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**RECOVERY OF RARE EARTH ELEMENTS FROM
COMPLEX AND LOW GRADE DEPOSITS**

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ABSTRACT

Rare earth elements (REE) have gained prominence over the last few years due to concerns over a sustainable supply to meet the growing global demand. A number of REE deposits have been studied over the past 5 years, and most of these deposits are of relatively low grade. One of the most complex aspects of the recovery of REE from low grade ores is that almost every ore is different and requires a specific metallurgical process to optimise its potential value.

The generation of a REE concentrate that would be suitable as refinery feed from low grade and complex REE ores can be divided roughly into three processing stages, namely physical beneficiation, 'cracking' to reject REE precipitants such as fluorides and phosphates, and leaching of REE. In some cases, hydrometallurgical purification of the leach liquor might also be required to generate a product suitable as refinery feed. The selection of the metallurgical treatment options is initially based on a detailed understanding of the ore mineralogy and the chemical composition of the ore.

This paper describes the testwork conducted on complex ore samples of different mineralisations. The correlation between the ore composition and the metallurgical response for different treatment options is illustrated. Concurrently the technical criteria for the selection of viable process flow sheets are discussed which facilitate the generation of a suitable refinery feed whilst maximising the REE recovery.

INTRODUCTION

Rare earth elements (REE) have gained prominence over the last few years due to concerns over a sustainable supply meeting the growing global demand. With increased effort at finding alternatives to Chinese supply for this critical commodity, all over the world attention has shifted to the exploitation of low grade REE deposits which are also complex in nature. Such deposits occur in a variety of geological settings, resulting in variability in the mineralogy of the REE and gangue minerals from one deposit to another.

The conventional recovery routes were characterised by multiple physical beneficiation steps to attain a high grade REE concentrate. Such concentrate was subsequently subjected to a hydrometallurgical cracking and leaching route to generate a very pure REE solution suitable for refining⁽¹⁾. A number of low grade and complex REE deposits have been studied by Mintek over the past 5 years and in many cases the conventional recovery routes were not applicable. This was due to the mineralogy of the ores as the REE bearing minerals were fine grained, needle-shaped, not liberated and intergrown within gangue.

The processing of complex REE ores distinguishes itself from the classical REE treatment routes in two main aspects.

The first aspect is that the beneficiation step is primarily aimed at rejecting the maximum amount gangue whilst minimising the compromise on recovery, which is not equivalent to the objective of generating a high grade REE concentrate. In the case of very complex or low grade ores this step may even be absent altogether. As a consequence, the second aspect will be that a purification step is required as integral part of the flowsheet, since this stage facilitates the comprehensive rejection of deleterious impurities.

As a result the selection of the most suitable recovery process is linked directly to the specific ore mineralogy such as mode of occurrence of REE minerals as well as type of gangue and impurities.

These treatment routes listed here are aimed at maintaining a high REE recovery whilst generating a pure REE solution suitable for refining. These process routes could be applied to either whole ore or upgraded ore and concentrates.

Three ore types (labelled Ore Type 1, 2 and 3) are discussed in this paper and have been selected as the object of the study, as it is believed that the solution to the treatment problems is generic enough to allow the understanding to be applied to other ores.

IMPORTANCE OF MINERALOGY

Within the majority of complex and low grade ore types, the gangue and REE mineralogy can differ from deposit to deposit, which is often a consequence of later-stage alteration effects. This has implications for the type of processing to be undertaken in the upgrading and extraction of the REE, as the choice of process steps and sequences is strongly dependent on ore and gangue mineralogy of the feed. In assessing the feasibility of REE extraction from possible resources, mineralogical investigations are proving indispensable for providing upfront ore characterisation to consider suitable process options and to understand the upgrading and extraction performance during extractive testwork⁽²⁾.

Mineralogical Analysis

Feed samples and the products from various treatment steps were subjected to a mineralogical examination. The mineralogical investigation encompassed analysis by X-ray diffraction (XRD) analysis to identify bulk mineral constituents and scanning electron microscopy (SEM) on polished sections of the ores. Electron microprobe analysis (EMPA) was used to establish the exact REE content within selected rare earth bearing mineral grains and phases.

Instrumentation used included a Bruker D8 Advance X-ray powder diffractometer, and a Zeiss EVO MA15 SEM with Bruker energy dispersive spectrometer (EDS) for compositional mapping (element maps). In the investigation manual SEM analysis was used for an initial qualitative assessment of the size, mode of occurrence and association as well as liberation characteristics of the REE bearing minerals with supplementary EDS analyses for identification of the identify the REE minerals.

In order to determine mineral abundances quantitatively, liberation characteristics and grain size distributions, an MLA (Mineral Liberation Analyser) and automated scanning electron microscopy (AutoSEM) was applied.

REE Mineralisation

The work presented in this paper focussed mainly on the extraction of REEs from the commercially most important REE minerals in complex ores and can be split into two main groups according to the chemical association of the rare earth elements. This distinction is of relevance when considering the downstream processing.

The first group are the fluorides, or more exactly fluoro-carbonates which mainly include synchysite and bastnaesite. The second group include the phosphates which include monazite and xenotime. REE-bearing apatite may also be classed here. These minerals and their ideal chemical formulae are presented in Table 1.

Table 1: Ideal chemical formulae of REE minerals investigated

Mineral	Ideal Chemical Formulae
Synchysite	$\text{Ca}(\text{Ce},\text{La})(\text{CO}_3)_2\text{F}$
Bastnaesite	$(\text{Ce},\text{La})(\text{CO}_3)\text{F}$
Monazite, Xenotime	$(\text{La},\text{Ce}, \text{Nd}, \text{Th})\text{PO}_4$, YPO_4

Ore Mineral Characterisation

The monazitic Ore Type 1 contains monazite with varying degrees of alteration, and the monazite is typically intergrown or also finely disseminated within the amorphous gangue matrix.

The complex ores in which REE occur in chemical association with fluoride, are represented by Ore Type 2 and 3. In Ore Type 2 fine textural intergrowths of the bastnaesite and synchysite with silica were present, whereas in Ore Type 3 synchysite was embedded within barite, strontianite, calcite and ankerite and also occurred with apatite.

An illustration of the textural complexity, poor liberation and the variety of problematic gangue minerals in the ore types investigated is illustrated below (Figure 1 to Figure 3).

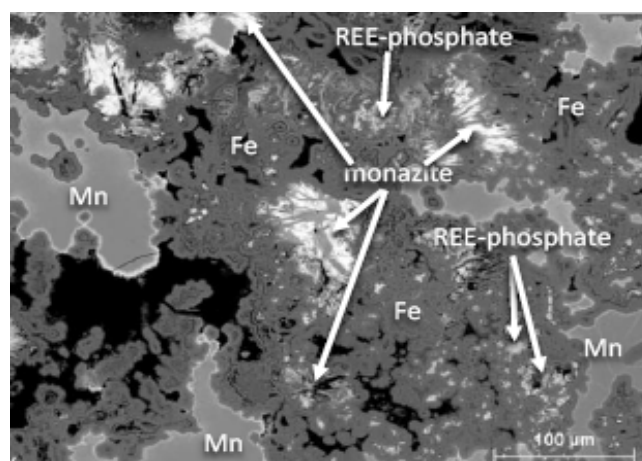


Figure 1: SEM BSE micrograph of Ore Type 1 showing disseminated and inter-grown monazite in the gangue matrix

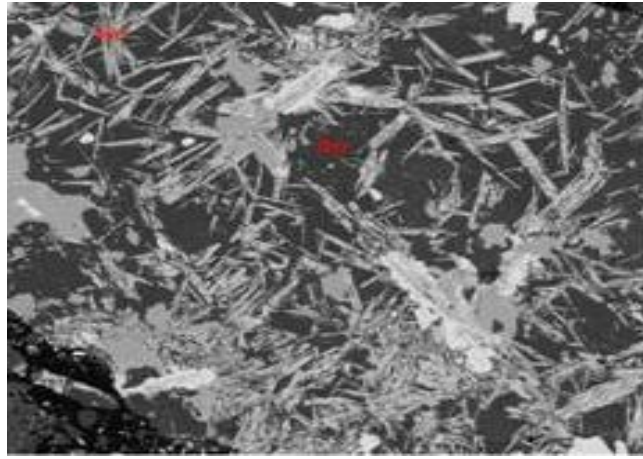


Figure 2: SEM BSE micrograph of Ore Type 2 showing the fine needle-like intergrowth of bastnaesite and synchysite within a silicate matrix resulting in poor liberation.

