conversely, the effect of recycling gypsum-saturated liquor back to a leach circuit. A high-purity brine is essential as feed for chlor-alkali plants and therefore additional purification circuits may be required. Molycorp (2014b) reported suffering from quality issues in its feed liquor, which impacted the overall plant operation.

Counter current leaching provides the advantage of lower overall acid consumption by using excess acidity from a strong acid leach stage to leach reactive ore components in a weak acid stage. In addition, the PLS moving forwards in the flowsheet typically requires less reagent to neutralize residual acidity (Fig. 2). Possible disadvantages include an additional liquid-solid separation step and the potential to lose soluble

**Table 3.** Overview of concentrate leach processes.

| Property        | % TREO Ore Grade | % TREO Concentrate Grade | REE Carrying Minerals   | Concentrate Leach Process  | Leach Extraction, % TREO |
|-----------------|------------------|--------------------------|---|--|--------------------------|
| Kvanefjeld      | 1.2              | 15                       | Steenstrupine (complex sodic phospho-silicate)  | Counter current atmospheric agitated leach with H <sub>2</sub> SO <sub>4</sub> to leach U. The leach residue is caustic cracked and subsequently HCl leached   | 70 <sup>1</sup>          |
| Strange Lake    | 0.93             | 1.5-2                    | Complex silicates, phosphates + zircon  | Selective Thermal Sulphation (STS) followed by water leaching of REE sulphates   | 88                       |
| Ashram          | 1.81             | 10                       | Monazite, trace bastnasite, xenotime  | Pre-leach (HCl), WHIMS to produce 39% TREO con, Acid Bake (250°C) in rotary kiln   | 95                       |
| Songwe Hill     | 1.6              | 4.7                      | Synchysite, apatite   | Gangue pre-leach (PL) with HCl. Pre-leach liquor is treated to regenerate HCl. Pre-leach residue is leached with HCl and its residue caustic converted and leached again with HCl. Both leach liquors are combined and advance to purification | 90                       |
| Montviel        | 1.5              | 3                        | Ba-Ce carbonates and monazite   | Atmospheric / agitated acid leach using regenerated and recycled HCl   | 99                       |
| Mt Weld         | 15.4             | 40                       | Monazite, apatite   | Acid Bake with H <sub>2</sub> SO <sub>4</sub> in rotary kiln, followed by water leach of sulphated minerals  | 95                       |
| Mountain Pass   | 8                | 65                       | Bastnasite  | Atmospheric / agitated acid leach using regenerated and recycled HCl. Leach residue is cracked (NaOH) and subsequently HCl leached   |                          |
| Norra Karr      | 0.59             | 1.6                      | Eudialyte   | Atmospheric / agitated leach with H <sub>2</sub> SO <sub>4</sub>   | 90                       |
| Zeus            | 0.41             | 0.75                     | Eudialyte   | Atmospheric / agitated leach with H <sub>2</sub> SO <sub>4</sub>   | 85                       |
| Bayan Obo       | 6                | 50                       | Bastnasite / monazite   | Acid Bake with H <sub>2</sub> SO <sub>4</sub> in rotary kiln, followed by water leach of sulphated minerals  | >90                      |
| Steenkampskraal | 14.4             | 30                       | Monazite  | Acid Bake with H <sub>2</sub> SO <sub>4</sub> in rotary kiln, followed by water leach of sulphated minerals  | 95                       |
| Nechalacho      | 1.72             | 6-8                      | LREE in bastnasite, synchysite, monazite and allanite. HREE in zircon, fergusonite and xenotime | Thermal crack followed by HCl Leach  | >93                      |
| Browns Range    | 0.66             | 20                       | Xenotime  | Dried concentrate is mixed with H <sub>2</sub> SO <sub>4</sub> in pug mill type device. Acid Bake in rotary kiln, followed by water leach of sulphated minerals  | 95                       |
| Ngualla         | 4.54             | 17                       | Bastnasite, monazite  | Atmospheric / agitated leach with H <sub>2</sub> SO <sub>4</sub>   | 96                       |
| Nolans Bore     | 2.6              | 8                        | Apatite, allanite   | Pre-leach with fresh H <sub>2</sub> SO <sub>4</sub> , Acid bake of pre-leach residue with fresh H <sub>2</sub> SO <sub>4</sub> . Preleach and acid bake water leach pregnant liquors are combined.   | 90                       |
| Eco Ridge       | 0.15             | 0.6                      | Monazite + U minerals   | Acid Bake with H <sub>2</sub> SO <sub>4</sub> in rotary kiln, followed by water leach of sulphated minerals  | 97                       |
| Bear Lodge      | 4.7              | ~10                      | Bastnasite, synchysite, monazite, cerianite,  | Atmospheric / agitated leach with fresh 35% HCl and recovered 18% HCl  | 87                       |
| Bokan Mountain  | 0.65             | ~2                       | Thalenite, bastnasite, xenotime, monazite   | Counter current atmospheric / agitated leach with HNO <sub>3</sub>   | 93                       |
| Lofdal          | 0.1              | 17-20 (after pre-leach)  | Xenotime  | Atmospheric / agitated gangue leach with HCl. Pre-leach residue is caustic cracked and subsequently leached with HCl   |                          |

REE due to formation of double salts or incorporation into gypsum formed in the weak acid leach stage. Two projects are considering using a counter current acid flowsheet. At the Kvanefjeld project, concentrate is counter currently leached with H<sub>2</sub>SO<sub>4</sub> to dissolve uranium, while the strong acid leach residue is metathesized with NaOH and subsequently leached with HCl to solublize REE. At the Bokan Mountain project, a counter current nitric acid leach process is being considered to dissolve REE (Bentzen et al., 2013).

