Recovery of Rare Earth Elements from Acidic Mine Waters by integration of a Selective Chelating Ion-Exchanger and a Solvent Impregnated Resin

M. Hermassi[a,c,*], M. Granados[b], C. Valderrama[c], C. Ayora[d] and J. L, Cortina[c,e]

[a]Thermochemical Energy Conversion Laboratory, Department of Applied Physics and Electronics, Umeå University, SE-90187 Umeå, Sweden

[b]Analytical Chemistry and Chemical Engineering Department, University of Barcelona, V. Diagonal 647, 08028, Barcelona, Spain

[c]Chemical Engineering Department, East Barcelona Engineering School, Barcelona TECHUPC, Eduard Maristany 10-14 (Campus Diagonal-Besòs), 08930 Sant Adrià de Besòs, Spain

[d] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18, 08034 Barcelona, Spain

[e]Water Technology Center CETaqua, Carretera d'Esplugues 75, 08940 Cornellà de Llobregat, Spain

(hermassi.mehrez@gmail.com)

Abstract

A polymeric ion-exchange resin, incorporating methyl-amino-phosphonic (TP260) functionalities, and a solvent impregnated resin (SIR) incorporating tri-methylpentylphosphinic acid (TP272), were evaluated for the selective separation of Rare Earth Elements (REE) from Transition (TE), post -Transition (PTE), and Alkaline Earth (AE) Elements in acidic mine waters (AMW). The influence of the functional groups nature and the acidity dependence were studied and their effects on efficiencies for REE removal and separation from TE/PTE were analysed Both resins provided good separation factors of REE from TE/PTE by acidity control of the treated effluent once Fe(III), the major component in AMW, had been removed by precipitation. The TP272 resin, containing tri-methylpentylphosphinic acid (Cyanex 272) onto the polymeric network, showed higher affinity towards Heavy REE (HRRE) than for Light REE (LRRE) by acidity control (pH>4).

Higher pre-concentration factors were achieved for TP272 impregnated resin (e.g., 20-30) in comparison with the TP260 phosphonic resin (2-5), as the pH extraction window is in the moderate pH region (1 to 5). The integration in series of both resins could be used to separate and recover HREE and LREE from TE/PTE from AMW generated concentrates could be used to recover REE as secondary resources for the clean energy technology industry.

Keywords: REE, aminophosphonic; aminophosphinic; ion-exchange resin; Cyanex 272; TP272; TP260

1. Introduction

Rare Earth Elements (REE) have been used in traditional sectors as metallurgy, petroleum, and textiles. Nowadays are also becoming indispensable and essential in high-tech industries, such as clean energy technologies, superconductor materials, batteries, plasma televisions, optical fibbers or military industry [1]. In fact, they are widely used in applications such as lasers, satellite communications, or radar systems, and consequently, they are considered strategically important [2, 3]. Some of them are also crucial in automotive catalytic convertors and petroleum cracking catalysts. REE represents a group of elements with a common electron configuration, that includes two pseudo lanthanides (Sc and Y) and 14 lanthanides. They possess large ionic radii and oxidation (III) states. Among the REEs, the elements with atomic numbers ranging from 57 (La) through 64 (Gd) are categorized as Light Rare Earth Elements (LREEs) while elements from 65 (Tb) through 71(Lu) are classified Heavy Rare Earth Elements (HREEs). According to the similarities in their properties, Sc is classified as LREE and Y as HREE.

Most of the REE are extracted from minerals such as bastanite, monazite, and xenotime, which are the main commercial sources of REE [4]. Another important source of REE are ion-adsorption clays. Deposits of those clays were originated by natural leaching as an effect of high temperatures and acid waters. Some of the most important deposits can be found in Ganzhou, Jiangxi, China [5]. On the other hand, it is difficult to find new primary sources of REE, and it is estimated that the increasing demand of REE will exceed the world's supply in a few years. In the European Union, without primary resources, REE have been included in the critical raw material list Elements List [6]. In this scenario, research on secondary sources of REE and production methods is essential [7].

Mining activity in the Iberian Pyrite Belt has led to the accumulation of a large number of abandoned pits, and dumps containing AMW [8, 9] along the basin of the main rivers of the area, such as Tinto or Odiel [10, 11]. AMW are characterized by a low pH (1–3), and high concentration levels of metal (e.g., Fe, Al, Zn, Cu) and non-metal (e.g., As, Se, Sb) ions. REE ions have been found in AMW at concentrations up to 1000 times higher than those of continental waters [12, 13].

Managing AMW is, by far, the largest sustainability challenge of the mining industry, due to the huge volumes and the high cost of treatments. AMWs are usually treated with lime or limestone, to increase the pH and precipitate metal ions as hydroxides [14, 15]. However, the high consumption of alkaline agents, accompanied by a water-rich sludge mainly composed of Fe, Al, and lesser amounts of Ca, Zn, Cu, make this process not economically viable [16]. The need to recover critical elements, combined with initiatives based on circular economy approaches, may help to overcome the traditional economic barriers, and to address solving a severe environmental problem [17]. This new strategy is based on considering AMW as potential secondary resource for REE and some TE (Zn, Cu) [18, 19], and developing low cost treatment options in order to recover valuable REE and TE, as well as promoting water reuse in the mining industry [20]. The development of a novel process should focus on the selective recovery of such valuable elements, which are present at low concentration values [12, 21]. Efforts addressed towards the integration of membrane technologies to treat AMW streams as reverse osmosis

[22], nanofiltration [23] or electrodialysis [24] are facing the problem of limited separation and concentration factors.

Nowadays, the hydrometallurgical processing of the REE, dealing with relatively high concentration levels in the processing circuits, mainly uses solvent extraction (SX) [25-27]. Ion exchange (IX) is also utilized, but to a lesser extent [28-30]. However, it is a need for more selective metal extraction reagents for SX and ion exchange resins [31-35] for new challenges as the recovery and separation of REE from transition elements, typically present on the processing streams, at relatively low concentrations (e.g. mg/L) [36-38].Taking benefit of the know-how developed on SX circuits of REE, different IX resins containing phosphonic and aminophosphonic groups have been identified as potential materials for hydrometallurgical processing [39, 40]. However, there is a lack of IX resins containing some selective extractants used on SX circuits. In this sense, the use of solvent impregnated resins, such as Lewatit TP272, which contains Bis-(2,4,4- trimethylpentyl-) phosphinic acid (Cyanex 272), could be an alternative. Cyanex 272 is a weaker acid than the two more widely used acidic organophosphorous extractants for REE solvent Extraction circuits, Di-ethylphosphoric acid (DEHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA). Cyanex 272 has higher acidity constant than DEHPA and EHEHPA [41] thus potentially allowing for lower acid requirement for regeneration.

The main objective of this work was to study the selective separation of REE from TE and post -TE (PTE) with Lewatit TP-260, a cation exchange resin with chelating aminomethylphosphonic acid groups, and Lewatit TP-272, a solvent impregnated resin containing bis-(2,4,4-trimethylpentyl-) phosphinic acid, and to evaluate the integration of the two resins to produce rich streams of REE or groups of REE (HREE and LREE) and TE/PTE. To this end, different experiments were performed, using batch and column configurations, to study the extraction and re-extraction performance of both resins evaluating the effect of pH as the main parameter to develop a pH-swing concept.

2. Experimental methodology

2.1 Reagents materials and solutions

Lewait TP260 is a cation exchange resin with a cross-linked polystyrene matrix, which contains amino methylphosphonic acid. Lewatit TP272 is a solvent impregnated resin with a cross-linked polystyrene matrix which contains Bis-(2,4,4-trimethylpentyl)-phosphinic acid (Cyanex 272). Both resins were provided by Lanxes (Germany) and were conditioned before used as described elsewhere [42]. Analytical grade reagents, such as NaOH, HCl and H_2SO_4 were used to adjust pH of working solutions. H_2O_2 30%(v/v) (Panreac) was used to oxidize Fe(II) to Fe(III) in AMW samples. All solutions were prepared using Milli-Q (Merck-Millipore) water quality.

2.2. Acidic mine water samples: sampling and pre-treatments

Acidic mine water samples were collected in Nueva Poderosa Mine, in the Tinto river basin (Huelva, Spain). AMW samples presented low pH (between 1.8-2.4), and yellow colour, due to high concentration of iron.