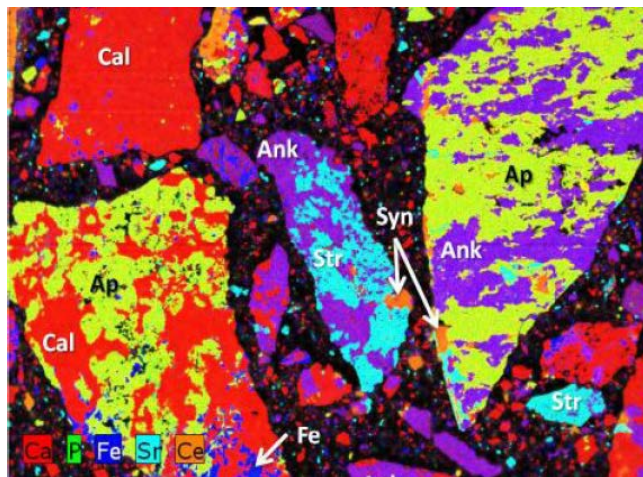


Figure 3: SEM BSE image of Ore Type 3 with element maps illustrating the textural complexity of a synchysite ore. The association of synchysite with apatite, ankerite and strontianite can be noted in conjunction with the presence of dolomite

EFFECT OF MINERALOGY ON PROCESS SELECTION

In order to devise potential processing approaches it was important to have a detailed understanding of the mineralogy of the ore to be treated. The mineralogical information was used to scope the metallurgical testwork program for each particular ore type.

The primary information gained was the amenability of the ore to physical beneficiation processes. For complex ores the physical (and chemical) beneficiation processes were not aimed at producing a pure high grade REE concentrate as due to the textural characteristics of the ore the result would be uneconomically high REE losses.

The objective was much rather to minimise the amount of gangue reporting to the hydrometallurgical downstream circuit. Specifically reagent consumers in the crack and gangue containing impurities deleterious in the hydrometallurgical circuit were targeted in this step.

In some instances the ore mineralogy precluded the use of physical beneficiation techniques. Therefore the investment into the investigation thereof was minimised whilst the shifting the focus to hydrometallurgical whole ore treatment.

Coarse Upgrading

Crushing and Sorting

The Mineralogical investigation can provide an indication as to whether sorting techniques such as X-Ray Fluorescence, X-Ray Transmission or even optical sorting can be a very effective waste rejection step after primary crushing of the ore. By this means, coarse barren waste could be rejected and very clean sorts with minimal REE losses (<3%) such as achieved on a sample of Ore Type 2. The limitation of sorting however is that material of <5mm would be too fine to treat. Sorting presents an option which in many cases is worthwhile investigating.

Dense Media Separation

In cases where the mineralogy indicates mostly liberated REE minerals (density of 4.0-5.0 g/cm³) or REE minerals hosted mostly in gangue minerals of high specific gravity (density of >3.0 g/cm³), then DMS should be investigated as rejection of barren silicates including quartz (density of 2.65 g/cm³) as well as reagent consuming carbonates such as dolomite ore calcite (density of 2.70 g/cm³) with the floats may be effected. DMS would be applicable in the particle size range between 1mm and 6mm due to liberation.

Fines Upgrading

Milling

When milling the ore, generally maximum liberation of REE bearing minerals with minimal slimes generation (<5µm to <20µm depending on ore and process) was targeted. The grain size and textural characteristics of the ore minerals determines the optimal grind for fines upgrading and is provided by the mineralogical liberation analysis for both the REE minerals and also of the gangue minerals. Coarser liberation sizes are advantageous as milling to a coarser target grind would typically decrease the slimes fraction generated.

Minimisation of slimes is of importance, as high slimes contents in the mill product are deleterious for the performance of gravity processes, and to some extent also for the performance of magnetic separation and flotation. If a de-slimes step is incorporated, the REE losses to the slimes reporting to tails can be economically significant.

Gravity Concentration

When considering gravity based separation processes the density difference between the gangue and the REE minerals has to be sufficient as a high amount of near density material would compromise the performance. Generally traditional table/spiral concentrators are not efficient for material finer than about 75µm.

Magnetic Separation

Low intensity magnetic separation (LIMS) is a very efficient process in removing ferromagnetic components potentially present in the ore. Depending on the ore mineralogy HIMS or WHIMS (High-, or Wet High Intensity Magnetic Separation) could be tested to recover the paramagnetic REE minerals monazite and bastnaesite/synchysite from non- or diamagnetic matrices of calcite/dolomite, apatite, barite and strontianite as well as various silicates. A further attraction thereof is that it can be applied to very fine grinds (sometimes down to 20µm depending on the magnetic properties of the particles).

Flotation

Flotation is another important process in the pre-concentration of REE minerals and the rejection of deleterious gangue. In order to achieve effective gangue rejection or upgrading of the REE ore by flotation, an understanding of the mineralogy is again critical. The mineralogy must confirm that it is possible to either float the REE minerals selectively (direct flotation) or the gangue minerals (indirect flotation). Factors such as shape of the particles (needle like, spherical), liberation (grind), slime content, and the mode of occurrence and association of minerals also affect the performance of this process. The flotation process should typically be recovery- and not grade-driven.

Complex and low grade REE ores often require complex flotation circuits with multiple cleaner, re-cleaner and scavenger stages. Thermal conditioning with long conditioning times is frequently required and reagent dosages are generally high. Depending on the type of gangue minerals multiple steps of direct flotation (often with gangue depression), indirect flotation, or both, are required.

A comprehensive discussion of the flotation options and other physical beneficiation options, flowsheets, reagents and conditions applied is beyond the scope of this paper. Information pertaining to this is available in the public domain in literature^(1,3).

Chemical Beneficiation

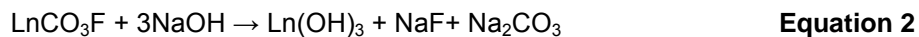
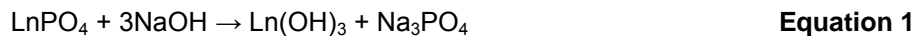
In cases where physical beneficiation processes are too inefficient or fail altogether, it may be necessary to remove certain gangue minerals, which could become deleterious in the cracking of the rare earth minerals and hydrometallurgical downstream processes, by chemical means.

Using the examples considered in this paper for Ore Type 3 the removal of residual dolomite was required to provide additional liberation and avoid operational difficulties related to excessive frothing in the downstream cracking step. This was accomplished by a mild (pH 3.0-3.5) hydrochloric acid leach. Minimal REE dissolution (5-8%) did occur, however these REE could be reclaimed in a neutralisation step with lime. Furthermore the HCl could be recovered by addition of H₂SO₄ to the CaCl₂ rich barren solution and recycled whilst forming clean gypsum.