Seven projects currently are using or considering using acid baking of mineral concentrate as part of the flowsheet (Strange Lake, Ashram, Mt Weld, Bayan Obo, Steenkampskraal, Browns

Range and Eco Ridge).

Acid baking is typically used for concentrates or ores where straight agitated leaching will not 'crack' the REE minerals and a more aggressive mineral attack (in terms of reagent dosage and operating temperature) is required (Fig. 3). Acid baking, though considered a mature technology in China on high-grade (~50% TREO) concentrates, is not a common processing technology on any material in the Western world. The challenges arise from the fact that the mixture of liquid acid and feed (wet or dry) forms a high yield strength pasty mass, which dries out as it moves through a rotary kiln or other high-temperature processing equipment. Free and/or reaction

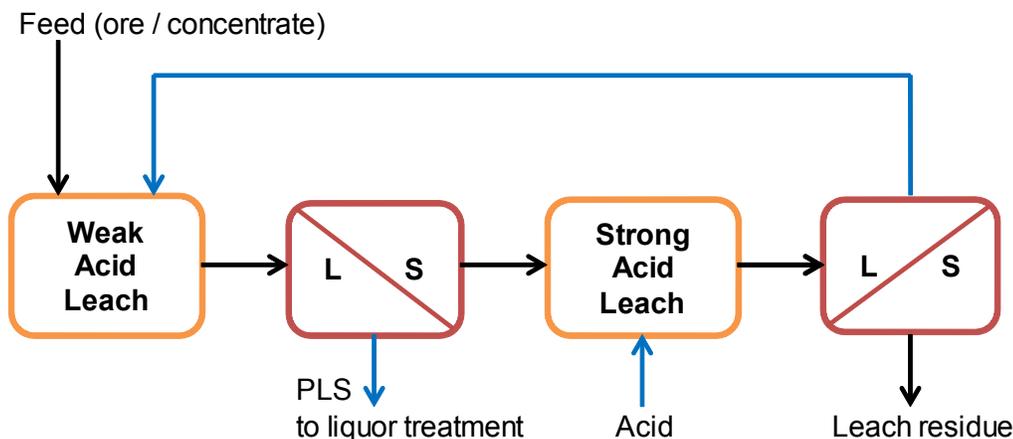


Fig. 2. Schematic counter current leach process.

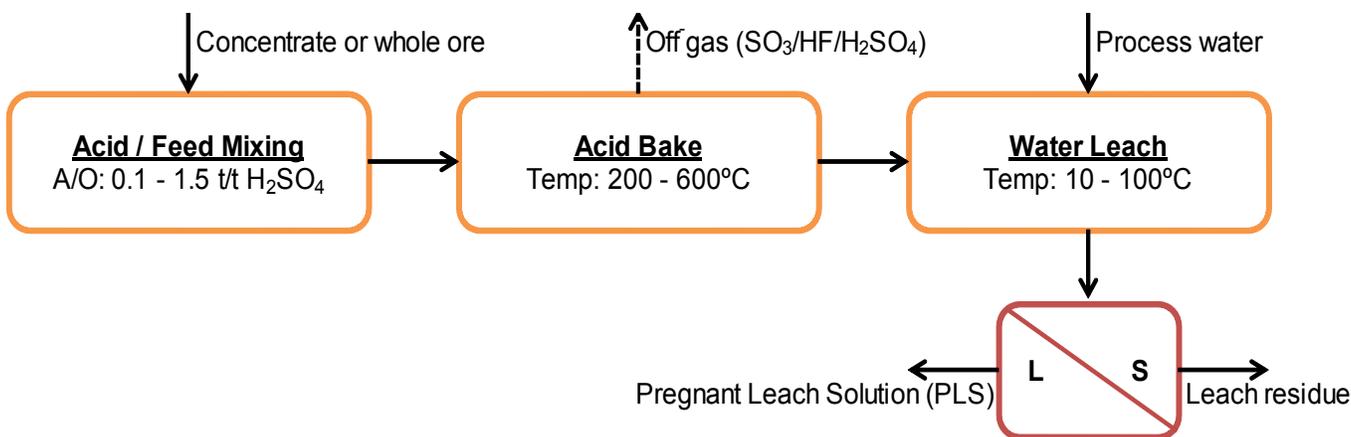


Fig. 3. Acid bake flowsheet schematic.

water and sulphuric acid are evaporated or otherwise consumed in the formation of hydrated metal sulphate salts. It is therefore commonly also referred to as a ‘sulphation’ step. The final kiln discharge is usually a dry, free-flowing powder or agglomerate, which is transferred into a leach circuit where sulphated salts (e.g., Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Ln<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) are dissolved in water.