Iron removal from acidic mine water samples. Iron present in AMW, either as Fe(II) or Fe(III), was removed following a procedure proposed by Ayora et al. [9]. Briefly, in a first stage Fe(II) is quantitatively oxidized to Fe(III) (>99,5%) by using H_2O_2 solutions, and then Fe(III) is precipitated by using NaOH. Volumes of 2-3 L of AMW were treated with an excess of H_2O_2 30% (v/v) and then equilibrated overnight, until the pH of the solution kept constant. Then, NaOH solution 4% (w/w) was added to the solution until pH reached a value of 3.7. This value, according to previous studies, assures a quantitative removal of Fe(III) from AMW as Schwertmannite, while minimum removal of TE, REE, and Al(III) occurs. Then the samples were left under magnetic stirring for 24 hours (Ovan, Multimix D). After completion of this stage, the solution was filtered by using quartz containing columns (15 cm diameter and 30 cm length). Filtration was performed using gravity (down flow mode). Filtered water samples of each treatment, named treated AMW (TAMW), were collected and stored for further sorption and precipitation trials. Composition of the

TAMW samples was determined by ion chromatography, and ICP-OES and ICP-MS. pH was measured by using a combined pH electrode (Crison).

2.3 REE concentration experiments by ion exchange and solvent impregnated resins: batch experiments

Batch equilibrium sorption experiments were carried out using standard methodology described elsewhere [42]. Weighted amounts of dry resin samples were shaken overnight with given volumes of aqueous solutions TAMW. All the experiments were carried out at room temperature, 22±1ºC. metal ions were determined by ICP-OES and/or ICP-MS.

Effect of acidity on metal extraction. TP272 (0.2 g) samples were added to 20 mL acidic mine water TAMW. Acidity was adjusted, with log[H^+] ranging from -4 to 0.5, and equilibrated for 24 h. On the other hand, TP260 (2 g) was equilibrated for 24 h with 50 mL of TAMW sample at different acidity values, with log[H^+] values ranging from -2 to 1.

2.4 REE concentration experiments by ion exchange and solvent impregnated resins: column experiments

Two Omnifit glass columns 100 cm long and 1.5 cm in diameter, filled with TP272 and TP260 resins respectively were used. A Peristaltic pump (Minipuls 3, Gilson MP) was used to pump the different TAMW solutions through the column. A fraction collector (FC 204 Gilson) was arranged at the exit of the column. Before the experiment, water was circulated at a flow rate of 1mL/min through the column for 2 h. Then, TAMW at pH=2.1 was circulated at 1mL/min through the column and 10 ml samples were collected with a fraction collector. Finally, the elution of the metals adsorbed was performed with 10 M H_2SO_4, which was passed through the column at 0.25 mL/min and different fractions were also sampled with the fraction collector. Collected samples from the loading and regeneration runs were analysed by ICP-OES and ICP-AES to determine the breakthrough curves and elution curves as a function of the treated bed volumes of TAMW or elution solution, respectively.

2.5 Analysis of aqueous solutions

Aqueous samples were collected from the different batch and column experiments. Measurement of pH was made with a Crison® pH-metter equipped with a Crison® glass electrode, and calibrated with buffer solutions of pH 7 and 2. Filtered samples using 0.22 µm pore size filter were acidified with HNO_3 for analysis of major and trace elements. Major cations (Ca, Mg, Zn, Fe, Al, Mn, Si) and total S were measured by ICP-AES (Perkin-Elmer® Optima 3200 RL) and trace metals (Ni, Cd, Co, Pb) and REE by ICP-MS (Perkin-Elmer®Sciex Elan 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 REE. The analytical precision error was estimated to be approximately 5% for ICP-AES and 4% for ICP-MS measurements. Two AMD laboratory standards supplied by P. Verplank (USGS) were also analysed for REE accuracy, giving deviations lower than 5% of the recommended values. Assuming all S to be sulphate, the charge balance error was usually less than 5%.

3. Results and discussion

3.1. Characterization of the Poderosa Mine AMW and removal of Fe(II)/Fe(III) from AMW

The REE, TE and Al(III) concentration values of a representative AMW sampled along two different campaigns in the Poderosa mine are summarized in Table 1. It is worth to mention the high content of Fe, 1.5 g/L, and the pattern for the concentrations of REE, which are consistent with those observed in previous field scale remediation studies in similar AMW from the Rio Tinto Basin [9]. 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 (La, Ce, Gd, Y, Nd). According to this classification the main effort on this study was focussed on the two last groups. In the case of TE and Al(III), the higher concentrations are associated to Fe, with 1.5 g Fe/L, followed by a group of elements between 100 and 380 mg/L (Al, Mg, Ca, Cu and Zn) and a group of elements below 2 mg/L (Co, Ni, and Cd, among others).

Table 1. REE, TE and PTE concentrations in a representative AMW sample, and removal percentage after treatment with H_2O_2/NaOH

TE/PTE	[TE] i (mg/L)	% Removal	LREE	[LREE] (mg/L)	% Removal	HREE	[HREE] (mg/L)	% Removal
Fe	1535±30	>99.9%	Eu	0.09±0.01	<1%	Lu	0.01±0.002	<1%
Al	375±20	7%	Pr	0.44±0.04	<2%	Tm	0.02±0.002	<2%
Ca	161±23	<1%	Sm	0.51±0.04	<1%	Ho	0.07±0.002	<1%
Mg	1826±25	<1%	Gd	0.54±0.07	<2%	Dy	0.40±0.04	<3%
Cu	111±15	<3%	La	1.21±0.2	<1%	Tb	0.09±0.01	<1%
Zn	101±15	<1%	Nd	1.94±0.3	<1%	Yb	0.10±0.02	<2%
Co	1.4±0.2	<1%	Ce	3.28±0.4	<3%	Er	0.15±0.02	<1%
Cd	0.4±0.05	<2%						
Ni	0.3±0.04	<1%						
Hf	0.40±0.04	<1%						
Y	1.79±0.2	<2%						

The removal (%) of both TE, Al(III) and RRE after oxidation of Fe(II) to Fe(III) by H_2O_2, followed by alkaline treatment with NaOH to pH 3.7, and filtration of the sample through a quartz sand filter, is also listed in Table 1. The losses of the most representative REEs are below 3%. In relation to iron removal the treatment was very effective, providing removal ratios >99.9 %. However, in terms of aluminium removal the procedure led to a reduction of the total aluminium concentration of 7%. The analysis of the generated brown to orange sludge by SEM-EDAX and XRD identified the presence of schwertmannite. The main effect of the treatment is the reduction of the total iron concentration to about 1 mg/L, with removal ratios of REEs below 3%. These results agree with the studies by Ayora et al. (2016) [9] about the behaviour of REE in AMW when pH was adjusted below 4, when schwertmannite precipitation occurs. They reported that no REE were lost in schwertmannite precipitates. However, at pH above 4.7, Al(III) precipitated as basaluminite (>95%) and REE co-precipitates (<90%). Therefore, to achieve maximum Fe(III) removal with minimum losses of RRE it is proposed to treat AMW with alkali to pH below 4.0 [43].

3.2 Separation of REE from TE and PTE from TAMW by using ion exchange resins: identification of the separation conditions

The separation factors of metal ions with ion exchange resins (e.g., phosphonic chelating and phosphinic impregnated) are mainly controlled by: i) the acidity of the solution; ii) the presence of complexing ions in the solution (e.g., HSO_4^-, Cl-, $H_2PO_4^-$), and iii) the acid-base properties of the resin functional acid groups (-POOH). As AMW are rich solutions in sulphate ions, sulphuric acid was used to adjust the acidity of the solutions, and thus both REE, TE (M^{+3}/M^{+2}) and Al (III) were partially complexed with SO_4^{2-} ions, typically forming MSO_4^+/MSO_4, but in some cases could be present as $M(SO_4)_2^-$/$M(SO4)_2^{-2}$. The extraction efficiency (%) as a function of proton concentration (in logarithm form) for TP260 and TP272 are shown in Figures 1 and 2, respectively; data are shown separately for REE, TE and Al (III).