Cracking and Leaching

Caustic Cracking and HCl Leaching

Caustic cracking of high grade REE concentrates is applied in industry and well described in literature⁽¹⁾. This process route was also applied to whole ore and low grade REE concentrates by Mintek. It entails leaching the feed material (ground ore or concentrate) in 50% w/w NaOH solution at 140°C at ambient pressure with the objective to convert the REE fluorides or phosphates into hydroxides soluble in mild acid according to the following reactions:



However when treating whole ore or low grade concentrates the additional contamination of the spent NaOH with soluble Al or Si species caused by dissolution of silicates may become problematic for potential recycling of the reagent, for example:



From an economic and environmental perspective it is desirable to recycle the excess NaOH in the spent lye solution. When processing pure monazite through this route this could be attained by the recovery of tri-sodium phosphate (TSP) by crystallisation from the lye solution. However with lower grade concentrates and whole ore, the TSP tenor would have to be built up significantly, but concurrently the Al and Si tenors in the lye solution would also increase and cause significant operational problems. The alternative of discarding spent lye is very costly and would also be associated with environmental/containment complications due to the high mobility of Na⁺.

The caustic crack is followed by multiple alkaline (pH 12-13) washing steps to remove entrained NaOH and NaF as well as sodium silicates and sodium aluminates. The washed solids are then subjected to a hydrochloric acid leach (pH of 1.5-2.5) in order to solubilise the REE from the REE hydroxides formed in the crack. The resulting pregnant liquor contains the REE as chlorides and may also contain certain impurities.

It should be noted that when applying this route, the use of a reductant is likely to be required in the subsequent hydrochloric acid leach. This is due to the oxidation of Ce(III) to Ce(IV) in alkaline media (Equation 4), as the resulting CeO₂·nH₂O is insoluble in mild hydrochloric acid⁽¹⁾.

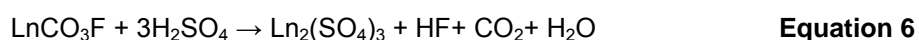
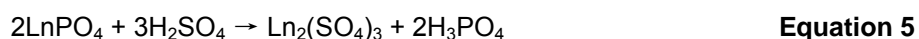
The oxidation of Ce(III) under these conditions is readily affected by oxidants such as dissolved O₂ or oxidants present in the gangue (especially Fe(III), Mn(III) and Mn(IV)).



If, with the intention to leave Ce behind in the tails a reductant is not used, the leach recovery of other REE could be compromised significantly, as their hydroxides may be locked in the amorphous CeO₂·nH₂O matrix. As to whether this is the case can be determined mineralogically by EMPA on the undissolved CeO₂·nH₂O phases in the leach residue.

Sulphuric Acid Cracking

The major alternative to cracking with caustic is the conversion of REE into water soluble sulphates by contacting the ore or concentrate with concentrated sulphuric acid⁽¹⁾. The mixture is then heated to 150-250°C followed by dissolution of the cracked product in a water leach:



Most impurities present would also be converted into soluble sulphates and will require removal from the REE containing water leach solution.

Selection of Cracking Option

From a processing perspective the following main criteria (although this list is by no means comprehensive) should be considered, and again the mineralogy of the ore or concentrate may ultimately be the decisive factor.

- Occurrence of REE

In case of poor liberation or fine dissemination of REE minerals in the gangue matrix, destruction of the gangue matrix to access and crack the REE minerals would be required. The selection of reagent is dependent on the mineralogical composition of the matrix. For the destruction of siliceous matrices including quartz a caustic crack would typically be the first choice to be investigated.

- REE recovery

Certainly an important factor for selection is the recovery of REE. It is critical that the cracking step is not seen in isolation for the assessment of this parameter. It must be taken into account that depending on the cracking route chosen and the type of impurities present after the leach, REE losses to different extents will occur in the downstream solution purification.

- Reagent consumption and cost

The type and abundance of certain gangue minerals is a significant, but by no means overriding factor for the choice of the cracking option. Certain reagent requirements, which are closely linked to the cracking option selected, may arise downstream. Therefore, as with the parameter of REE recovery, the reagent requirement in the solution purification circuit will also have to be taken into account.

In addition the, potential for recycling or regeneration of reagents for the crack (NaOH in particular) as well as the quantity and cost of reagents used further downstream need to be factored in.

- Solid/liquid separation

An assessment of the solid/liquid separation performance after the crack should be conducted early on in the testwork stages. This is particularly advisable if due to other favourable factors a caustic cracking route is envisaged. The nature, viscosity and temperature of the pulp however could potentially make conventional solid/liquid separation options such as settling or filtration

ineffective. Alternatively the use of centrifuges may be evaluated, however due to the corrosiveness of the medium the materials of construction and maintenance of such equipment may be costly.

At the throughput of high tonnages, the option of diluting the pulp in order to address the problems caused by its viscosity enabling the application of conventional solid/liquid separation equipment may be discarded due to problems arising around the water balance associated with handling of dilute caustic streams.

➤ Implications on downstream solution processing

A certain advantage provided by the caustic cracking route in this regard is the rejection of fluoride and phosphate with the caustic stream, whereas when applying the sulphuric acid crack option fluorides and phosphates will deport to the impure REE containing leach solution. This tends to be problematic in the subsequent neutralisation of the leach solution for the rejection of impurities. During neutralisation REE losses are likely to occur due to precipitation of mostly insoluble REE phosphates or REE fluorides even at low pH values. This is largely avoided when following a caustic cracking route, assuming that entrained TSP and NaF could be removed efficiently in the preceding washing steps.

The operation in a chloride medium after cracking and leaching is furthermore advantageous as it provides greater flexibility in the selection of reagents for the downstream purification and in addition increases the potential for the regeneration and recycle of reagents. The use of NaOH for the removal of impurities and subsequent precipitation of an intermediate REE hydroxide (this applies similarly to Na_2CO_3) product results in a NaCl rich barren stream. This stream can be treated electrochemically to regenerate NaOH and HCl from the NaCl.

The use of relatively inexpensive lime for the same purpose would result in the generation of a CaCl_2 rich barren stream from which HCl can be regenerated by addition of sulphuric acid, thereby forming HCl and gypsum as by-product. This would constitute a substitution of the cost of HCl with the cost of H_2SO_4 , without actually operating a sulphate based REE processing circuit.

In the sulphuric acid cracking approach the presence of sulphate however precludes the use NaOH (or any other neutralising agent with monovalent cations, such as K^+ , NH_4^+) due to the formation of light rare earth double sulphate salts. These have limited solubility which is an undesirable effect in these stages of the process. Therefore the use of lime and limestone would remain the only options for the removal of impurities by means of precipitation. In order to precipitate a high grade intermediate REE hydroxide product from the sulphate liquor, the use of MgO should typically be considered as the use of lime would cause significant dilution of the product with gypsum.

In some instances it will however be the case that the mineralogy of the ore or concentrate will preclude the use of either one of the cracking options. In such case the listed criteria must be considered to be an unavoidable consequence of the mineralogy rather, and dealt with as such in the process development.

Calcination as Alternative Option to Cracking for Bastnaesite/Synchysite

For complex bastnaesite and synchysite ores an alternative pyrometallurgical option was investigated in order to remove fluoride and carbonate from the ore on Ore Types 2 and 3 as pre-treatment to leaching^(1,4). The first ore type (Ore Type 2) had a TREE grade of 11% with an Fe grade of 1.3%, a Si grade of 17% and a Ca grade of 8.5%.