Whereas the acid bake flowsheet is fairly easily tested at bench scale using crucibles in a muffle furnace or tube furnaces, it can be very challenging to test continuously for extended periods of time in a pilot plant. Primary challenges exist around the acid-feed mixing system and the associated material handling equipment. In addition, the movement of material through the kiln can be problematic and the actual properties depend on many factors, such as the concentrate/ore mineralogy and if, at the optimum (from a metal extraction point of view) acid dosage, the acid-feed mixture is amenable to agglomeration. In certain situations it is recommended to take a deliberate reduction in metal extraction to obtain more favourable material handling characteristics (Fig. 4a). Plugging of a rotary kiln (Fig. 4b) may only become apparent when a test program is advanced from extensive bench testing to continuous piloting. Selecting materials of construction for the severe and corrosive acid bake

applications has also led to significant challenges during the piloting stages of various test programs. Possible solutions may include pre-bake formation of cured agglomerates (Fig. 4c), if the feed mineralogy and required acid addition are amenable.

Lynas’ Mount Weld hydrometallurgical operation in Malaysia is an example of an operating project that has selected the acid bake route. The ore is mined and concentrated in Western Australia and concentrate is shipped to Lynas’s Advanced Material Plant in Malaysia. The hydrometallurgical plant was commissioned in late 2012, and ramp-up commenced in January 2013. The flowsheet consists of acid baking of the flotation concentrate, followed by water leaching of the calcine, impurity removal and solvent extraction to recover REE (Lynas, 2005). Various press releases have commented on lower than design production rates (Lynas, 2014) and issues with premature wearing of “some equipment of the cracking unit” and “clogging of filters” in the leach circuit (Lynas, 2013). After nine quarter-year periods, current production (Fig. 5) seems to remain well below design capacity, and follows a McNulty Category 4 ramp-up behaviour, one that is typically observed in plants with complex metallurgy, poor understanding of feed and/or chemistry, and limited pre-operation piloting testwork



**Fig. 4.** Photographs of **a)** an easy flowable material, **b)** a plugged rotary kiln, and **c)** an agglomerated product.

(McNulty, 1998 and McNulty, 2004). The Lynas plant output is comparable to the ramp-up of Western Australian nickel laterite projects in the 1990s (Verbaan et al., 2014), which were also characterized by complex metallurgy and a similar ‘race to production’.

Metathesis or caustic crack step has been identified at four projects. Two (Kvanefjeld, and Lofdal) include phosphate minerals, such as xenotime, which are converted or metathesized

to soluble sodium phosphate and insoluble REE hydroxides. Excess sodium hydroxide and sodium phosphate is washed out, the sodium phosphate can be crystallized to produce a tri-sodium phosphate by-product. Excess NaOH can be evaporated back to the original strength (50-60%) and re-used. The washed REE hydroxides are subsequently leached in acid.

The Mountain Pass and Songwe Hill properties contain bastnasite and synchysite, which both contain fluoride. We assume that REE precipitated in the primary HCl leach as REE fluorides are metathesized into REE hydroxides and soluble sodium fluoride. REE hydroxides are then leached with more HCl (or with the primary HCl PLS).

## 6. Whole Ore Treatment

Despite low ore grades, six projects do not include mineral beneficiation to produce an upgraded mineral concentrate. These projects use whole ore treatment processes (Table 4). As described below, the four hard rock projects use processes that differ from the two ionic clay projects.

The low grade Round Top project is pursuing a sulphuric acid heap leach operation using crushed (1/2 inch) ore. Hulse et al. (2014) reported testwork showing that extraction of up to 80% HREE is achievable with acid consumption as low as 30 kg/t.

The Port Hope Simpson project originally considered a beneficiation flowsheet comprising gravity separation, magnetic separation, and flotation (Dreisinger et al., 2012). However, more recent work (Dreisinger et al., 2014) revealed that a whole ore acid bake process using crushed ore (6 mesh) and an acid dosage of 100 kg/t ore feed is effective. Reported advantages of this approach include: 1) significant flowsheet simplification and improved REE recovery by removal of the beneficiation flowsheet; 2) removal of the energy-intensive grinding circuit (feed to the hydrometallurgical plant is 6 mesh material); 3) improved material handling characteristics of the acid/feed mixture and calcine in acid bake process equipment; and 4) improved filtration of the water leach pulp due to coarse particle size.

Few process details are available on the Dubbo zirconia process flowsheet. Milled ore is mixed with sulphuric acid and then roasted in a rotary kiln. Based on the environmental impact statement (Irwin, 2013), an acid consumption of 325 kg/t ore can be calculated. Calcine is subsequently leached with water, during which double salts are formed in the solid leach residue. LREE-rich double salts are re-leached and recovered, while HREE remain in solution with Zr and Nb and advance to sequential solvent extraction to recover zirconium and niobium and recover HREE by precipitation. Overall REE extractions in the Dubbo flowsheet are low and range from 32 to 61%. It is unclear from the public data (Alkane, 2013) where most of the REE losses occur.

Frontier’s Zandkopsdrift deposit contains approximately 3-4 times as much manganese as REE. Though ore beneficiation was attempted, results were unsatisfactory and a whole ore leach approach was examined instead. The whole ore leach process consists of the following steps (Harper et al., 2015).

