An insight into REEs recovery from spent fluorescent lamps: Evaluation of the affinity of an NH4-13X zeolite towards Ce, La, Eu and Y

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An insight into REEs recovery from spent fluorescent lamps: evaluation of the affinity of an NH_4-13X zeolite towards Ce, La, Eu and Y

Francesco Colombo[a], Riccardo Fantini[a], Francesco Di Renzo[b], Gianluca Malavasi[a], Daniele Malferrari[a], Rossella Arletti[a]

corresponding author: Rossella Arletti rossella.arletti@unimore.it

[a]*Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, Modena, Italy*

[b]*ICGM, University of Montpellier, CNRS, ENSCM, Place Eugène Bataillon, 34095, Montpellier, France*

Abstract: The constantly increasing demand of Rare Earth Elements (REEs) made them to be part of the so-called "critical elements" indispensable for the energy transition. The monopoly of only a few countries, the so-called balance problem between demand and natural abundance, and the need to limit the environmental costs of their mining, stress the necessity of a recycling policy of these elements. Different methods have been tested for REEs recovery. Despite the well-known ion-exchange properties of zeolites, just few preliminary works investigated their application for REEs separation and recycle. In this work we present a double ion exchange experiment on a NH_4-13X zeolite, aimed at the recovery of different REEs from solutions mimicking the composition of liquors obtained from the leaching of spent fluorescent lamps.

The results showed that the zeolite was able to exchange all the REEs tested, but the exchange capacity was different: despite Y being the more concentrated REE in the solutions, the cation exchange was lower than less concentrated ones (16 atoms p.u.c. vs 21 atoms for Ce and La

solutions), suggesting a possible selectivity. In order to recover REEs from the zeolite, a second exchange with an ammonium solution was performed. The analyses of the zeolites show that almost all of Ce and Eu remain in the zeolite, while nearly half of La and Y are released. This, once again, suggests a possible selective release of REEs and open the possibility for a recovery process in which Rare Earths can be effectively separated.

Keywords: Zeolite X, Cation exchange, REE, recovery

1. Introduction

Rare Earth Elements (REEs) are a group of seventeen elements, fifteen of which are the Lanthanides with the addition of scandium and yttrium. Their demand is constantly increasing due to their extensive use in many technological applications such as computer memory, DVDs, rechargeable batteries, autocatalytic converters, super magnets, mobile phones, LED lighting, superconductors, glass additives, fluorescent materials, phosphate binding agents, solar panels and magnetic resonance imaging (MRI) agents (Balaram, 2019).

An European foresight study on Critical Raw Materials (Bobba et al., 2020) shows how REEs are part of a group of raw materials fundamental for the energy transition. The report displays how the use of some REEs for the mentioned technologies will more than double from 2030 to 2050. The risk in the supply of these elements is higher than others because they have a very high demand rate against the number of known ores. Moreover, as reported in the study, the REEs market is mastered by China which is the world's largest producer, consumer, and exporter of REEs (e.g., the 98% of the EU's supply of REEs is provided by China). To achieve resource security, it is crucial to diversify the supply from primary and secondary sources enabling reduced dependency on a single country and, most importantly, improving resource efficiency and circularity (European Commission, 2020).

A lot of work has been done to find and characterize REEs-rich waste materials from which to recover these elements; among them, phosphogypsum, red muds (bauxite processing residue), mine tailings, coal and incinerator ashes, metallurgical slags, wastewater and different electronic and electrical equipment wastes (WEEE) have been identified as suitable candidates (Binnemans et al., 2015). Phosphogypsum, the calcium sulfate hydrated waste from the production of phosphate fertilizers, occurs in large quantities and can contain a lot of different REEs, mainly depending on the source rock (Cánovas et al., 2019); moreover, it may also contain radionuclides, making it a material of environmental and health concern. The concentration of REEs in red muds depend strongly on the lithologies of the bauxite host-rock (Borra et al., 2016) which can be of three types: Tikhvin-type bauxites (0.5 %) lying on aluminosilicate rocks, the “classical” lateritic bauxites (88 %) and karst bauxites (11.5 %), deposits lying on carbonates which may contain the highest amounts of REEs. Waste materials like acid mine drainage (AMD) (Ayora et al., 2016; González et al., 2020; Hedin et al., 2019; Li and Wu, 2017), mine tailings (Zhang et al., 2014) and ashes (Blissett et al., 2014; Funari et al., 2016) have a REEs concentration strongly related to the primary material, thus each case study requires a proper evaluation.

WEEEs comprehend, among others, NdFeB magnets, Ni-MH batteries, and phosphors from fluorescent lamps. NdFeB magnets contain about 31-32 wt% of REEs (Yang et al., 2017). The content of REEs in spent NiMH batteries is approximately 90 mg/kg for La, 27 mg/kg for Ce and 26 mg/kg for Nd (Lie and Liu, 2021), and they also contain fair amounts of Mn, Co, Zn, Cd and Al. Fluorescent lamps are based on different phosphor types: white phosphor (HALO), red phosphor (YOX), green phosphors (LAP, CAT and CBT) and blue phosphor. HALO does not contain REEs, while in the others Y, Eu, La, Ce, Tb and Gd occur (Gijsemans et al., 2018). A major requirement of WEEEs recycling is to previously optimize their physical dismantling and concentration in diversified scraps (Jowitt et al., 2018). As the separation of different phosphor types is rarely

achieved in this process, the recovery of REEs requires their selective separation from a common leaching solution, generally obtained after a series of physicochemical processes aimed at the beneficiation of REEs (Ambaye et al., 2020; Xie et al., 2023; Yuksekdag et al., 2022). An effective separation can be achieved through various methods. For example, a selective precipitation can be done though different reagents favouring the precipitation of double salts, hydroxides, oxalates and carbonates (Mao et al., 2022; Pavón et al., 2018; Porvali et al., 2018; Silva et al., 2019). Solvent extraction, or liquid-liquid extraction is highly used and is commercially exploited to produce high purity single REEs; however, it is an inefficient, labour-intensive and time-consuming method (Opare et al., 2021). Adsorption of REEs can also be carried out with either organic or inorganic compounds, depending on the element considered; the effectiveness of this method is strongly related to contact time, adsorbent dose, initial concentration, solution pH and temperature (Anastopoulos et al., 2016; Iannicelli-Zubiani et al., 2015; Pinto et al., 2023). Ion exchange is another widely exploited method that is generally carried out exploiting different resins (Chen et al., 2017; Hérès et al., 2018) and MOFs.

Zeolites are a family of microporous materials, natural and synthetic, which are classified according to their structure (framework types) and chemism. Zeolites are usually exploited for their cation exchange property which mainly depend on the Al^{3+} for Si^{4+} substitutions in tetrahedra. The REEs adsorption on zeolite faujasite (framework type FAU) (Baerlocher et al., 2007) from concentrated solutions has been extensively studied, notably but not exclusively for the preparation of fluid catalytic cracking (FCC) (Chen et al., 1990; Guzzinati et al., 2018). Despite this, only few studies evaluated the possible exploitation of zeolites for the recovery of REEs (Barros et al., 2019; Confalonieri et al., 2022; Eremin et al., 2017; Kocasoy and Şahin, 2007; Mosai et al., 2019; Mosai and Tutu, 2021; Motsi et al., 2009).

The use of zeolites as cation exchangers in the acidic conditions typical of mineral extraction processes can be limited by the acid hydrolysis of the Si-O-Al bonds, easier for Al-rich zeolites. This has prompted experimentation on natural (clinoptilolite) or synthetic (zeolite-L (LTL)) zeolites, with a relatively high Si/Al ratio. The cheapest synthetic zeolites, like zeolite-A (LTA) and faujasite (FAU), are produced with a low Si/Al ratio, slightly above unity, which gives a very high ion exchange capacity; nevertheless, these materials are more prone to dealumination and amorphization in acidic solution than those with higher Si/Al ratios.

