

Final degree project

## **Bachelor's degree in Chemical Engineering**

# **Recovery of rare earth elements from acid mine waters by using phosphate based precipitation processes**

### **MEMORY**

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## Abstract

The market of rare earths (RE) is currently being controlled by China. In 2010 abruptly reduced its exportation quota creating supply disruptions. This, along with the fact that huge increase of their demand for supplying new technologies have created a scarcity of rare earth elements (REE) and nowadays have been classified by the EU as critical elements and it is a need to extract and recover them from secondary sources.

The recovery of REE as phosphate salts from acid mine water (AMW) samples as a potential secondary REE resources has been evaluated in this study. The work has been developed using acid mine waters (AMWs) collected in abandoned mines along the Rio Odiel Basin (Huelva). Specifically, for this study samples from La Poderosa Mine were used. As many of the AMW of the Odiel Basin are characterized by high presence of transition elements (TE), especially Fe, Al, Zn, Cu; and alkaline earths (Ca and Mg). REE recovery efforts were developed after removal of Fe, by total oxidation of Fe(II) to Fe(III) and precipitation as Fe(III) hydroxides by using a strong alkaline reagent (e.g. NaOH, CaO, and MgO).

The main objective of this study was to evaluate the precipitation of REE in a pH where the precipitation of TE is minimized and then the purity of REE content on the by-product recovered is maximized. The total initial REE concentration, the pH of precipitation and the molar ratios of phosphate/REE were studied.

The results show that it is possible to obtain moderate REE recovery (<15%) when using acid mine water with a total content of REE lower than 10 mgREE/L. However, using a previous concentration stage of REE from AMW using ion exchange resin the concentration could be increased by factors of 15 to 20. Under these conditions, and using an excess of phosphate (P/REE (40)) REE recovery ratios of 90±5% were achieved. Furthermore, for pH values below 2.5 a selective separation of REE and TE were achieved.

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## 1. Glossary

- AMW: acid mine water.
- TAMW: treated acid mine water.
- REE: rare earth elements.
- REO: rare earth oxides.
- TE: transition elements
- BV: bed volume



## 2. Introduction

The rare earth elements (REEs), which include the 15 lanthanide elements ( $Z = 57$  through 71), yttrium ( $Z = 39$ ) and Scandium (Sc), less frequently included, are so called because most of them were originally isolated in the 18th and 19th centuries as oxides from rare minerals. (Castor, S.B., Hendrick, 2006)

The IUPAC definition divides the REE, into the light REE (lanthanum (La) – samarium (Sm)) and heavy REE (europium (Eu) - lutetium (Lu)). Yttrium behaves as a heavy REE. The terms 'mid', 'middle' and 'medium REE' are also sometimes used to denote samarium (Sm) – dysprosium (Dy). The lanthanides are members of the 'f elements' or 'f block' in the Periodic Table as is shown at Figure 1. Some authors prefer to use the abbreviation REY instead of REE to denote Y and the lanthanides. (Wall, 2013).

Rare Earth Elements															<div>Y 39</div>		
La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71			
Lanthanides																	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mn	Uu	Uu	Uu

Figure 1. Chemical periodic table delineating the 16 rare earth elements (REE): the lanthanides, La through Lu, plus Y, whose geochemical behaviour is virtually identical to that of the heavier lanthanides (Haxel, Hedrick, and Orris 2002).

### 2.1. Physical and chemical properties

The REE are soft, silver-coloured metals that tarnish quickly in air and have high melting points. The lanthanide series results from filling of the 'f' electron shell in the atoms. This gives rise to the magnetic and spectroscopic properties that make REE so useful in many applications.

These inner electrons are shielded and so maintain the distinct elemental properties in various bonding situations. The electronic properties give the REE distinct and sharp absorption and emission spectra, including distinct colours in solution. Most REE are strongly paramagnetic

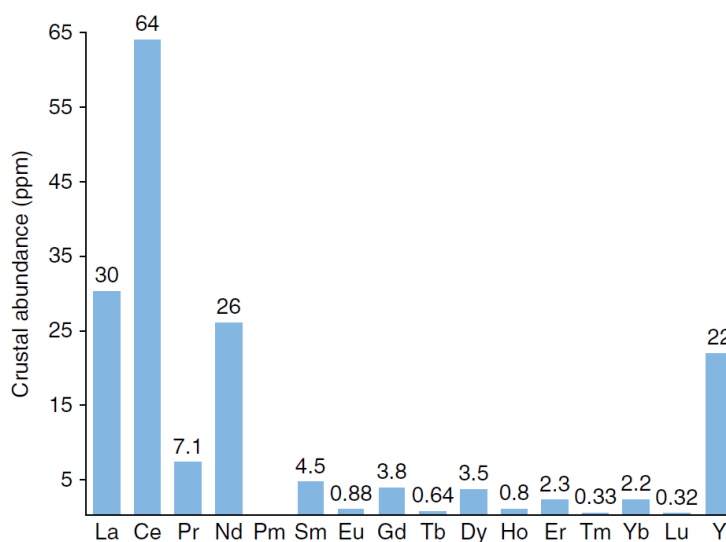


and the strong magnetism that results from their combination with transition metals such as iron and cobalt is one of their most important features.

One of the most important properties in determining chemical behaviour is cation size and, conversely to what might be expected, the size of lanthanide cations (and atoms) decreases smoothly with increasing atomic number. In nature, REE almost always occur in the +3 valency state (i.e. they form the oxide  $\text{REE}_2\text{O}_3$ ) but there are two important exceptions in natural environments (Castor, S.B., Hendrick, 2006): in oxidising environments, such as weathered deposits and seawater deposits, Ce forms  $\text{Ce}^{4+}$  ( $\text{CeO}_2$ ), a much smaller cation, and in reducing environments, Eu forms the larger  $\text{Eu}^{2+}$  cation. In the laboratory, +2 valencies are also known for Sm, Tm, Yb;  $\text{Pr}_6\text{O}_{11}$  is a mixed synthetic oxide ( $4\text{PrO}_2 \cdot \text{Pr}_2\text{O}_3$ ). (Wall, 2013).

## 2.2. Distribution and abundance in the Earth's crust

The more abundant REE are each similar in crustal concentration to commonplace industrial metals such as chromium, nickel, copper or zinc, molybdenum. Even the two least abundant REE (Tm, Lu) are nearly 200 times more common than gold (Haxel et al., 2002). However, in contrast to ordinary base and precious metals, REE have very little tendency to become concentrated in exploitable ore deposits. Consequently, most of the world's supply of REE comes from only a handful of sources. A summary of each rare element abundance in the Earth's crust is provided in Figure 2.



*Figure 2. Crustal abundances of rare earth elements (Data from (Taylor et al., 1981)). The light rare earths, lanthanum (La), cerium (Ce) and neodymium (Nd), are the most abundant rare earth elements in the Earth's crust.*

Naturally, REEs occur as salts and are associated with other metals. They often occur together in a deposit. More than 250 rare earth minerals have been identified. However, only four are the major industrial rare earth minerals bastnaesite, monazite, xenotime, and fluocerite. (Wang D, 1996; Zhang et al., 2016). A summary of the major industrial rare earth minerals is provided in Table 1.

Mineral	Formula	Wt % REO
<b>CARBONATES/ FLUORCARBONATES</b>		
bastnaesite-(Ce)	CeCO <sub>3</sub> F	75
<b>PHOSPHATES</b>		
florencite-(Ce)	(Ce)Al <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	32
monazite-(Ce)	CePO <sub>4</sub>	70
xenotime-(Y)	YPO <sub>4</sub>	61

*Table 1. The major industrial rare earth minerals, including an indication of the percentage by weight (Wt %) of the rare earth oxide (REO) (Chakhmouradian and Wall, 2012).*

## 2.2.1. Primary REEs Sources

### Iron-REE Deposits.

Some iron deposits contain REE resources, and such deposits have been exploited in only one area Bayan Obo, China. These deposits constitute the largest known REE resource in the world and are now one of the most important REE source in the world. (Castor, S.B., Hendrick, 2006). The REE ore consists of three major types: REE-iron ore, the most important type; REE ore in silicate rock; and REE ore in dolomite (Zhongxin et al., 1992).

### Carbonatite-related REE deposits

Carbonatites, which are igneous rocks composed of more than 50 per cent carbonate, are the main economic source of REE. Minerals include bastnaesite, monazite, and ancylite. The two most famous REE-rich carbonatites are in Mountain Pass, USA and Bayan Obo, China. (Wall, 2013)

### Ion-adsorbed clays

Ion-adsorbed clays are very important sources of REO, with over 60% of its content in REO coming from Y and little requirement for physical beneficiation needed, can be considered one of the most important source of RE, and can be processed almost directly using hydrometallurgical methods. Some of the most important deposit can be found in Ganzhou, Jiangxi in China. (Yang et al., 2013)

## 2.3. REE Applications and their roles in the modern world

Due to their unique magnetic, luminescent, and chemical properties, REEs play an important role in the development of alternative power and energy efficient technologies.(Seredin and Dai, 2012).

Yttrium is a basic component of superconducting electric power lines, whilst Nd, Pr, Sm, Dy and Tb are important components for super-power permanent magnets (Seredin et al., 2013). They are needed in industrial generators, since they can transform renewable energies into electricity effectively (Seredin et al., 2013). Moreover, REEs are commonly used in hybrid and electric vehicles, while phosphors of Y, Eu, and Tb are components of compact fluorescent lights and light-emitting diodes (Seredin and Dai, 2012; Seredin et al., 2013). These elements were therefore considered critical by the European Commission in 2010, since their use is increasing rapidly in several clean technologies, which include alternative power and energy saving applications.

REEs have now become a “corner stone” for modern technologies, especially in alternative power and energy saving applications(Seredin and Dai, 2012). REEs consumption has shown an exponential growth in recent years and no doubt will continue to grow in the foreseeable future.(Seredin et al., 2013).

## 2.4. The problem of REEs raw materials

As shown above, there are two main sources of REEs at present, carbonatite and weathered crust elution-deposited (ion-adsorbed) ores, both of which are almost exclusively mined in China and have been supplying the world industry for many years. Less than 5% of world REEs production is from other sources (Seredin and Dai, 2012). Due to this complete control of its own mining supply chains, the Chinese government has the ability to greatly influence the availability and affordability of REEs to the rest of the world.

Over recent years, China has been steadily decreasing its exports to rare earth importing nations, because of newly-instated production quotas by China's Ministry of Land and Resources Each year, these quotas have become increasingly stringent; since 2005, China has halved these REE export quotas (Morrison, 2012).

In this connection, the price of some critical metals in the middle of 2011 reached the highest in historical record, as shown in Figure 3: Dy> \$3 000 000, Tb> \$5 000 000, and Eu> \$6 000 000 per ton, 10 times higher than some years ago. (Seredin and Dai, 2012).

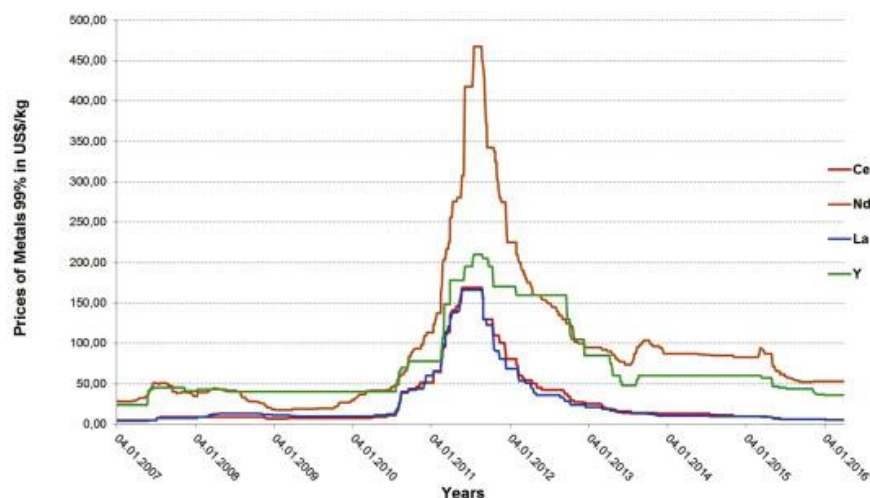


Figure 3 Metal prices development during the last 10 years for selected REE (Argus Metals International - Argus Media)

Under this situation, all countries in the world are now facing the problem of seeking new REEs sources, especially those for crucial metals.

## 2.5. REE Secondary sources

### Recycling in-use stocks

Recycling in-use stocks can be an alternative source, especially for the “big four,” i.e., La, Ce, Nd, and Pr (Beltrami et al., 2015). This is possible for metallurgical applications, auto-mobile catalysts, and magnets in wind turbines and automobiles, where REE are used in fairly large quantities as seen in Figure 4. The availability of less-abundant REE, however, continues to be a challenge.

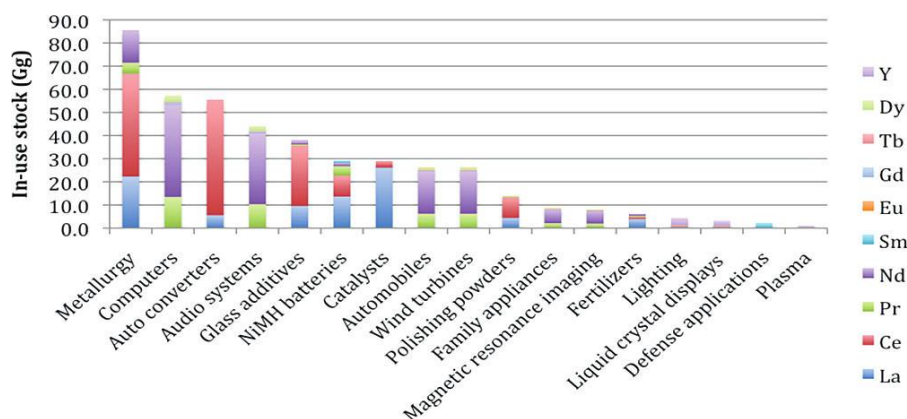


Figure 4. Rare earth in-use stocks in principle applications, by element (2007)(Du and Graedel, 2011)

## Acid mine waters

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Acid mine waters (AMW) is commonly considered an environmental pollution issue. However, REE concentrations in AMW can be several orders of magnitude higher than in naturally occurring water bodies. With respect to shale standards, the REE distribution pattern in AMW is enriched in the less-abundant REE, such as Tb and Dy (Ayora et al., 2016).

The reasons for the REE enrichment in AMW with respect to the rest of natural waters are grounded in their aqueous geochemistry. The majority of REE in igneous and sedimentary rocks are occasionally located as major components of carbonates (bastnaesite) and phosphates (monazite). Weathering of these minerals in conventional soils occurs due to the aggressive action of CO<sub>2</sub> and humic acids. Once in solution, REE in soil pore water remain as trivalent cations or, at neutral to alkaline pH complexed with CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup>. Due to its large positive charge and ionic potential, trivalent cations are strongly sorbed onto the negative charged surface of clays, (Bradbury and Baeyens, 2002). As a consequence, REE are mainly concentrated in clays, which become a major reservoir of REE in sedimentary rocks.

A strong correlation between high REE concentrations and acidity has been reported in both the surface and ground waters (Beltrami et al., 2015). When acid mine water (AMW) effluents mix with neutral waters, the pH increases accordingly and the concentrations of REE are greatly increase in these mixing zones as a consequence.

**The Odiel and Tinto basins** in the province of Huelva, south-western Spain, has great historical significance as well as environmental interest. They are ones of the most polluted fluvial-estuarine systems in the world as well as the city of Huelva has become the site of one of the most polluted industrial too (Davis et al., 2000).

The Iberian Pyrite Belt is one of the major provinces of massive sulphide deposits, its mining of near the headwaters of the Odiel river produce the dissolution of Fe sulfides and generate acidic solutions with pH values around 2,5. Furthermore, there were quite elevated concentrations of many transition elements and other metals (e.g. Cu, Ca, As, Zn, Fe, Al) in the estuaries as a consequence of the mining activities.