The study entailed fine grinding of the ore (P80 of 75 μm) with subsequent calcination without any additives. The effect of different calcination temperatures from 600°C to 1200°C for 4h on the deportment of REE and impurities was investigated. The calcined material was then leached at a temperature of 60°C with HCl, targeting a pH value of 0.8. The ORP of the leach slurry was maintained below 600 mV (vs. Ag/AgCl electrode) in order to reduce any Ce(IV) generated in the calcination process to soluble Ce(III).

The results are illustrated in Figure 4. It was notable that lower temperatures (600°C to 800°C) in the calcination step resulted in lower leach extractions of TREE of ~60%, while the leach extractions of impurities, notably Th, Ca, Mg and Mn was high. This was also reflected by the amount of acid consumed for the leaching of gangue (~270 kg of 32% HCl/ ton of leach feed).

As from a calcination temperature of 900°C the TREE extraction improved to 77% of TREE and remained constant until the highest calcination temperature (1200°C) tested. The leaching of impurities decreased significantly, particularly that of Mg, Ca and Mn as well as that of Th and Fe. Concurrently the acid consumed for the leaching of gangue decreased to 145 kg of 32% HCl/ ton of leach feed when applying a temperature of 1200°C in the calcination step.

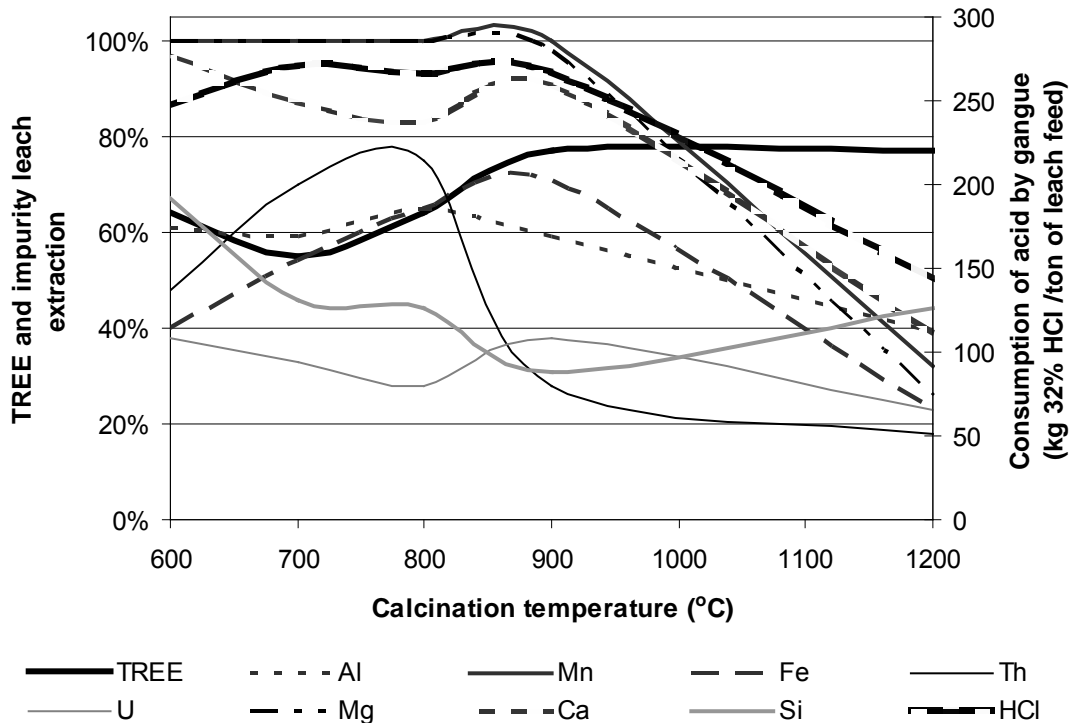


Figure 4: Rare earth and impurity leach extraction as a function of calcination temperature, Ore 2

This approach was also tested on a synchysite sample of different composition (Ore Type 3). The main difference between the ores was a higher Fe grade of 9.7% and lower TREE grade of 1.2% in Ore Type 3. The Si grade was also lower at 3.3% with a Ca grade of 30% in this ore. The response of this ore type to the calcination step was significantly different to the response of Ore Type 2. In this case the TREE extraction in the leach was significantly compromised, and decreased with increasing calcination temperature from 35% (900°C) to 10% (1200°C). The co-extraction of impurities in the leach also decreased with increasing calcination temperature and was already suppressed at a calcination temperature of 900°C, particularly for Mg, Ca, Fe and Al. This is illustrated in Figure 5.

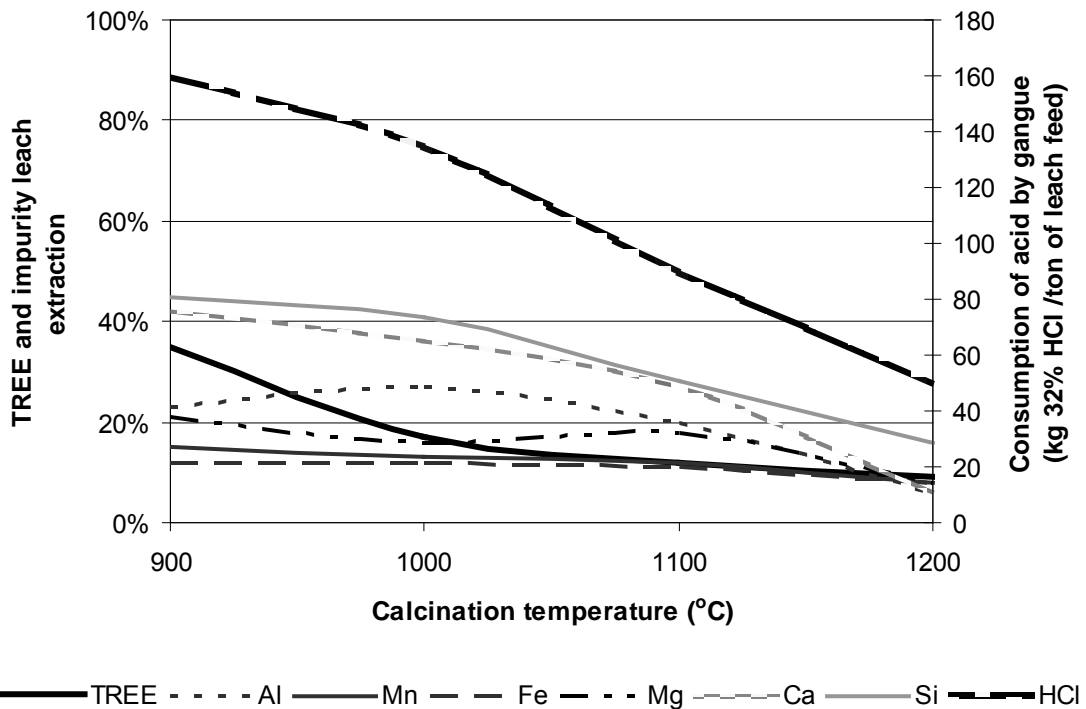


Figure 5: Rare earth and impurity leach extraction as a function of calcination temperature, Ore 3

In order to explain the different metallurgical response the use of Mineralogy as diagnostic tool was again invaluable.