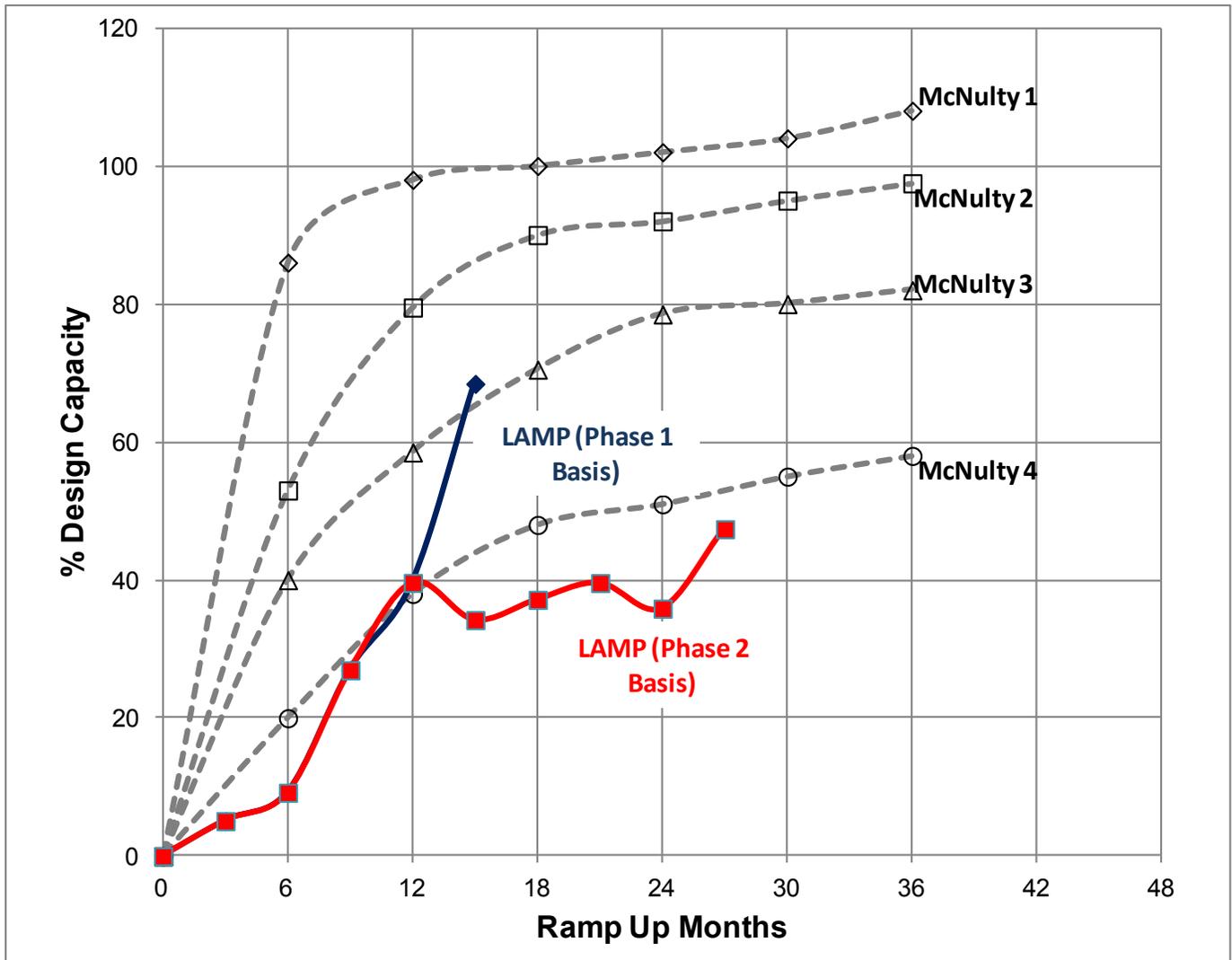


Fig. 5. Ramp-up curve Lynas LAMP (Mount Weld project).

- Reductive pre-leach to pre-extract about 90% of the Mn at an acid addition of ~100 kg/t  $H_2SO_4$  and 70 kg/t  $SO_2$ .
- The Mn pre-leach residue is contacted with about 1 t/t sulphuric acid in a high shear mixer, which leads to the production of a dry, stable, granular, free flowing and competent material that allows the use of fluidized bed reactors rather than rotary kilns.
- The granular material is then cracked or baked at low temperature (250-350°C), where gangue and REE minerals are sulphated.
- The low-temperature calcine is heated further in a high temperature calcination step during which ferric sulphate decomposes to hematite and gaseous  $SO_2$  and  $SO_3$ . This needs to be done under careful temperature control to avoid the decomposition of REE sulphates.
- High-temperature calcine is leached with water, during which REE sulphates are dissolved and hematite remains in the leach residue.
- Gaseous  $SO_2$  and  $SO_3$  are treated in an acid plant and reconstituted to sulphuric acid. It is reported in the PFS that around 80% of the added sulphur to the Mn leach residue is regenerated to sulphuric acid. This would mean that the overall acid consumption (pre-leach + acid bake) is near 300 kg/t  $H_2SO_4$ .