In this work, the samples of the acid mine waters were obtained of the collected in abandoned mines along the river Odiel Basin. Specifically, for this study samples from La Poderosa Mine were used which is on the mines located in Iberian Pyrite Belt (IPB, southwest Spain), as is shown in Figure 5.

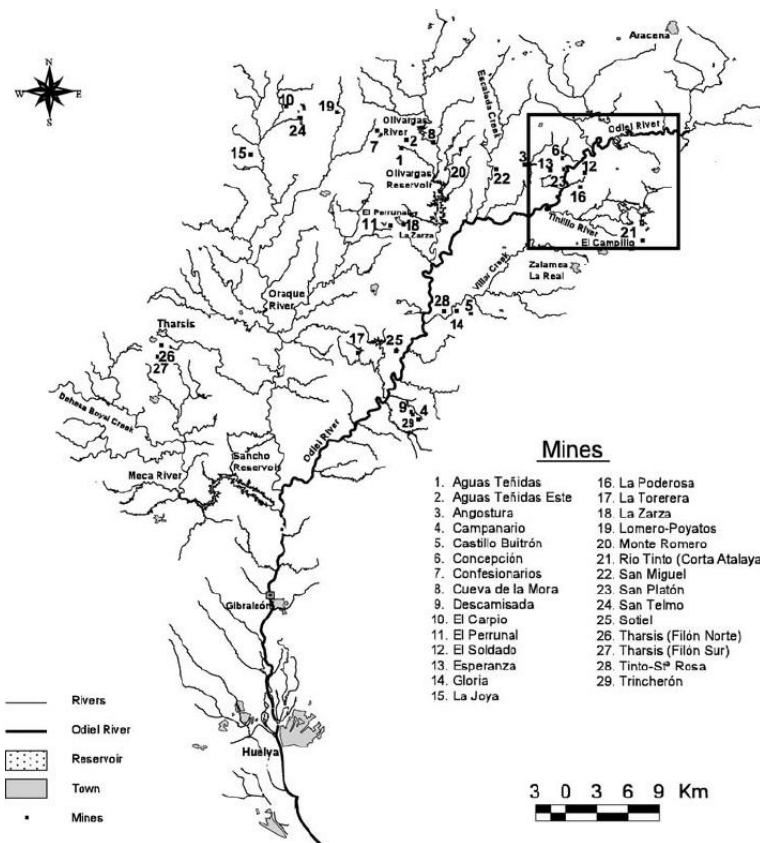


Figure 5. Hydrological map of the Odiel basin with location of the most important mines. La Poderosa mine is highlighted by a squared area (Sánchez España et al., 2006).

The transition elements (TE) and other metals concentration presents in the Odiel basin is provide in Figure 6.

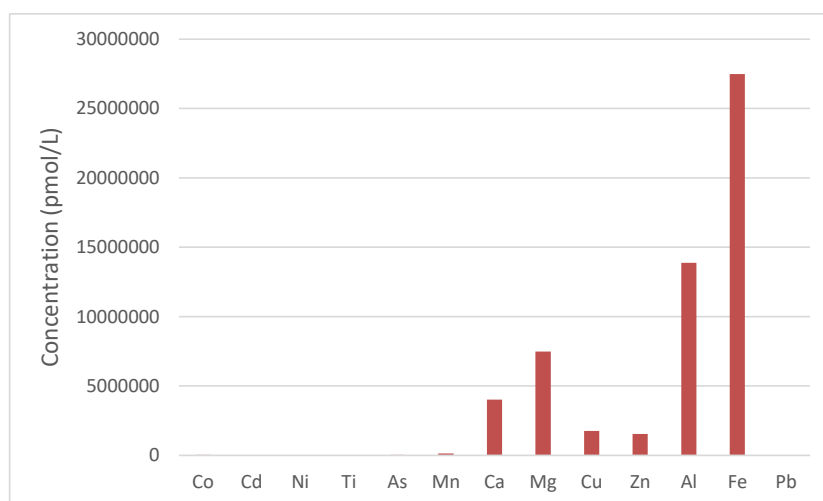


Figure 6. Transition elements concentration (pmol/L) in AMW from Odiel basin.

REE contents in acid mine water (AMW) from our Odiel basin data consistently show a range between 4000 and 23 000 pmol/L, as shown in Figure 7

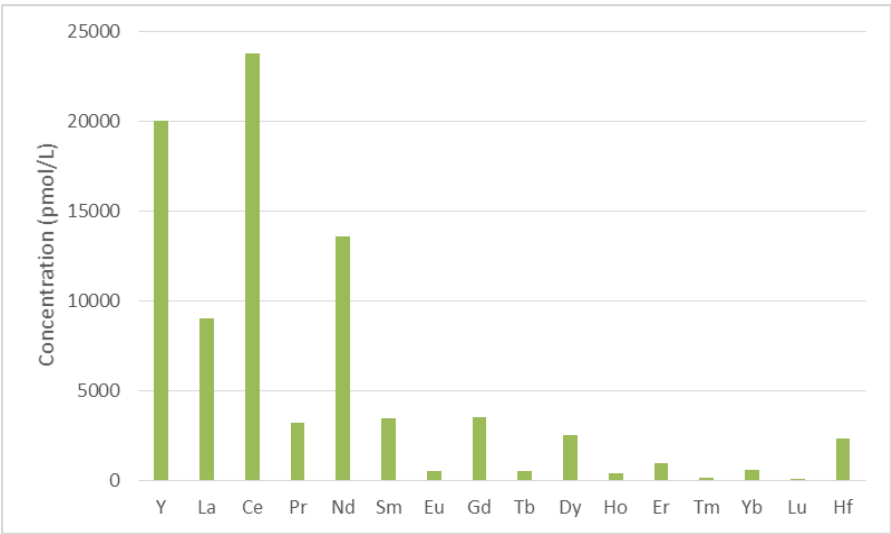


Figure 7. REE concentration (pmol/L) in an AMW sample from Odiel basin.

## **2.6. REE Extraction and Recovery Technologies**

The REE occur together in ore bodies and the chemical similarity of these element makes their extraction and their separation a challenging task.

Different technologies can be used for the recovery of REE depending on their origin (minerals, clays, wastes...) and the REE content. Such as gravity, magnetic, electrostatic and photochemical separations, or solvent extraction and ion exchange methods. Especially the last two methods, solvent extraction and ion exchange, are used for REE recovery and separation from aqueous streams generated among the hydrometallurgical processing stages.

### **2.6.1. Solvent extraction (SX)**

Solvent extraction (SX) also recognized as liquid-liquid extraction has been widely used for separation of REE is most of the hydrometallurgical processing schemes. This technique allows to separate REE into different currents, at first (light REE, medium REE and heavy REE), and after separate them from each other (Tang and Steenari, 2015). The most common and used extractants have functional groups as phosphinic, and phosphoric acids. Also, chelating groups, such as hidroxyquinolines are used (Jha et al., 2016).

### **2.6.2. Ion exchange (IX):**

Ion-exchange is a liquid-solid extraction process where REE metal ions are retained at the solid phase taking benefits of its functional groups. This technique separates and produces very high-purity rare earth products but with limited quantities due to its lower capacity and efficiency compared to SX (Zhang et al., 2016).

Different ion exchange resins are used (Jha et al., 2016), using batch or continuous mode in column for extracting REE from leached solutions. In particular, continuous mode and an ion exchange resin has been investigated in this study.

### **2.6.3. Precipitation of REE as phosphate minerals**

Phosphate rocks such as fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) often contain significant amounts of rare earth minerals and considered as rare earth ores. They can be processed to produce phosphoric acid as well as rare earth metals. For this reason, processing of apatite ores has become more prominent recently. These deposits however, often require a pre-leach stage prior to the acid bake stage at elevated temperature where the latter converts REE-phosphates to water soluble REE-sulphates (Stone et al., 2016). The aim of the pre-leach stage of ores/concentrates is to remove the calcium which otherwise interfere with liberation of REEs in acid bake stage due to formation of gypsum.



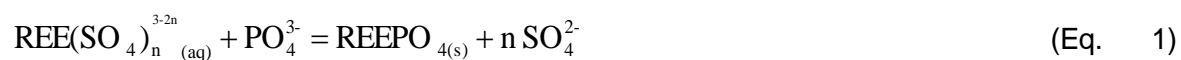
Recent studies have shown a positive impact on selecting  $\text{H}_3\text{PO}_4$  as a pre-leaching agent. Their results show maximum leaching efficiencies of calcium (100%) keeping dissolution of REEs at a minimum level in  $\text{H}_3\text{PO}_4$  at high acid concentrations. (Stone et al., 2016)

On the other hand, a huge number of minerals bearing phosphates REEs have been found, a fact which shows that REEs have a natural tendency to precipitate with phosphates. A summary of the varieties of minerals bearing phosphates REEs is provided in Figure 8.

Phosphate REEs bearing minerals	Chemical formula
Britholite (Ce)	$(\text{Ce,Ca})_5(\text{SiO}_4\text{PO}_4)_3(\text{OH,F})$
Britholite (Y)	$(\text{Y,Ca})_5(\text{SiO}_4\text{PO}_4)_3(\text{OH,F})$
Brockite	$(\text{Ca,Th,Ce})(\text{PO}_4) \cdot \text{H}_2\text{O}$
Chevkinite (Ce)	$(\text{Ca,Ce,Th})_4(\text{Fe}^{2+}, \text{Mg})_2(\text{Ti,Fe}^{3+})_3\text{Si}_4\text{O}_{22}$
Churchite (Y)	$\text{YPO}_4 \cdot \text{H}_2\text{O}$
Crandallite	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$
Florencite (Ce)	$\text{CeAl}_3(\text{PO}_4)_2(\text{OH})_6$
Florencite (La)	$(\text{La,Ce})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$
Florencite (La)	$(\text{Nd,Ce})\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$
Fluorapatite	$(\text{Ca,Ce})_5(\text{PO}_4)_3\text{F}$
Gorceixite	$(\text{Ba,REE})\text{Al}_3[(\text{PO}_4)_2(\text{OH})_5] \cdot \text{H}_2\text{O}$
Goyazite	$\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$
Monazite (Ce)	$(\text{Ce,La,Nd,Th})\text{PO}_4$
Monazite (La)	$(\text{La,Ce,Nd,Th})\text{PO}_4$
Monazite (Nd)	$(\text{Nd,Ce,La,Th})\text{PO}_4$
Rhabdophane (Ce)	$(\text{Ce,La})\text{PO}_4 \cdot \text{H}_2\text{O}$
Rhabdophane (La)	$(\text{La,Ce})\text{PO}_4 \cdot \text{H}_2\text{O}$
Rhabdophane (Nd)	$(\text{Nd,Ce,La})\text{PO}_4 \cdot \text{H}_2\text{O}$
Vitusite (Ce)	$\text{Na}_3(\text{Ce,La,Nd})(\text{PO}_4)_2$
Xenotime (Y)	$\text{YPO}_4$

Figure 8. Minerals containing rare earth phosphates (Jha et al., 2016).

The present study investigated the precipitation of yttrium and lanthanides from acid mine waters by the addition of sodium dihydrogen phosphate and  $\text{H}_2\text{PO}_4$ . Due to the strong affinity of  $\text{Y}^{3+}$  and  $\text{Ln}^{3+}$  ions for  $\text{PO}_4^{3-}$  compared to  $\text{SO}_4^{2-}$  (Firsching and Brune, 1991; Kim and Osseo-Asare, 2012) the addition of  $\text{Na}_2\text{PO}_4$  to acid mine water that have yttrium and lanthanides was expected to trigger the precipitation of REE phosphate (Eq. (1)) even at low concentration of REE.



The precipitation of rare earth elements (REE) and transition elements (TE) is pH dependent as it could be observed in Figure 9, where the solubility-pH functions for a total phosphate concentration is shown.

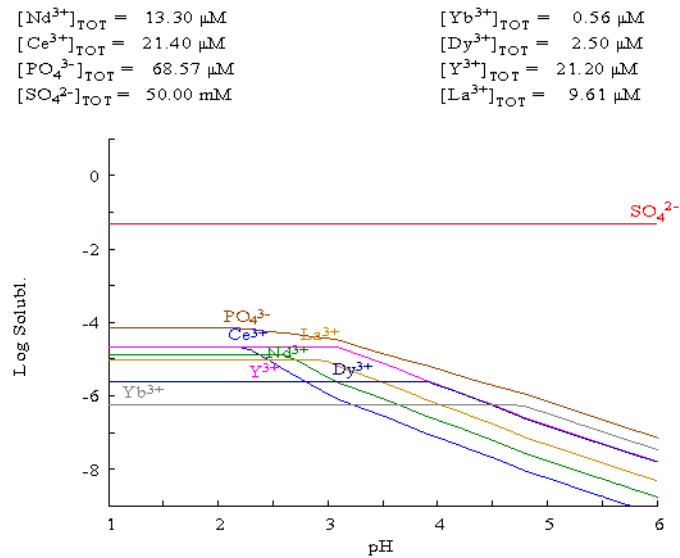


Figure 9. Solubility diagram for the REE-phosphates in acid mine waters. Thermodynamic data from MEDUSA database (Puigdomènech, 2010).

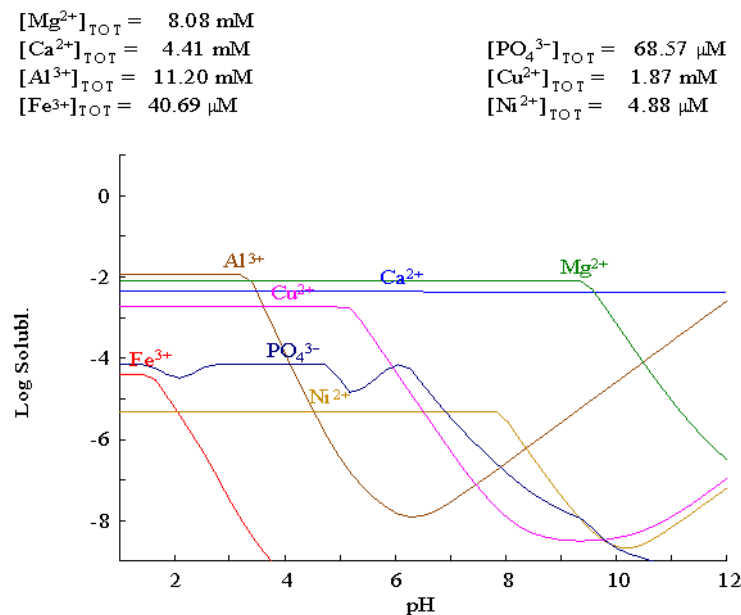


Figure 10. Solubility diagram for the TE-phosphates in acid mine waters. Thermodynamic data from MEDUSA database (Puigdomènech, 2010).

As it could be observed precipitation of divalent TE occurs at higher pH values than for REE with the exception of the trivalent TE, specially Fe(III) forming insoluble phosphate and or hydroxides at acidic pH values where REE are precipitating as phosphates and Al(III) forming insoluble phosphates and hydroxides at pH values higher than 4. This pH window has been used as the main separation principle.

## 2.7. Objectives

Nowadays, recycling in-use stocks of rare earth elements (REE) are being investigated. Even though there are large quantities of REE on different industrial and urban waste products, currently their recovery is still economically unviable. This is the reason why new sources of REE containing wastes and new technologies for their recovery should be identified.

The main objective of this work is to study the recovery of REE from river waters contaminated by acid mine drainage, taking benefit of their tendency to form phosphate minerals. In this manner it is integrated in one step the treatment of a polluted effluent as the acid mine water (AMW) and its valorisation to recover REE. In this way, a pollutant is transformed into by-product with added value.