For Ore Type 2 the calcination at temperatures above 900°C resulted in the formation of secondary silicate structures (Fe-Al-Ca-Mg silicates) thereby minimising the leaching of impurities. Calcination at 1200°C resulted in partial melting of the ore which required a regrind of the calcine. At calcination temperatures of 600 and 700°C synchysite was still present in the calcine and occurred as needles locked in quartz. Liberated REE oxides and REE-Ca oxides were present. From 800°C the synchysite appeared altered, the occurrence of fluorite and a REE oxyfluoride was detected in the calcine. Liberation of REE-bearing particles was more evident, although a fraction of altered synchysite needles still occurred locked in quartz, possibly limiting the leach extraction to the maximum of 77%. The bulk mineralogical composition and corresponding photomicrographs of the calcines from the various calcination temperatures are presented in Table 2 and Figure 6 respectively.

The mineralogical investigation of the calcines from Ore Type 3 revealed that the calcination step caused the formation of mineralogical phases which included hematite, magnetite, leucite, cerianite and Ce-britholite. Calcination at 900°C formed Fe-oxide phases in the form of hematite and the liberated REE phases occurred predominantly as carbonates and oxides. Calcination at 1000°C indicated that the REE, which occurred predominantly as carbonates and oxides, were locked in a secondary silicate phase and as a result were mostly refractory to the leaching process. Samples treated at 1100°C and 1200°C showed the occurrence of a Ce-britholite phases which locked the REE, thereby further minimising their dissolution during the leaching step. The bulk mineralogical composition and corresponding photomicrographs at various calcination temperatures are presented in Table 3 and Figure 7 respectively.

**Table 2: Bulk mineralogical composition of Ore Type 2
after calcination at varying temperatures**

Mineral	Formula	Calcination temperature		
		600°C	700°C	800°C
Quartz	SiO ₂	major	major	major
Barite	Ba(SO ₄)	minor	minor	minor
Dolomite	Ca(Fe,Mg)(CO ₃) ₂	minor	√	√
Bastnaesite	CeCO ₃ F	√		
Strontianite	SrCO ₃	minor	minor	√
Cerium Lanthanum Calcium Oxide	(Ce,La,Ca)O	minor	major	major
Strontium Lanthanum Oxide	Sr ₃ La ₄ O ₉	trace	trace	trace
Lime	CaO		minor	trace
Periclase	MgO		minor	trace
Fluorite*	CaF ₂			minor
Cerium Lanthanum Oxide Fluoride*	CeLa ₂ O ₃ F ₃			trace
Synchysite	CaCe(CO ₃) ₂ F	√√	√	√

*major – 20-50 mass%; minor- 5 -20 mass%; trace - <5 mass%; blank - not detected;
√ - observed by SEM; √√-more abundant; √- less abundant*

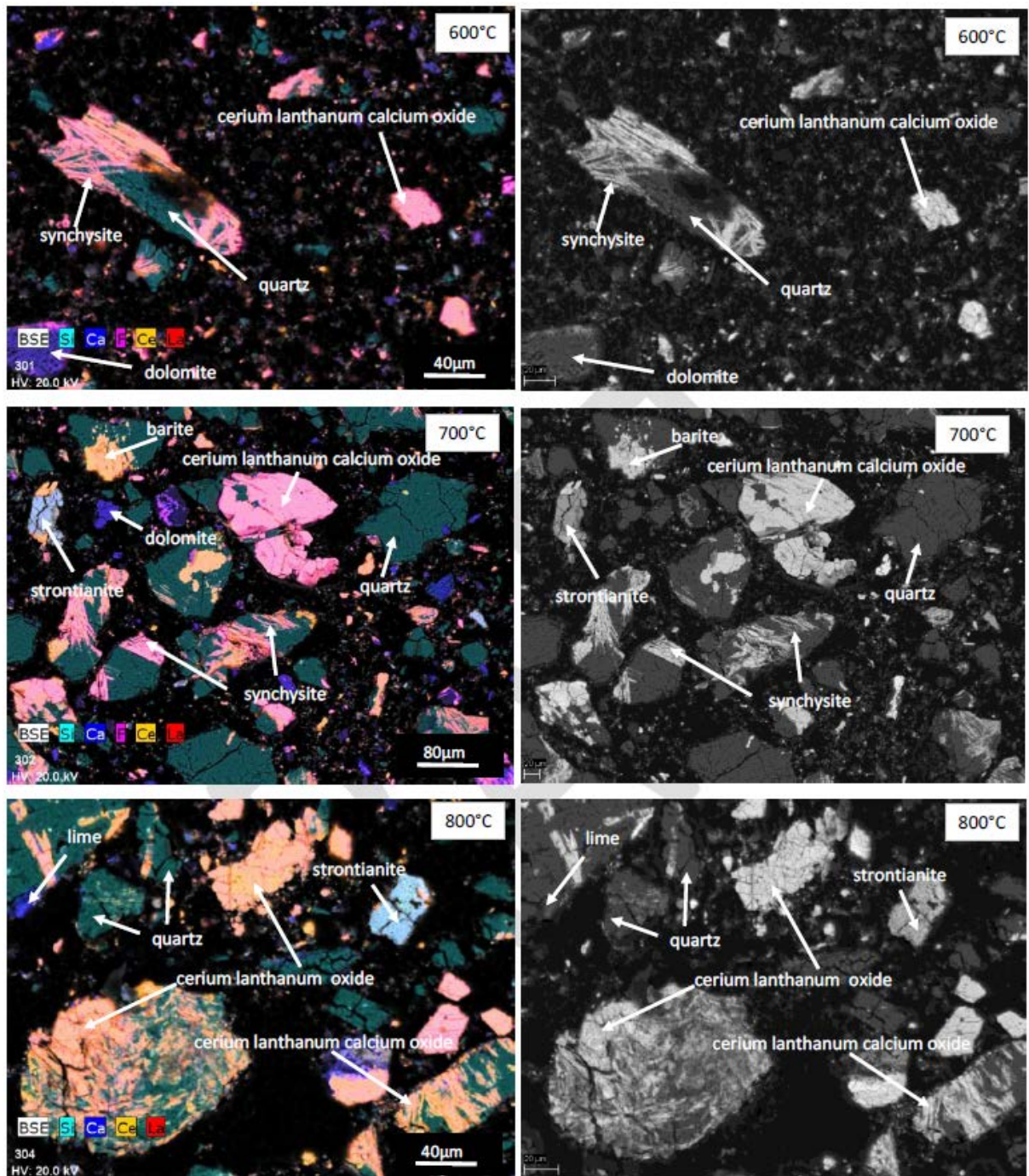


Figure 6: Element maps (left) and backscattered electron (BSE) images of the calcined samples of Ore Type 2 at varying temperatures.