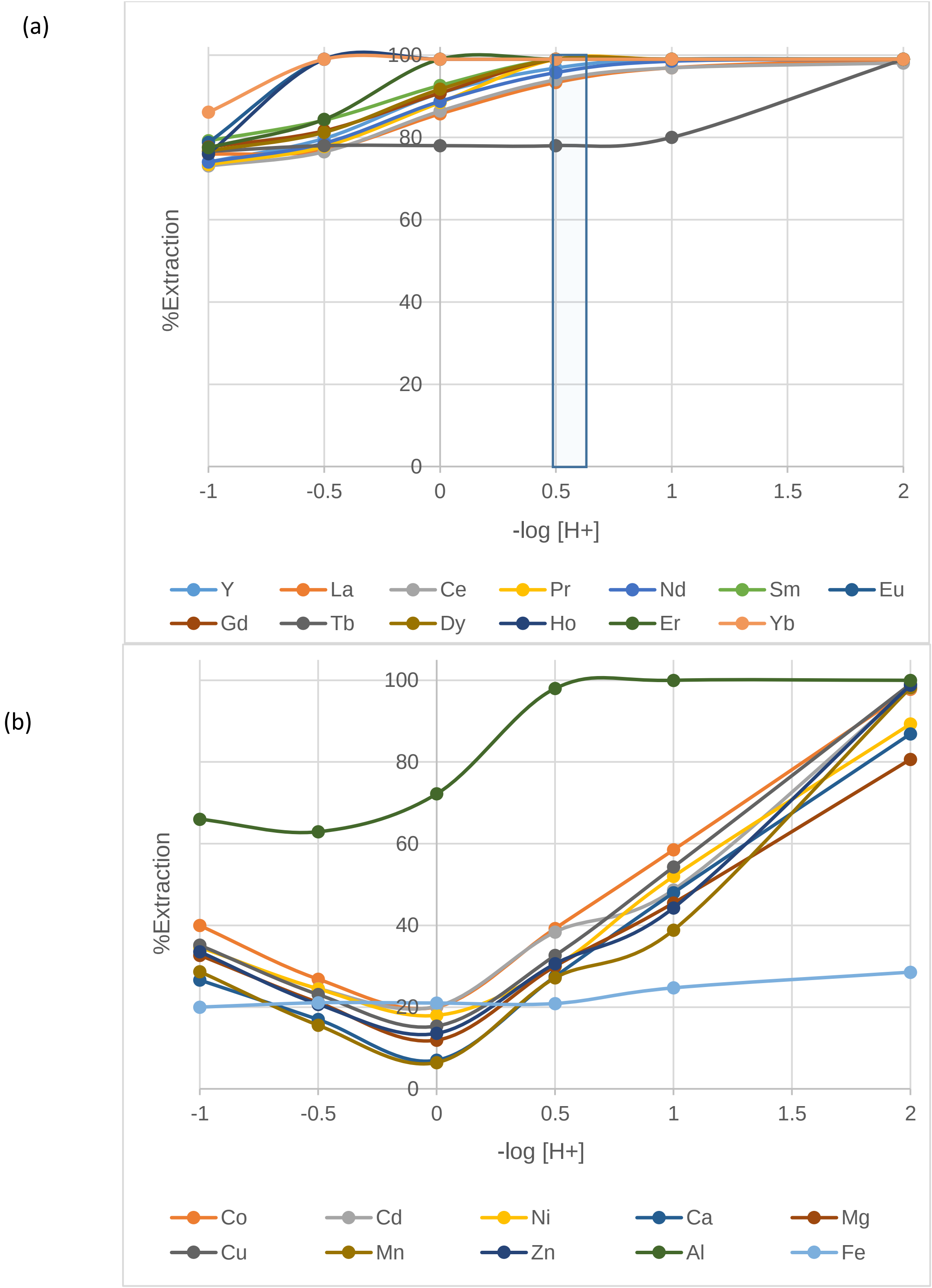

Figure 1. TP260 resin: variation of the extraction percentage versus pH for a) REE and b) TE and Al(III). The solid/liquid ratio used was 20 mL of TAMW (table 1) and 0.2 g of TP-260 Resin. Box indicate the acidity range where the maximum REE extraction efficiency is reached.

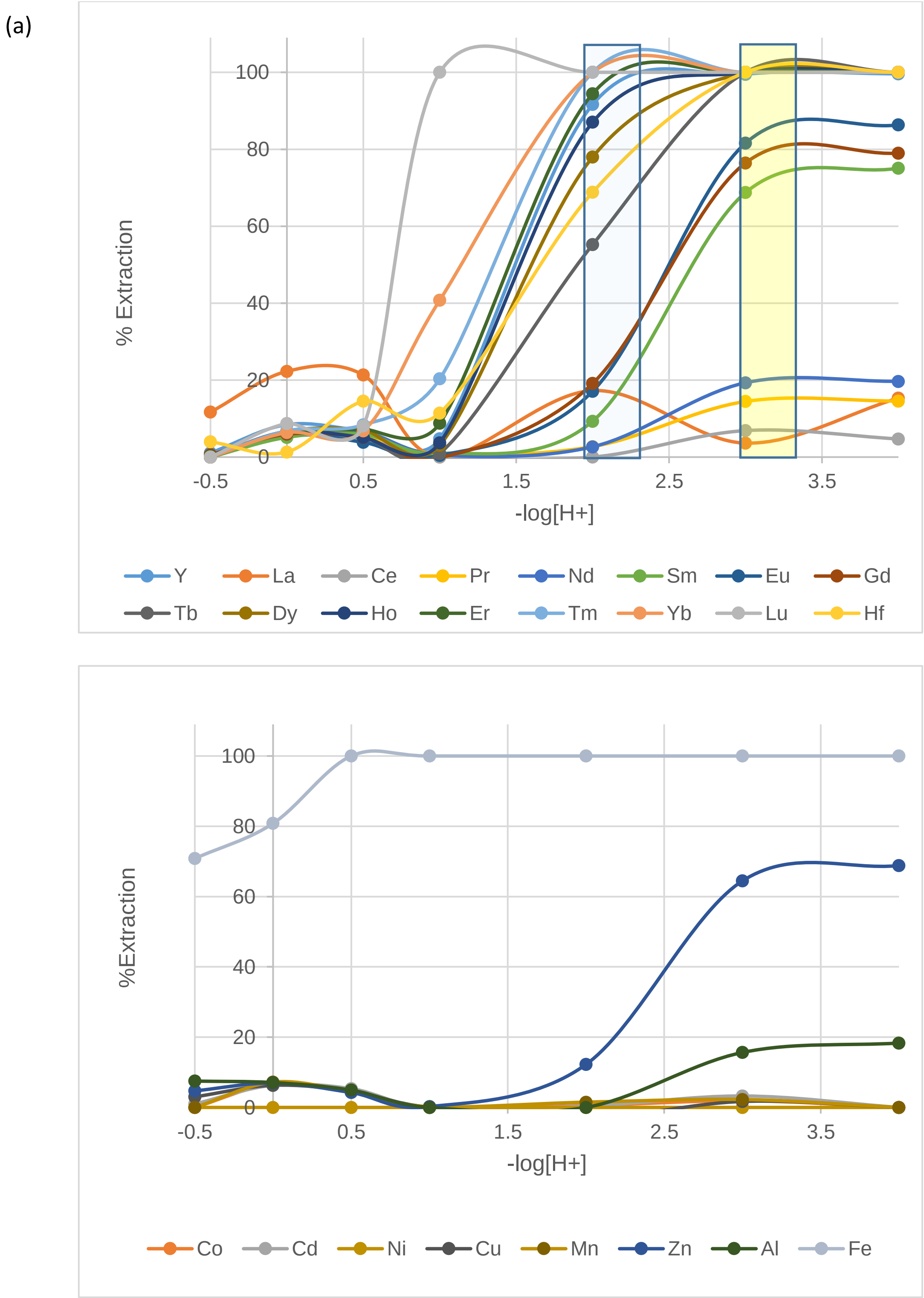

Figure 2. TP272 resin: extraction percentage versus pH for a) REE and b) TE and Al(III). The solid/liquid ratio used was 0.2 g of TP-272 resin/20 mL of TAMW (Table 1). Boxes indicate the acidity range where the maximum REE extraction efficiency is reached (blue box HREE, yellow box for LREE).

For both resins the extraction of REE occurs at more acidic pH than TE and Al(III). It is worth to mention that with TP260 resin, quantitative extraction of REE, as well as Al(III) is achieved at strong acidic conditions ($[H^+]$=1 M), while Fe(III) is only partially extracted. whereas for divalent metal ions the extraction percentage growths from $[H^+]$= 1 M to attain quantitative extraction at pH 2. At high acidity values ($[H^+]$ =10 M), the extraction of divalent TE ions increases, and may be associated to the role of the protonated amine group ($-NH_2^+$) and the extraction of negatively charged M-SO_4 complexes, such as $M(SO_4)^{2-}$ as it will be discussed below.

On the other hand, TP272 shows a typical S shape for REE, TE and Al(III). At log$[H^+]$ =-3 those classified as HREE (Y, Yb, Tm, Ho, Dy,) presented extraction values close to 100%, those classified between HREE and LREE (Sm, Gd, Eu) showed extraction values from 70 to 90%, and the lowest extraction values (5-20%) were measured for the LREE group (Ce, Pr, Nd, La, Sc). For the case, Fe(III) is quantitatively extracted from strong acidic conditions (-log[H+]= 0.5), while extraction of Al(III) was observed from -log[H+]= 2, being less efficiently extracted than Zn(II). Zn(II) shows the highest selectivity factors over the divalent TE group, being extracted quantitatively above log$[H^+]$=-3. For the rest of TE, limited extraction was observed for Cu, Ni, Co, Cd, and Pb, and also for earth alkaline elements, such as Ca and Mg. This low selectivity factor for Ca(II) and Mg(II) in front of TE is a relevant property when at industrial scale low cost neutralizing reagents as caustic magnesia or calcite are used in the Fe(III) removal stage.