In order to achieve this objective, a previous stage was needed in order to remove the large amount of Fe present in the AMW samples. As typically Fe is present in such solutions as mixtures of Fe(II) and Fe(III), Fe was oxidized by using  $\text{H}_2\text{O}_2$  and then precipitated by addition of strong bases (e.g. NaOH, CaO, and MgO). The resulting solutions are identified as treated AMWs (TAMW).

Finally, working with this treated acid mine waters, different experiments were performed to investigate the best conditions of pH and phosphate concentration to optimize in a single step their maximum recovery and their separation from transition elements (TE) present on TAMW.

## 2.8. Project scope

The experimental work has covered two different scenarios:

- a) Direct precipitation of rare earth elements (REEs) from treated acid mine waters (TAMWs) where the rare earth elements are present in concentrations ranges from 0.1 to 4 mgREE/L, and a total REE concentration below 11 mgREE/L.
- b) Precipitation of REE from REE concentrates generated from the treatment of TAMW by using ion-exchange resins where REE are present in concentration ranges of 4 to 77 mgREE/L and a total REE concentration below 240 mgREE/L.

When necessary synthetic solutions of REE were used to study the precipitation reactions and determining the optimal conditions in terms of acidity and total phosphate concentration needed.

This project is centred on experimental work at laboratory scale using AMW from the Odiel River Basin. It is not inside the scope of the study any environmental study at full scale level and similarly any study devoted to analyze the economic viability of the REE separation process.

### 3. Experimental section

#### 3.1. Reagents and solutions

- **REE standard solutions:**  $\text{Ce}^{3+}$ ,  $\text{Y}^{3+}$  and  $\text{La}^{3+}$ , solutions of 1000 mgREE/L were prepared using  $\text{CeCl}_3$ ,  $\text{La}_2(\text{SO}_4)_3$  and  $\text{Y}_2\text{O}_3$  salts after appropriate dissolution with deionized water  $\text{H}_2\text{SO}_4$  in 1% .  **$\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Yb}^{3+}$  standard solutions** of 1000 mg/L in  $\text{HNO}_3$  1% were also used.

-  **$\text{H}_2\text{SO}_4$  solutions:**  $\text{H}_2\text{SO}_4$  solutions (0.1 and 1.8 M) were prepared by dilution of 96%  $\text{H}_2\text{SO}_4$ .

- **HCl solution:** HCl solution 1.1 M was prepared by dilution of 37% HCl.

-  **$\text{H}_3\text{PO}_4$  solution:**  $\text{H}_3\text{PO}_4$  solution 1.47 M was prepared by dilution of 85%  $\text{H}_3\text{PO}_4$ .

-  **$\text{NaH}_2\text{PO}_4$  solutions;**  $\text{NaH}_2\text{PO}_4$  solutions of 1 and 0.2 M were prepared by using appropriate amounts of  $\text{NaH}_2\text{PO}_4$  (98% purity).

-  **$\text{H}_2\text{O}_2$  solution:** 30% v/v (Panreac) was used to oxidize to Fe(III).

NaOH solutions, CaO (99% purity) and MgO (98% purity) were used for the pH adjusting on the acid mine water samples.

Aqueous solutions were prepared using deionized water (Milli-Q, Merck-Millipore).

- **Ion exchange resins for REE extraction and concentration: SPC 11706 resin**

SPC 11706 is a macroporous of polystyrene sulfonate, and it have as a functional group sulfonic acid and sodium as counter-ion. A summary of the SPC 11706 proprieties is provided in Table 2.

*Table 2. General Characteristics of SPC 11706 Resin*

	SPC 11706 Resin proprieties
Functional group	Sulfonic acid
Structure	Macroporus
Counter-ion	$\text{Na}^+$
Density (mg/L)	1,3
Minimum Capacity (g/L)	23
pH range	0-14
Regeneration agents	Strong acid

- **Auxiliary and expendable material for precipitation assays were:** 50 mL Centrifuge Tubes of PET (Scharlau); 25 mm nylon filters (Phenomenex, 25mm) and 3 mm nylon syringe filter with pore size 0.45  $\mu\text{m}$  (SimplePlure 13 mm).

## 3.2. Experimental methodology

### 3.2.1. Characterization of acid mine water samples.

Acid mine water samples (AMW) from the Iberian Pyrite Belt (IPB), Rio Odiel basin (Huelva) in southwest Spain with pH values between 1.8 and 2.4 were used in the laboratory experiments. They were sampled at the outflow of a gallery of the Poderosa mine and represented a strong interaction with a shale enclosing rock. Samples present an orange colour, due to high concentrations of Fe(II) and Fe(III).

### 3.2.2. AMW pre-treatment for removal of Fe(III) by oxidation with $H_2O_2$ and pH control.

Fe was removed from AMW samples in a two stages process. In a first stage 3 mL of  $H_2O_2$  30% v/v per liter of acid mine water was added to oxidize Fe(II) to Fe(III). Then in a second stage Fe was precipitated as  $Fe(OH)_3$  by increasing the pH up to pH = 3.7-3.8. In order to evaluate the cost of the precipitation stage three alkaline reagents were used: NaOH (50% concentration), CaO (99% purity), MgO (98% purity). Precipitation assays were carried out using 3L of AMW pre-oxidized by  $H_2O_2$  and adding an alkaline agent: 9.9 mL NaOH or 8.7g CaO(s) or 5.1g MgO(s).

For solid reagents (CaO(s) and MgO(s)) and due to their low solubility in aqueous solutions after each addition of 2g of solid the sample was exposed to ultrasound for 20 minutes using a water bath, until a pH = 3.7 was reached. Then the samples were left under magnetic stirring for 24 hours (Ovan, Multimix D).

Treated AMW liquid samples, containing REE were prepared by two filtration stages process to separate the precipitate iron hydroxides. In a first stage samples were filtered using a Kitassato and Whatman N42 paper filter and followed by a filtration using two sand columns (10 cm length) in series to remove colloidal matter. The final solution was let in agitation 24h, and if the pH decreased below 3.6, the process was repeated. The two sand columns and the vacuum filter are exposed in Figure 11.

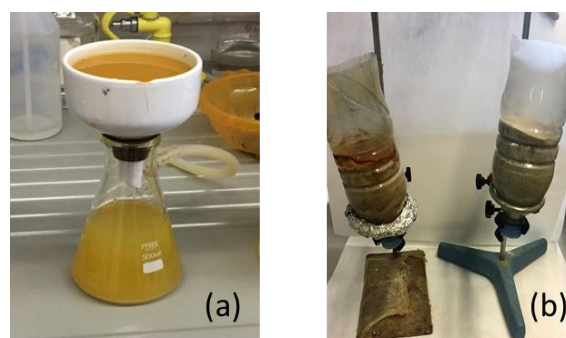


Figure 11. System filtration by using a Kitassato (a)) and sand columns (b)).

### 3.2.3. Precipitation experiments with phosphate solutions.

The global objective of this study is to find the optimal conditions to obtain the maximum recovery of REE, precipitation of  $\text{REE}(\text{PO}_4)_{(s)}$ .

The conditions studied were:

- Precipitation as a function of pH: different pH values.
- Precipitation as function of the nature of acid to control pH: acid solutions of  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$  y  $\text{H}_2\text{SO}_4$  were used to decrease the pH from 3.7 to pH chosen for REE precipitation. This study with different acids was carried out to study the potential complexation effects as prices could have a potential cost implication.
- Molar ratio of the total phosphate concentration and to the total REE concentration (SQ) defined by Eq 2:

$$SQ = \frac{\sum H_x PO_4^{x-3} \text{ added}(\text{mol})}{\sum REE_{\text{initial}}(\text{mol})} \quad (\text{Eq. 2})$$

The pH was first fixed with the appropriate acid and in each sample the required mass of  $\text{NaH}_2\text{PO}_4$  for a given SQ value was added. Finally, the samples were let in agitation for 24 h in an overhead shaker (Figure 12) and if the pH increased it was fixed again and let in agitation for 24 h more.

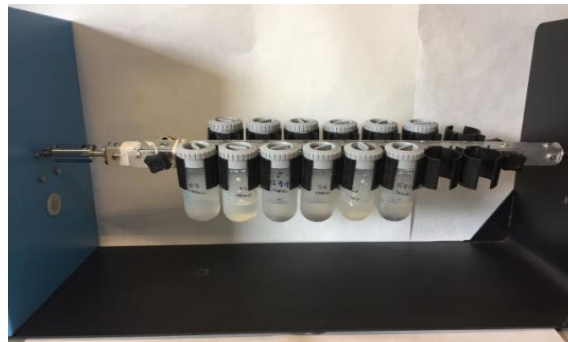


Figure 12. Rotatory mechanical agitation system.

At the end of the experiments, samples were filtered (SimplePlure 13 mm) and metal concentration and total sulphur concentrations were measured by ICP-OES and ICP-MS depending on the concentration range present, as it is described in section 3.3.

### Test 1. Evaluation of REE recovery from Fe free treated AMW

According to the experimental planning a total number of 28 samples of 50 mL of pre-treated AMW with NaOH were prepared. Each sample has a different pH, in the range 1.7 to 2.3, different molar P/REE ratio (SQ) and different nature of the acid used (HCl, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>). A summary of the different conditions for each sample is given in Table 3. The variation range of pH was selected taking into account the solution chemistry of the systems (PO<sub>4</sub>)–(SO<sub>4</sub>)–H<sub>2</sub>O at 25 °C using the Hydro-Medusa code (Puigdomènech, 2010). Hydra-Medusa code was used to estimate equilibrium concentration as it is shown in the solubility diagrams (function of pH and the total phosphate concentration) in Figure 17. The molar P/REE ratio (SQ) was varied from 1 to 2. Both REE and transition elements (TE) were evaluated as one of the objectives to be achieved is the maximum separation of both types of metal groups.

*Table 3. pH, molar P/REE ratio (SQ) and nature of acid used for each 50 mL aliquot of AMW pre-treated with NaOH.*

Reduction in pH with	SQ	pH	
H <sub>2</sub> SO <sub>4</sub> (1.8 M)	1	2,3	Sample1
		2,1	Sample2
		1,9	Sample3
		1,7	Sample4
	1.5	2,3	Sample5
		2,1	Sample6
		1,9	Sample7
		1,7	Sample8
	2	2,3	Sample9
		2,1	Sample10
		1,9	Sample11
		1,7	Sample12
HCl (1.2 M)	1	2,3	Sample13
		2,1	Sample14
		1,9	Sample15
		1,7	Sample16
	1.5	2,3	Sample17
		2,1	Sample18
		1,9	Sample19
		1,7	Sample20
	2	2,3	Sample21
		2,1	Sample22
		1,9	Sample23
		1,7	Sample24
H <sub>3</sub> PO <sub>4</sub> (1.47 M)	2*	2,3	Sample25
	16*	2,1	Sample26
	26*	1,9	Sample27
	41*	1,7	Sample28

\*The samples which H<sub>3</sub>PO<sub>4</sub> was used were not added NaH<sub>2</sub>PO<sub>4</sub> since they have stoichiometric excess of PO<sub>4</sub><sup>3+</sup> in relation to REE.

## Test 2. Evaluation of REE precipitation from treated acid mine waters (TAMW) using excess of phosphate

A total number of 18 samples 100 mL of pre-treated AMW with NaOH, CaO, and MgO were prepared each with pH=2.3 and 2.5, more details were given in section 4.3 Test 2. Molar P/REE ratio 40 was chosen to work since the results obtained in Test 1.

*Table 4. pH, molar P/REE ratio (SQ) and nature of acid used for each 100mL aliquot of AMW pre-treated with NaOH, MgO and CaO.*

AMW treated with:	Reduction in pH with	pH	SQ	
NaOH	H <sub>2</sub> SO <sub>4</sub> (1.8 M)	2,3	40	Sample29
		2,5	40	Sample30
	HCl (1.2 M)	2,3	40	Sample31
		2,5	40	Sample32
	H <sub>3</sub> PO <sub>4</sub> (1.47 M)	2,3	88*	Sample33
		2,5	53*	Sample34
CaO	H <sub>2</sub> SO <sub>4</sub> (1.8 M)	2,3	40	Sample35
		2,5	40	Sample36
	HCl (1.2 M)	2,3	40	Sample37
		2,5	40	Sample38
	H <sub>3</sub> PO <sub>4</sub> (1.47 M)	2,3	88*	Sample39
		2,5	53*	Sample40
MgO	H <sub>2</sub> SO <sub>4</sub> (1.8 M)	2,3	40	Sample41
		2,5	40	Sample42
	HCl (1.2 M)	2,3	40	Sample43
		2,5	40	Sample44
	H <sub>3</sub> PO <sub>4</sub> (1.47 M)	2,3	88*	Sample45
		2,5	53*	Sample46

\*This samples have SQ>40 since the addition of H<sub>3</sub>PO<sub>4</sub> to reach the pH= 2.3 and 2.5.



### Test 3. Evaluation of Ce and La precipitation with phosphate solutions using synthetic acidic solutions.

A study of the precipitation behaviour of the two representative REEs in the AMW (La and Ce) was made using 18 aliquots of 50 mL of La 25 mg/L and another 18 of Ce 25 mg/L as well. After the % REE recovery results obtained in Test 1 (Section 4.3 Test 1) in SQ=41 in this experiment SQ=40 and 100 were chosen to work. Furthermore, each of them was brought to different precipitation conditions (Table 5).

*Table 5. Precipitation conditions (pH, nature of acid used and molar P/REE ratio (SQ)) for solutions La and Ce 25 mg/L.*

Reduction in pH with	pH	SQ
<b>HCl (1.2 M)</b>	2,3	40
		100
	2,5	40
		100
	2,7	40
		100
<b>H<sub>2</sub>SO<sub>4</sub> (1.8 M)</b>	2,3	40
		100
	2,5	40
		100
	2,7	40
		100
<b>H<sub>3</sub>PO<sub>4</sub> (1.47 M)</b>	2,3	50**
		100*
	2,5	30**
		100*
	2,7	17**
		100*

\*The samples which H<sub>3</sub>PO<sub>4</sub> was used were added NaH<sub>2</sub>PO<sub>4</sub> until reach SQ=100.

\*\* The SQ=50, 30 and 17 were reached only adding H<sub>3</sub>PO<sub>4</sub> for reach the pH= 2.3, 2.5 and 2.7 in that order.

### 3.2.4. Concentration REE from AMW by using ion exchange resin (S11706 resin) in column experiments.

An Omnifit glass column 100 mm long and 15 mm in diameter has been used, which was filled with  $9.5 \pm 0.5$  g of resin. Peristaltic pump (Minipuls 3, Gilson MP) was used to pass the different solutions through the column. A fraction collector (FC 204 Gilson) was arranged at the exit of the column.

Before the experiment,  $H_2O$  for 2 h and a flow rate of 1 mL/min was circulated through the column. Then, TAMW at pH=2.1 was circulated at 1 mL/min through the column and the fractions was collected by the fraction collector. Finally, the elution of the metals adsorbed was performed with  $H_2SO_4$  10 M, which was passed through the column at 0.25 mL/min and different fractions were also sampled with the fraction collector. A scheme of the experiment is exposed in Figure 13.