Table 3: Bulk mineralogical composition of Ore Type 3 after calcination at varying temperatures

Mineral	Formula	Calcination temperature			
		900°C	1000°C	1100°C	1200°C
*Apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)	major	intermediate	intermediate	major
**K-feldspar	KAlSi ₃ O ₈	* major	* major	minor	
Leucite	KAlSi ₂ O ₆		minor	intermediate	major
Celsian	(Ba,K)(Al,Si) ₃ O ₈		minor	minor	trace
Goethite	FeOOH				
Hematite	Fe ₂ O ₃	intermediate	intermediate	major	major
Magnetite	Fe ₃ O ₄ /(Mn,Fe,Mg)(Fe,Mn) ₂ O ₄			minor	minor
Synchysite-(Ce)	CaCO ₃ CeFCO ₃				
Cerianite-(Ce)	CeO ₂	trace	minor	trace	
***Ce-britholite	(Ce,Ca,Th,La,Nd) ₅ (SiO ₄ ,PO ₄) ₃			minor	minor
Mica	KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂				
Quartz	SiO ₂	trace			
Ankerite	Ca(Fe,Mg,Mn)(CO ₃) ₂				
Calcite	Ca ₂ SiO ₄				

predominant (>50 mass%); major (25-50 mass%); intermediate (15-25 mass%); minor (5-15 mass%); trace (< 5 mass%); blank – not detected

**Also includes other Ca phosphates with a similar crystalline structure.*

***Although a single type of K-feldspar is indicated, the formation of a second, probably, sanidine, is noted at 900°C and higher.*

****Ce-britholite has a similar crystal structure to apatite; this phase is abundant in the SEM analysis*

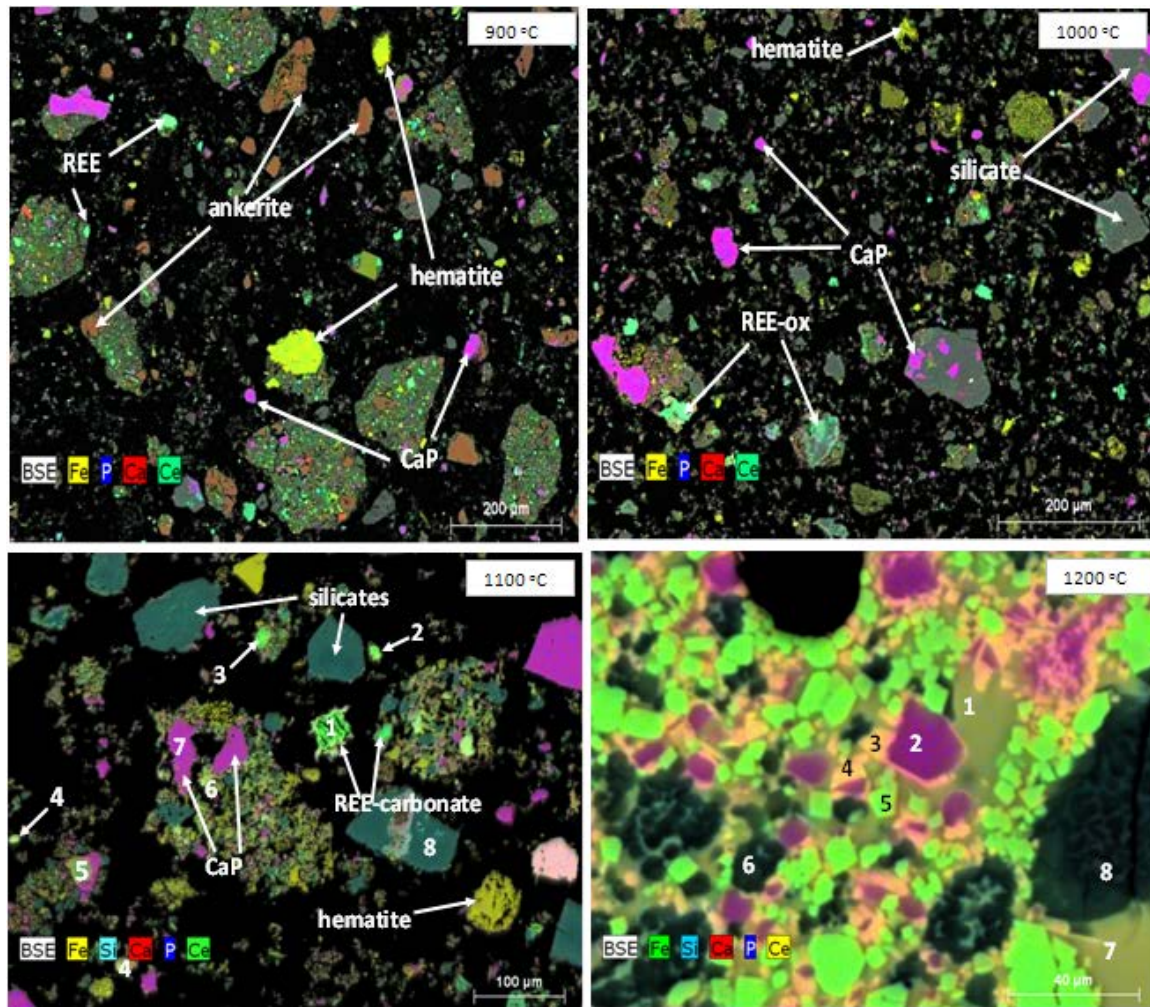


Figure 7: Element maps of the calcined samples of Ore Type 3 at varying temperatures.

PURIFICATION OF CRUDE RARE EARTH LEACH SOLUTION

Bulk Impurity Removal

It will likely be inevitable that the treatment of complex REE ores will result in impure leach solutions which are not suitable as refinery feed, irrespective of the cracking option selected.

The bulk impurity removal step is aimed the removal of deleterious metals which precipitate typically at a low pH already. This step targets mainly the precipitation of Fe, Th, Si and Al whilst aiming to minimise the co-precipitation of REE. A typical pH vs. precipitation curve using NaOH as neutralising agent on a medium grade (20 g/L) impure REE leach solution after a caustic crack followed by HCl leach is shown in Figure 8. In the case presented, it was possible to comprehensively reject all Fe, Al, Si and Th at a pH of 5.5 with a corresponding REE loss of 2.2%. At this pH it was only possible to remove 50% of the U.

The shape of such curves is a function of operating temperature, tenor of REE and concentration of individual impurities. The medium (sulphate or chloride) is also an important factor as illustrated in Figure 9. The curves were generated by neutralising an impure medium grade REE solution (22 g/L) in a sulphate medium. The difference in selectivity for these specific cases was clearly visible, which was mainly caused by the precipitation of REE at a low pH already due to the presence of phosphates in the liquor after the sulphuric acid crack.

Therefore the optimum pH and operating conditions in order to maximise selectivity in the bulk impurity rejection step will have to be determined on a case-by-case basis through detailed testwork.

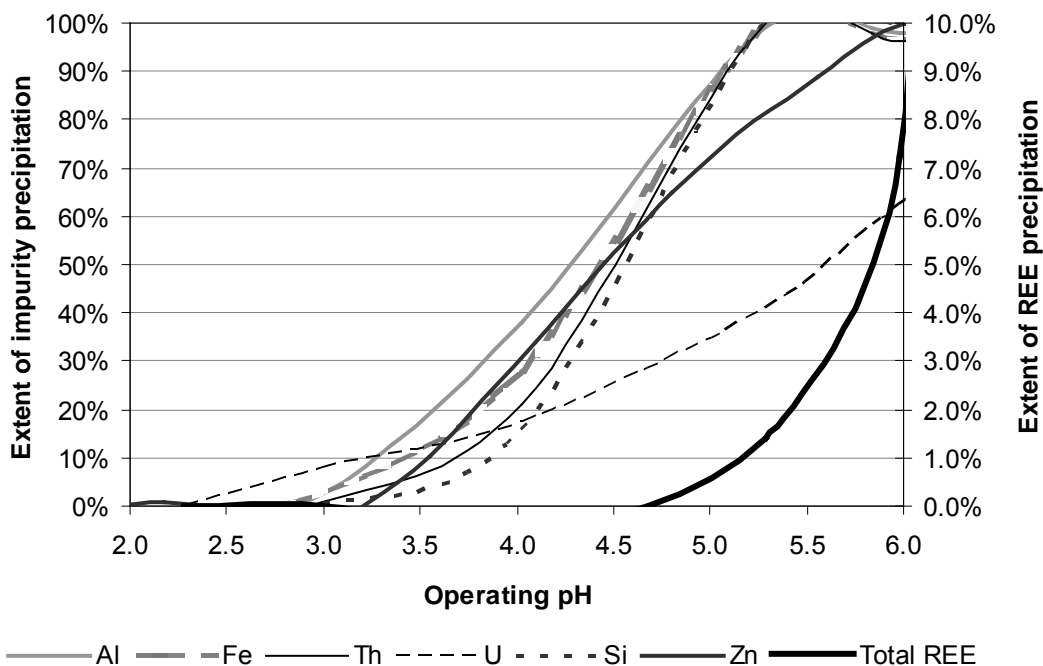


Figure 8: Precipitation vs. pH curve with NaOH on medium-grade impure REE solution, chloride medium