Metal extraction reactions with the methyl-amino-phosphonic resin (TP260).

The metal extraction process of the amino-phospoinic ($R-CH_2-NH-POOH_r$) TP260 resin is a complex system due to the presence of two functional groups: an internal secondary amine group (-NH-) and the terminal phosphonic acid group ($-POOH_r$). The aminophosphonic group is considered as a polyampholyte that can bind metal ions via oxygen atoms from the phosphonic group and via a nitrogen atom from a secondary amino group [44]. Phosphonic groups are moderately acidic and contain active centres of two kinds: phosphonic oxygen and hydroxyl acid groups, and the sorption of REE/TE/PTE ions can proceed via their coordination interaction with the former, and through their ionic interaction with the latter.

In most of the acidic range evaluated both the phosphonic and the secondary amine will be protonated as it is described in Eq. 1:

$$HSO_4^- + H^+ + R - NH - POOH_r \leftrightarrow R - (NH_2^+ HSO_4^-) - POOH_r \quad K_{NH2/HSO4} \text{ (1)}$$

Where $R - NH_2 - POOH_r$ represents the aminophosphonic group of the ion-exchange resin.

REE, TE and PTE extraction is described by a main reaction involving the phosphonic acid group (Eq. 2).

$$M(SO_4)_m^{(n-2m)+} + nR - (NH_2^+ HSO_4^-) - POOH_r \leftrightarrow (R - (NH_2^+ HSO_4^-) - POO)_n M_r + nH^+ + mSO_4^{-2} \quad K_{M1} \text{ (2)}$$

The metal extraction reaction describing the results observed for TE and PTE in strongly acidic solutions of sulphuric acid ([H_2SO_4]>0.5 M) involves an anion-exchange reaction with the HSO_4^- ions of the amine group as described by Eq.3:

$$M(SO_4)_2^- + R - (NH_2^+ HSO_4^-) - POOH_r \leftrightarrow R - (NH_2^+ M(SO_4)_2^-) - POOH_r + HSO_4^- \quad K_{M2} \text{ (3)}$$

Metal ions recovery involving the anion exchange reaction described by Eq. 3 was postulated by Kertman et al., (1994) [44] when studying polyampholyte resins as TP260, incorporating a methylene group present between the aromatic ring of the STD and nitrogen atom of the amine group. At low loads, both functional groups may act as tridentate ligands, while when metal loading increases act as bi and mono-dentate ligands. TP260 has been reported for a range of applications, most of them related to the extraction of trivalent elements, such as Fe(III) and Bi (III), from strong acidic solutions. Kervit and

Dreissinger (2009)[45] reported the removal of Fe(III) and other impurities as Bi(IIII), from copper tank electrolytes in the copper metallurgical processing industry.

Metal ions could be eluted by using concentrated electrolytes such as HCl, or H_2SO_4. As it could be seen in Figure 2, metal ions are complexed to form anionic complexes in 5 M H_2SO_4 solutions. However, the fact that extraction occurs at strong acidic conditions has limited the application of separation and extraction routes using the acid regeneration cycles; the use of complexing agents (*e.g.* EDTA), or reduction to Fe(II) by SO_2(g), has been proposed as alternative.

Metal extraction reactions with the 2,4,4-trimethylpentyphosphinic acid impregnated resin (TP272).

The metal extraction process could be described as a similar approach as for SX, where the active component, bis-(2,4,4-trimethylpentyl) phosphinic (HL) is dissolved on the porous structure of the polystyrene di-vinyl-benzene polymeric network as described by Eq. 4 [42]:

$$M(\,SO_4\,)_m^{(n-2m)+} + n\overline{HLr} \leftrightarrow \overline{ML_{n,r}} + nH^+ + mSO_4^{-2} \qquad K_M \qquad (4)$$

where HL_r represents di-(2,4,4-trimethylpentyl) phosphinic acid and $ML_{n,r}$ represents the formed metal-HL on the resin phase. For simplicity HL_r has been considered not associated, however, as demonstrated Cortina et al., (1992) [42] is partially present associated as dimer form ($(HL)_{2,r}$).

3.4 Separation of REE from TE/PTE from TAMW by using selective ion exchange resins: column experiments

Separation of REE from TE/PTE by TP260. As described in section 3.2, the acidity-value to achieve the highest separation factors for both metal groups could be at $-\log[H^+]=0.5$ (Figure 2a-b). Then, samples of TAMW (Table 1) were acidified with H_2SO_4. Figures 3a-b show the breakthrough curves (C/C_0) as a function of the solution bed volumes (BV) for REE, TE and PTE, and the variation of the acidity along the column run.

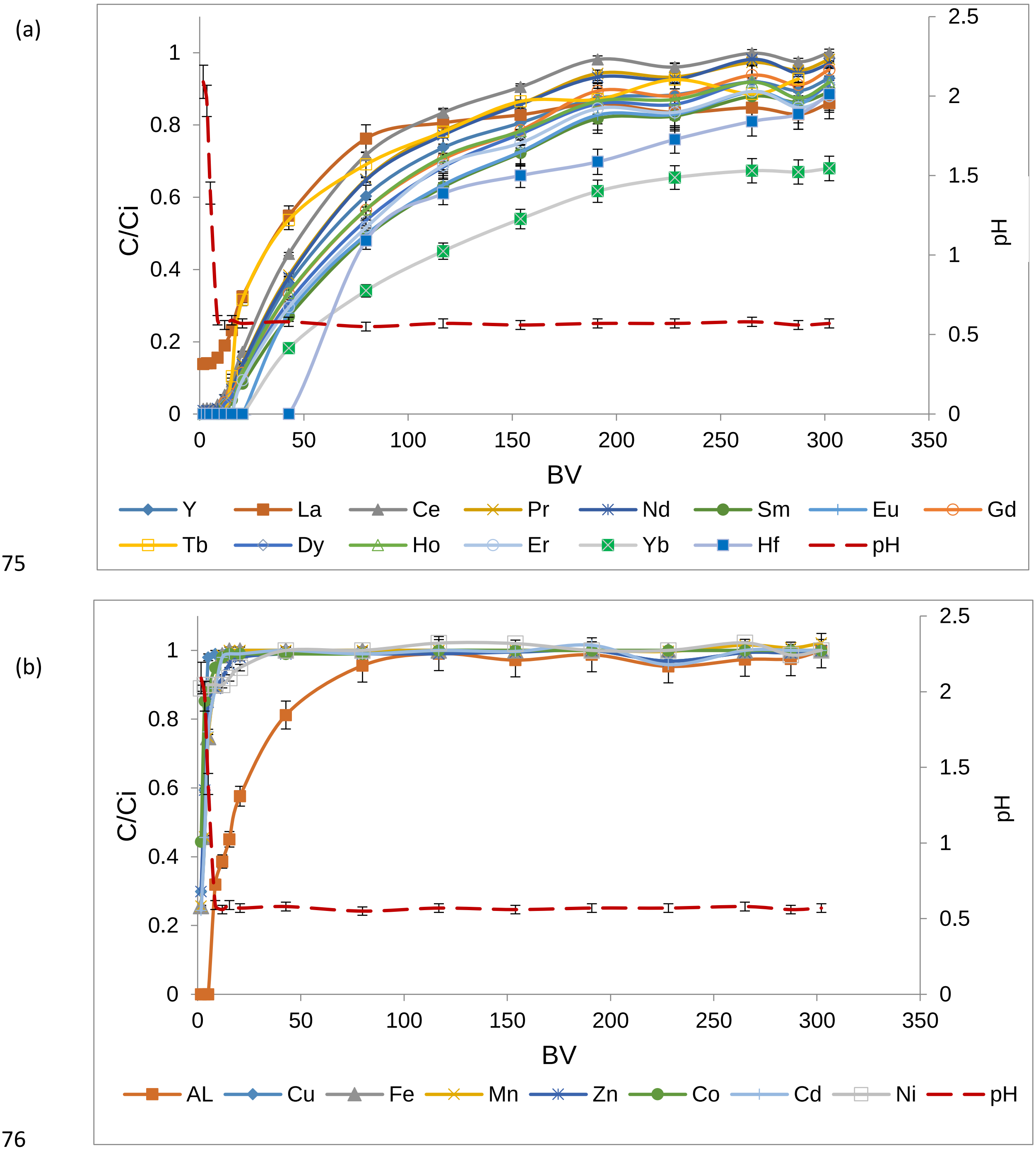

Figure 3: TP260 column: Breakthrough curves (C/C_0) and evolution of the acidity at the column exit as a function of the TAMW solution in BV for (a) REE and (b) TE/PTE.

