Recovery Alternatives for Rare Earths Elements (REE) Contained in Monazite and in Cathode ray Tubes (CRT)

LIZET ALVARADO-HERNÁNDEZ AND GRETCHEN T. LAPIDUS*

Depto. Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana - Iztapalapa, Avenida Ferrocarril San Rafael Atlixco número 186, Colonia Leyes de Reforma 1a sección, Alcaldía de Iztapalapa, Ciudad de México, 09310 México

Abstract : In the present study, ultrasonic energy was employed to assist in the recovery of rare earth elements contained in cathode ray tube phosphors and the mineral monazite, (Ce, La, Pr, Nd, Th, Y) PO_4 . Metallic iron (Fe°) was added to the ultrasonic leaching process, which acts as a collector for phosphate ions, the principal deterrent for REE leaching from both materials. In each case, after sonication in pyrophosphate solution (0.1 M Na₄P₂O₇), the leach liquor and two solids were detected, one magnetic (M+) and the other non-magnetic (NoM+). The phosphate ion transfer into the M+ phase was 83% for the CRT and 94% for the monazite, while over 90% of the REE remained in the NoM+ phase. The NoM+ was later contacted with boiling 1 M H₂SO₄ solution, leaching nearly all of the REE.

Keywords: Sono-leaching, Monazite, CRT powder, Pyrophosphate

1. INTRODUCTION :

The demand for rare earth elements (REEs) has significantly increased in recent years, due to their use in diverse technological applications, such as for clean energy applications and in high-performance airplane fuselages. The USA imports 97% of its yttrium oxide from China and projections show that this will increase, fore shadowing supply issues in the near future [1].

One of the main primary sources of REE is the mineral monazite (Ce, La, Pr, Nd, Th, Y)PO₄. However, REE extraction, separation and purification procedures are normally quite complicated due to its inherent structure [2 - 5]. For that reason, the search for a radical change in processing practices is warranted. Furthermore, REE recovery from different e-wastes, especially cathode ray tube kinescopes (CRT) from analogue televisions, would constitute a competitive source.

While monazite contains an average of 55% of its weight in REEs, it is generally refractory due to the presence of the phosphate ion [6], which is also the case for the CRT's [7]. Structural disruption and removal of the phosphate ion usually requires substitution by sulfate or hydroxide at elevated temperatures, which generates leach liquors that is itself constitute an unwanted liquid waste. Emerging recovery technologies, such as bioleaching and alkali pug bake-leaching have been proposed with limited success or excessive reagent use [8].

*Corresponding Author : E-mail: gtll@xanum.uam.mx

The present study proposes the use of ultrasonic technology, as an alternative to previously suggested pretreatments to assist in REE recovery from monazite as well as from waste CRT. Sonochemistry, consisting in the application of ultrasound radiation (20 kHz – 10 MHz) to solid-liquid systems, have been used to increase diffusion of soluble species in the liquid phase and induce the creation of microfissures, as well as particle breakage, in the solid due to cavitation [9,10]. Furthermore, acoustic cavitation creates localized pressure and temperature elevations, which lead to the homolytic dissociation of water, generating H and OH radicals; these combine to form H₂O₂, represented by the following reactions (Eq. 1-3)[11-12]:

$$\begin{array}{ll} H_2O & \rightarrow & HO + H \cdot & (1) \\ H \cdot + & H \cdot & \rightarrow & H_2 & (2) \\ \cdot OH + \cdot OH & \rightarrow & H_2 O_2 & (3) \end{array}$$

The presence of H_2 y H_2O_2 generates physical and chemical effects since they are strong reducing agents that could improve the leaching conditions of the REE.

In recent investigations, REE's, contained in liquid crystal displays (LCD), were leached into an aqueous pyrophosphate solution ($Na_4P_2O_7$) and some were simultaneously incorporated into a magnetic solid generated in the ultrasonication process [13]. The magnetic solid was formed by the reduction of iron oxide present in the starting material and assisted by quelation with the pyrophosphate ion, which preferentially forms complexes with metal ions in their +III oxidation state, such as the ferric ion and REE's [14].

Notwithstanding, the compositions of monazite and CRT powder differ from that of the LCD in that the former materials contain very little iron, while the latter consists basically of oxides with negligible phosphate ions. For that reason, although similar leaching conditions were employed to study the behavior of monazite and CRT powders in this system, metallic iron powder was added to the solid mixture.