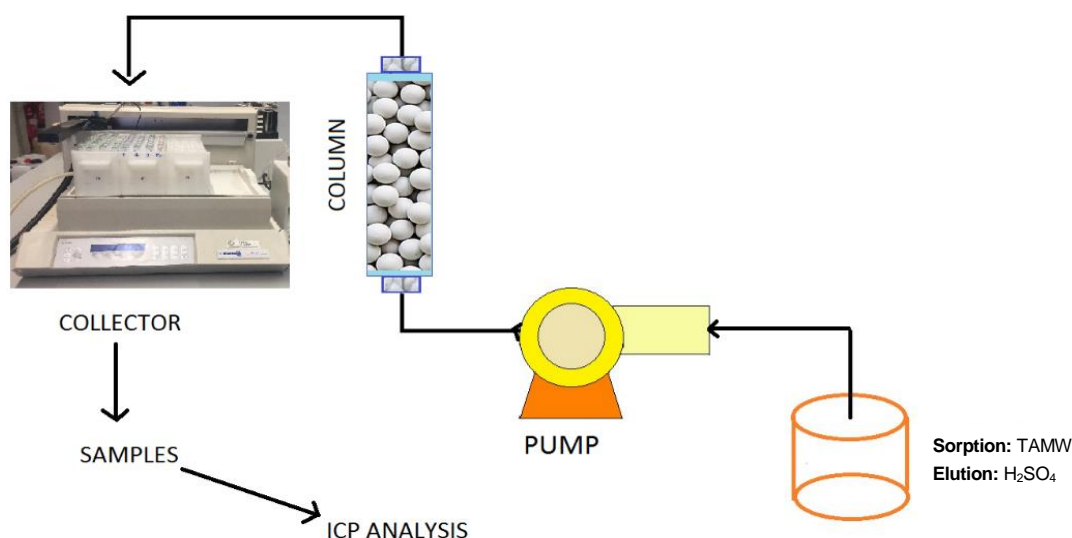


Figure 13. Column experiment scheme system for the concentration of REE from treated acid mine water (TAMW) using ion-exchange resins.

### Test 4. REE recovery from synthetic solutions from concentrates generated in treatment of TAMW with ion-exchange resins (total REE concentration <130 mgREE/L)

Treated acid mine waters (TAMW) aliquots of 50 mL were prepared under the same conditions of pH and acid used in Table 4. The concentration of Y, La, Ce, Nd, Yb and Dy in each sample was increased to reach concentrations of column elution (Table 6) by using standard solutions 1000 mg/L in  $HNO_3$  1%. After adding the necessary amount of La, Ce, Nd, Yb and Dy the processed used is the same that the previous experiments: fixed the pH, control the pH adding the stoichiometric quantity of  $NaH_2PO_4$ , and let in agitation for 24h.

This experiment worked in SQ=2.5 and 5. To choice the experimental condition a fraction diagrams of the system were done, they are given in Annex E. A total of 38 samples were filtered by using 25 mm nylon filters (Phenomenex, 25mm) to be analysed by ICP-OES and ICP-MS.

*Table 6. REE Concentrations (mg/L) in the Test 4 samples reached adding solutions standard 1000mg/L HNO<sub>3</sub> 1%.*

Y	La	Ce	Nd	Dy	Yb
25	20	40	20	10	4

A summary of the experimental conditions of Test 4 is given in Table 7 .

*Table 7. Experimental conditions of the different samples in Test 4*

AMW treated with:	Reduction in pH with	pH	SQ	
NaOH	H <sub>2</sub> SO <sub>4</sub> (1.8 M)	2,3	2,5	Sample47
			5	Sample48
		2,5	2,5	Sample49
			5	Sample50
	HCl (1.2 M)	2,3	2,5	Sample51
			5	Sample52
		2,5	2,5	Sample53
			5	Sample54
CaO	H <sub>2</sub> SO <sub>4</sub> (1.8 M)	2,3	2,5	Sample55
			5	Sample56
		2,5	2,5	Sample57
			5	Sample58
	HCl (1.2 M)	2,3	2,5	Sample59
			5	Sample60
		2,5	2,5	Sample61
			5	Sample62
MgO	H <sub>2</sub> SO <sub>4</sub> (1.8 M)	2,3	2,5	Sample63
			5	Sample64
		2,5	2,5	Sample65
			5	Sample66
	HCl (1.2 M)	2,3	2,5	Sample67
			5	Sample68
		2,5	2,5	Sample69
			5	Sample70

### Test 5. REE recovery from synthetic solutions from concentrates generated in treatment of TAMW with ion-exchange resins (total REE concentration <240 mgREE/L)

A total number of 6 aliquots (200mL) of AMW pre-treated with NaOH, CaO and MgO were used in this experiment. The concentration of Y, La, Ce, Nd, Yb and Dy in each sample was increased to reach the maximum concentrations of column elution (Table 8) making use of standard solutions 1000 mg/L in HNO<sub>3</sub> 1%. The aliquots pH was decreased from 3.7 to 2.5 by using a H<sub>2</sub>SO<sub>4</sub> solution (1.8 M). Then the necessary amount of NaH<sub>2</sub>PO<sub>4</sub> was added to reach the SQ=2.5 and 40. In total, 6 samples were analyzed in this experiment Table 9.

*Table 8. REE concentrations (mg/L) in the Test 5 samples reached adding solutions standard 1000mg/L HNO<sub>3</sub> 1%.*

Y	La	Ce	Nd	Dy	Yb
64	42	77	35	13	8

*Table 9. Test 5 experimental conditions.*

AMW treated with:	Reduction in pH with	pH	SQ	
NaOH	H <sub>2</sub> SO <sub>4</sub>	2,5	2,5	Sample71
			40	Sample72
CaO	H <sub>2</sub> SO <sub>4</sub>	2,5	2,5	Sample73
			40	Sample74
MgO	H <sub>2</sub> SO <sub>4</sub>	2,5	2,5	Sample75
			40	Sample76

The precipitate obtained had an amorphous form. In order to be determined by X-ray diffraction (XRD), the precipitate has been given a heat treatment in an oven at 1050°C for four hours to its crystallization.

### 3.3. Chemical and Mineralogical Analyses.

Measurement of pH was made with a Crison® glass electrode calibrated with buffer solutions of pH 7 and 2. Redox potential was measured using a Pt combination electrode (ThermoOrionSureFlow®) that was calibrated with standard buffer solutions of 220 and 468 mV. Measurements were corrected to the Standard Hydrogen Electrode to calculate pE. Total (gross) alkalinity was measured by acid titration using an Alkalinity Test from Aquamerck® (limit of detection 0.1 mmol H<sup>+</sup>/L, analytical error of 0.1 mmol H<sup>+</sup>/L). Filtered samples (0.1 µm nylon) were acidified with HNO<sub>3</sub> for the analysis of major and trace elements by inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS), respectively. Details of the analytical procedures are described following. Filtered samples (0.1 µm) were acidified with HNO<sub>3</sub> for analysis of major and trace elements. Major cations (Ca, Mg, Zn, Fe, Mn, Si) and total S were measured by ICP-AES (Perkin-Elmer® Optima 3200 RL) and trace metals (Ni, Cd, Co, Pb) with ICP-MS (PerkinElmer® SciexElan 6000). Detection limits were 0.1 mg/L for S; 0.05 mg/L for Ca, Mg, Si; 0.02 mg/L for Fe, Zn, Mn; 5 µg/L for Al; 1.5 µg/L for Cu, Ni; 0.5 µg/L for Pb; 0.2 µg/L for Cd, Co and REY. The analytical precision error was estimated to be approximately 6% for ICP-AES and 4% for ICP-MS measurements. Two AMW laboratory standards supplied by P. Verplank (USGS), were also analyzed for REE accuracy, giving deviations lower than 5% of the recommended values S1, with the exception of Eu, giving values 25% below the recommended value. Assuming all S to be sulfate, the charge balance error was usually less than 5%.

Once the precipitation experiments were concluded, the solids were recovered by filtration and dried at room temperature. The solid samples consisted almost precipitated REE-phosphates. The mineralogy was determined by X-ray diffraction (XRD) and field emission scanning electron microscopy with energy-dispersive analysis (FESEM-EDS). The major mineral phases forming the solid samples were identified by X-ray diffraction (XRD) using a Bruker® D5005 X-Ray Diffractometer (XRD) with Cu K $\alpha$  radiation. The samples were scanned from 0 to 60 degrees 2 $\theta$  with a continuous scan at a rate of 0.025°/18 s. Granular material was also observed under a JEOL® JSM840 Field Emission Scanning Electron Microscope with Oxford Link® Energy Dispersive System (SEM-EDS).

## 4. Results and discussion

### 4.1. Characterization of the La Poderosa acid mine water.

The REE concentrations in the Poderosa acid mine water are summarized in Table 10 . The pattern is consistent with the observation that the concentration of REE in similar AMW of the Rio Tinto Basin (Ayora et al., 2016) or the country rock of the Sitai coal mine (China) is one order of magnitude higher than those of pyrite and coal samples (Zhao et al., 2007).

*Table 10 REEs concentration in the acid mine water sample (mg/L).*

Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
1,79±0.2	1,21±0.2	3,28±0.4	0,44±0.04	1,94±0.3	0,51±0.04	0,07±0.01	0,54±0.07	0,09±0.01
Dy	Ho	Er	Tm	Yb	Lu	Hf		
0,40±0.04	0,07±0.01	0,15±0.02	0,02±0.002	0,10±0.02	0,01±0.002	0,37±0.04		

The concentration of REE ranged from 0.01 mg/L for Lu up to 3.3 mg/L for Ce. Three main groups could be defined: REE in the range 0.01 to 0.10 mg/L (Lu, Tm, Ho, Eu), REE in the range 0.1 to 0.5 mg/L (Yb, Er, Hf, Dy, Pr, Sm) and REE in the range 0.5 to 3.3 mg/L (Gd, La, Y, Nd, Ce). According to this classification the main effort on this study was centred on the two last groups.

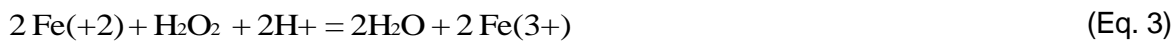
In the case of transition elements (TE) the higher concentrations are associated to Fe, with 1.5 g Fe/L, followed by a group of elements between 100 and 400 mg/L (Al, Mg, Ca, Cu and Zn) and a group of elements below 10 mg/L (Co, Ni, Cd between others).

*Table 11. Transition elements (TE) concentrations in the acid mine water sample (mg/L).*

Co	Cd	Ni	Ca	Mg	Cu	Zn	Al	Fe
1,4±0.2	0,4±0.05	0,3±0.04	161,0±23	181,6±25	111,1±15	100,9±15	374,6±50	1534,78±220

## 4.2. AMW pre-treatment for removal of Fe(III) by oxidation with $\text{H}_2\text{O}_2$ and pH control.

As described in Table 11, raw acid mine water samples contain large quantities of iron (e.g.  $1534.7 \pm 220$ ). According to (Ayora et al., 2016) with similar AMW most the iron is present as Fe(II). To simplify the separation process in the REE concentration process using ion exchange Fe should be removed in a two stage process: a) oxidation of Fe(II) to Fe(III) by using  $\text{H}_2\text{O}_2$  (1 mL of  $\text{H}_2\text{O}_2$  30% per liter of AMW) as it is shown in Eq 3; and b) precipitation of Fe(III) as hydroxide by increasing the pH by using alkaline agents.



In Figure 14 is shown the variation of the total Fe(III) and Al(III) concentration, in logarithmic form, as a function of pH, assuming the formation of  $\text{Al}(\text{OH})_3(\text{s})$  and  $\text{Fe}(\text{OH})_3(\text{s})$  as preliminary hypothesis. As it has been described by (Ayora et al., 2016) precipitation of Fe(III) and Al(III) happens by formation of complex hydroxi-sulphates (e.g. schwermanite and basaluminite) however their solubility constants are under determination. Accordingly to precipitate  $\text{Fe}(\text{OH})_3$  the acidic water sample was adjusted to pH = 3.7-3.8 as shown in Figure 14. Under this conditions more than 99% of Fe(III) could be totally removed from solution and Al(III) removal starts above pH 3 with values below 5%. In order to evaluate REE recovery rate against the cost of the sample pre-treatment, three reagents with different chemical and physical properties and with different cost were used: NaOH (50% concentration), CaO (99% purity), MgO (98% purity). To treat 3L of sample was needed 9.9 mL NaOH, 8.7g CaO and 5,1g MgO.

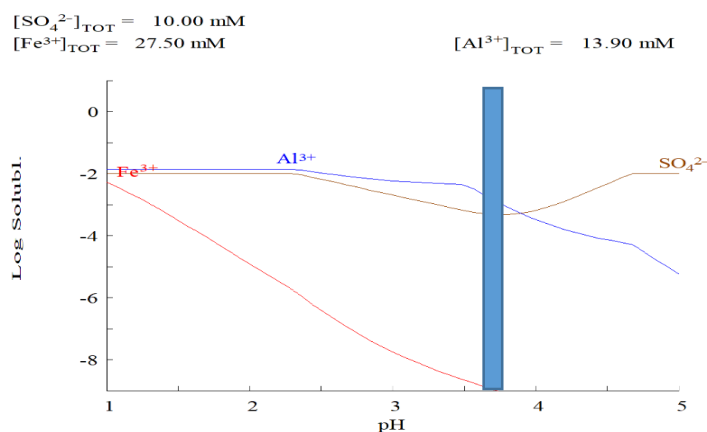


Figure 14. Variation of Al and Fe concentrations with pH using the speciation code HYDRA (Puigdomènech, 2010). The shaded rectangular field indicates the best pH range to precipitate  $\text{Fe}(\text{OH})_3$ .

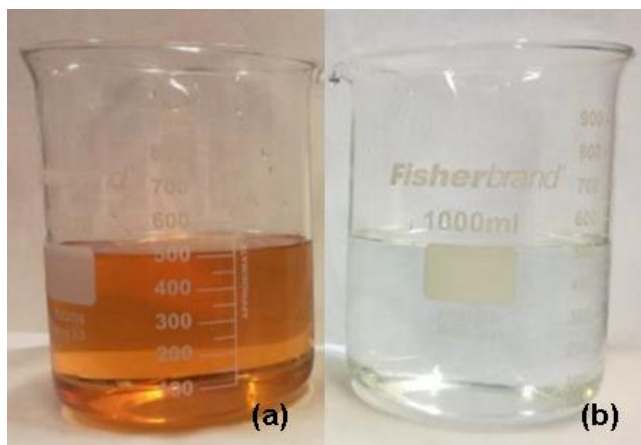


Figure 15. Samples treated (a)) Acid mine water, (b)) Acid mine water treated to remove Fe.

The change of the sample after treatment can be seen in Figure 15. The REE and TE concentration changes on the solution composition after the treatment with the different reagents is summarized on Table 12.

Table 12. Concentration (mg/L) of transition elements and REEs after oxidation pre-treatment of acid mine water (AMW)

	Co	Cd	Ni	Ca	Mg	Cu	Zn	Al	Fe
AMW treated with CaO	1,4±0.2	0,4±0.05	0,3±0.04	582,0±80	195,0±30	109,5±15	107,6±15	331,1±45	2,3±0.3
AMW treated with NaOH	1,4±0.2	0,4±0.05	0,3±0.04	147,0±20	171,5±25	108,0±15	102,9±15	302,2±40	2,2±0.3
AMW treated with MgO	1,5±0.2	0,5±0.05	0,3±0.04	273,0±40	1025,0±145	107,3±15	105,1±15	302,2±40	2,8±0.3
AMW	1,4±0.2	0,4±0.05	0,3±0.04	161,0±23	181,6±25	111,1±15	100,9±15	374,6±50	1534,78±220

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd
AMW treated with CaO	1,81±0.2	1,16±0.1	3,00±0.4	0,40±0.04	1,78±0.2	0,47±0.04	0,07±0.01	0,54±0.07
AMW treated with NaOH	1,78±0.2	1,21±0.2	3,24±0.4	0,43±0.04	1,89±0.2	0,51±0.04	0,07±0.01	0,54±0.07
AMW treated with MgO	1,83±0.2	1,27±0.2	3,11±0.4	0,43±0.04	1,86±0.2	0,50±0.04	0,07±0.01	0,55±0.07
AMW	1,79±0.2	1,21±0.2	3,28±0.4	0,44±0.04	1,94±0.3	0,51±0.04	0,07±0.01	0,54±0.07



	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
AMW treated with CaO	0,08±0.01	0,41±0.04	0,07±0.01	0,15±0.02	0,02±0.002	0,10±0.02	0,01±0.002	0,41±0.04
AMW treated with NaOH	0,09±0.01	0,40±0.04	0,07±0.01	0,15±0.02	0,02±0.002	0,10±0.02	0,01±0.002	0,33±0.04
AMW treated with MgO	0,08±0.01	0,40±0.04	0,07±0.01	0,15±0.02	0,02±0.002	0,10±0.02	0,01±0.002	0,43±0.04
AMW	0,09±0.01	0,40±0.04	0,07±0.01	0,15±0.02	0,02±0.002	0,10±0.02	0,01±0.002	0,37±0.04

As shown in Figure 16 the AMW treated with CaO has higher loss percentages of the most representative REEs (around 8 %). The treatment with NaOH provided the lower removal ratios of REEs. In relation to iron elimination the three pre-treatment provided similar removal ratios (99.9 %). However, in terms of aluminium removal the pre-treatment with CaO had the lowest percentage of removal.