The aim of this work is to evaluate the extent to which instability in acid solution is limiting for the use of low Si/Al zeolites in REE recovery. The cation exchange capacity of a synthetic NH_4 exchanged 13X zeolite (FAU framework type) (Baerlocher et al., 2007) was studied against four different rare earth elements (Ce, La, Eu and Y) and the recovery of the exchanged REEs was also evaluated. Solution concentrations were chosen by mimicking those resulting from a two-step leaching on spent fluorescent lamps with hydrochloric acid (Eduafo et al., 2015).

2. Materials and Methods

2.1 NH_4-13X zeolite

As will be better detailed below, an NH_4 saturated zeolite was prepared to test the counter-exchange of NH_4 for the recovery of the REEs from a solution containing only REEs and readily removable ammonium.

Molecular Sieve 13X is the sodium form of synthetic zeolite X, and it is characterized by a low Si/Al ratio, high porosity, and high cation exchange capacity of 300 meq/100g (Mondale et al., 1995; Rees, 1970). One of the main properties of this material is its great ability to exchange cations. This zeolite is characterized by the primary building block SOD (*i.e.* sodalite cage) (Supplementary

Figure 1) and cages are connected by double six-rings to form accessible larger cavities (Baerlocher et al., 2007; Zhu and Seff, 1999).

Starting from the 13X zeolite of BDH Chemicals Ltd Poole England, about 30 grams of NH_4 exchanged 13X form was prepared by putting 4g of zeolite in contact with 1L of a 0.5M NH_4Cl solution (Carlo Erba analytical grade reagent), under stirring, for 24h at room temperature; zeolite was then separated from the solution via filtration (Filter: Cat No 1005125, Whatman), washed three times with MilliQ and dried at 60°C.

Major elements composition was determined by WDS-XRF (Wavelength-Dispersive Spectrometer X-ray Fluorescence) Philips PW1480, while ammonium and water content were measured by TGA (Thermogravimetric Analyses) with a Seiko SSC/5200 thermal analyser in air flow, with heating range and gradient 25-1050°C and 10°C/min, respectively. The chemical formula of the obtained material is $(NH_4)_{55.5}\ Na_{24.7}\ Mg_{0.8}\ Ca_{0.06}\ Ti_{0.02}\ Fe_{0.04}\ Al_{90.6}\ Si_{103.5}\ O_{384}$ x 205 H_2O.

2.2 13X stability tests

To assess whether the 13X zeolite maintains the crystallinity during the REE-exchange procedure, preliminary stability tests were performed by interacting the zeolite with HCl solutions at the pH value of 4.4 for 24h at room temperature. Treated zeolite was separated by centrifugation (8000 rpm, 5 min.), washed three times with MilliQ water and then dried at 60°C. A second stability test was then performed with the same procedure on the material recovered after the first test at pH 4.4, to evaluate the possibility of zeolite re-use for more exchange cycles. The occurrence of amorphous material was then evaluated on X-ray powder diffraction (XRPD) patterns collected with an X'Pert PRO diffractometer and analysed by applying the Rietveld - RIR method using GSAS software (Larson and Dreele, 2000) and methods described in Gualtieri (2000) and Gualtieri et al. (2019).

2.3 REEs exchange tests

Four single-element solutions mimicking the concentrations found in leaching solutions of fluorescent lamps (Ce 0.03M, La 0.04M, Eu 0.006M and Y 0.17M) (Eduafo et al., 2015) were prepared. For Ce and La cation exchange tests proper amounts of $Ce(NO_3)_3 \cdot 6H_2O$ (99%, Aldrich) and $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Alfa Aesar) were dissolved in MilliQ with a final pH of 4.66 and 4.33, respectively. For Eu and Y cation exchange tests, Eu_2O_3 (99.9%, Aldrich) and Y_2O_3 (99.9%, Alfa Aesar) were dissolved in MilliQ with the addition of HNO_3 (Carlo Erba, analytical grade reagent), obtaining a final pH of 2.67 and 1.55, respectively. Since pH values below 4 can induce zeolites dealumination and/or amorphization, while pH values higher than 5 can lead to REE precipitation (Han, 2020), TRIS (tris(hydroxymethyl)aminomethane, 99.9%, Aldrich) was used to buffer the pH at about 4.4 for both the Eu and Y solutions.

The REEs exchange tests were performed by putting the NH_4-13X zeolite in contact with the single-element REE solutions under stirring for 24h at room temperature using three different liquid-to-solid (l/s) ratios: 10/1, 50/1 and 100/1 ml/g. The zeolites were then separated from the solutions by centrifugation (8000 rpm, 5 min.), washed three times with MilliQ water and dried at 60°C. The solutions, once separated from the zeolite, were filtered with a 0.45 µm filter. Elemental Analyses (FLASH 2000 CHNS Analyzer) were performed to evaluate the nitrogen content in zeolite samples in "FLASH" dynamic combustion (modified Dumas' method), a method that allows to heat sample at 1800 °C and analyse the released elementary gases, separated through a chromatographic column, using a highly sensitive thermal conductivity (TCD) detector. SEM-EDS analysis were performed on REE exchanged zeolites powders compressed into thin discs and coated with carbon. Thermogravimetric characterization was carried out applying the same experimental conditions used for NH_4-13X zeolite.

The final exchange solutions were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) Perkin Elmer Optima 4200 DV to evaluate the content of Ce, La, Eu and Y (Supplementary Table 2). The pH of the solutions was measured at the beginning of the exchange test, after 1h, 2h, 20h, 22h and 24h, data are reported in Supplementary Table 3.

2.4 REEs recovery from zeolite

In order to recover REEs from the exchanged zeolites, REEs were extracted by a further exchange with a 0.8M NH_4Cl solution. The REEs enriched zeolites were put in contact with the solution for 24h at room temperature under stirring, using a solid/liquid ratio of 1/125 g/ml. The zeolite powders were then separated from the solution and characterized as described above.

3. Results and discussion

3.1 pH stability tests

Stability tests at pH 4.4 (Supplementary Table 1) showed a considerable increase in amorphous content after the first treatment (24h), while no significant changes occurred after the second treatment. It is therefore possible to assume that the amorphization stabilised at less than 30 wt%. The amorphization could derive from zeolite dealumination and the consequent precipitation of EFAL (extra-framework aluminium species) on the surface and inside the porosity of the zeolite (Janssen et al., 2001). The XRPD patterns of the sample before and after pH tests do not show other major differences (Figure 1).

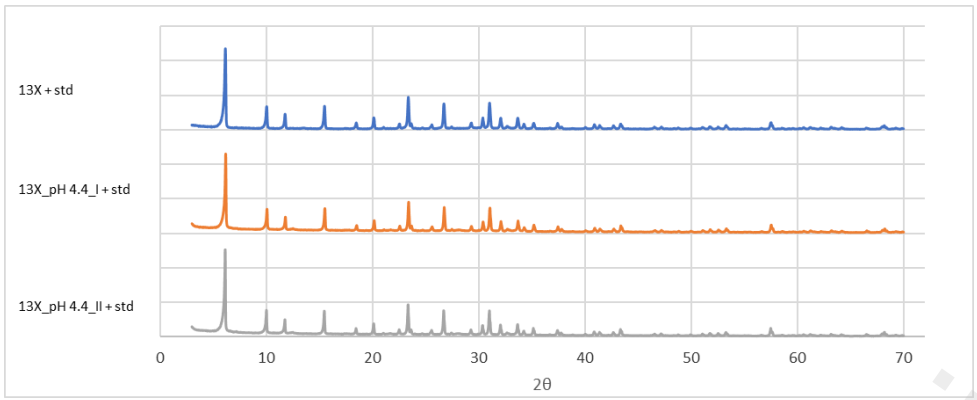

Figure 1. XRPD pattern of the samples before and after the pH test. 10 wt% of corundum was added to the samples as internal standard (std in labels) to calculate the amount of amorphous material.