The Tantalus and Serra Verde projects (Table 4) are ionic clay projects that are not amenable to mineral upgrading. Ionic clay projects do not use aggressive leach systems as outlined above for the hard-rock deposits. Instead, REE sorbed onto clays are simply desorbed using an ion-exchange-based elution process with eluants such as sodium chloride or ammonium sulphate. Current practice in China is to use in-situ or heap leaching methods (for review, see Chi and Tian, 2008). The Serra Verde and Tantalus clay properties share many similarities to the Southern China clay projects, which produce much of the global HREE. The Serra Verde project is described in detail by Rocha et al. (2013, 2014), and the Tantalus clay desorption

**Table 4.** Whole ore treatment processes.

| Property          | Host Rock Minerals       | % TREO Ore Grade | Whole Ore Leach Process   | Acid Consumption kg/t |
|-------------------|--------------------------|------------------|---|-----------------------|
| Round Top         | Alkaline rock-associated | 0.06             | Crush ore to 1/4-1/2 inch. Heap leaching with H <sub>2</sub> SO <sub>4</sub> .  | 30                    |
| Port Hope Simpson | Alkaline rock-associated | 1.07             | Crush ore to 6 mesh. Whole ore acid baking at low A/O of 100 kg/t H <sub>2</sub> SO <sub>4</sub> and hot water leaching.  | 100                   |
| Dubbo             | Alkaline rock-associated | 0.9              | Acid bake with H <sub>2</sub> SO <sub>4</sub> and water leach. Double salts are formed in the WL. HREE remain in solution. DSP is re-leached.   | 325                   |
| Zandkopsdrift     | Carbonatite              | 1.9              | Reductive pre-leach (PL) with H <sub>2</sub> SO <sub>4</sub> /SO <sub>2</sub> to remove Mn. Agglomeration of PL residue in high shear mixer, Low temperature sulphation in fluidized bed reactor (FBR). High temperature calcination in FBR. Two stage water leach. | 300                   |
| Tantalus          | Ionic clay               | 0.09             | Heap leach (i.e. desorption) with NaCl or Na <sub>2</sub> SO <sub>4</sub> .   | N/A                   |
| Serra Verde       | Ionic clay               | 0.16             | Heap leach (i.e. desorption) with NaCl or Na <sub>2</sub> SO <sub>4</sub> . In situ leach is under consideration.   | N/A                   |

processes are detailed by Moldoveanu and Papangelakis (2013) and Desharnais et al. (2014). Typical REE grades are low (ranging from 0.1 to 0.4%) and consequently, the logistics of moving large quantities of ore and solution poses challenges.

Rocha et al. (2013) reported that about 50% of the total REE are adsorbed onto clay and are therefore recoverable by the desorption process, with the remainder in primary minerals or partially decomposed minerals. Testwork results indicated that about 50% La, Pr-Lu can be desorbed using either NaCl or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> eluants. Cerium and thorium extraction is significantly limited due to their presence in cerianite minerals.

## 7. Pregnant leach solution (PLS) treatment options

Most processes will dissolve deleterious impurities into the leach solution along with REE during the leaching step. Hydrometallurgical methods are then used to separate the REE from impurities. Though most process routes (Table 5) differ, they can be grouped into five main categories: 1) Impurity Removal – REE Precipitation and Re-Leach (IR-RP-RL); 2) direct ion exchange or solvent extraction (IX/SX); 3) IR-direct IX/SX; 4) double salt precipitation (DSP); and 5) direct REE precipitation with oxalic acid.

### 7.1. IR-RP-RL process route

In this route, elements such as Fe, Al, Th, P are removed upstream of REE recovery. Impurity Removal (IR) usually uses reagents such as NaOH, MgCO<sub>3</sub>, MgO, or CaCO<sub>3</sub>. In addition, ion-exchange may be used to remove U. REEs are precipitated from the IR filtrate in a REE Precipitation circuit (RP) using MgO, Na<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub> or NaOH. The REE precipitate is subsequently re-leached using acid. Secondary impurity removal is likely carried out on the re-leach liquor. This

flowsheet, or variations thereof, is exercised by 11 projects. These include alkaline granite projects such as Nechelacho, Port Hope Simpson, Strange Lake, Zeus, and Browns Range, and carbonatite projects such as Ashram, Lofdal, Montviel, Songwe Hill, and Zandkopsdrift.

### 7.2. Direct ion exchange or solvent extraction (IX or SX) process route

In this route, REEs are extracted selectively (against impurities) directly from impure leach solution without prior neutralization or impurity removal. Three projects use this approach. The Bokan Mountain project proposes using a SuperLig® resin based on Molecular Recognition Technology (MRT) to extract REE as a group first, away from other dissolved metals, in a nitric acid medium. The REE are subsequently separated into individual elements using MRT. At the Kvanefjeld project, an HCl-based leach solution is treated by direct solvent extraction (SX). REEs are subsequently separated to produce individual La, Ce, LaCe and Pr-Lu+Y product streams. The feasibility study (Greenland Minerals, 2015a) does not elaborate on impurity handling and it is unknown where impurities such as Fe, Al, Th report to or how they are dealt with. Although it is feasible, depending on mineralogy and leach conditions, that many of the impurities such as Fe, Al, and U will end up in the H<sub>2</sub>SO<sub>4</sub> based uranium leach solution, elements such as thorium are expected to follow REE. A recent press release (Greenland Minerals, 2015b) indicates the presence of an impurity removal circuit upstream of SX, which would place this project into the IR-Direct IX/SX category. At the Round Top project, low-grade heap leach solutions are treated in an initial CIX (Continuous Ion Exchange) system to separate the REEs from the dilute PLS into a concentrated mixed REE