Breakthrough point, arbitrarily taking a value of 0.1 for C/C_0, ranged from 15 to 50 BV. The breakthrough order follow the elution of LREE (La< Ce < Pr < Nd < Pm < Sm < Eu < Gd), followed by HREE (Y< Tb< Dy < Er < Tm < Lu< Yb < Ho). The measured sequence is related to the strength of the metal-phosphinic complexes; the weightier the element, the higher the K_M constant, and thus the higher the breakthrough values [41]. When analysing the performance of the TP260 resin with trivalent TE and PTE while Fe(III) is not retained with a breakthrough volume below 0.1 BV, however for the base of Al(III) the breakthrough volume was reached after 9 BV. Divalent TE were weakly retained and in less than 2 BV. The selectivity sequence followed K_M values were Ni<Co<Cu<Zn<Cd<Mn. The potential interference of the co-extration of Al(III) could be removed if the pre-treatment of the acidic waters is carried out as described in section 3.1, but reaching a final pH of 5 as has been demonstrated recently by Vecino et alt (2020) [46], where removal of 99% for Fe(III) and 90% for Al(III) were achieved. The selectivity factors are much higher than those reported for strong cation resins [47, 48].

Results on elution performance of the column using 10 M H_2SO_4, after treating 300 BV, are shown in Figure 4. Elution profiles of divalent TE (Fig 4b) show sharp peaks, indicating the efficiency of the regeneration step, with more than 95% eluted in less than 1 BV.

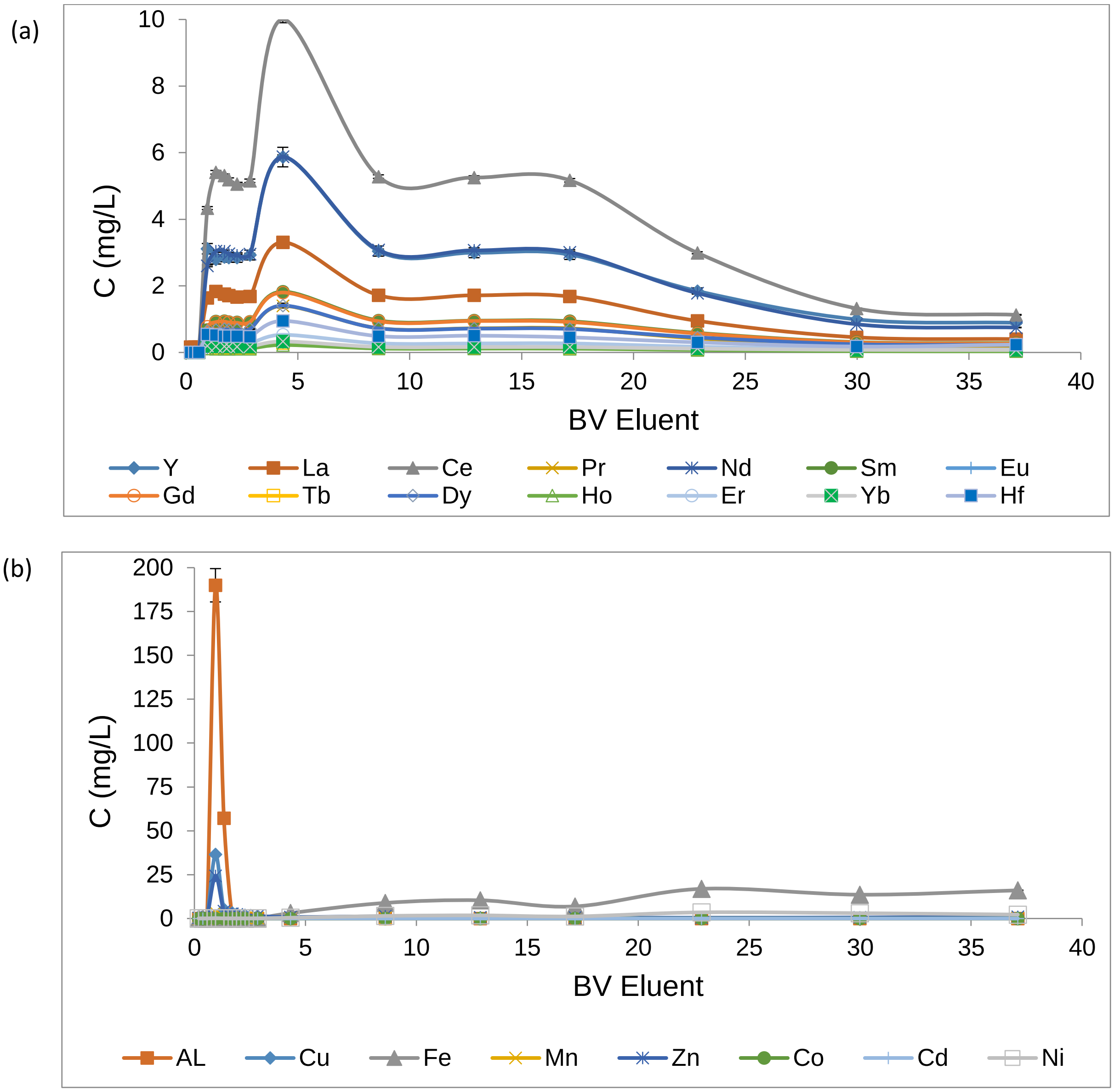

Figure 4. TP260 elution curves: variation of metal concentration at the exit of the column as a function of the BV of the stripping solution for REE (a) and TE/PTE (b). 3 g of TP 260 resin, column d=1cm, flow rate=0.25mL/min, using 10 M H_2SO_4.

Similar behaviour was observed for REE, with a double elution peak This behaviour can be related to the two metal extraction mechanisms described by Eqs. 2-3. Quantitative recovery of REE (>95%) was reached after 30 BV. Due to the strong metal-phosphonic complexes (K_M) low concentration factors (CFs) were achieved. In general, CFs for LREE and HREE reached values below 3.2. Then, TP260 could be used to separate efficiently REE from TE and small amounts of residual Fe(III) from the precipitation stage. A potential treatment scheme is depicted in Figure 5, including a nanofilltration stage [23]. The regenerant H_2SO_4 solution could be partially recovered in only one stage and at the same time the RRE stream could be concentrated up to 1.5 times.