3.2 REEs exchange of NH_4-13X

NH_4-13X samples were put in contact with different volumes of solutions having concentration of each REE chosen as typical of the effluent of WEEE waste acid leaching (Eduafo et al., 2015). Liquid-to-solid ratios of 10, 50 and 100 ml/g were used, and the concentrations of the solutions were 0.029, 0.037, 0.005 and 0.13 for Ce, La, Eu and Y, respectively (Supplementary Table 2). The composition of the initial 13X and of the REE-exchanged zeolites are reported in Supplementary Table 4, while the calculated chemical formulas are given in Table 1.

Sample	**Chemical Formula**	**C. U. [%]**
NH_4-13X	$(NH_4)_{55.48}\ Na_{24.73}\ Mg_{0.83}\ Ca_{0.06}\ Ti_{0.02}\ Fe_{0.04}\ Al_{90.65}\ Si_{103.47}\ O_{384}$ x 206 H_2O	11.53
NH_4-13X _Ce0.03M_1/10	$Ce_{5.61}\ (NH_4)_{40.98}\ Na_{17.57}\ Al_{85.95}\ Si_{108.69}\ O_{384}$ x 250.27 H_2O	12.29
NH_4-13X _Ce0.03M_1/50	$Ce_{21.02}\ (NH_4)_{12.59}\ Na_{9.6}\ Al_{86.81}\ Si_{105.57}\ O_{384}$ x 276.87 H_2O	1.79
NH_4-13X _Ce0.03M_1/100	$Ce_{22.88}\ (NH_4)_{10.2}\ Na_{9.29}\ Al_{85.08}\ Si_{106.20}\ O_{384}$ x 280.19 H_2O	-3.39
NH_4-13X _La0.04M_1/10	$La_{6.93}\ (NH_4)_{36.51}\ Na_{17.06}\ Al_{85.75}\ Si_{109.10}\ O_{384}$ x 252.61 H_2O	13.30

NH_4-13X _La0.04M_1/50	$La_{21.93}$ $(NH_4)_{11.35}$ $Na_{8.29}$ $Al_{85.65}$ $Si_{106.04}$ O_{384} x 277.62 H_2O	0.26
NH_4-13X _La0.04M_1/100	$La_{20.42}$ $(NH_4)_{9.52}$ $Na_{7.87}$ $Al_{85.69}$ $Si_{108.07}$ O_{384} x 274.16 H_2O	8.22
NH_4-13X _Eu0.006M_1/10	$Eu_{0.78}$ $(NH_4)_{52.02}$ $Na_{19.18}$ $Mg_{0.30}$ $P_{0.04}$ $Ca_{0.12}$ $Al_{87.10}$ $Si_{107.97}$ O_{384} x 242.49 H_2O	15.57
NH_4-13X _Eu0.006M_1/50	$Eu_{3.82}$ $(NH_4)_{42.46}$ $Na_{17.87}$ $Mg_{0.40}$ $P_{0.05}$ $Ca_{0.08}$ $Al_{87.09}$ $Si_{108.36}$ O_{384} x 247.56 H_2O	17.57
NH_4-13X _Eu0.006M_1/100	$Eu_{7.64}$ $(NH_4)_{32.60}$ Na_{17} $Mg_{0.89}$ $P_{0.03}$ $Ca_{0.10}$ Al_{87} $Si_{108.05}$ O_{384} x 254.68 H_2O	16.64
NH_4-13X _Y0.17M_1/10	$Y_{14.11}$ $(NH_4)_{21.31}$ $Na_{17.46}$ $Mg_{0.18}$ $P_{0.42}$ $Ca_{0.11}$ $Al_{86.95}$ $Si_{105.32}$ O_{384} x 266.51 H_2O	6.74
NH_4-13X _Y0.17M_1/50	$Y_{15.97}$ $(NH_4)_{16.45}$ $Na_{17.51}$ $Mg_{0.17}$ $P_{0.45}$ $Ca_{0.15}$ $Al_{87.03}$ $Si_{104.98}$ O_{384} x 269.07 H_2O	5.94
NH_4-13X _Y0.17M_1/100	$Y_{16.40}$ $(NH_4)_{14.25}$ $Na_{17.01}$ $Mg_{0.47}$ $P_{0.61}$ $Ca_{0.17}$ $Al_{87.17}$ $Si_{104.66}$ O_{384} x 271.59 H_2O	7.70

Table 1. Atomic composition of the REE-exchanged zeolites. The charge unbalance (C.U. %) was calculated with the formula below.

$$C.U.\% = \frac{Al\ cations - (\Sigma\ monovalent\ cations) - 2 * (\Sigma\ bivalent\ cations) \ldots - n * (\Sigma\ n\ valent\ cations)}{Al\ cations} * 100$$

The fraction of REE extracted from solution is reported in Figure 2A as a function of the liquid-to-solid ratio. At a liquid-to-solid ratio of 10 ml/g, virtually all Ce, La, and Eu passes from the solutions to the zeolite, while, in the same conditions, only nearly half of Y is extracted from the solution. At increasing liquid-to-solid ratio (up to 100 ml/g), Eu is still completely extracted while the fractions extracted from Ce, La and Y solutions decreases with the increasing of the solution volume, reaching extraction levels of 40, 29 and 7%, respectively for Ce, La and Y, at liquid-to-solid ratio of 100 mL/g. The REE adsorbed by zeolite increases with the volume of contacting solution (Figure 2B) with a trend strongly dependent on the initial concentration of the REE solution. The amounts of REEs exchanged are reported in mg REE/g zeolite, instead of meq, to give a clearer vision of the applicative potential of this recovery process. In the case of the very diluted Eu solution, the amount adsorbed is linearly dependent on the volume of solution, reaching a value of 69 mg REE/g zeolite at a liquid-to-solid ratio 100 mL/g. The observed linearity suggests that, in these

experimental conditions, the affinity of Eu for the solution does not depend on the adsorbed amount; this trend usually indicates that the adsorbent capacity is far from being saturated. For the more concentrated solutions of Ce, La and Y, the adsorbed amount is in the 40-60 mg/g range already for 10 ml solution per g of zeolite. At higher liquid-to-solid ratios, the adsorbed amount of Ce and La increases nonlinearly with solution volume, reaching values of 135-160 mg/g at liquid-to-solid ratio of 50 ml/g. At a liquid-to-solid ratio 100 ml/g the amount of REE incorporated remain almost in the same range (150-160 mg/g), indicating the saturation of the zeolite is approaching. This behaviour suggests that the affinity of the zeolites for REE cations is decreasing when the amount of adsorbed REE is near the saturation capacity of the exchanger. A different response can be identified for Y. At higher liquid-to-solid ratios, the amount of Y incorporated in the zeolite remains almost the same, indicating that the saturation conditions for Y are reached at the liquid-to-solid ratio of 10 ml/g.