**Table 5.** Leach liquor Purification processes.

| Property          | % HREO relative  | PLS Chemistry                  | Downstream Flowsheet Category                               | Primary Purification  | Primary REE Recovery  | Secondary Purification  |
|-------------------|------------------|--------------------------------|---|---|---|---|
| Bokan Mountain    | 40               | HNO <sub>3</sub>               | Direct IX/SX  | -   | Direct REE IX (MRT) in multiple steps   | -   |
| Browns Range      | 87               | H <sub>2</sub> SO <sub>4</sub> | IR-RP-RL  | Neutralization with Ca(OH) <sub>2</sub> , Fe(III) and MgO to remove Fe, P and Th. U is removed by conventional IX | FS: Primary REE precipitation with Na <sub>2</sub> CO <sub>3</sub> . Hadley and Catovic (2014) reported on direct oxalic precip   | -   |
| Dubbo             | 25               | H <sub>2</sub> SO <sub>4</sub> | DSP   | Zr/NbSX from WL PLS. Various undisclosed unit ops   | Double sulphate precipitation in WL. DSP is re-leached to form a LREE product. An HREE product is produced from Zr/Nb raffinate   | -   |
| Kvanefjeld        | 11.8             | H <sub>2</sub> SO <sub>4</sub> | Direct IX/SX  | -   | Direct SX of REE. Production of La, Ce, LaCe and Pr-Lu  | -   |
| Nechalacho        | 27.3             | HCl                            | IR-RP-RL  | Impurity removal by neutralization  | REE Precipitation   | -   |
| Norra Karr        | 52               | H <sub>2</sub> SO <sub>4</sub> | IR-Direct IX/SX   | Neutralization with MgO or Ca(OH) <sub>2</sub> to remove impurities (Si,...)                                      | Direct SX (primary amine) of REE coupled with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> stripping and precipitation of REE. REE solids are separated by centrifugation and filtration                    | -   |
| Port Hope Simpson | 19.6             | H <sub>2</sub> SO <sub>4</sub> | IR-RP-RL  | Fe, Al, Th, removal by Na <sub>2</sub> CO <sub>3</sub> / MgCO <sub>3</sub> / MgO neutralization                   | Bulk REE precipitation with Na <sub>2</sub> CO <sub>3</sub>   | RP cake is re-leached in HCl and the PLS is treated for secondary Th removal prior to REE precipitation with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . Final REE cake is calcined to make a 98-99% REO product |
| Round Top         | 72               | H <sub>2</sub> SO <sub>4</sub> | Direct IX/SX  | -   | IX to separate REE from other elements in Heap Leach PLS  | -   |
| Strange Lake      | 39               | H <sub>2</sub> SO <sub>4</sub> | IR-RP-RL  | Fe/Al/Th removal by MgO neutralization  | Bulk REE Precipitation  | REE Precip is re-leached. REE will be re-precipitated with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> and finally calcined  |
| Zeus              | 37               | H <sub>2</sub> SO <sub>4</sub> | IR-RP-RL  | Fe/Al/Th removal by CaCO <sub>3</sub> neutralization followed by IX to (presumably remove U and residual Zr)      | Primary REE precipitation with Na <sub>2</sub> CO <sub>3</sub>  | Secondary impurity leaching with undisclosed reagent. REE are re-leached in acid, followed by SX to separate LREE from HREE   |
| Ashram            | 4.7              | H <sub>2</sub> SO <sub>4</sub> | IR-RP-RL  | Impurity removal by NaOH  | Na <sub>2</sub> CO <sub>3</sub> precipitation   | -   |
| Bear Lodge        | 4.4              | HCl                            | Direct RP with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> | -   | Direct REE Precipitation with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . REE oxalates are subsequently calcined at 700°C  | RP is leached with HNO <sub>3</sub> . Th is precipitated with NH <sub>4</sub> OH in 2 steps. REE are then precipitated with NH <sub>4</sub> OH  |
| Lofdal            | 76               | HCl                            | IR-RP-RL  | Neutralization with Ca(OH) <sub>2</sub> to remove Fe, Th  | Primary REE precipitation with Ca(OH) <sub>2</sub>  | -   |
| Montviel          | 1.8              | HCl                            | IR-RP-RL  | Fe/Al/Th removal by NaOH (from chlor alkali plant) neutralization   | REE Precipitation with NaHCO <sub>3</sub>   | -   |
| Mountain Pass     | 1                | HCl                            | IR-Direct IX/SX   | Fe and Pb removal   | Direct SX   | Ce redox circuit  |
| Mt Weld           | 3                | H <sub>2</sub> SO <sub>4</sub> | IR-Direct IX/SX   | Fe/Al/Th removal by MgO/FeCl <sub>3</sub> neutralization  | Direct SX of REE with D2EHPA. Production of La, Ce, NdPr, Sm-Lu+Y   | -   |
| Ngualla           | 1.9              | H <sub>2</sub> SO <sub>4</sub> | DSP   | -   | Double sulphate precipitation (rejects Fe, Al, U). Conversion of DSP to hydroxide. RL with HCl and Ce rejection   | Fe/Al removal from RL liquor by addition of NaOH. Final REE precip by Na <sub>2</sub> CO <sub>3</sub>   |
| Songwe Hill       | 6.8              | HCl                            | IR-RP-RL  | Fe/Al/Th removal by CaCO <sub>3</sub> neutralization  | Primary REE precipitation with NaOH. RP filtrate is treated to regenerate HCl.  | RP cake is dried in air atmosphere and subsequently re-leached in HCl to reject Ce. REE are precipitated with NaOH  |
| Zandkopsdrift     | 7.8              | H <sub>2</sub> SO <sub>4</sub> | IR-RP-RL  | Fe, Al, Th, U, PO <sub>4</sub> removal by MgO neutralization  | Bulk REE Precipitation with MgO   | RP is re-leached with HCl   |
| Serra Verde       | 25 (37 if no Ce) | SO <sub>4</sub> or Cl          | IR-RP-RL  | Neutralization to remove Fe, Al, Th   | Primary REE precipitation with H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> or (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>  | -   |
| Eco Ridge         | 11.4             | H <sub>2</sub> SO <sub>4</sub> | IR-Direct IX/SX   | Uranium SX (Alamine 336)  | Direct REE SX with D2EHPA/TBP   | -   |
| Nolans Bore       | 4                | H <sub>2</sub> SO <sub>4</sub> | DSP   | -   | Double sulphate precipitation (rejects Fe, Al, U). Conversion of DSP to hydroxide. RL with HCl and Ce rejection   | Various, UIX  |
| Steenkampskraal   | 3.8              | H <sub>2</sub> SO <sub>4</sub> | DSP   | The flowsheet allows for a split LREE (double salt) and HREE process route.                                       | LRE route: Double sulphate precipitation (rejects Fe, Al, U). DSP is converted to REE hydroxide, which is re-leached with HCl, while rejecting Ce. HRE Route: HREE precipitation from purified DSP filtrate | IX to remove Cu and U (on LREE process route). Cu/ base metal removal by precipitation with NaHS in HREE process route  |