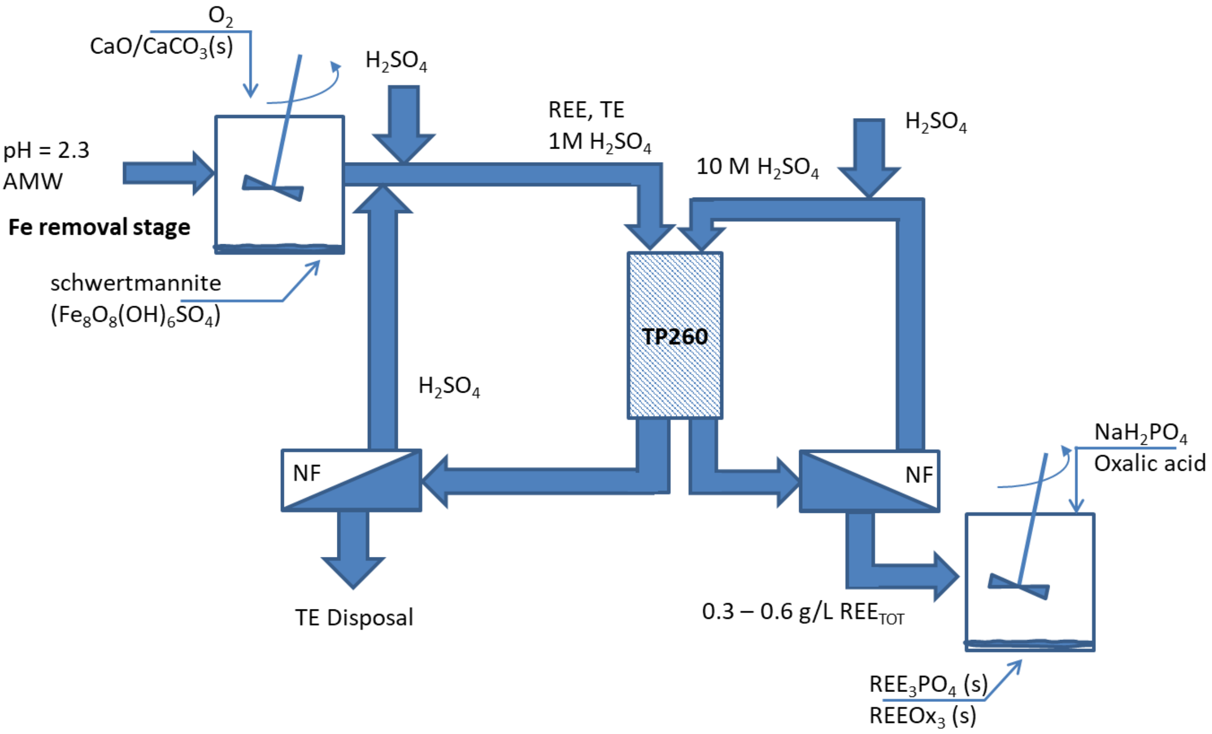

Figure 5. Proposed treatment of AMW including: i) total oxidation of Fe(II) to Fe(III) and precipitation with $CaO/CaCO_3$; ii) concentration of valuable metals with TP260 resins, iii) recovery of H_2SO_4 and concentration of valuable metals RRE with NF, and iv) selective precipitation of REE as oxalates or phosphates.

With the proposed scheme TP260 resin is suitable for REE recovery from AMW and separation from TE, but does not provide high CFs when using an elution cycle via acidic regeneration with H_2SO_4. The potential regeneration with other complexing reagents as EDTA, as has been proposed for sulphonic acid resins [49], should be evaluated. The use of redox regenerants, such as $SO_2(g)$, may be also evaluated for REE.

Separation of REE from TE/PTE by TP272. As described in section 3.2, the acidity value to achieve the highest separation factors both metal groups could be at -log[H+]=4 (Figure 2a-b). Then samples of TAMW were used directly in the dynamic experiments. Figure 6 shows the breakthrough curves as a function of BV of TAMW solution for REE and TE/PTE. The variation of acidity along the column run is also shown.

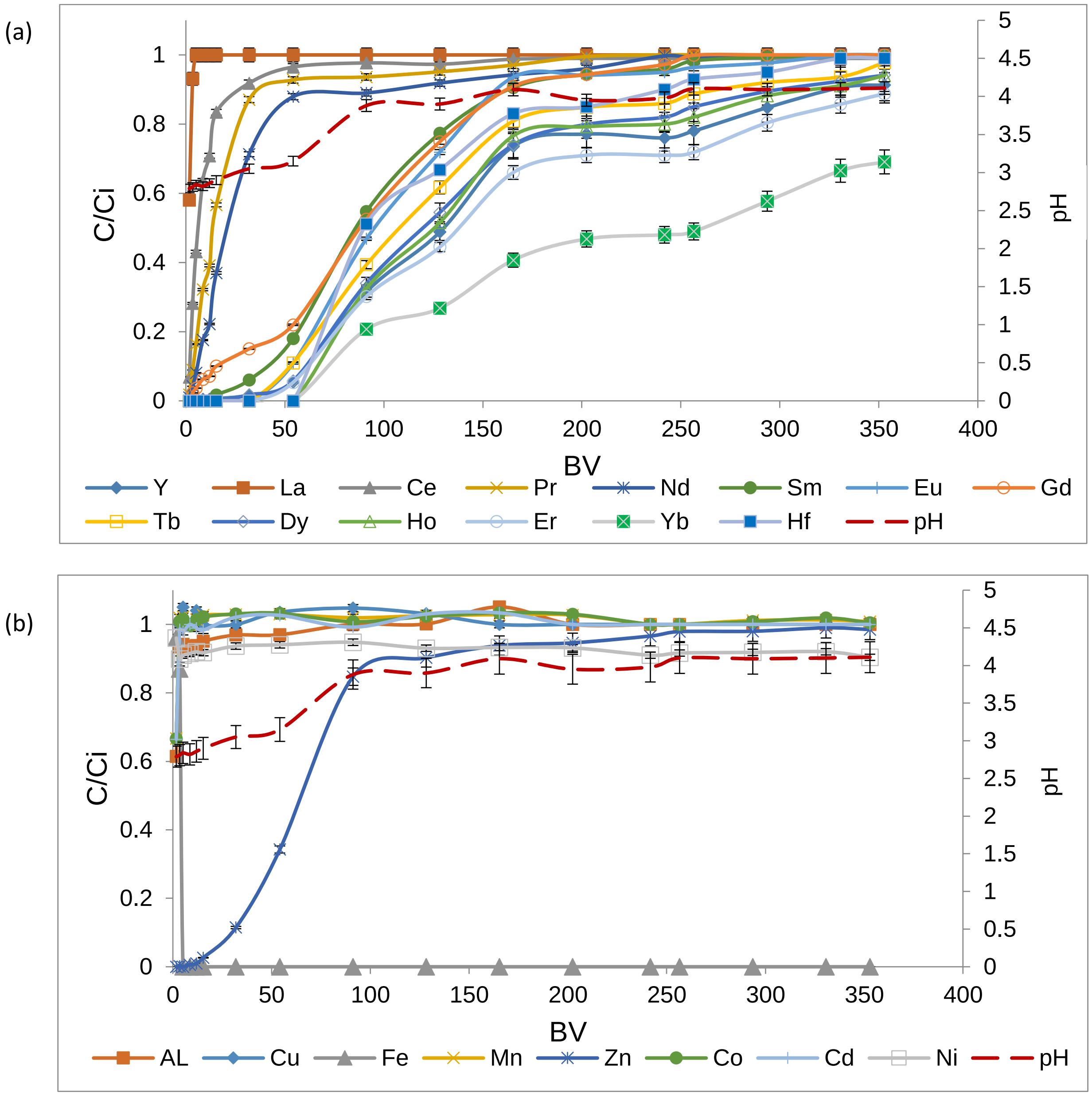

Figure 6. Breakthrough curves (C/C_0) of TP272 columns and evolution of the acidity at the column exit as a function of the -TAMW solution in BV for a) REE and b) TE/PTE.

REE profiles showed a steeply performance, with breakthrough for LREE (La, Ce, Pr, Nd, Pm, Sm, Eu Gd) bellow 5 BV, and between 50 to 60 BVs for HREE (Y, Tb, Dy, Er, Tm, Lu with Yb and Ho). This different behaviour cannot be associated with the changes of pH along the sorption test, as values ranged from 3.5 to 4. The pH initially decreased (3.2±0.2) as the sorption of the elements decreased, according to Eq. 5. The measured sequence can be related with the strength of the metal-phosphinic complexes, the weightier the element the higher the KM constant and thus the higher the breakthrough values [41].

When analysing the performance of the TP272 resin with TE/PTE elements, residual Fe(III) (<2 mg/L) is efficiently extracted and breakthrough was not reached after 350 BV; confirming the batch results, Al(III) is not retained, but Zn(II) is retained with a breakthrough value of 20 BV. None of the other divalent metal ions (Ni, Co, Cd, Mn, Ca and Mg) are retained. The selectivity sequence is Ni<Co<Cu<Zn<Cd<Mn.

Elution from the loaded resin after treating 350 BV of TAMW was carried out using 20 g/L H_2SO_4 solution and the elution curves for TE and REE are shown in Figures 7 and 8, respectively. Elution of TEs and REEs occurs between 0.5-2 BV. Elution profiles of TE for the minor (Ni, Co, Cd, Fe) and the major TE/PTE (Zn, Al) show sharp peaks indicating the efficiency of the regeneration step, *e.g.* more than 95% of the loaded TE are eluted in less than 1 BV. According to the ratio of BV values for loading and elution curves, CFs of 5 were achieved for TE and Al(III). It is confirmed the high affinity of the resin for Zn, providing more than 2000 mg/L at the maximum of the elution peak, followed by Al(III) (almost 1000 mg/L) and Fe (up to 300 mg/L). As it was observed in the sorption curve (Figure 2), TP-272 presents as affinity sequence Fe(III)>Zn(II)>Al(III).