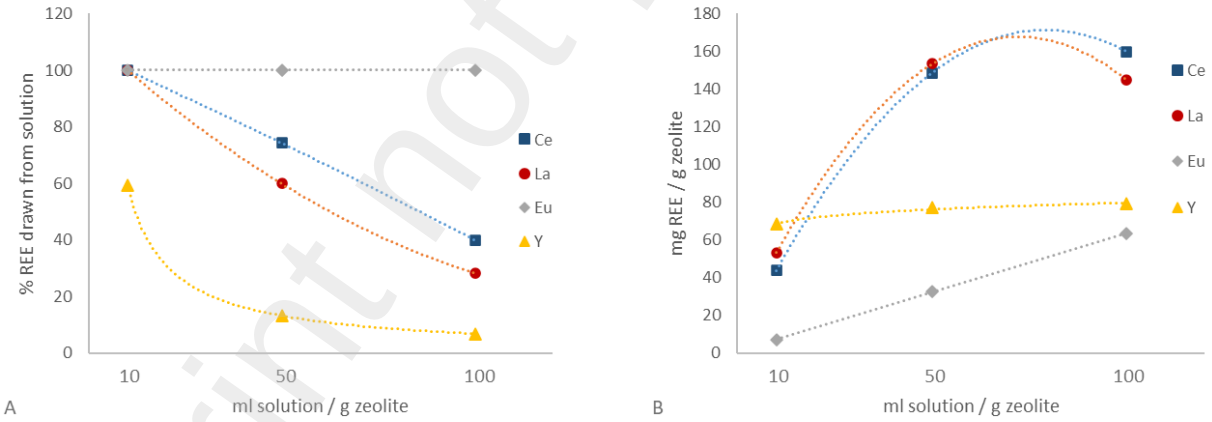

Figure 2. REE fraction drawn from solution (A) and amount of REE incorporated in the zeolite (B) as a function of the solid/liquid ratio. Initial concentrations (mg/L): Ce 0.029, La 0.037, Eu 0.005 and Y 0.13. The lines are guides for the eye.

The composition of the exchanged zeolites provides some information about their stability; in fact, the Si/Al ratio of 1.23 ± 0.03 (Figure 3A) is almost unaffected by the amount of REE in the solid and the volume of solution with which the sample interacted. These Si/Al ratios, significantly higher than the 1.14 value of the parent 13X, derive from the partial dissolution of Al, as would be expected by treating an Al-rich zeolite with an acid solution. The virtual constancy of the Si/Al when the solid is treated with larger volumes of acid solution suggests that the extraction of aluminium by acid hydrolysis has reached a stable state related to the pH of the solution. The pH behaviour of the solution depends on the exchanged REE, initial pH and liquid-to-solid ratio (Supplementary Table 3). In general, when the experimental conditions limit NH_4 exchange, pH tend to increase while, high NH_4 exchange results in a slight decrease in pH. The decrease of pH may be due to an increment of NH_4^+ concentration in the solution that promote acid hydrolysis. On the other hand, the increase in pH may be related to a smaller increase of NH_4^+ concentration and to the possible competition between H^+ protons and REE cations adsorbed in the NH_4-13X (Sánchez-Hernández et al., 2018), reasonable stabilizing over time at values close to neutrality.

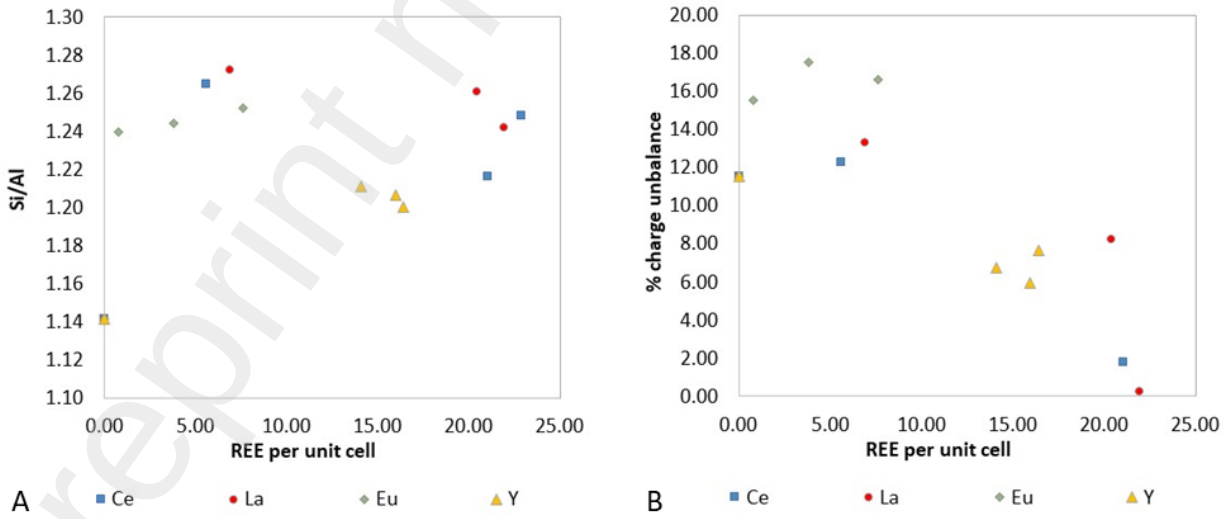

Figure 3. Modification of the zeolite with REE exchange: (A) Si/Al ratio and (B) fraction of Al not contributing to the compensation of the cation charge ((Al-cation charge)/Al) vs. REE cations per unit cell.

Hydrolysis of the Al-O-Si bonds passes through the formation of extra-framework aluminium species (EFAL) which no more form lattice anions whose charge has to be compensated by exchanged cations. The unbalance between cation charge and aluminium content in the sample, reported in Figure 3B, provides a first indication on the fraction of aluminium not forming lattice anions. The pristine 13X already has a significant charge unbalance (about 11 % of Al not requiring charge compensation), probably due to the presence of amorphous aluminium oxyhydroxides left over from zeolite synthesis. The charge unbalance of the exchanged samples is strictly related to their REE content. Samples with low REE content present a larger charge unbalance, suggesting that the dealumination of the samples has formed EFAL species not dissolved by the acid treatment. In samples characterized by the highest REE exchange, the charge unbalance systematically decreases with the REE content. Samples with 20 REE p.u.c. exhibit nearly perfect charge compensation, suggesting that virtually all aluminium is part of the framework.
This effect is probably related to the well-known stabilisation of the faujasite framework by REEs, which is the basis of the use of REE-Y catalysts in FCC (fluid catalytic cracking) (C. Vogt and M. Weckhuysen, 2015). Indeed, the highest thermal and hydrothermal stability of REE-exchanged zeolite Y allowed its use in the high-temperature steam-ridden conditions of the FCC plan regenerator (Li and Rees, 1986). This lattice stabilisation has been variously attributed to the polarization effect of REE clusters or REE cations in specific positions in the zeolite cages (Guzman et al., 2005; Scherzer et al., 1975; Schüßler et al., 2011). This effect was mainly observed for Al-poor zeolite Y under high-temperature steaming conditions; it is now relevant to observe a similar

stabilization also in the REE exchange Al-rich zeolite X in acidic environments. It can also be observed that the initial 13X zeolite was not completely in NH_4 form and a significant amount of Na cations were still present. This means that both NH_4^+ and Na^+ can be exchanged by REE cations, as showed by the results reported in Table 1. The fraction of Na and NH_4 cations in the exchanged zeolites are reported in Figure 4 as a function of the REE charge fraction. It may be noted that the NH_4 content decreases nearly linearly with the amount of REE exchanged. The Na fraction takes a different trend, remaining almost constant until at least half zeolite anions are compensated by REE cations and decreasing only for further REE exchange. This indicates a preferential exchange of NH_4 by REE and, significantly, this trend is common to all REE. Clearly, the affinity of the zeolite for REE is much higher than for ammonium, while residual sodium is much less easily exchanged.