stream. Continuous Ion Chromatography (CIC) is then used to further isolate the REEs into ‘lights’, ‘mids’ and ‘heavies’ and reject co-extracted impurities. These solutions are then further processed to produce selected separated groups of REEs.

### 7.3. IR-direct IX/SX process route

This route is similar to the Direct IX/SX process route, but includes an upstream impurity removal step. Four projects are currently or considering using this type of process route. In the flowsheet for the Norra Kärr project, a sulphate based

leach solution is neutralized with MgO or Ca(OH)<sub>2</sub> to remove impurities such as silicon. A primary amine is then used in an SX step to extract REEs. Oxalic acid is used to simultaneously strip REE from organic material and precipitate the REEs. Precipitated REE oxalates are recovered through centrifugation and filtration (Short et al., 2015). It will be of interest to monitor organic losses (associated with filtered solids) in future testwork results. The Mountain Pass operation has recently been placed on care and maintenance. Few details are available, but it seems that iron and lead are removed upstream of the SX circuit. A cerium redox circuit is employed to reduce the amount of cerium advancing to the SX circuit. At Mount Weld, sulphate-based leach solutions are initially treated with a mixture of MgO and FeCl<sub>3</sub> to promote co-precipitation of Th into a FePO<sub>4</sub> compound. The FeCl<sub>3</sub> is presumably balanced to promote a Fe:P molar ratio of 1:1. REEs are subsequently extracted from the partial purified filtrate using SX (D2EHPA extractant). The LAMP produces La, Ce, NdPr and mixtures of heavy REE (Sm-Lu+Y) products. A recent quarterly report (Lynas Corporation, 2015) reveals that the production of NdPr and LaCe products was harmed by unstable SX operations. The key issue was identified to be organic degradation in the LaCe|PrNd separation circuit, which is considered the most complex part of the LAMP REE separation. The LaCe|PrNd SX circuit has 110 stages and long residence times including about three weeks for Pr. This means that any adjustments to production settings take time to resolve through the system (Lynas Corporation, 2015). At Eco Ridge, uranium is recovered from sulphate-based leach solutions through an Alamine 336 SX circuit. USX raffinates are subsequently neutralized using lime in an Impurity Removal circuit. REEs contained in the IR filtrate are then extracted in a D2EHPA SX circuit (Cox et al., 2012). This flowsheet is based on the historic Elliot Lake yttrium production flowsheets as described by Goode (2012).

#### 7.4. Double salt precipitation (DSP) process route

The double salt (Na<sub>2</sub>SO<sub>4</sub>·Ln<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O) route is very common for predominantly LREE projects due to the higher preference of LREE to form double sulphate salts compared to HREE. However, the DSP route can also be applied in projects with considerable HREE, and in such projects, a crude separation between lights and heavies is accomplished. Double salts are formed by the addition of sodium sulphate to a REE leach solution. In most flowsheets, the double salt is metathesized to a hydroxide form by slurring the DSP in caustic. The moist hydroxide cake can be subsequently oxidatively dried at 150°C and ultimately re-leached in acid (usually HCl). The drying step leads to oxidation of Ce(III) to Ce(IV), which has limited solubility in dilute acid. Therefore, the DSP route allows for the early rejection of cerium.

Four projects are considering using the DSP route. Three predominantly LREE projects (Ngualla; Peak Resources, 2014; Nolans Bore, Arafura, 2014; and Steenkampskraal, Clay et al., 2014) apply the DSP process on dilute H<sub>2</sub>SO<sub>4</sub> leach solution and also use the cerium oxidation removal step. The

Steenkampskraal project also recovers HREE from the DSP filtrate and has reported using IX to remove Cu and U from the LREE stream. In addition, copper and other base metals are removed from the HREE stream by sulphide precipitation (using NaHS). At the Dubbo project, double salts appear to be formed naturally in the Dubbo project acid bake-water leach circuit, probably by operating the water leach circuit at high pulp densities and maybe because of high Na/K levels from the ore in the PLS. The leach solution (enriched in HREE) is first treated by SX to extract Zr and Nb, which are both recovered as products and then precipitated. The WL residue (enriched in LREE) appears to be re-leached and the solution treated to recover a LREE product.