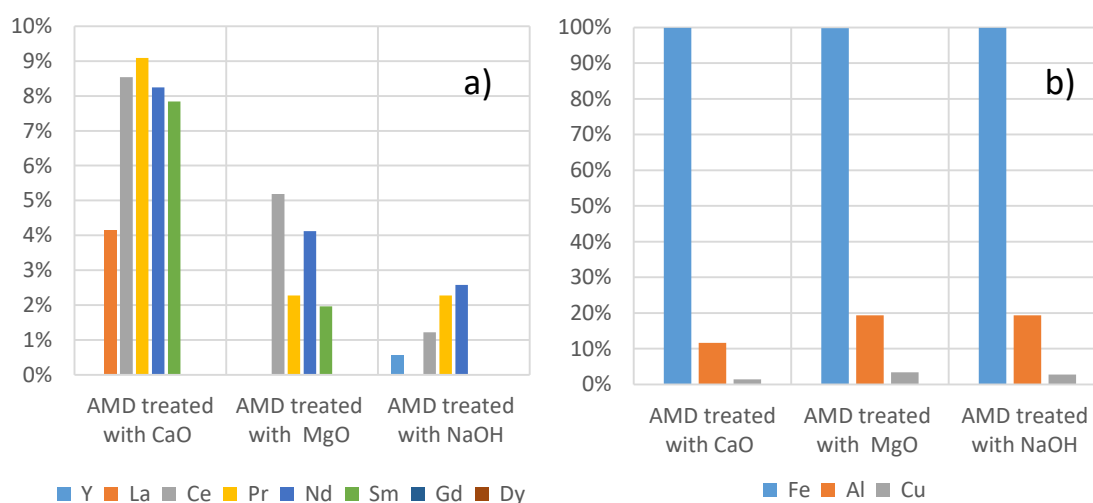


Figure 16. Loss percentages of the most representative REEs (a)), Al and Fe (b)) in the AMW.

The pre-treatment stage of Fe removal by pre-oxidation with  $H_2O_2$  was successfully achieved and the solution could be treated increasing the pH with removal efficiencies of Fe higher than 99.9% and low removal ratios of REE (values below 5%).

The percentages of the concentration variation of each element is given in Annex A.

### 4.3. Precipitation experiments with phosphate solutions results.

#### Test 1. Evaluation of REE recovery from Fe free treated AMW

Initial molar ratios selected ranged from 1 to 2.3. According to the precipitation conditions (Figure 17 ) as a function of pH and for different molar ratios (phosphate/REE), experiments at pH 1.7, 1.9, 2.1 and 2.3 were carried out . According to Figure 17 and using the composition of the acid mine water (Ayora et al., 2016) it could be seen that precipitation of Al(III) by phosphate occurs at pH values higher than 2.3, assuming the precipitation of  $\text{AlPO}_4(\text{s})$ .

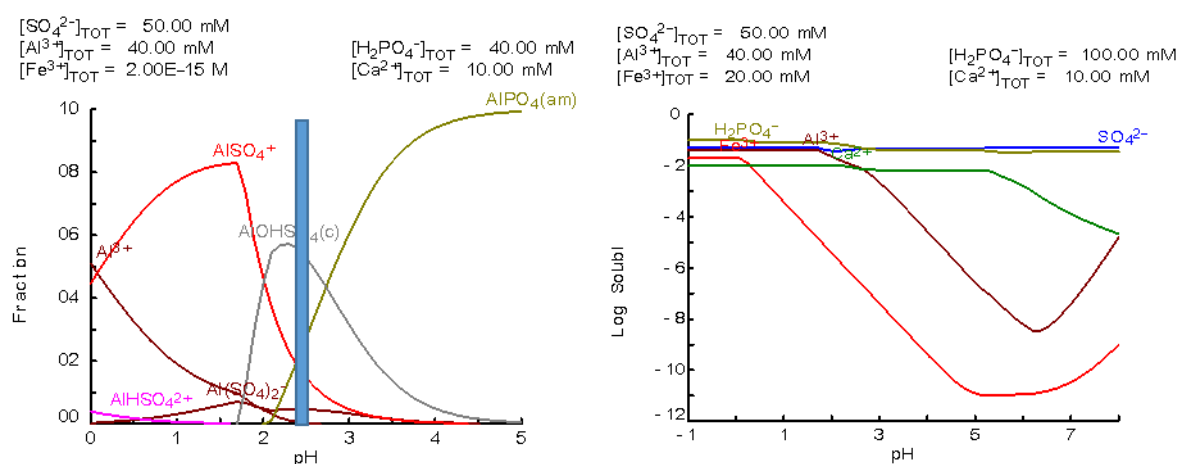


Figure 17. Solubility and fraction diagram of Ca(II), Fe(III) and Al(III) aqueous species with pH in acid media and  $[\text{PO}_4^{3-}] = 40 \text{ mM}$ . Thermodynamic data from MEDUSA database (Puigdomènech, 2010)

In terms of REEs recovering results, 3 samples (25, 27, and 28) from the 28 samples prepared had a total REE recovery percentage higher than 7%. As can be seen in Table 3, these samples were decreased in pH by using  $\text{H}_3\text{PO}_4$  and had an excess of stoichiometry of  $\text{PO}_4^{3-}$  as a consequence of the use  $\text{H}_3\text{PO}_4$  to reach at pH=2.3, 1.9 and 1.7. A summary of the conditions of the 3 samples is given in Table 13.

Table 13. Experimental conditions of the 3 samples with % total REE recovery > 7%

Reduction in pH with	SQ	pH	
<b>H<sub>3</sub>PO<sub>4</sub> (1.47 M)</b>	2,3	2,3	Sample25
	26,0	1,9	Sample27
	41,3	1,7	Sample28

The REEs and TE recovery percentages of samples 25, 27 and 28 are represented in Figure 18 and Figure 19. Global results for other samples are summarized in Annex B.

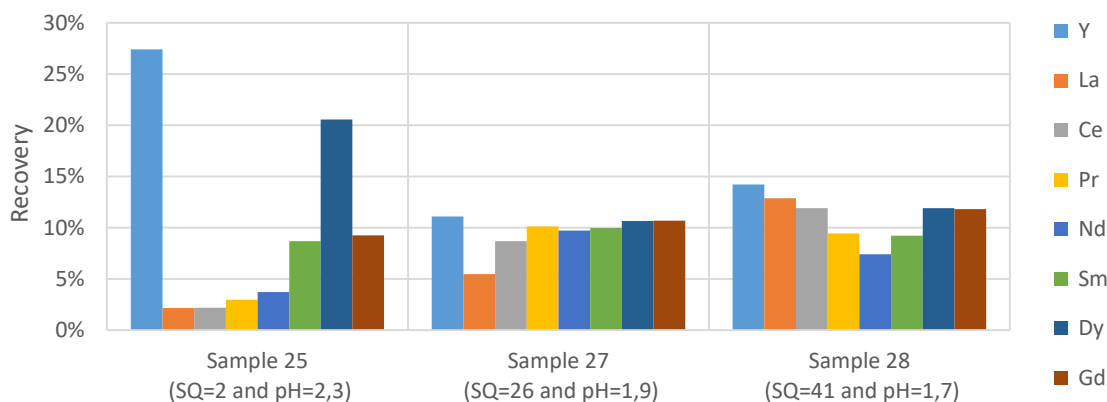


Figure 18. %REE Recovery in the samples 25, 27 and 28 described in Table 13.

An increase in the % REEs recovery is observed when SQ increase (sample 28). In this samples  $H_3PO_4$  were used and consequently the SQ increase to achieve the lower pH values. In terms of the transition elements the higher precipitation ratios were also observed for sample 28.

Results on Figure 18 and Figure 19 indicate the higher contribution of the excess of phosphate on the recovery efficiency of REE, however also the TE precipitation increases. As TE are present with concentrations up to three orders of magnitude than REE in the raw AMW and being a potential problem on the final purity of the solids recovered, the reduction of the removal ratios should be an objective. For this reason, the selection of the phosphate excess will be compromise between recovery efficiency of REE and presence of TE.

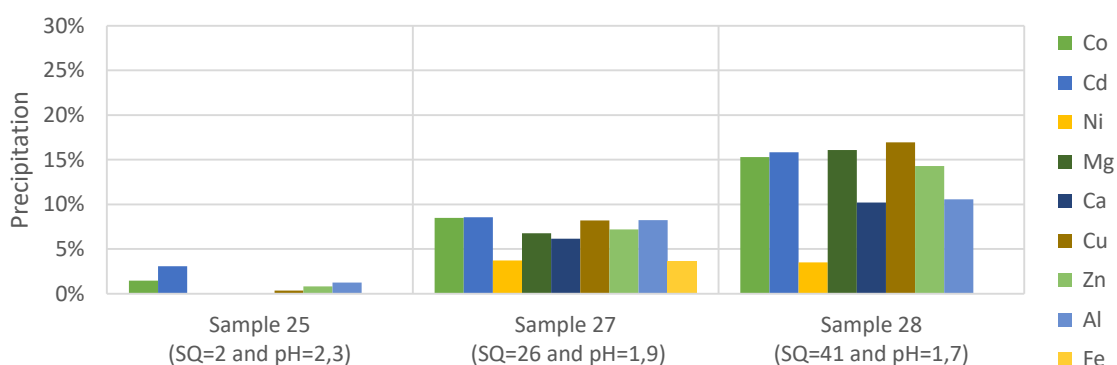


Figure 19. % Transition elements precipitation in the samples 25, 27 and 28 described in Table 13.

## Test 2. Evaluation of REE precipitation from TAMW using excess of phosphate

Molar ratio 40 (SQ=40) was selected to work in this experimental. Unlike Test 1, the pH points chosen to work in this test were pH=2.3 and pH=2.5. As it can see in Annex C, in the REE fraction diagrams, at pH= 2.3 and 2.5 most of REEs should be precipitated for a SQ=40. However, the REE recovery results in real AMW samples from this experiment have not exceeded 10% as shown in Figure 20.

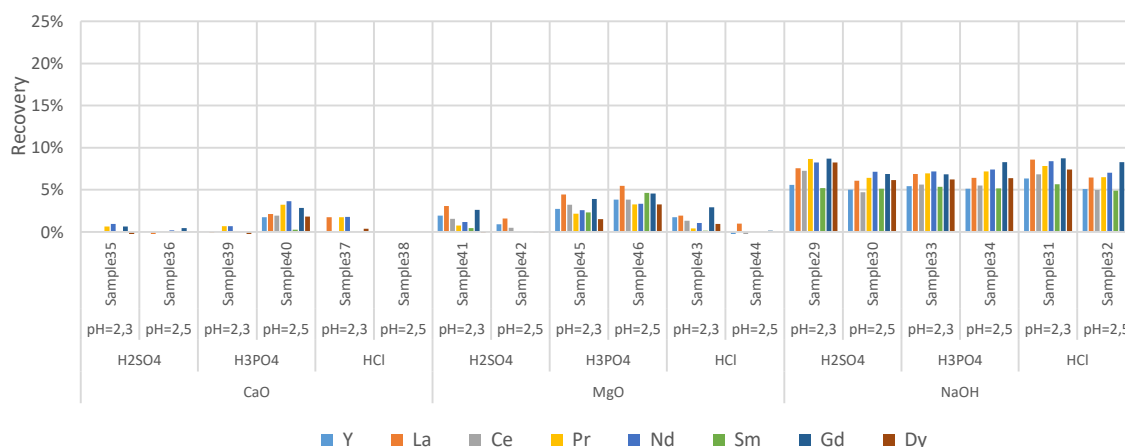


Figure 20. %REE recovery in the samples conditions described in Table 4.

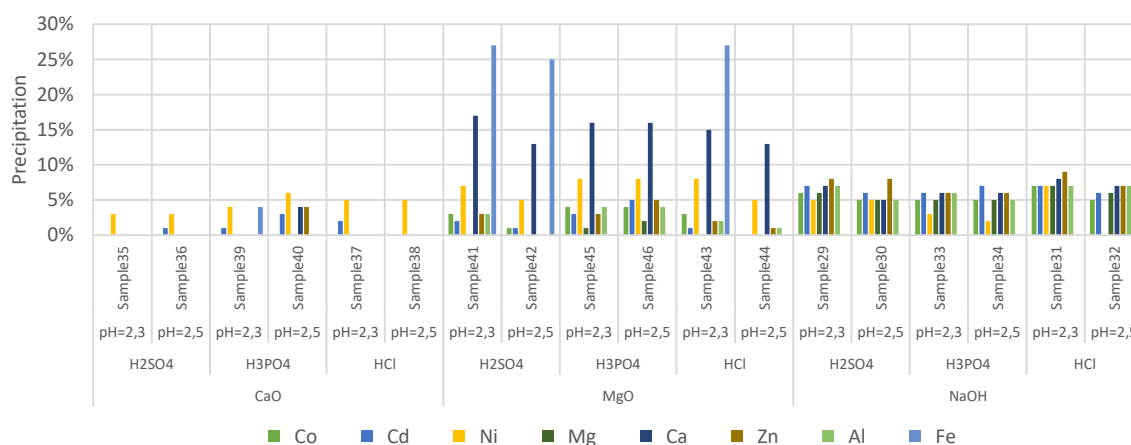


Figure 21. %Transition elements precipitation in the samples conditions described in Table 4.

As it is shown in Figure 21 AMW pre-treated with MgO have higher aluminium and iron precipitation in comparison to the samples pre-treated with CaO and NaOH. The percentage of REE recovery and the transition elements precipitation is in the same order in the samples pre-treated with CaO and MgO (around 8%).

Molar Fraction versus total phosphate concentration ( $-\text{Log}([\text{PO}_4^{3-}])$ ) diagrams were developed for different pH values to study the excess of phosphate needed for the REE precipitation. These diagrams showed that the  $[\text{PO}_4^{3-}]$  needed to obtain  $\text{REEPO}_4(\text{s})$  increase when the target working pH is lower Diagram a) and b)).

However, taking into account that the total initial concentration of Y (III) (as example) was 21.7  $\mu\text{mol/L}$  and total phosphate concentration was 2,7 mmol/L at pH=2.5, this value of total phosphate concentration is lower than 10 mmol/L (logarithmic values lesser than -2) and then it could not provide high recovery efficiencies of REE. This could explain the recovery rates of approximately 8% obtained in this Test 2.