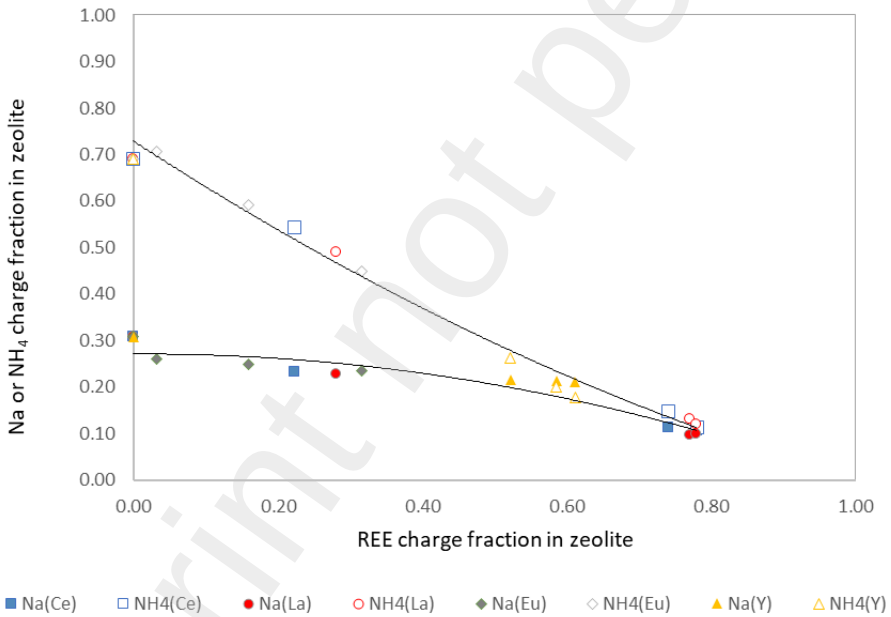

Figure 4. Na (filled symbols) and NH_4 (void symbols) content of the exchanged zeolites as a function of the REE content. Zeolites exchanged with Ce (squares), La (circles), Eu (diamond), Y (triangles). The lines are polynomial fittings for Na and NH_4 content.

3.3 REEs recovery from zeolite

The chemical formula and composition of the zeolites after the counter-exchange test in ammonium solution are reported in Table 2 and Supplementary Table 4, respectively. The fraction of REE extracted from the zeolites by the NH_4 solution vs. the initial amount of REE in the zeolite are reported in Figure 5. Two well-defined patterns appear. La and Y can be recovered by cation exchange with NH_4^+ at 30-45% while, under the same conditions, Ce and Eu are only recovered at 10-18% suggesting a higher affinity of the zeolitic framework for the latter two elements. This behaviour could be related to the variation of charge unbalance before and after the recovery process; in fact, in the case of La and Y the charge unbalance increases after the recovery with a consequent release of great amount of charge compensating ions while, in the case of Ce and Eu, the variation of charge unbalance before and after the recovery is low, suggesting a major stabilization of 13X zeolite after the ionic exchange.

Sample	**Chemical Formula**	**C. U. (%)**
Ce recovery_1/10	$Ce_{6.22}\ (NH_4)_{55.35}\ Na_{5.94}\ Mg_{0.60}\ P_{0.03}\ Ca_{0.21}\ Al_{86.94}\ Si_{106.33}\ O_{384}$ x 256.61 H_2O	8.06
Ce recovery_1/50	$Ce_{18.23}\ (NH_4)_{32.64}\ Na_{2.53}\ Mg_{0.79}\ P_{0.03}\ Ca_{0.11}\ Al_{86.67}\ Si_{104}\ O_{384}$ x 277.94 H_2O	-3.69
Ce recovery_1/100	$Ce_{18.16}\ (NH_4)_{31.06}\ Na_{2.59}\ Mg_{1.08}\ P_{0.02}\ Ca_{0.07}\ Al_{87.21}\ Si_{103.93}\ O_{384}$ x 277.64 H_2O	-1.07
La recovery_1/10	$La_{4.93}\ (NH_4)_{48.37}\ Na_{5.08}\ P_{0.04}\ Al_{86.24}\ Si_{110.16}\ O_{384}$ x 258.17 H_2O	20.86
La recovery_1/50	$La_{11.03}\ (NH_4)_{29.98}\ Na_{2.28}\ Mg_{0.45}\ P_{0.08}\ Ca_{0.08}\ Al_{88.53}\ Si_{108.79}\ O_{384}$ x 260.86 H_2O	26.18
La recovery_1/100	$La_{11.38}\ (NH_4)_{29.77}\ Na_{2.41}\ Mg_{0.33}\ P_{0.02}\ Al_{88.21}\ Si_{109.05}\ O_{384}$ x 260.98 H_2O	24.79
Eu recovery_1/10	$Eu_{0.68}\ (NH_4)_{61.27}\ Na_{8.5}\ Mg_{0.41}\ P_{0.01}\ Ca_{0.10}\ Al_{86.25}\ Si_{109.09}\ O_{384}$ x 254.16 H_2O	16.75
Eu recovery_1/50	$Eu_{3.84}\ (NH_4)_{54.83}\ Na_{6.51}\ Mg_{0.43}\ Ca_{0.17}\ Al_{84.60}\ Si_{110.29}\ O_{384}$ x 266.02 H_2O	15.14
Eu recovery_1/100	$Eu_{6.74}\ (NH_4)_{47.81}\ Na_{3.93}\ Mg_{0.21}\ Ca_{0.19}\ Al_{88.01}\ Si_{107.80}\ O_{384}$ x 262.49 H_2O	18.24
Y recovery_1/10	$Y_{8.62}\ (NH_4)_{43.90}\ Na_{5.96}\ Mg_{0.28}\ P_{0.13}\ Ca_{0.16}\ Al_{86.99}\ Si_{107.29}\ O_{384}$ x 262.07 H_2O	12.98
Y recovery_1/50	$Y_{9.38}\ (NH_4)_{42.62}\ Na_{5.13}\ Mg_{0.29}\ P_{0.10}\ Ca_{0.15}\ Al_{86.31}\ Si_{107.83}\ O_{384}$ x 263.97 H_2O	12.09

Y recovery_1/100	$Y_{10.01}\ (NH_4)_{41.29}\ Na_{5.29}\ Mg_{0.45}\ P_{0.05}\ Ca_{0.13}\ Al_{87.90}\ Si_{106.51}\ O_{384}$ x 263.77 H_2O	12.82

Table 2. Chemical formulas of the REE-exchanged zeolites after ammonium counter exchange. The charge unbalance was calculated as described in Table 1.

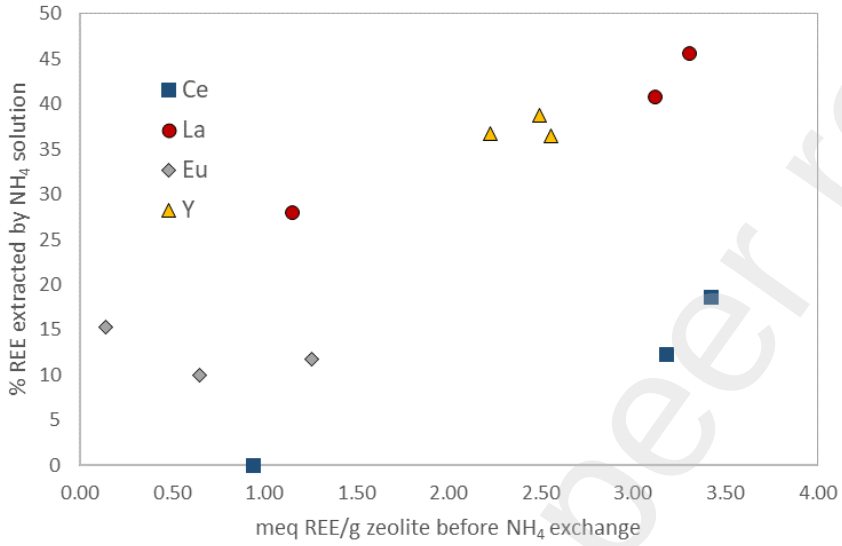

Figure 5. Fraction of REE extracted by ammonium solution as a function of the initial REE content in the zeolite.