1.1. THERMODYNAMIC CONSIDERATIONS

The pyrophosphate ion $(P_2O_7^{4^-})$ was selected to assist in the quelation of REE ions in the leaching solution. Speciation diagrams as a function of pH for Ce³⁺, Y³⁺ and Eu³⁺ in the CRT and Nd³⁺, Tb³⁺ and La³⁺ in the monazite with pyrophosphate were elaborated using the MEDUSA© software suite (Making Equilibrium Diagrams Using Simple Algorithms), complemented with critical stability constants obtained from the NIST database [14]. Figure 1 (A, B) shows the soluble complexes, as well as the solid species, formed in a 0.1 M $P_2O_7^{4^-}$ solution at 25°C.



Figure 1. Species distribution diagrams for A) Ce³⁺, Y³⁺ and Eu³⁺ for the CRT and B) Nd³⁺, Tb³⁺ and La³⁺ for the monazite, as a function of pH in 0.1 MP 207⁴⁻ solution at 25 °C with the following concentrations: 0.001 M Ce³⁺, 0.001 M Y³⁺, 0.0001 Eu³⁺, 0.001 Nd³⁺, 0.001 Tb³⁺ and 0.001 M La³⁺.

As may be observed in the figure, all of the REE ions form soluble complexes with the pyrophosphate ion between pH 2 and 9, in the absence of phosphate ion.

However, if the phosphate is present in equal amounts with the pyrophosphate ion (0.1 M), the solubility of the REE is severely affected, as shown in Figure 2 (A, B). For that reason, the successful removal of phosphate from the starting material is a necessary prerequisite for REE leaching.



Figure 2. Species distribution diagrams for A) Ce³⁺, Y³⁺ and Eu³⁺ for the CRT and B) Nd³⁺, Tb³⁺ and La³⁺ for the monazite, as a function of pH in 0.1 MP 207⁴ solution at 25 °C with the following concentrations: 0.001 M Ce³⁺, 0.001 M Y³⁺, 0.0001 Eu³⁺, 0.001 Nd³⁺, 0.001 Tb³⁺ and 0.001 M La³⁺

2. MATERIALS AND METHODS

2.1. Materials

The monazite for this study, originally from Petaca, New Mexico, was provided by Excalibur Mineral Corp. The total rare earth content was approximately 21.5% by weight, the majority of which were Nd, Tb and La. The rare earth composition of the preponderant elements is shown in Table 1. Since Nd reports the highest concentration among the rare earth elements, it is considered a monazite-(Nd). Monazite particles were ground in an agate mortar to avoid contamination, especially by iron and alumina. The resulting particles were sieved and classified by size fractions: -60 + 100 mesh (149-250 µm), -100 + 140 mesh (105-149 µm), -270 + 400 mesh (37-53 µm) and -400 mesh (-37 µm). The size fraction used for this study was that of -60 + 100 mesh (149-250 µm).

Table	1 Average	rare earth	elemental	content of	monazite*.

Element	Y	La	Eu	Nd	Gd	Tb	Dy	Sm
Content (wt%)	1.5	4.2	0.1	6.1	3.7	4.1	1.7	0.05
$T_{oto1} DEE = 21.50/$								

Total REE = 21.5%

*Table 1. does not include elements whose content is <0.05%

One hundred television sets (TV's) were collected from individuals and donated by the Reciclatón program, a program of the Secretariat for the Environment of Mexico City. The TVs were dismantled, removing the casing, metals and plastics, while the kinescopes or cathode ray tubes (CRT) were separated. The CRT were discharged by short circuiting. The kinescopes were opened to access the phosphor layer, which contains the rare earth compounds as a very thin coating (Table 2). This operation was performed manually, harvesting for each 20-inch TV approximately 2.5 g of the target sample.

Table 2. Metallic	content of the	CRT phosphor	[.] sample.
-------------------	----------------	---------------------	----------------------

Element	Eu	Y	Ce	Sm	Al	P	Zn	Pb	Fe	S
Content (wt%)	0.9	14.2	14.3	0.9	4.8	2.0	26.3	0.4	0.24	11.1

Total REE = 75.14%

2.2. Sono-leaching Conditions

100 mL of 0.1 M Na₄P₂O₇ (NaPP) was combined with 0.7, 1.4 or 2.8 g Fe^{\circ} (7, 14 and 28 g/L Fe^{\circ}) and 1 g of monazite or CRT powder (10 g/L) and the pH was adjusted to 3 with sulfuric acid. An ultrasound probe [9], with a piezoelectric transducer at 90 kHz frequency and a titanium tip of 9.5 mm, was introduced and energy was applied for 3 hours at 100% amplitude (Figure 3) The experiments were performed at a sonication output power of 120 W. Unless otherwise specified, the temperature was controlled at 25°C.

Three products resulted from the leaching process: the leach liquor, a magnetic solid (M+) and a non-magnetic residue (NoM+).



Figure 3. Schematic diagram of the experimental leaching system with in-situ ultrasonic energy application and the resulting products.