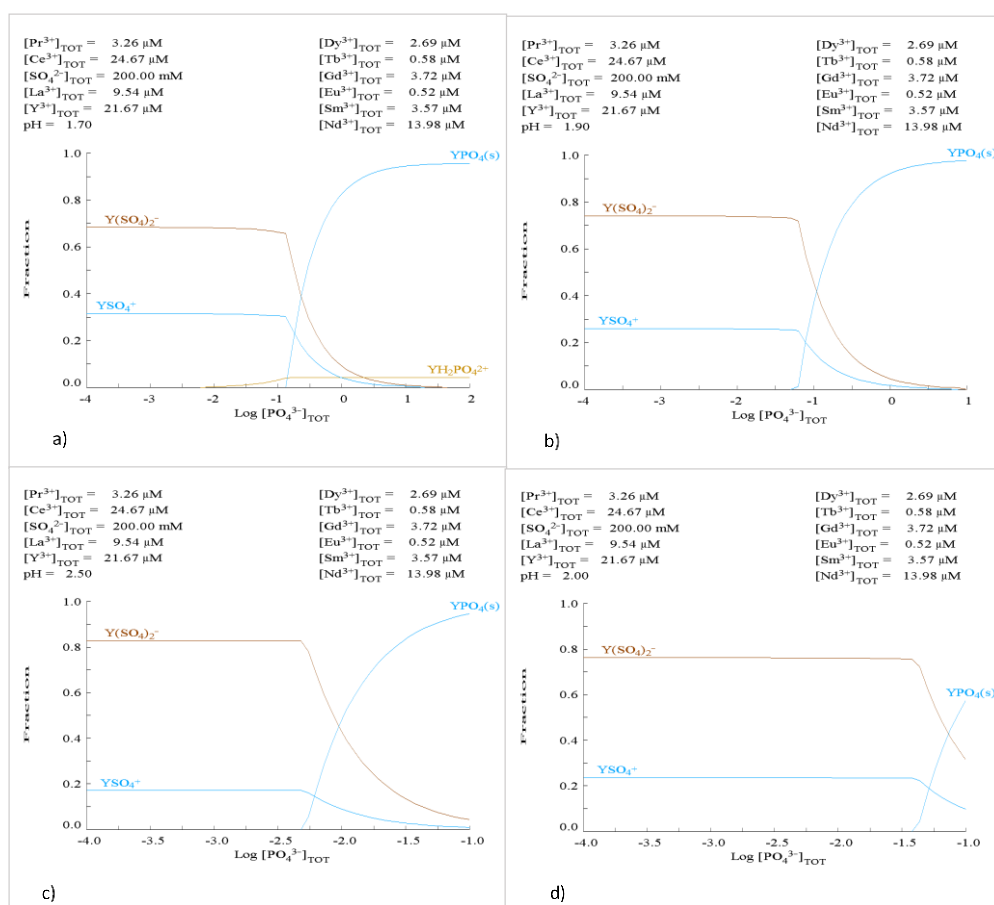


Figure 22. Yttrium Fraction- $\text{Log}([\text{PO}_4^{3-}])$  diagrams of La Poderosa acid mine water system in different pH: (a)) pH=1.7, (b))pH=1.9, (c))pH=2.5 and (d))pH=2. Thermodynamic data from MEDUSA database (Puigdomènech, 2010).

The limited removal ratios of REE, below 10% indicates that higher phosphate concentration is needed when working at low concentrations of REE ( $<11 \text{ mgREE/L}$ ), however the increase of phosphate also will promote and increase on the removal ratios of TE that could reduce the purity of the formed precipitated in terms of REE content.

### Test 3. Evaluation of Ce and La precipitation with phosphate solutions using synthetic acidic solutions.

The aim of this experiment is to study the precipitation behaviour of La and Ce in high concentration (25 mg/L) without interference of the others metals and a high molar P/REE ratio (SQ =40 and 100). For this reason samples of 50 ml of La and Ce 25mg/L were prepared.

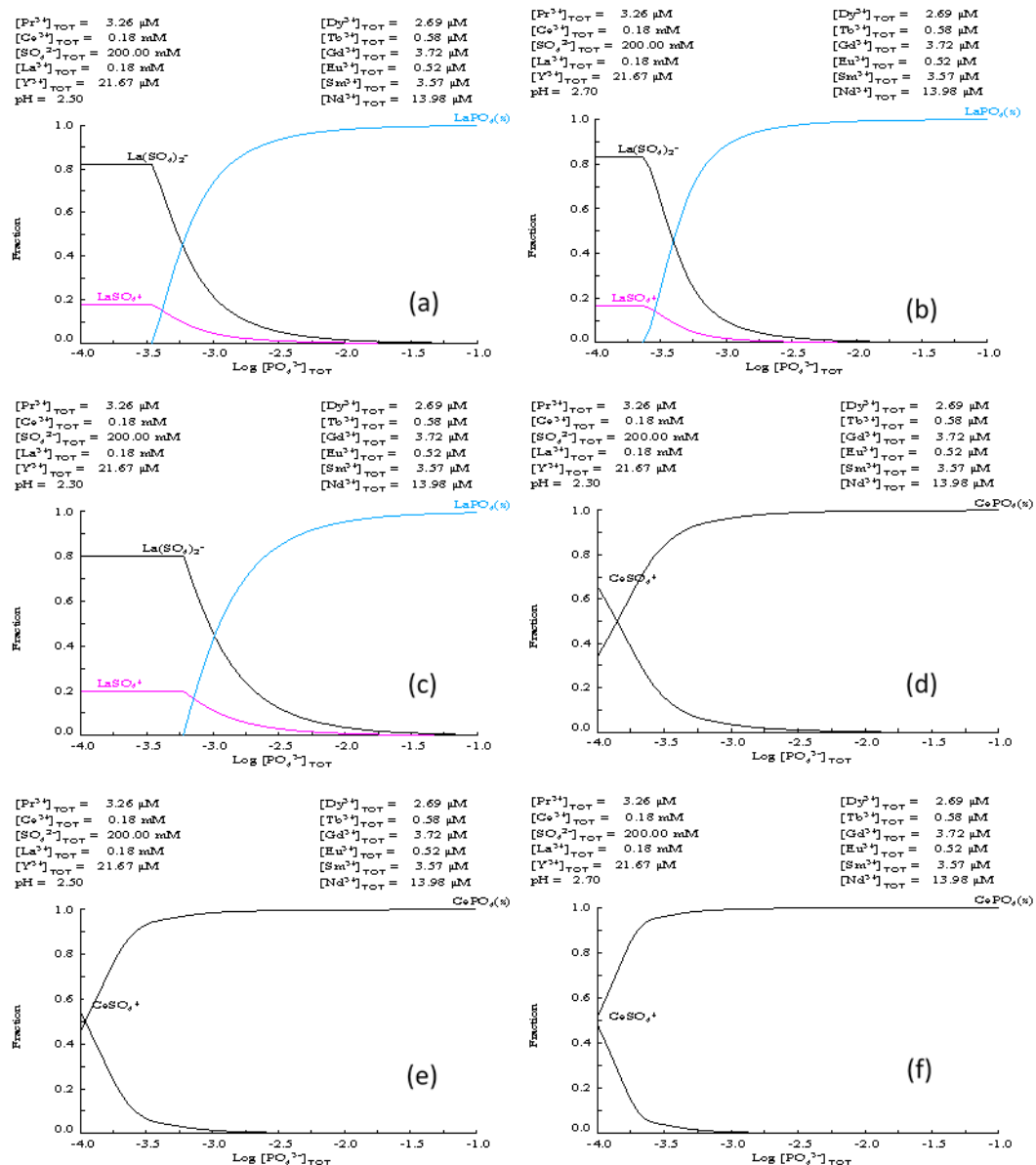


Figure 23. La and Ce Fraction– $\text{Log}[\text{PO}_4^{3-}]$  diagrams of La and Ce 25 mg/L and La Poderosa acid mine water system in different pH; (a)) La at pH=2., (b)) La at pH=2.7, (c)) La at pH=2.3, (d)) Ce at pH=2.3, (e)) Ce at pH= 2.5 and (f)) Ce at pH= 2.7. Thermodynamic data from MEDUSA database (Puigdomènech, 2010).

The molar Fraction–total phosphate concentration ( $\text{Log}([\text{PO}_4^{3-}])$ ) diagrams of La and Ce were calculated and they are shown in Figure 23. For a total initial concentration of La(III) and Ce(III) was 25 mgREE/L, equivalent to approximately 0.18 mmol/L, the value of total phosphate concentration for a molar P/REE ratio 40 was fixed at 7.2 mmol/L. This value is higher than 0.001 mol/L (logarithmic values higher than -3) and it could provide removal efficiencies higher than 99.9% according to Figure 23. For that reason pH values of 2.3 2.5 and 2.7 were chosen to work.

For both elements measured removal ratios were <99% for most of the SQ and pH values evaluated as could be seen in Figure 24.

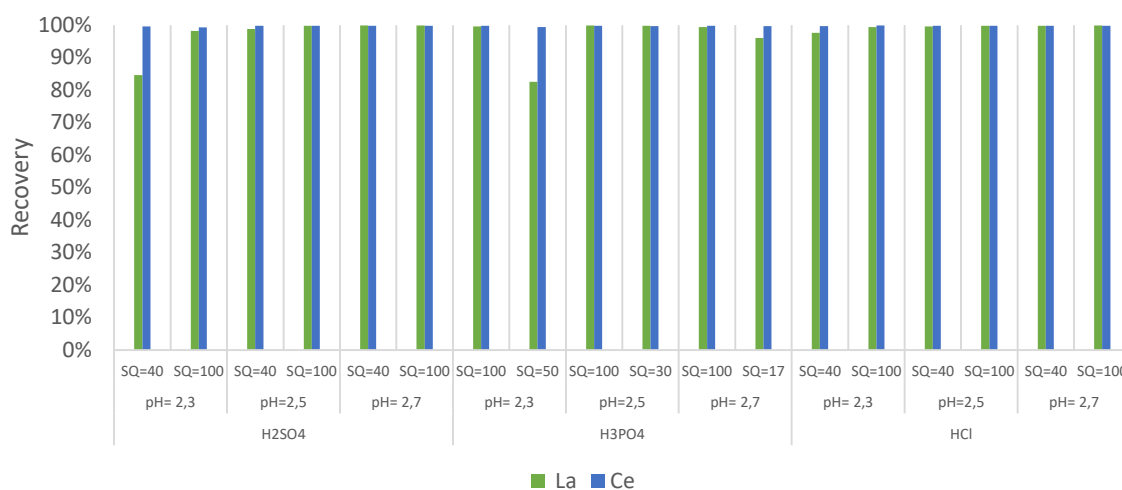


Figure 24. % La and Ce Recovery in samples prepared at pH= 2.3, 2.5 and 2.7 decreased with H<sub>2</sub>SO<sub>4</sub>, HCl and SQ=40 and 100 except the samples where were used H<sub>3</sub>PO<sub>4</sub> which have SQ= 17, 30, 50 and 100.

#### 4.4. Concentration REE from AMW by using ion exchange resins (S11706 resin) in column experiment.

A preliminary study on the possibility to concentrate REE in TAMW was carried out using ion-exchange resins. The main mechanism of the resin used is provided in Eq 4.



The breakthrough curves representing the evolution of the ratio  $C/C_0$  as a function of the treated effluent quantified as bed volume is shown in Figure 25. For simplicity REE and TE breakthrough curves are shown separately. Further details of these experiments are found in Annex D.

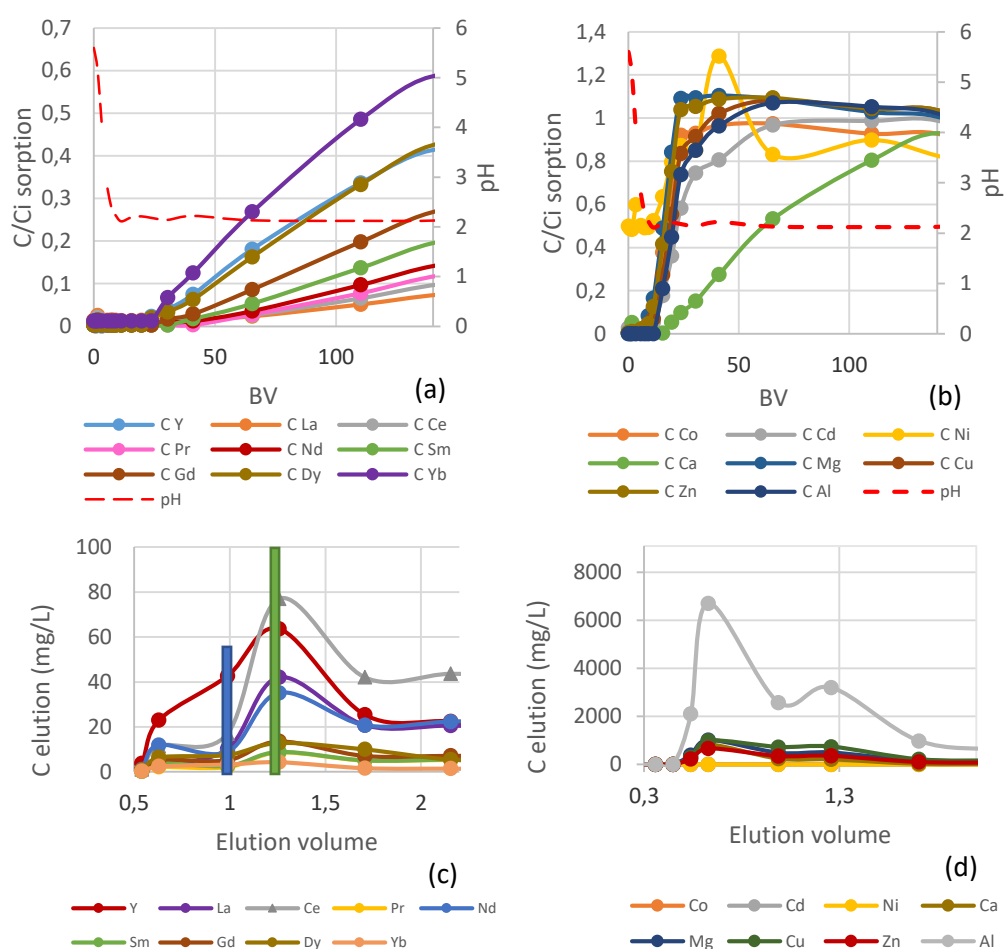


Figure 25. Column extraction results working with SPC11706 resin and AMW treated with NaOH: REEs sorption results (a)) and transition elements sorption results (b)); Elution curves carried out with  $\text{H}_2\text{SO}_4$  (10 M): REEs elution results (c)), Transition elements elution results (d)).



As Figure 25 shows, the REEs breakthrough starts from 35 BV ( $C/Co > 0.02$ ) and at the maximum volume tested (140 BV) saturation has not yet been reached ( $C/Co = 1$ ). Therefore the maximum sorption capacity for REE was not achieved along the experiment. Contrary for TE, the rupture occurs from 10 BV, with typical S shape curves and saturation is reached from 35 BV, except for Ca (II).

Elution of the loaded resin was carried out using concentrated sulphuric solutions and the elution curves are shown on the bottom part of Figure 22. Elution curves of REE and TE are shown separately. Elution of REEs and TEs occurs between 1.5-2 BV, and it is not possible to separate both groups. According to the ratio of the BV values for breakthrough and the elution curves concentration factor of 5 were achieved for TE and concentration factors higher than 20 could be achieved for most of the REE

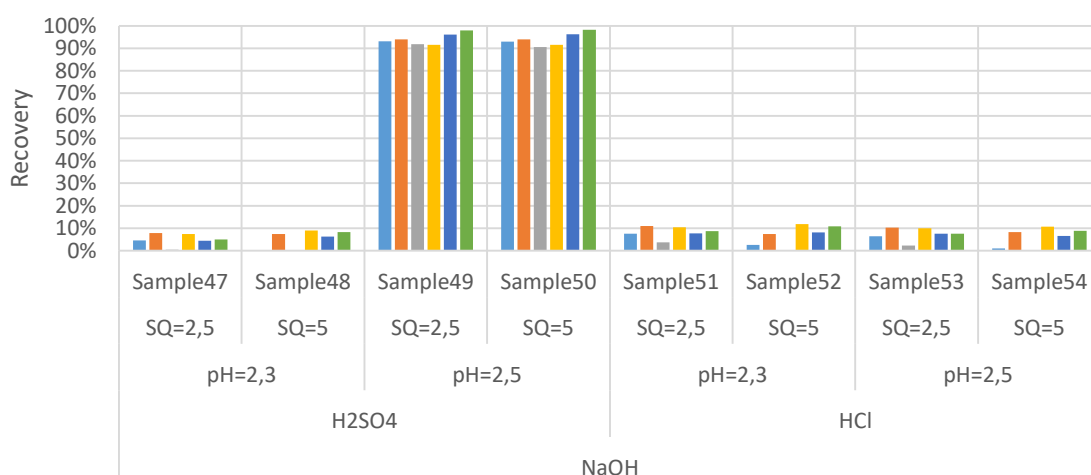
Then as specified in the methodology section (Test 4 and Test 5), the concentration of Y, La, Ce, Nd, Dy and Yb in the treated acid mine water (TAMW) was increased until reach concentration factors higher than 20. The two levels selected corresponds for given volumes indicated in Figure 25 (green mark for the Test 5 and blue mark for the Test 4). As is shown in the results of Test 3 and Test 2, the  $REEPO_4(s)$  precipitation did not show high % recovery at low concentration of REEs (Test 2) but working with high concentration (La and Ce 25 mg/L) in Test 3 the % recovery is of the order of 99 %. For that reason Test 4 and Test 5 were carried out.