3.4 Exchange isotherms

The affinity of the zeolite for trivalent REE cations is much higher than the affinity for monovalent Na and NH_4. Therefore, both REE exchange and NH_4 counter-exchange can be used to plot exchange isotherms of REE in 13X. The charge fraction of REE - defined as the ratio charge of REE / the total positive charges - in the zeolite is reported for all samples vs. the relative normality in solution (Figure 6). All exchange isotherms present a sharp rise of exchanged REE at the lowest concentration in solution, confirming the high affinity of REE for the 13X sites. The isotherms show

that Ce and La present a saturation plateau at about 0.78 charge fraction, which corresponds to a capacity of about 66 charges p.u.c. In contrast, yttrium presents a less well-defined plateau at lower REE content. A lower exchange capacity of 13X for Y than for heavier REE has been already observed (Guzzinati et al., 2018). The Langmuir isotherm $q=K*qmax*c/(1+K*c)$, where q is the fraction of exchange sites in the zeolite occupied by REE cations, q_{max} is the fraction of sites occupied by REE cations at the saturation of the exchanger, K is the affinity constant and c is the C/C° fraction between REE normality and total cation normality in solution, can be used to verify if the exchange occurs with the same chemical potential throughout the concentration field. The isotherms of Ce and Y can be satisfactorily fit by a Langmuir isotherm, suggesting a good homogeneity of their exchange sites. The q_{max} values for Ce and Y are very close (0.79 and 0.60 for Ce and Y, respectively), while the affinity constants significantly differ being 45 and 8, respectively. In the case of La, the isotherm cannot be fitted by a Langmuir isotherm, suggesting a heterogeneity of exchange site affinity for REE. However, the trend of the isotherm suggests an average affinity between those of Ce and Y. In the case of Eu all the experimental points are at very low C/C° values and the fitting with an isotherm model cannot be considered reliable.

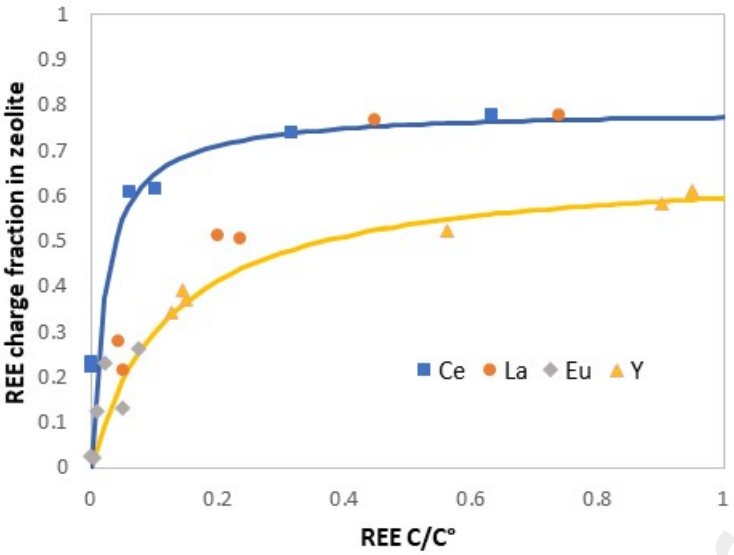

Figure 6. Charge fraction of REE in the zeolite vs. REE concentration fraction in equilibrium solution. The lines are Langmuir fit of the Ce and Y data.

4. Conclusions

This research has provided indications on the possible use of zeolites for the recovery of Ce, La and Y from simulated waste solutions highlighting the strengths and weaknesses of these materials. NH_4-13X zeolite revealed a good affinity towards REEs. For Ce, La and Y a maximum value of respectively 23, 22 and 16 atoms p.u.c. exchanged was found, while the starting concentration of Eu was too low to saturate the zeolite for every liquid-to-solid ratio, and the data obtained are not sufficient to evaluate the Eu affinity. The best exchange condition in terms of liquid-to-solid ratio for Ce and La is 50/1: the zeolite reaches amounts of REE p.u.c. near the saturation values, and a little REE remains in the solution. Y is concentrated enough to already saturate the zeolite also at a liquid-to-solid ratio of 10/1, yet leaving a lot of REE in the solution. With higher liquid to solid ratios, either for Ce, La and Y the amount of REE p.u.c. exchanged slightly increase, but not enough

to account for the consequent increase of REEs remaining in the solutions. Although Y is the most concentrated REE in the starting solution (0.13M), it is less exchanged than Ce and La, which were significantly less concentrated (respectively 0.03M and 0.04M). While Ce and La have a similar behaviour in exchanging with NH_4 and the residual Na, Y exchanges NH_4 in the same way, but is unable to exchange Na like Ce and La. Ce and La have therefore a higher affinity for the zeolite than both NH_4 and Na, while Y is more affine than NH_4 but less than Na. This could be due to the significantly smaller ionic radius of Y with respect to that of Ce, La and Na, suggesting that zeolite NH_4-13X is selective toward REEs with larger ionic radii. For applicative purposes, the Na remaining in the zeolite can thus play a relevant role; therefore, further experiments should be aimed at the total removal of Na from the zeolite before the REE-exchange tests, in order to evaluate the variations of the affinities in a fully NH_4-exchanged 13X.

The recovery of REEs from the exchanged zeolites is another aspect to work on. Ce and Eu recoveries were almost nil, while almost half of La and Y were recovered. With a view to the work of Eduafo et al. (2015), from which the concentrations of the starting solutions were taken, these findings are crucial. In fact, considering that this behaviour was observed by the interaction with two different solutions, one enriched in Ce and La and the other one in Eu and Y, NH_4-13X zeolite can potentially selectively release La over Ce and Y over Eu.

5. References

Ambaye, T.G., Vaccari, M., Castro, F.D., Prasad, S., Rtimi, S., 2020. Emerging technologies for the recovery of rare earth elements (REEs) from the end-of-life electronic wastes: a review on progress, challenges, and perspectives. Environ. Sci. Pollut. Res. 27, 36052–36074. https://doi.org/10.1007/s11356-020-09630-2

Anastopoulos, I., Bhatnagar, A., Lima, E.C., 2016. Adsorption of rare earth metals: A review of recent literature. J. Mol. Liq. 221, 954–962. https://doi.org/10.1016/j.molliq.2016.06.076

Ayora, C., Macías, F., Torres, E., Lozano, A., Carrero, S., Nieto, J.-M., Pérez-López, R., Fernández-Martínez, A., Castillo-Michel, H., 2016. Recovery of Rare Earth Elements and Yttrium from Passive-Remediation Systems of Acid Mine Drainage. Environ. Sci. Technol. 50, 8255–8262. https://doi.org/10.1021/acs.est.6b02084

Baerlocher, C., McCusker, L.B., Olson, D., Meier, W.M., 2007. Atlas of zeolite framework types, 6th rev. ed. ed. Published on behalf of the Structure Commission of the International Zeolite Association by Elsevier, Amsterdam Boston.