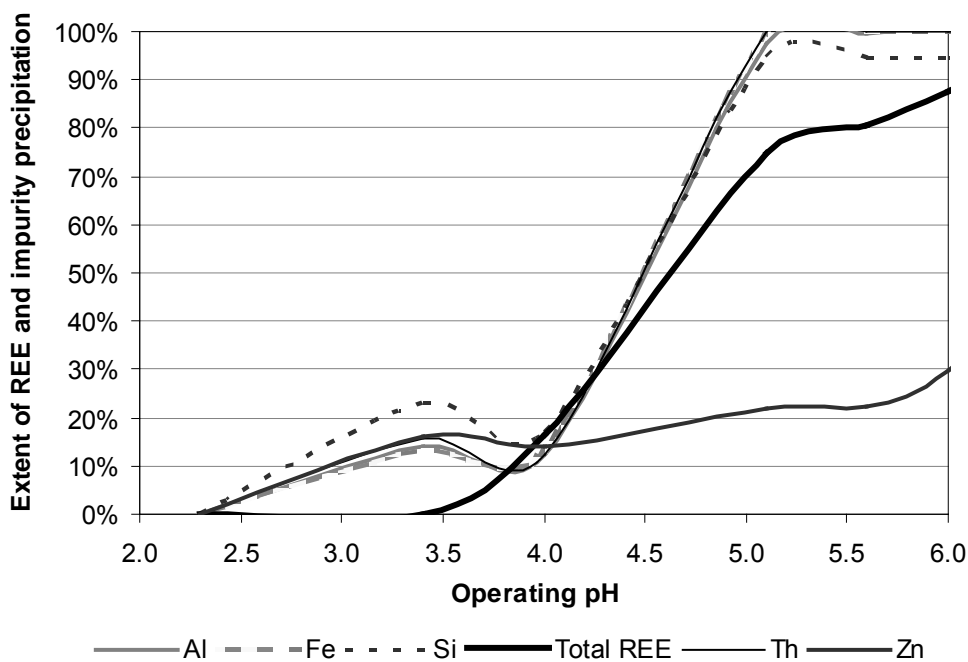


Figure 9: Precipitation vs. pH curve with lime on medium-grade impure REE solution, sulphate medium with phosphate background

Intermediate Rare Earth Product Precipitation

The precipitation of an intermediate REE product may either be considered as a further impurity rejection step or to generate a saleable product.

After the bulk removal of impurities a relatively high grade rare earth product can be generated either for sale or as feed to subsequent treatment steps for generating a feed solution suitable for a refining and separation plant. This step also provides the opportunity to switch from the sulphate circuit to a chloride circuit for subsequent refining.

A variety of neutralising agents can be selected if the REE are already present in a chloride medium. These could include NaOH, lime, sodium carbonate, oxalate and MgO. In the case of a sulphate medium the options are more limited as the use of lime would again result in the contamination and dilution of the product with gypsum, and the use of NaOH and Na₂CO₃ would cause the undesired formation of double rare earth sulphate salts. This would leave MgO and in some cases oxalate as the reagents of choice.

The pH vs. precipitation curve for the precipitation of an intermediate REE hydroxide using NaOH on the medium grade REE solution in a chloride medium from the above example (after bulk impurity removal) is shown in Figure 10. The precipitation step was conducted at ambient temperature. The graph illustrates that in this case the heavy rare earth element (HREE) precipitation was complete at a pH of 6.8 and the light rare earth element (LREE) precipitation was complete at a pH of 7.7.

Mg (and in this case also Ba) could be rejected comprehensively with the barren solution. Some selectivity over Mn is also evident, in a single precipitation step 40% of the Mn could be rejected with the barren. If comprehensive Mn rejection was required, a two stage precipitation targeting 70% LREE (>99% HREE) precipitation could be applied.

The curves also indicate that any U and Zn would report to the REE hydroxide product.

The pH vs. precipitation curves using MgO for a sulphate medium after bulk impurity removal is shown in Figure 11 and illustrates that similar deportment could be expected.

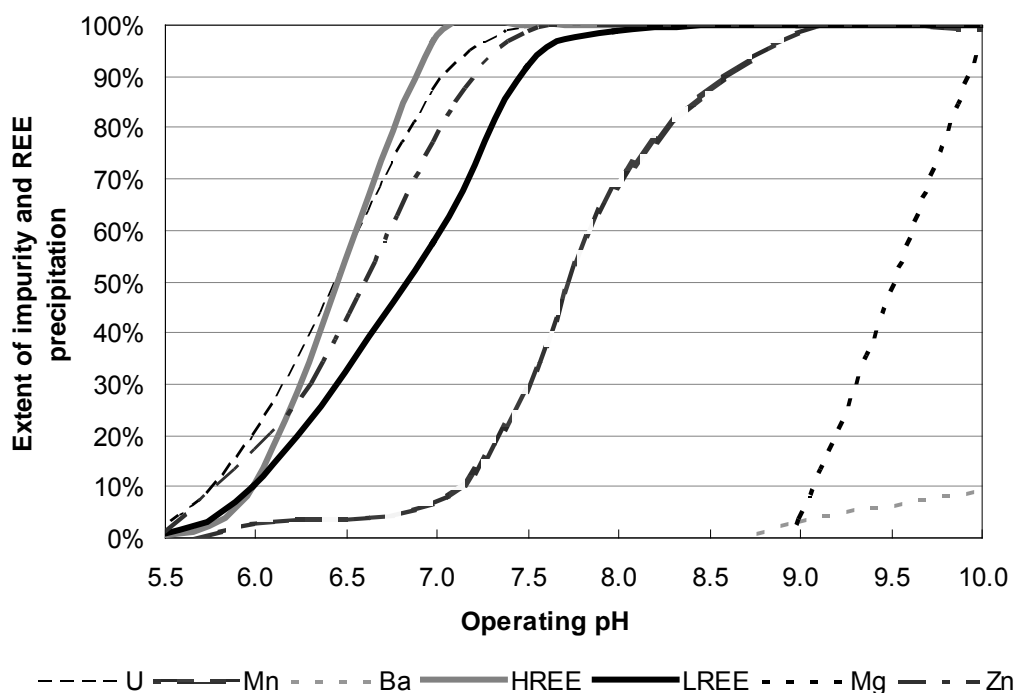


Figure 10: Precipitation vs. pH curve with NaOH on medium-grade REE solution after bulk impurity removal in a chloride medium