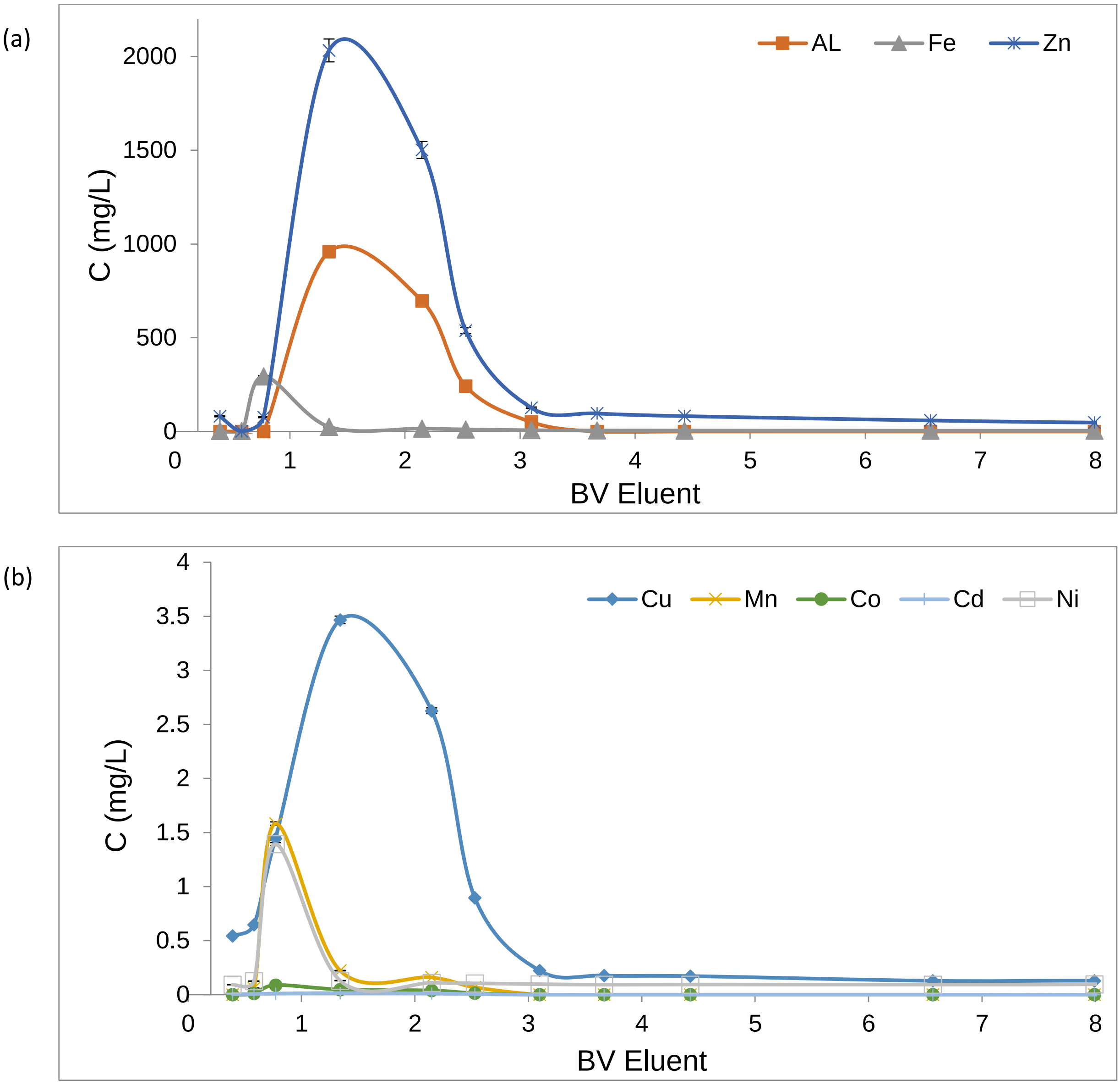

Figure 7. Regeneration curves for TE/PTE as a function of the elution solution for the TP272 resin using 0.2 M H_2SO_4.

The optimization of the pre-treatment stage of the AMW, when the presence of Al(III) is high, as were the samples from The Poderosa Mine, should be considered. The high values measured in the eluted effluents was high as its initial value, around 220 mg Al/L, compared with Zn (90 mg/L) and Iron (5 mg/L). The maximum concentration for other base metals are below 4 mg/L.

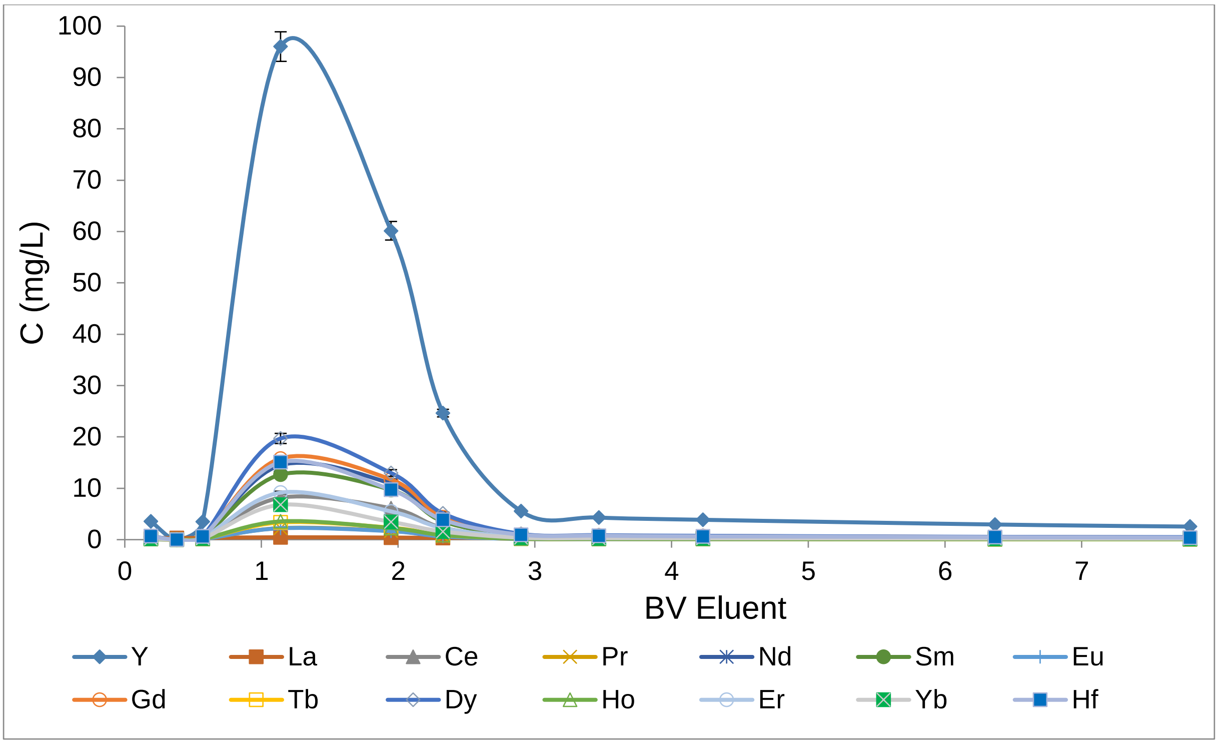

Figure 8. Regeneration curves for REE as a function of the elution solution for the TP272 resin.

Similar behaviour was observed for REE, with quantitative recovery of REE (>95%) after 2 BV. In general, as HREE reported CFs of 20-50 whilst 10 to 25 where the highest reached values were for Y and CFs higher than 20 were achieved for most of the REE. In consequence, high CF were achieved in comparison with TP260 resin. Elution profiles showed concentration peaks nearly 100 mg/L for Yttrium, between 10-20 mg/L for Hf, Dy, Gd, Sm, Nd, between 5-10 mg/L for Ce and Er, and less than 5 mg/L for the other REEs. Nevertheless, the initial concentration of Y, La, Ce and Nd was much higher than the other REE. So, it is confirmed the low selectivity of the phosphinic impregnated resin for LREE.

The maximum of the elution peaks for REE in these conditions occurs at 1.2 BV, and there is strong overlapping with the peaks of base metals. To achieve separation of REEs from TE by resin TP 272 a modification of the extraction acidity window should be done when the concentration of Zn(II)> 100 mg/L. The elution should be carried out at pH 1.5 (e.g $>0.2MH_2SO_4$), where the extraction of HREE is still totally favoured.

From the elution experiments the REE concentration factors achieved with both resins as summarized in table 2.

Table 2. Concentration factors achieved in the treatment of AMD with TP260 and TP272 resins.