#### **Test 4. REE recovery from synthetic solutions from concentrates generated in treatment of TAMW with ion-exchange resins (total REE concentration <130 mgREE/L)**

In this experiment the concentration factor was set up for an Elution BV of 1 in Figure 25 (blue mark). The concentrations reached in the samples are given in Table 6. This experiment was done at  $SQ=2.5$  and 5.

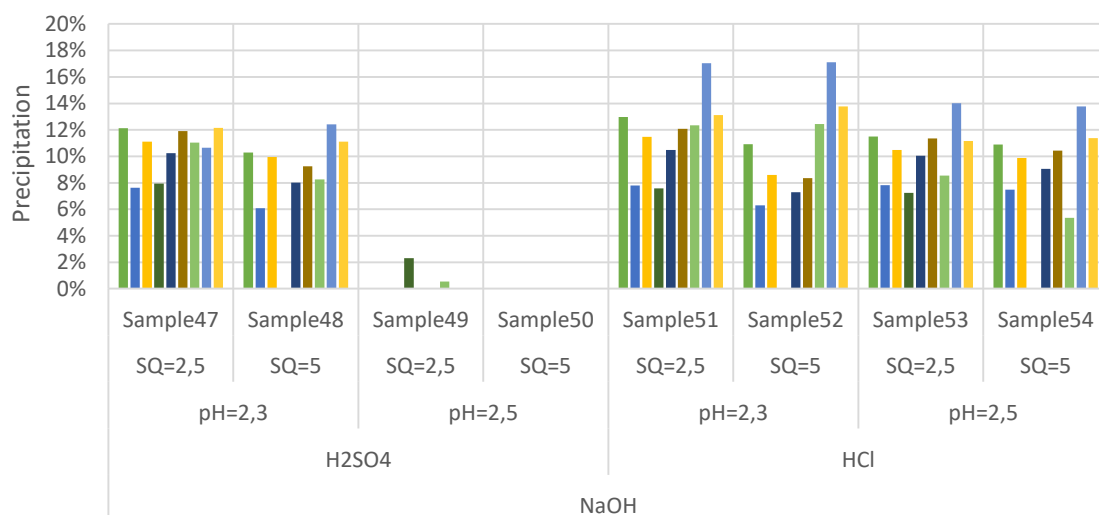
The samples which have the best results are Sample 49 and 50, it have the highest results of % REE recovery (e.g. La, Ce, Y with 94%, 92%, 93% respectively ) and the lowest % precipitation of transition elements.

The experimental condition of the Samples 49 and 50 were: AMW pre-treated with NaOH ,  $H_2SO_4$  was used to decrease the pH until 2.5 and  $SQ=2.5$  and 5. In order to compare the %REE recovery and the % transition elements precipitation of the samples 49 and 50 to the others samples Figure 26 shows the results of the samples pre-treated with NaOH also.



(a)

■ Y ■ La ■ Ce ■ Nd ■ Dy ■ Yb



(b)

■ Cu ■ Zn ■ Al ■ Fe ■ Ca ■ Mg ■ Ni ■ Cd ■ Co

Figure 26. (a))%REE recovery and b))%Transition elements precipitation in the experimental conditions describe in Table 7.

### Test 5. REE recovery from synthetic solutions from concentrates generated in treatment of TAMW with ion-exchange resins (total REE concentration <240 mgREE/L)

In this experiment the concentration factor was increased at it was set up an Elution BV of 1.25, green mark in Figure 25. Solution pH was adjusted by using  $H_2SO_4$  at pH=2.5, these conditions were chosen to work since the good results that had in Test 4 in the Samples 49 and 50. The molar P/REE ratio was SQ= 2.5 and (Table 9).

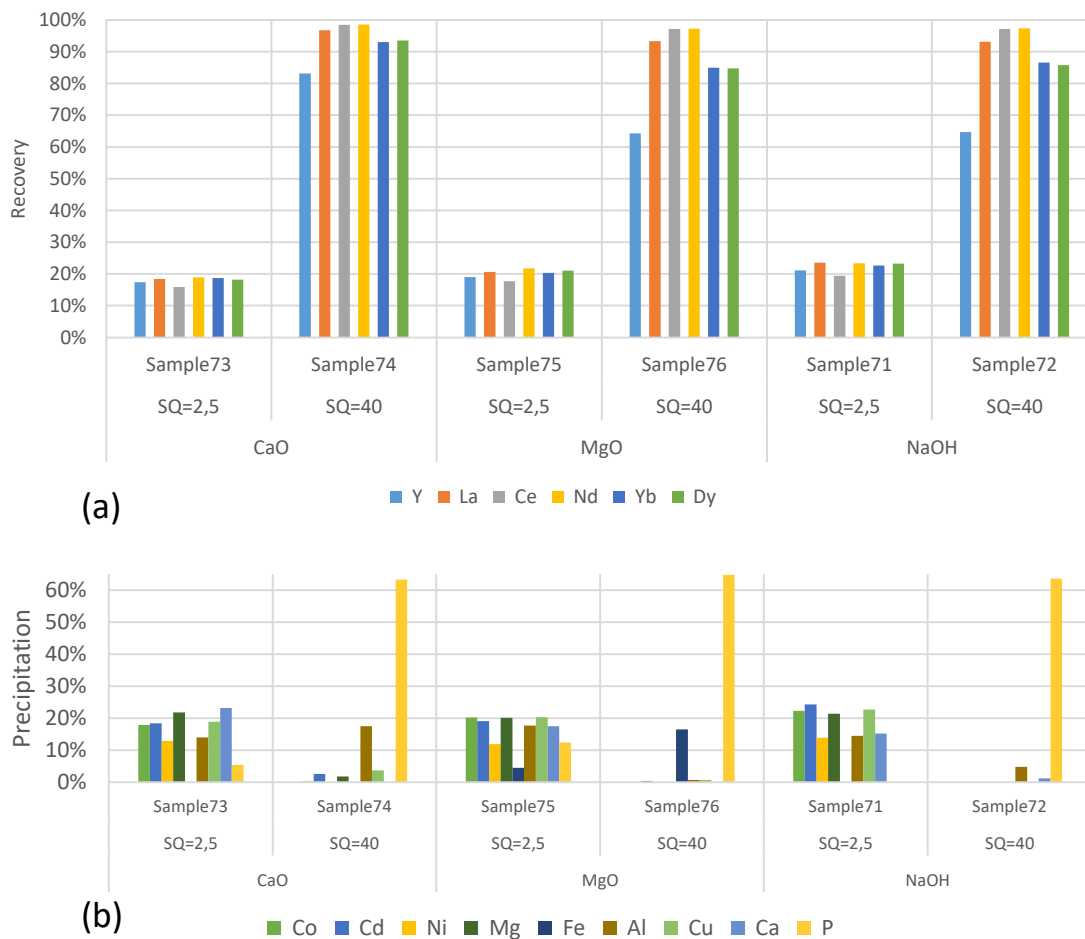


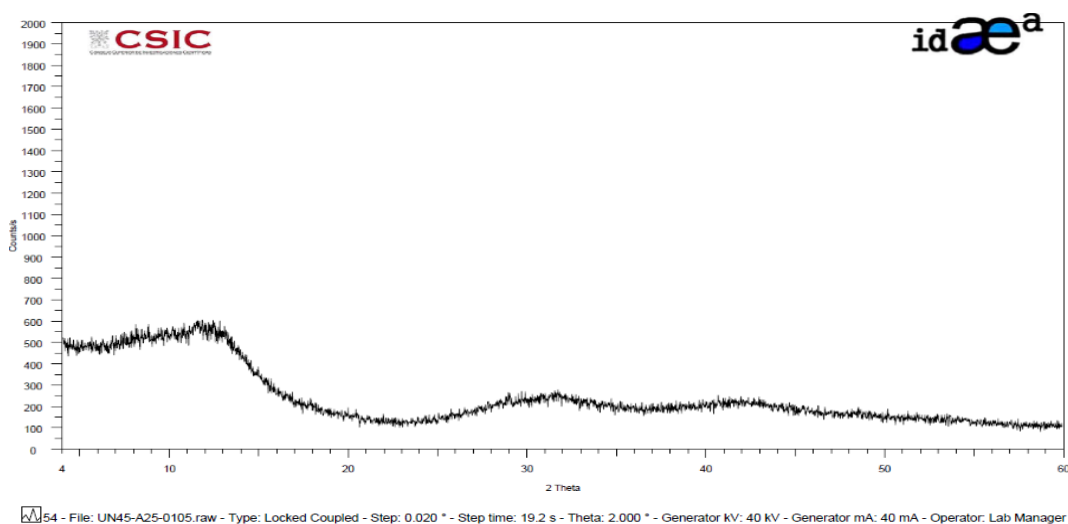
Figure 27.(a))%REE recovery ad (b)) %transition elements precipitation in the samples conditions described in Table 9.

As it is shown in Figure 27 the higher REE recovery achieved was for samples 74, 76 and 72, which were prepared with the higher molar ratios SQ=40. The increase of phosphate concentration increases the recovery ratio of REE. Furthermore, the recovery of TE were below 20%

On the other hand, as is shown in Figure 27 (b) % precipitation of P is represented and it is around %60. This means that the experiment could have worked at a molar ratio lower than 40. For that reason, optimization of molar ratio in these conditions could continue to be studied.

Finally, in this test unlike Test 4, REE precipitation is obtained in samples pre-treated with MgO and CaO also. This leads us to believe that phosphate precipitation works independently of the pre-treatment in samples with high concentration of REE and high molar ratio. However, for samples with low REE content and low molar ratio the working pre-treatment should be NaOH.

Recovered precipitates were analysed by XRD and in general samples analysed showed an amorphous form as it is shown in Figure 28 for one of the samples. For that reason samples were subjected to a heat treatment at 1050 ° C for 4h for its crystallization, the results is shown in Figure 29, 27 and 28.



*Figure 28. XRD result of the samples without heat treatment, which presented an amorphous.*

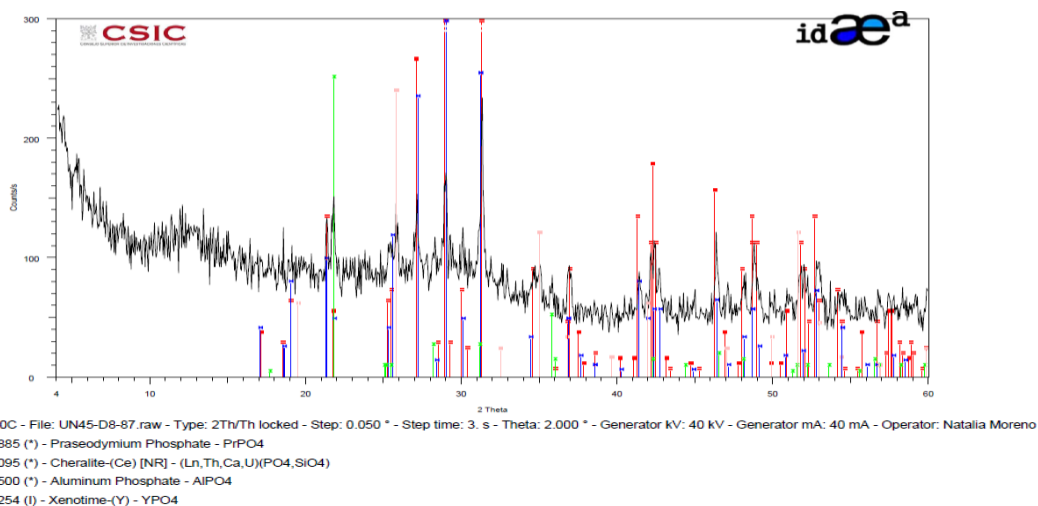


Figure 29. XRD result for the Sample72 (pre-treated with NaOH, reduced in pH with H<sub>2</sub>SO<sub>4</sub>, and SQ=40).

As it is shown in Figure 29, for the Sample 72 XRD results, the major mineral phases (red and blue) were Preseodymium Phosphates (PrPO<sub>4</sub>) and Cheralite (CePO<sub>4</sub>) in which the Ce could be replaced by other lanthanide, Th, Ca or U. Xenotime (YPO<sub>4</sub>), whit pink colour, is also notably present in the precipitated Finally, the other minor phase (green) identified was Aluminium phosphate (AlPO<sub>4</sub>).

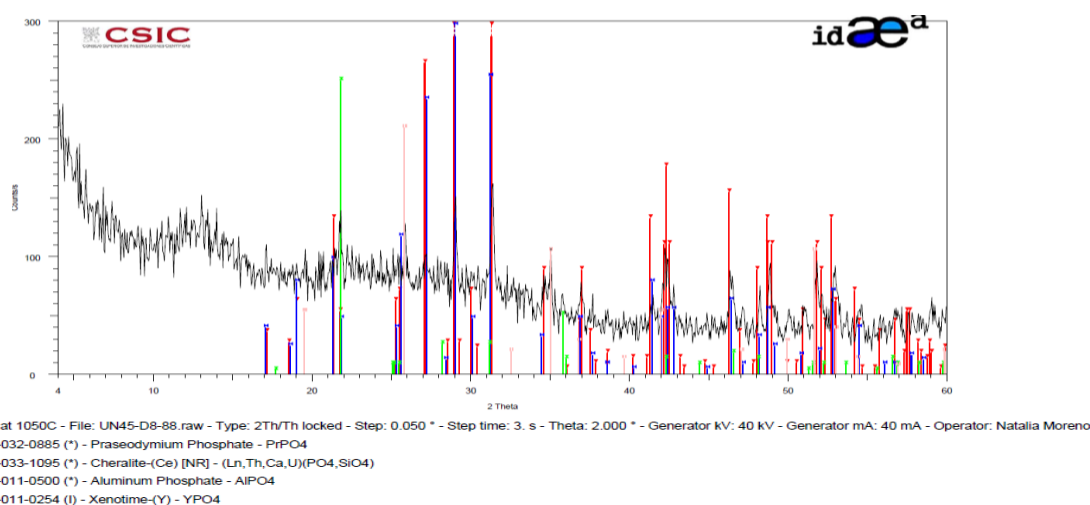


Figure 30. XRD result for the Sample 74 (pre-treated with CaO, reduced in pH with H<sub>2</sub>SO<sub>4</sub>, and SQ=40).

Sample 74 has similar results to sample 72 and the major phases were (red, blue and pink: Praseodymiun Phosphate (PrPO<sub>4</sub>) and Cheralite (CePO<sub>4</sub>), Xenotime (YPO<sub>4</sub>) and Aluminium Phosphate (AlPO<sub>4</sub>) was present as minor phase.