Balaram, V., 2019. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geosci. Front. 10, 1285–1303. https://doi.org/10.1016/j.gsf.2018.12.005

Barros, Ó., Costa, L., Costa, F., Lago, A., Rocha, V., Vipotnik, Z., Silva, B., Tavares, T., 2019. Recovery of rare earth elements from wastewater towards a circular economy. Molecules 24. https://doi.org/10.3390/molecules24061005

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Pontikes, Y., 2015. Towards zero-waste valorisation of rare-earth-containing industrial process residues: A critical review. J. Clean. Prod. 99, 17–38. https://doi.org/10.1016/j.jclepro.2015.02.089

Blissett, R.S., Smalley, N., Rowson, N.A., 2014. An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content. Fuel 119, 236–239. https://doi.org/10.1016/j.fuel.2013.11.053

Bobba, S., Carrara, S., Huisman, J., Mathieux, F., Pavel, C., 2020. Critical raw materials for strategic technologies and sectors in the EU. A Foresight Study.

403 Borra, C.R., Blanpain, B., Pontikes, Y., Binnemans, K., Van Gerven, T., 2016. Recovery of Rare Earths
404 and Other Valuable Metals From Bauxite Residue (Red Mud): A Review. J. Sustain. Metall.
405 2, 365–386. https://doi.org/10.1007/s40831-016-0068-2
406 Cánovas, C.R., Chapron, S., Arrachart, G., Pellet-Rostaing, S., 2019. Leaching of rare earth elements
407 (REEs) and impurities from phosphogypsum: A preliminary insight for further recovery of
408 critical raw materials. J. Clean. Prod. 219, 225–235.
409 https://doi.org/10.1016/j.jclepro.2019.02.104
410 Chen, P., Yang, F., Liao, Q., Zhao, Z., Zhang, Y., Zhao, P., Guo, W., Bai, R., 2017. Recycling and
411 separation of rare earth resources lutetium from LYSO scraps using the diglycol amic acid
412 functional XAD-type resin. Waste Manag. 62, 222–228.
413 https://doi.org/10.1016/j.wasman.2017.02.020
414 Chen, S.H., Chao, K.J., Lee, T.Y., 1990. Lanthanum-NaY zeolite ion exchange. 1. Thermodynamics
415 and thermochemistry. Ind. Eng. Chem. Res. 29, 2020–2023.
416 https://doi.org/10.1021/ie00106a007
417 Confalonieri, G., Vezzalini, G., Maletti, L., Di Renzo, F., Gozzoli, V., Arletti, R., 2022. Ion exchange
418 capacity of synthetic zeolite L: a promising way for cerium recovery. Environ. Sci. Pollut.
419 Res. 29, 65176–65184. https://doi.org/10.1007/s11356-022-20429-1
420 C. Vogt, E.T., M. Weckhuysen, B., 2015. Fluid catalytic cracking: recent developments on the grand
421 old lady of zeolite catalysis. Chem. Soc. Rev. 44, 7342–7370.
422 https://doi.org/10.1039/C5CS00376H
423 Eduafo, P.M., Strauss, M.L., Mishra, B., 2015. Experimental investigation of recycling rare earth
424 metals from waste fluorescent lamp phosphors. Presented at the TMS Annual Meeting, pp.
425 253–259. https://doi.org/10.1002/9781119093244.ch29

Eremin, O.V., Epova, E.S., Filenko, R.A., Rusal', O.S., Bychinsky, V.A., 2017. Use of Zeolite Rocks in Metal Recovery from Mine Water. J. Min. Sci. 53, 915–924. https://doi.org/10.1134/S1062739117052957

European Commission, 2020. Critical raw materials resilience: Charting a path towards greater security and sustainability. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0474

Funari, V., Bokhari, S.N.H., Vigliotti, L., Meisel, T., Braga, R., 2016. The rare earth elements in municipal solid waste incinerators ash and promising tools for their prospecting. J. Hazard. Mater. 301, 471–479. https://doi.org/10.1016/j.jhazmat.2015.09.015

Gijsemans, L., Forte, F., Onghena, B., Binnemans, K., 2018. Recovery of rare earths from the green lamp phosphor LaPO4:Ce3+,Tb3+ (LAP) by dissolution in concentrated methanesulphonic acid. RSC Adv. 8, 26349–26355. https://doi.org/10.1039/c8ra04532a

González, R.M., Cánovas, C.R., Olías, M., Macías, F., 2020. Rare earth elements in a historical mining district (south-west Spain): Hydrogeochemical behaviour and seasonal variability. Chemosphere 253. https://doi.org/10.1016/j.chemosphere.2020.126742

Gualtieri, A.F., 2000. Accuracy of XRPD QPA using the combined Rietveld-RIR method. J. Appl. Crystallogr. 33, 267–278. https://doi.org/10.1107/S002188989901643X

Gualtieri, A.F., Gatta, G.D., Arletti, R., Artioli, G., Ballirano, P., Cruciani, G., Guagliardi, A., Malferrari, D., Masciocchi, N., Scardi, P., 2019. Quantitative phase analysis using the Rietveld method: towards a procedure for checking the reliability and quality of the results. Period. Mineral. 88. https://doi.org/10.2451/2019PM870

Guzman, A., Zuazo, I., Feller, A., Olindo, R., Sievers, C., Lercher, J.A., 2005. On the formation of the acid sites in lanthanum exchanged X zeolites used for isobutane/cis-2-butene alkylation.

Microporous Mesoporous Mater. 83, 309–318. https://doi.org/10.1016/j.micromeso.2005.04.024

Guzzinati, R., Sarti, E., Catani, M., Costa, V., Pagnoni, A., Martucci, A., Rodeghero, E., Capitani, D., Pietrantonio, M., Cavazzini, A., Pasti, L., 2018. Formation of Supramolecular Clusters at the Interface of Zeolite X Following the Adsorption of Rare-Earth Cations and Their Impact on the Macroscopic Properties of the Zeolite. ChemPhysChem 19, 2208–2217. https://doi.org/10.1002/cphc.201800333

Han, K.N., 2020. Characteristics of Precipitation of Rare Earth Elements with Various Precipitants. Minerals 10, 178. https://doi.org/10.3390/min10020178

Hedin, B.C., Capo, R.C., Stewart, B.W., Hedin, R.S., Lopano, C.L., Stuckman, M.Y., 2019. The evaluation of critical rare earth element (REE) enriched treatment solids from coal mine drainage passive treatment systems. Int. J. Coal Geol. 208, 54–64. https://doi.org/10.1016/j.coal.2019.04.007

Hérès, X., Blet, V., Di Natale, P., Ouaattou, A., Mazouz, H., Dhiba, D., Cuer, F., 2018. Selective extraction of rare earth elements from phosphoric acid by ion exchange resins. Metals 8. https://doi.org/10.3390/met8090682

Iannicelli-Zubiani, E.M., Cristiani, C., Dotelli, G., Gallo Stampino, P., Pelosato, R., Mesto, E., Schingaro, E., Lacalamita, M., 2015. Use of natural clays as sorbent materials for rare earth ions: Materials characterization and set up of the operative parameters. Waste Manag. 46, 546–556. https://doi.org/10.1016/j.wasman.2015.09.017

Janssen, A.H., Koster, A.J., de Jong, K.P., 2001. Three-Dimensional Transmission Electron Microscopic Observations of Mesopores in Dealuminated Zeolite Y. Angew. Chem. Int. Ed. 40, 1102–1104. https://doi.org/10.1002/1521-3773(20010316)40:6<1102::AID-ANIE11020>3.0.CO;2-6