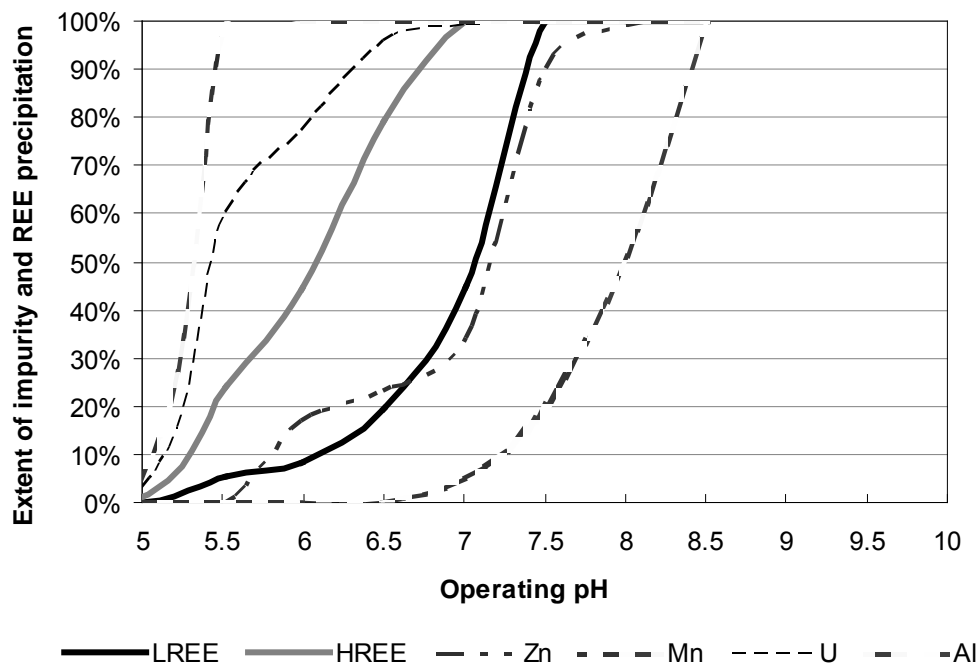


Figure 11: Precipitation vs. pH curve with MgO on medium-grade REE solution after bulk impurity removal in a sulphate medium

Rare Earth Re-Dissolution

The REE re-dissolution step was carried out on the intermediate rare earth hydroxide precipitate using concentrated (32% w/w) hydrochloric acid. The target of this processing step was to determine the operating conditions and process options for generating a pure high grade solution as feed for a refining circuit.

Figure 12 shows the curves for the re-dissolution of REE and various critical impurities from the intermediate rare earth hydroxide cake as a function of pH. The graph indicates that a multi-stage re-dissolution circuit would provide a very selective re-dissolution of REE whilst rejecting specific impurities in specific stages. Using this example, in a primary leach stage at a pH of 5.0 most Mg and Mn would be rejected.

In a subsequent re-leach stage at pH 3.4, TREE dissolution of ~70% would be targeted, thereby rejecting 80% of Al and 75% of Zn with the residue. In a tertiary stage operated at a pH of between 2.5 and 3.0 the residual REE would be re-leached and the residue containing mainly Zn and Al as well as some Fe and Th which may have slipped through would be rejected with the tails, whereas the liquor could be recycled to the first stage of the re-dissolution circuit.

In such manner the REE losses could be minimised (<2.5%) and the liquor generated in the second stage would be suitable as feed to the refining circuit. Notably U tends to deport with the REE and its removal would require a separate treatment step prior to the REE separation.

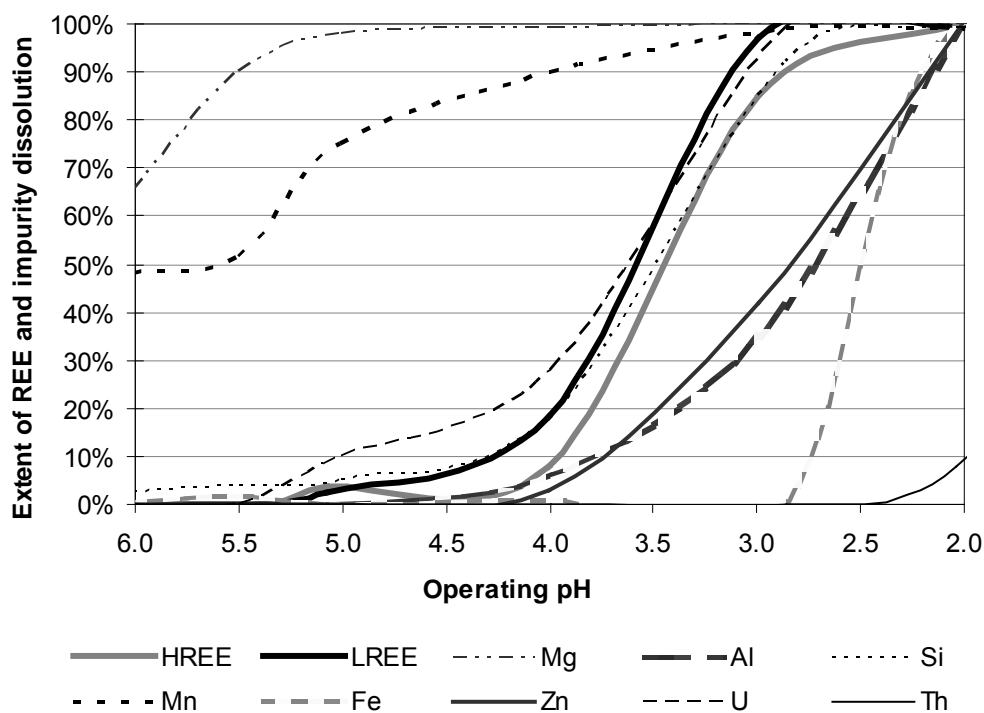


Figure 12: Re-dissolution vs. pH curve with HCl of an intermediate Rare Earth hydroxide product

CONCLUSIONS

Prior to defining a metallurgical testwork program for the recovery of REE it is critical to gain a detailed understanding of the ore mineralogy. Relatively inexpensive qualitative or semi-quantitative methods such as XRD or SEM suffice as tools for selecting a metallurgical testwork program at the initial stages of a project. As the level of detail of the study increases, a quantitative REE and gangue department study on a representative sample of the ore must be conducted.

The initial study should focus on the amenability of the ore for upgrading of coarse and fines by physical means with the methods outlined in this paper. The focus is more on waste rejection at maximum recovery to minimise reagent consumptions and tonnages of throughput downstream, although in some cases a whole ore treatment route may be indicated.

The selection of the appropriate cracking option for conversion of the REE bearing minerals into an acid leachable form is governed by specific criteria, although it may be that one of these criteria can override all others in the selection process.

As illustrated with the example of applying a calcination process, two completely different outcomes in terms of metallurgical performance were determined, although the ores compared had a similar REE mineralisation. As confirmed by the mineralogical analysis, the difference in interaction of the gangue with the rare earth minerals had the determining effect on the metallurgical performance of this particular process. This outlined that each ore type, although certain ore types may appear very similar and therefore a similar metallurgical response would be expected, has to undergo detailed testwork as such similarity is in most cases merely superficial. It also showed that mineralogical analysis can be an invaluable diagnostic tool for parts of the flowsheet where difficulties are experienced or optimisation is required.

After attaining solubilisation of REE from complex ores, a sequence of impurity rejection steps is required to produce a solution suitable as feed to a refinery and separation plant. Again each liquor stream has to be tested individually to define the exact operating conditions in each step of the sequence as the conditions are very sensitive to the composition of the specific liquor to be purified.

In order to recover REE economically from complex and low grade deposits a renewed understanding of processing routes to be taken will inevitably be required. The type of mineralisation, as well as the products formed in the various stages of processing must be characterised in order to select and optimise a particular process option. The examples, criteria and tools described above should aid in the decision process for scoping of a focussed metallurgical testwork programme which maximises the REE recovery and purity of the REE product generated. By following a clear defined scope the cost and time spent on the testing of processing options not viable from the outset will be minimised and the value extracted from each REE deposit will be maximised.

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