LREE/ HREE	Concentration Factors-TP260 resin	Concentration Factor -TP272 resin
Eu	3,1±0,2	18,0±0,5
Pr	2,6±0,2	5,0±0,2
Sm	3,2±0,2	15,5±0,5
Gd	2,7±0,2	14,4±0,5
La	1,5±0,2	0,3±0,05
Nd	2,6±0,2	4,8±0,2
Ce	2,4±0,2	1,8±0,2
Y	2,4±0,2	17,8±0,5
Lu	2,5±0,2	9,7±0,5
Tm	2,4±0,2	9,5±0,5
Ho	2,6±0,2	27,2±0,5
Dy	2,7±0,2	21,7±0,5
Tb	2,7±0,2	21,8±0,5
Yb	2,8±0,2	32,6±1,0
Er	2,6±0,2	29,7±1,0

As it could be seen in Table 2, much higher concentration factors were achieved with the impregnated resin TP272 when compared with the results for TP260, although the optimization of the elution stage was not evaluated in this study. The weak nature of the REE bond with the organo-phosphinic group provided higher concentration factors that those obtained with the amino methylphosphonic acid group of TP260. It should be also mentioned the low concentration factors, reached for Ce(III) and La(III) ions with TP272 impregnated resin Due to their lower price their absence in the produced concentrate is giving and additional added value to the mixture of REE to be recovered in the further processing stages.

A proposed scheme to recover and separate RRE from AMW is described in figure 10. TAMW at pH 3.7 is treated with TP272 for selectively removal of HREE, and in a second stage, after conditioning the TE/PTE and LHREE stream with sulphuric acid solution (1M), the TP260 resin is used to separate LREE from TE/PTE as described in Figure 9.

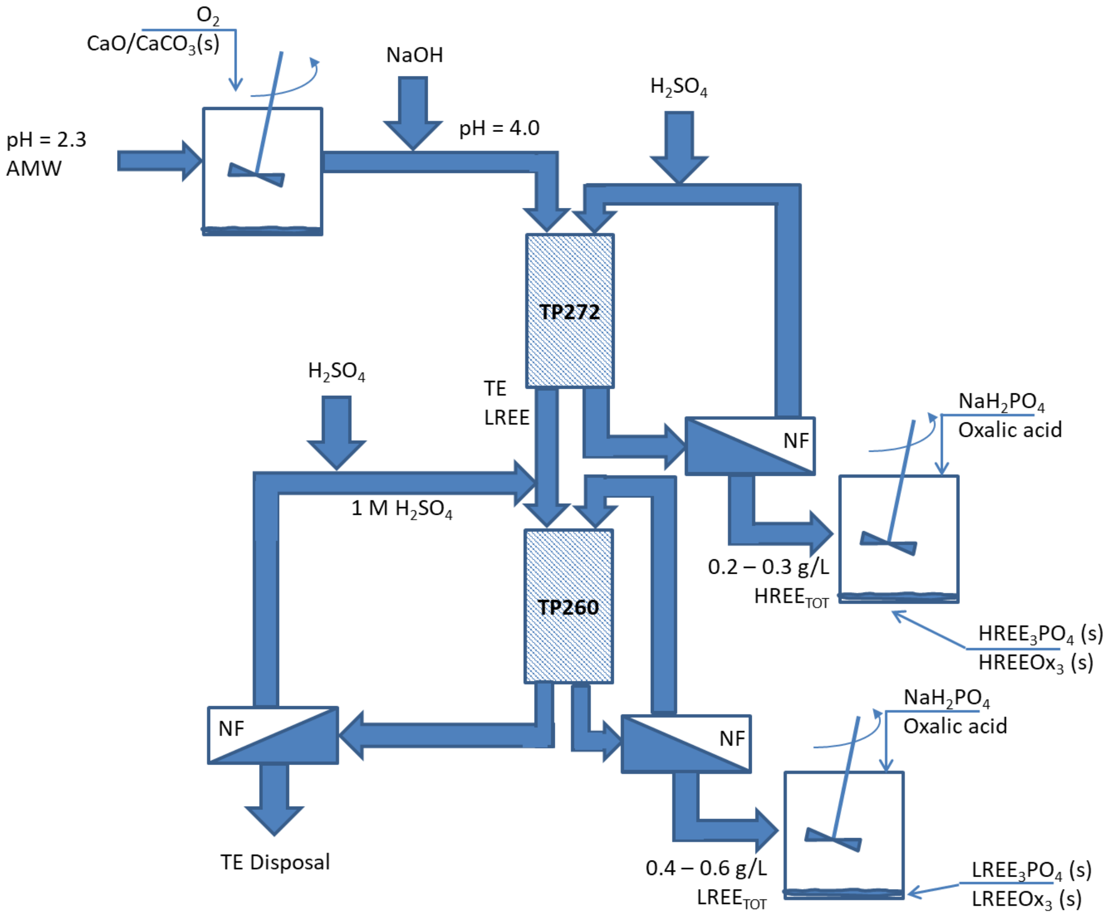

Figure 9. Proposed treatment of an AMW including: i) total oxidation of Fe(II) to Fe(III) and precipitation with CaO/CaCO$_3$; ii) separation of HRRE (from LREE and TE) and concentration by using TP272 impregnated resins and production of HREE phosphates/oxalates; iii) separation of HREE (from TE) and iv) concentration by using an amonino-phosphinic IX resin (TP260) and production of LRRE phosphates or oxalate. Each in IX stage is coupled with the use of acidic nanofiltration membranes to recover the elution solution (e.g., H$_2$SO$_4$) and to concentrate the generated HREE and LHREE streams before precipitation as phosphates or oxalates.

Elution of TP272 column with 0.5 M H$_2$SO$_4$ and TP260 with 10 M H$_2$SO$_4$ will provide two streams, the first containing HREE, and the second one containing LREE. As the separation factors and CFs are not as high as needed, these factors could increase by integration of a Nano-filtration (NF) stage after the IX step. NF membranes provide high rejection for multi-charged ionic species (>90%), whereas the single charged ones can permeate across the membrane. In the case of using sulphuric solutions as stripping, as strong acid (pK_{a2}=1.9), in most of the solutions generated it will be present mainly as HSO_4^- and H^+ ions and then transported through the membrane. Contrary most of the metals eluted from the columns are present as multi-charged species and highly rejected by the membrane active layer due to size or steric hindrance as the exclusion mechanism [50]. In a previous work, acidic solutions containing mixtures of TE and REE were filtered with different NF membranes (Desal DL and HydraCoRe 70pHt and NF270) with different active layers as semiaromatic polypiperazine-amide (Desal DL, NF270) and sulphonated polyethersulphone (HydraCoRe 70pHT) membrane exhibited low sulphuric rejection values while metallic ions were effectively rejected (>98%) [51]. Accordingly, the integration of NF membranes on the IX recovery scheme will provide the possibility to reuse the free acid sulphuric concentration and provide an additional concentration factor for the eluted metal ions. This reduction of the free sulphuric acid is providing a second benefit as it will be a reduction of the alkali needs to reduce the acidity of the REE containing solutions before its precipitation as oxalates.

Finally, modifying the metal complexing properties, especially for the methyl-aminophosphonic group by selecting a more selective metal extractant or using counter-current chromatography could be an alternative option [52, 53]. In this way, high CFs could be achieved using an elution cycle via acidic regeneration with H_2SO_4 or by using other complexing reagents as EDTA, as ben proposed for sulphonic acid resins [48]. Additionally, the pre-treatment stage for Fe(III) removal could be extended to the removal of Al(III) if the neutralization stage reaches values of pH 4.4, where most than 99% of Fe(III) and 90% of Al(II) with not losses of the REE. Reduction of the Al(III) will increase the ion-exchange resins capacity for trivalent metal ions as REE [9,17].

4. Conclusions

The experimental work developed on the evaluation of the potential routes to recover REE and separate TE/PTE from AMW by using two selective sorbents provide the conclusions summarized below:

- The acidity window for the recovery of REE by a complexing resin containing a methyaminophosphonic group (TP 260) is situated at strong acidity conditions (0.5 to 1 M H_2SO_4) where REE are selectively extracted and separated from TE. Regeneration requires concentrated H_2SO_4 solutions (10 M H_2SO_4.) The CFs achieved are between 1.5-3.2. and if higher CFs are needed a weaker functional group, such as sulphonic group, will be needed.

- The acidity window for the recovery of REE by an impregnated resin containing an organo-phosphinic acid extractant (TP 272) is situated around pH 1.5 to 4, where HREE could be separated from REE and TE, and regeneration can be achieved with moderate H_2S0_4 solutions (20-30 g/L). The CF factors could reach values up to 20-30.

- The organophosphinic resin showed competitive sorption equilibrium data, and its kinetic performance is similar to that achieved with conventional ion-exchange resin, and confirms the improved properties of these materials when compared with the homologues applications using organic solvents.

REEs being in low concentration and in the presence of high concentrations of other metals within the acid mine waters, these results give a promising perspective into selective extraction schemes. The utilization of phosphinic and amino phosphonic functional groups could allow for the easy separation of REE from TE in acid mine waters after removal of Fe(III) and Al(III) by precipitation with alkaline solutions

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