#### 7.5. Direct REE precipitation with oxalic acid process route

In this route, which is used only at the Bear Lodge project, REE are precipitated directly out of an HCl-based leach solution using oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>). A significant separation of REE versus other metal occurs due to the selectivity of oxalate precipitation, though thorium is one of the main contaminants that follow the REE. REE oxalates are subsequently calcined at 700°C and then re-leached in nitric acid. A series of consecutive precipitation steps employing ammonium hydroxide are subsequently used to separate Th from the REE.

#### 8. REE separation

The conventional method to separate REEs is based on SX (P507) technology, as described by Liao et al. (2013) and Yan et al. (1999). Recent new developments in REE separation are being considered by some projects, although few details are publically available.

Free Flow Electrophoresis (FFE) is under consideration for the Montviel project (GeoMega, 2015). In FFE, a solution of mixed dissolved elements (REE) is passed through a separation channel, which is affected by a static perpendicular electrophoretic force, exerted by side-wall electrodes. The magnitude of this force and the charge to size ratio of each ion affects the deviation of ions from a straight trajectory along the channel. REE separation is achieved by using multiple channels and flow splitters. The FFE process is patented by Innord Inc, a wholly owned private subsidiary of GeoMega (Hajjani, 2014).

The Bokan Mountain project is considering using Molecular Recognition Technology (MRT) by IBC Advanced Technologies Inc, to produce high-purity separated REEs. MRT is a selective non-ion exchange process using custom designed organic chelating ligands (SuperLig®) and uses supramolecular ‘lock and key’ chemistry as the basis for its high selectivity. Elution of the loaded REE resin is accomplished by using an acidic eluent, which leads to the production of concentrated REE solutions, either as group or as individual elements.

Other methods include: Continuous Ion Chromatography (CIC) by K-technologies Inc (which is being considered for the Round Top project); micro-fluidics, membrane-supported SX, “Fast SX”, and other variants on the P507 route; and Tri-n-butyl phosphate (TBP) extraction from nitrate solution, as used

by Solvay and other refiners.

### 9. Reagent regeneration

Due to the high costs and/or high dosages required of some reagents, reagent regeneration is a key component of some projects. Although regeneration reduces operating costs, it usually adds to process complexity. Some projects have introduced water recovery and NaOH, HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> recycling strategies (Table 6). Bedrossian and Connell (2014) review HCl regeneration by gypsum crystallization and by the chlor-alkali process. The Molycorp plant experienced significant issues in the operation of its chlor-alkali plant (Molycorp, 2014b).

### 10. Conclusions

It is clear that after a potential ore deposit has been found and described by geologists, much work is required by metallurgists to develop an economical and effective flowsheet suitable for the commonly complex overall ore mineralogy. Although flowsheet selections are driven primarily by ore mineralogy and specific project conditions, extractive metallurgists have many choices to make as is shown by the current wide array of metallurgical flowsheets. This applies to the beneficiation, chemical extraction (leaching), purification and separation areas of the overall treatment flowsheets. To mitigate risks, full tests of a selected flowsheet under continuous processing conditions are demanded.

**Table 6.** Reagent regeneration processes.

| Property       | PLS Chemistry                  | Reagent Regeneration   |
|----------------|--------------------------------|--|
| Bokan Mountain | HNO <sub>3</sub>               | HNO <sub>3</sub> recycling.  |
| Dubbo          | H <sub>2</sub> SO <sub>4</sub> | Reverse osmosis to treat process water for re-use.   |
| Strange Lake   | H <sub>2</sub> SO <sub>4</sub> | Excess H <sub>2</sub> SO <sub>4</sub> and SO <sub>2</sub> /SO <sub>3</sub> from decomposed Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> from calciner.                                |
| Bear Lodge     | HCl                            | HCl distillation from RP filtrate to form 20.2% HCl. H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> regeneration by crystallization (cooling) from distillation bottoms.                   |
| Lofdal         | HCl                            | HCl from the gangue leach will be regenerated by means of H <sub>2</sub> SO <sub>4</sub> addition and CaSO <sub>4</sub> precipitation. NaOH regeneration is also assumed to be required. |
| Montviel       | HCl                            | Chlor-Alkali plant for HCl/NaOH regeneration. Feed (RP Filtrate) is treated with Na <sub>2</sub> CO <sub>3</sub> and IX to prepare for Chlor-Alkali.                                     |
| Mountain Pass  | HCl                            | HCl / NaOH via Chlor-Alkali.   |
| Songwe Hill    | HCl                            | HCl regeneration via CaSO <sub>4</sub> precipitation with H <sub>2</sub> SO <sub>4</sub> .   |
| Zandkopsdriif  | H <sub>2</sub> SO <sub>4</sub> | Excess H <sub>2</sub> SO <sub>4</sub> and SO <sub>2</sub> /SO <sub>3</sub> from decomposed Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> from calciner.                                |
| Serra Verde    | SO <sub>4</sub> or Cl          | Reverse osmosis to recycle process water and regenerate eluant ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> or NaCl).  |

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