473 Jowitt, S.M., Werner, T.T., Weng, Z., Mudd, G.M., 2018. Recycling of the rare earth elements. Curr.
474 Opin. Green Sustain. Chem., Reuse and Recycling / UN SGDs: How can Sustainable
475 Chemistry Contribute? / Green Chemistry in Education 13, 1–7.
476 https://doi.org/10.1016/j.cogsc.2018.02.008
477 Kocasoy, G., Şahin, V., 2007. Heavy metal removal from industrial wastewater by clinoptilolite. J.
478 Environ. Sci. Health - Part ToxicHazardous Subst. Environ. Eng. 42, 2139–2146.
479 https://doi.org/10.1080/10934520701629617
480 Larson, A.C., Dreele, R.B.V., 2000. General Structure Analisys System (GSAS) 86–748.
481 Li, C.-Y., Rees, L.V.C., 1986. The thermal stability of faujasites with different SiAl ratios. Zeolites 6,
482 60–65. https://doi.org/10.1016/0144-2449(86)90013-8
483 Li, X., Wu, P., 2017. Geochemical characteristics of dissolved rare earth elements in acid mine
484 drainage from abandoned high-As coal mining area, southwestern China. Environ. Sci.
485 Pollut. Res. 24, 20540–20555. https://doi.org/10.1007/s11356-017-9670-5
486 Lie, J., Liu, J.-C., 2021. Selective recovery of rare earth elements (REEs) from spent NiMH batteries
487 by two-stage acid leaching. J. Environ. Chem. Eng. 9.
488 https://doi.org/10.1016/j.jece.2021.106084
489 Mao, F., Zhu, N., Zhu, W., Liu, B., Wu, P., Dang, Z., 2022. Efficient recovery of rare earth elements
490 from discarded NdFeB magnets by mechanical activation coupled with acid leaching.
491 Environ. Sci. Pollut. Res. 29, 25532–25543. https://doi.org/10.1007/s11356-021-17761-3
492 Mondale, K.D., Carland, R.M., Aplan, F.F., 1995. The comparative ion exchange capacities of
493 natural sedimentary and synthetic zeolites. Miner. Eng., Minerals Engineering ’94
494 Proceedings of the International Conference 8, 535–548. https://doi.org/10.1016/0892-
495 6875(95)00015-I

Mosai, A.K., Chimuka, L., Cukrowska, E.M., Kotzé, I.A., Tutu, H., 2019. The Recovery of Rare Earth Elements (REEs) from Aqueous Solutions Using Natural Zeolite and Bentonite. Water. Air. Soil Pollut. 230. https://doi.org/10.1007/s11270-019-4236-4

Mosai, A.K., Tutu, H., 2021. Simultaneous sorption of rare earth elements (including scandium and yttrium) from aqueous solutions using zeolite clinoptilolite: A column and speciation study. Miner. Eng. 161. https://doi.org/10.1016/j.mineng.2020.106740

Motsi, T., Rowson, N.A., Simmons, M.J.H., 2009. Adsorption of heavy metals from acid mine drainage by natural zeolite. Int. J. Miner. Process. 92, 42–48. https://doi.org/10.1016/j.minpro.2009.02.005

Opare, E.O., Struhs, E., Mirkouei, A., 2021. A comparative state-of-technology review and future directions for rare earth element separation. Renew. Sustain. Energy Rev. 143. https://doi.org/10.1016/j.rser.2021.110917

Pavón, S., Fortuny, A., Coll, M.T., Sastre, A.M., 2018. Rare earths separation from fluorescent lamp wastes using ionic liquids as extractant agents. Waste Manag. 82, 241–248. https://doi.org/10.1016/j.wasman.2018.10.027

Pinto, J., Colónia, J., Abdolvaseei, A., Vale, C., Henriques, B., Pereira, E., 2023. Algal sorbents and prospects for their application in the sustainable recovery of rare earth elements from E-waste. Environ. Sci. Pollut. Res. 30, 74521–74543. https://doi.org/10.1007/s11356-023-27767-8

Porvali, A., Wilson, B.P., Lundström, M., 2018. Lanthanide-alkali double sulfate precipitation from strong sulfuric acid NiMH battery waste leachate. Waste Manag. 71, 381–389. https://doi.org/10.1016/j.wasman.2017.10.031

Rees, L.V.C., 1970. Chapter 9. Ion exchange in zeolites. Annu Rep Prog Chem Sect Gen Phys Inorg Chem 67, 191–212. https://doi.org/10.1039/GR9706700191

520 Sánchez-Hernández, R., Padilla, I., López-Andrés, S., López-Delgado, A., 2018. Al-Waste-Based
521 Zeolite Adsorbent Used for the Removal of Ammonium from Aqueous Solutions. Int. J.
522 Chem. Eng. 2018, e1256197. https://doi.org/10.1155/2018/1256197
523 Scherzer, J., Bass, J.L., Hunter, F.D., 1975. Structural characterization of hydrothermally treated
524 lanthanum Y zeolites. I. Framework vibrational spectra and crystal structure. J. Phys. Chem.
525 79, 1194–1199. https://doi.org/10.1021/j100579a010
526 Schüßler, F., Pidko, E.A., Kolvenbach, R., Sievers, C., Hensen, E.J.M., Van Santen, R.A., Lercher, J.A.,
527 2011. Nature and Location of Cationic Lanthanum Species in High Alumina Containing
528 Faujasite Type Zeolites. J. Phys. Chem. C 115, 21763–21776.
529 https://doi.org/10.1021/jp205771e
530 Silva, R.G., Morais, C.A., Teixeira, L.V., Oliveira, É.D., 2019. Selective Precipitation of High-Quality
531 Rare Earth Oxalates or Carbonates from a Purified Sulfuric Liquor Containing Soluble
532 Impurities. Min. Metall. Explor. 36, 967–977. https://doi.org/10.1007/s42461-019-0090-6
533 Xie, B., Liu, C., Wei, B., Wang, R., Ren, R., 2023. Recovery of rare earth elements from waste
534 phosphors via alkali fusion roasting and controlled potential reduction leaching. Waste
535 Manag. 163, 43–51. https://doi.org/10.1016/j.wasman.2023.03.029
536 Yang, Y., Walton, A., Sheridan, R., Güth, K., Gauß, R., Gutfleisch, O., Buchert, M., Steenari, B.-M.,
537 Van Gerven, T., Jones, P.T., Binnemans, K., 2017. REE Recovery from End-of-Life NdFeB
538 Permanent Magnet Scrap: A Critical Review. J. Sustain. Metall. 3, 122–149.
539 https://doi.org/10.1007/s40831-016-0090-4
540 Yantasee, W., Fryxell, G.E., Addleman, R.S., Wiacek, R.J., Koonsiripaiboon, V., Pattamakomsan, K.,
541 Sukwarotwat, V., Xu, J., Raymond, K.N., 2009. Selective removal of lanthanides from
542 natural waters, acidic streams and dialysate. J. Hazard. Mater. 168, 1233–1238.
543 https://doi.org/10.1016/j.jhazmat.2009.03.004

544 Yuksekdag, A., Kose-Mutlu, B., Zeytuncu-Gokoglu, B., Kumral, M., Wiesner, M.R., Koyuncu, I., 2022.
545 Process optimization for acidic leaching of rare earth elements (REE) from waste electrical
546 and electronic equipment (WEEE). Environ. Sci. Pollut. Res. 29, 7772–7781.
547 https://doi.org/10.1007/s11356-021-16207-0
548 Zhang, B., Liu, C., Li, C., Jiang, M., 2014. A novel approach for recovery of rare earths and niobium
549 from Bayan Obo tailings. Miner. Eng. 65, 17–23.
550 https://doi.org/10.1016/j.mineng.2014.04.011
551 Zhu, L., Seff, K., 1999. Reinvestigation of the Crystal Structure of Dehydrated Sodium Zeolite X. J.
552 Phys. Chem. B 103, 9512–9518. https://doi.org/10.1021/jp991817l