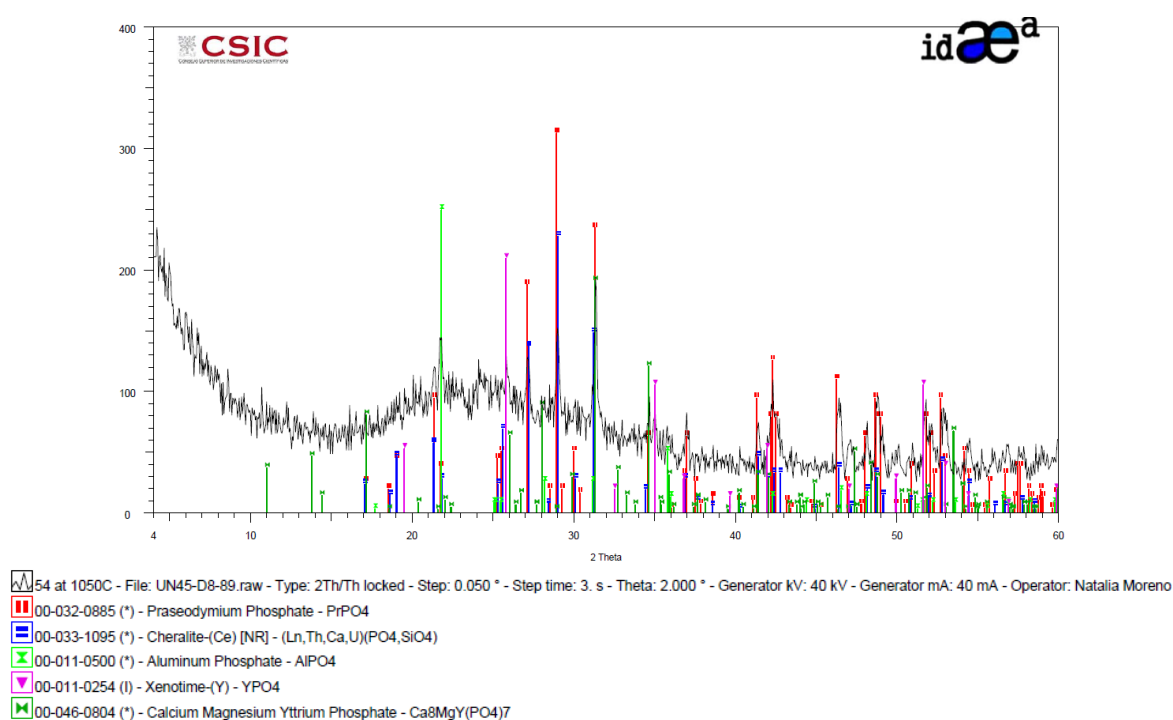


Figure 31. XRD result for the Sample 76 (pre-treated with  $\text{MgO}$ , reduced in pH with  $\text{H}_2\text{SO}_4$ , and  $\text{SQ}=40$ ).

Finally, sample 76 has similar results to sample 72 and 74 although it was also identified a Calcium Magnesium Yttrium Phosphate phase that is not present in the other samples.

## 4.5. Economical evaluation.

A simple preliminary cost evaluation in terms of reagents consumption and value of the recovered by products was carried out. Additionally to the ion-exchange process, were also the main cost is associated to reagents the main processes involved are pre-treatment stage typically carried out at industrial scale using limestone and air-oxidation and the precipitation reactions where the main operational cost is associated to reagents consumption. Cost of the main reagents used are summarized in Table 14. Values were provided by chemical companies providing reagents for laboratory scale. Then, results could not be used for being extrapolated at process scale level.

*Table 14. Market prices of the most representative reagent used and the indicative price of Ce*

Reagent	Price		Format	Source
<b>H<sub>2</sub>SO<sub>4</sub> (98%)</b>	1,12	€/l	25L	(Productos químicos industriales - Vadequímica)
<b>HCl (35%)</b>	1,08	€/l	25L	(Productos químicos industriales - Vadequímica)
<b>H<sub>3</sub>PO<sub>4</sub> (85%)</b>	4,40	€/l	25L	(Productos químicos industriales - Vadequímica)
<b>NaH<sub>2</sub>PO<sub>4</sub></b>	3,40	€/Kg	25Kg	(Productos químicos industriales - Vadequímica)
<b>NaOH</b>	1,54	€/Kg	25Kg	(Productos químicos industriales - Vadequímica)
<b>CaO</b>	0,44	€/Kg	25Kg	(Materiales Incera. Tienda online - Materiales Incera)
<b>MgO</b>	2,52	€/Kg	25Kg	(Productos químicos industriales - Vadequímica)
<b>Ce</b>	1870	€/Kg	100 g	(Merck Millipore. Productos químicos industriales y de laboratorio)
<b>La</b>	4320	€/Kg	25 g	(Merck Millipore. Productos químicos industriales y de laboratorio)
<b>Y</b>	8440	€/Kg	25 g	(Merck Millipore. Productos químicos industriales y de laboratorio)
<b>Nd</b>	3820	€/Kg	25 g	(Merck Millipore. Productos químicos industriales y de laboratorio)
<b>Yb</b>	22600	€/Kg	5 g	(Merck Millipore. Productos químicos industriales y de laboratorio)
<b>Dy</b>	12000	€/Kg	10 g	(Merck Millipore. Productos químicos industriales y de laboratorio)

With the results obtained in the experiments, calculations were performed for the case, use of sulphuric acid, where the higher recovery percentage (90% of REE) was achieved and with the minimum presence of TE. Then, it is not possible to discuss the economic difference in the use of the three different acids since HCl and H<sub>3</sub>PO<sub>4</sub> did not recover REE.

Regarding the use of NaOH, MgO and CaO as can be seen in Figure 16 the alkaline reagent that precipitates less REE is NaOH pre-treatment with precipitation of Fe 99%. MgO and CaO precipitate about 8% each of REE. The price (Table 14) of losses of REE (from 1870 to 22600 €/ kg) is very high compared to the savings given between using CaO and NaOH. Finally, MgO is more expensive than NaOH and gives more REE losses, so it is discarded as a reagent.

#### 4.5.1. The economic evaluation of the expenses to perform the project.

Three different categories have been considered to have an estimation of the total cost of the project: Materials and Reagents, Energy consumption and Human resources.

*Table 15. Reagents used during experimental phase*

	Amount (L)	Cost (€/L)	Total (€)
H <sub>2</sub> SO <sub>4</sub>	0,036	1,12	0,04032
H <sub>3</sub> PO <sub>4</sub>	0,01	4,4	0,044
HCl	0,01	1,08	0,0108
	Amount (kg)	Cost (€/kg)	Total (€)
NaOH	0,05	1,54	0,08
CaO	26,10	0,44	11,48
MgO	15,30	2,52	38,56
NaH <sub>2</sub> PO <sub>4</sub>	9,38E-02	3,40	0,32
La	1,00E-04	2030	0,20
Ce	1,00E-04	4320	0,43
Y	1,00E-04	8440	0,84
Yb	1,00E-04	22600	2,26
Nd	1,00E-04	3820	0,38
DY	1,00E-04	12000	1,20
<b>Sum</b>			<b>55,85</b>

*Table 16. Cost of sample's analysis*

	Amount of samples	Unit cost (euro)	Total cost (€)
ICP-MS/ICP-OES	112	21,13	2366,56
XRD	6	40	240
<b>Sum</b>			<b>2606,56</b>



Table 17. Energy consumption

	Consumption (kWh)	Unit cost (euro/kWh)	Total cost (€)
<b>Agitator</b>	280	0,15	42
<b>Oven</b>	130		19,5
<b>Vacuum</b>	15		2,25
<b>Sum</b>			63,75

Table 18. Cost of human resources

	Amount	Salary (euro/h)	Time(h)	Total cost (€)
<b>Engineer</b>	1	15	800	12000
<b>Supervisor</b>	2	40	40	3200
<b>Sum</b>				15200

In Figure 32 cost breakdown is provided, its shows the percentage of each category cost regarding the total cost of the project.

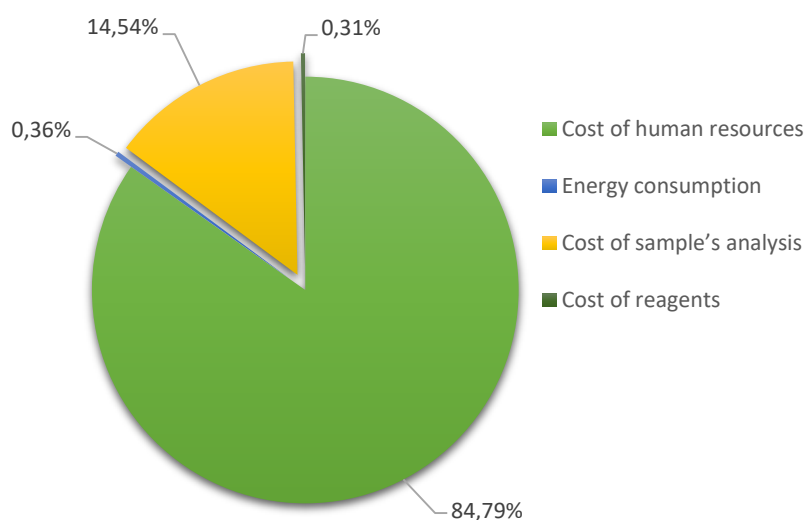


Figure 32. Cost breakdown.

## 4.6. Project planning

The overall planning of the entire project is summarized in the following Figure 33 and Table 19.

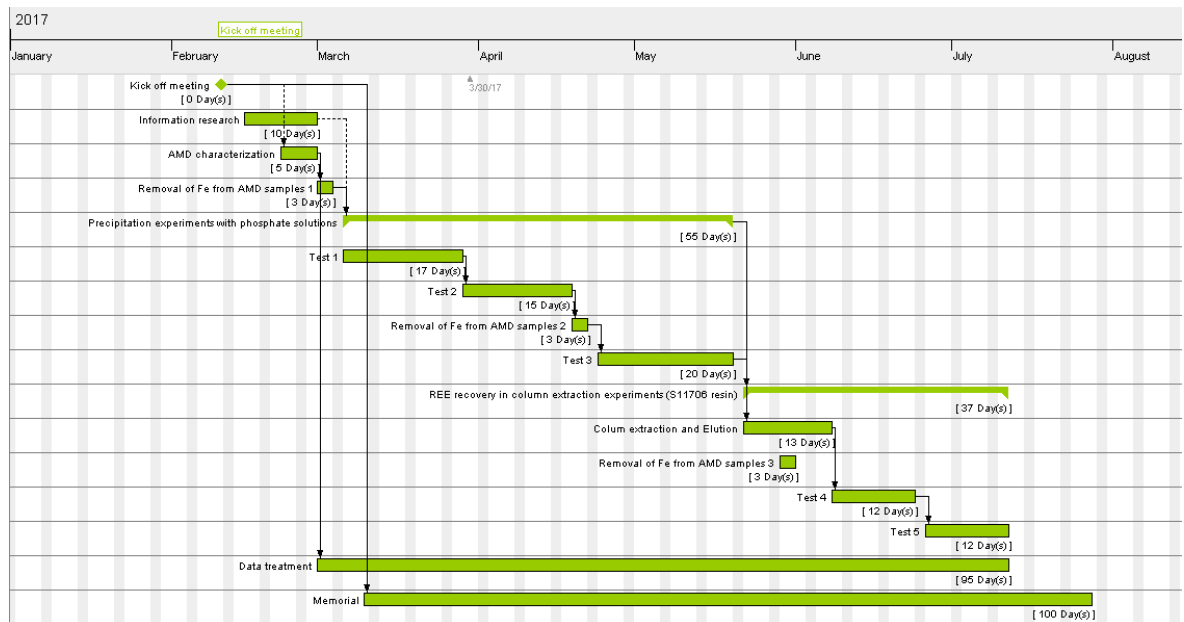


Figure 33. The Project planning

Table 19. Details of the project planning

Tasks			
Name	Begin date	End date	Duration
Kick off meeting	2/10/17	2/10/17	0
Information research	2/15/17	2/28/17	10
AMD characterization	2/22/17	2/28/17	5
Removal of Fe from AMD samples 1	3/1/17	3/3/17	3
Precipitation experiments with phosphate solutions	3/6/17	5/19/17	55
Test 1	3/6/17	3/28/17	17
Test 2	3/29/17	4/18/17	15
Removal of Fe from AMD samples 2	4/19/17	4/21/17	3
Test 3	4/24/17	5/19/17	20
REE recovery in column extraction experiments (S11706 resin)	5/22/17	7/11/17	37
Column extraction and Elution	5/22/17	6/7/17	13
Removal of Fe from AMD samples 3	5/29/17	5/31/17	3
Test 4	6/8/17	6/23/17	12
Test 5	6/26/17	7/11/17	12
Data treatment	3/1/17	7/11/17	95
Memorial	3/10/17	7/27/17	100

## 4.7. Environmental assessment/sustainability issues.

The project is purely experimental in laboratory scale. It is not valued within the scope of the project to make a comprehensive assessment of the environmental impact generated by the project both on a large scale and on a small scale. However, this project has as main objective to solve an environmental problem: the contamination of the water mine of La Poderosa. In addition, it was sought to obtain an economic benefit from this contamination: rare earth elements (REE). That is why if this project were carried out on a large scale the environmental benefits would be very large, since REE and transition elements could be separate and eliminate in the river water.

On the other hand, in this project it has been evaluated that the precipitate of  $\text{REEPO}_4(s)$  would be sent for its purification, obtaining two elements of economic interest: REE and  $\text{H}_3\text{PO}_4$ .

The good laboratory practice: The wastes generated during the experimental phase were disposed accordingly; the solutions with pH below 4 were disposed in the container for residual pH solution. The solution containing REE were saved separately for later uses. The solutions with concentration of transition elements were disposed in the respectively container.

## Conclusions

The experimental work developed on the evaluation of the potential routes to recover REE from acid mine waters from the Odiel River Basin provide the conclusions summarized below.

- In the evaluation of AMW pre-treatment for removal of Fe(III).
  - The alkaline agent which gives less REE losses is NaOH. However, in terms of the Fe elimination CaO, MgO and NaOH give a 99% of removal.
- In the evaluation of the rare earth recovery in the acid mine water by means of precipitation with phosphates.
  - REE precipitation in pre-treated AMW for the elution of Fe (III) by the use of phosphates is possible after a concentration of REE performed by column extraction.
  - The percentage of  $\text{REEPO}_{4(s)}$  precipitation is maximum with the highest of REE content and molar ratio. Under these conditions, the acid used to set the working pH which gives better results is  $\text{H}_2\text{SO}_4$  and the alkaline agent used in the pre-treatment (CaO, MgO or NaOH) do not have any influence.
  - In AMW samples with high REE content but low molar ratio the alkaline agent used in the pre-treatment have big influence since the  $\text{REEPO}_{4(s)}$  precipitation only take place in the sample pre-treated with NaOH. Furthermore, the acid used should be  $\text{H}_2\text{SO}_4$  also.
  - In AMW samples with low REE content is not possible to precipitate  $\text{REEPO}_{4(s)}$  in a pH range around 1.7-2.3 at room temperature and in a molar ratio range of 1 to 80.
  - Analysis of the precipitates by XRD generated indicated the formation of in general non-crystalline mineral phases.
  - Analysis of the precipitates, after being treated thermically at 1050°C, shown for most of the samples analysed the presence of Preseodymium Phosphates ( $\text{PrPO}_4$ ) and Cheralite ( $\text{CePO}_4$ ) where Ce could be replaced by other lanthanide, Th, Ca or U and Xenotime ( $\text{YPO}_4$ ) as major phases. However, also were identified as minor phase aluminium phosphate ( $\text{AlPO}_4$ ) and Calcium Magnesium Yttrium Phosphate.

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