Samples of both solid products were subjected an aqua regia digestion $(2:1 \text{ ratio HCl:HNO}_3)$ and their REE and P content in the leach liquor was determined by microwave-induced plasma atomic emission spectrometry (MP-AES 4210, Agilent Technologies). Likewise, the leach liquor was analyzed directly by the same method.

Subsequently, the monazite NoM+ was subjected to leaching with nitric or sulfuric acid to extract the REE and the pregnant solutions were analyzed by MP-AES.

3. RESULTS AND DISCUSSION

In preliminary studies, it was observed that the metallic iron, which formed the magnetic solid, acted as an attracter for the phosphate ion, leaving most of the REE as an oxides in the non-magnetic residue (NoM+). The largest quantity of Fe^o resulted in greater removal of phosphate from the original material, being incorporated mostly into the magnetic solid. Table 3 shows the distribution of phosphate (% P) in the leach liquor (LL) and the magnetic solid (M+), as well that which remains in the non-magnetic residue (NoM+), after 3 hours of sono-leaching (application of ultrasonic energy) for both CRT powder and monazite. The fact is that the phosphate was concentrated in an independent, magnetically separable phase represents a clear advantage compared to other REE dissolution methods, where the leach liquor contains a large amount of contaminating species, limiting its reuse after REE recovery.

Table 3. Distribution of the phosphate ion in the CRT and monazite leaching products after the
application of ultrasonic energy for 3 hours in contact with 28 g/L Fe*. Initial content of CRT
or monazite powder: 10 g/L of 0.1 M sodium pyrophosphate solution.

Fe° (g/L)	% P in LL		% P i	in M+	% P in NoM+		
	CRT Mon		CRT	Mon	CRT Mon		
28	13.7	2.9	82.7	94.6	3.6	2.5	

Fe° addition to the sodium pyrophosphate (NaPP) impacts directly on the amount of phosphate removed from the original materials (96.4% for CRT and 97.5% for the monazite). This pretreatment disrupted the structure of the materials, allowing them to be attacked and dissolved in a subsequent leach.

The quantity of REE lost to the sono-leaching solution and to the magnetic solid (M+) was very small as can be observed in Table 4 for the CRT powder using different quantities of Fe[°] powder. This implies an efficient transformation of the REE phosphates.

Table 4.	% Eu and	Y remaining i	n the non-magne	tic residue (NoM	(+) after leaching	CRT powder
----------	----------	---------------	-----------------	------------------	--------------------	------------

Fe° (g/L)	% Eu	% Y		
7	100	82		
14	100	73		
28	96	94		

Although the percentage of REE loss was hardly affected by the amount of Fe^{\circ} in the sono-leach, the removal of phosphate and its concentration into the metallic phase (M+) was superior at larger doses. For that reason, 28 g Fe^{\circ}/L was used for the remainder of experiments on both materials.

3.1. Sono-leaching Time

Increasing the duration of the sono-leach also affected the percentage of phosphate removal from the CRT material and its ultimate fate, as shown in Table 5 for 1 and 3 hours of sonication. Although the phosphate remaining in the non-magnetic residue (NoM+) from the original material does not vary significantly from 1 to 3 hours, the longer time enabled more phosphate to be incorporated into the magnetic solid (M+).

Table 5. % P in Leach liquor (LL), magnetic solid (M+) and non-magnetic residue (NoM+).

Leach time (h) with ultrasound	%P in LL	%P in M+	%P in NoM+	
1	39	54	6	
3	14	83	4	

For that reason, further experimentation with monazite was performed for 3 hours in 0.1 M pyrophosphate solution at pH 3.

3.2. With And Without Temperature Control

Initially the experiments were carried out with strict temperature control (25° C); to this end, the sono-leach reactor was placed in a jacketed water bath cooled with ice. Due to cavitation phenomena, the uncontrolled temperature reached 40°C in the 3-hour experiment. Figure 4 shows that the incorporation of phosphate into the magnetic solid (M+) is relatively unaffected by temperature, but there would appear to be a better separation of neodymium. It is interesting to note that, of all the REE, due to its magnetic characteristics, Nd tends to be attracted to the Fe°.



Figure 4. P (phosphate ion) and Nd concentrated in the magnetic solid (M+), with and without temperature control, in the experiments with monazite. Sono-leaching conditions: 3 hours at pH 3.

In Figure 5, an analysis of the non-magnetic residue confirms that almost all of the REE (< 90%) remain in this phase, both with and without temperature control, with the exception of Nd. It might be observed, the most significant finding is that, in both cases, less than 5% of the original phosphate ion was still present, have been concentrated in the M+ phase by sono-leaching with the presence of iron.



Figure 5. Phosphate ion (P) and REE remaining in the non-magnetic monazite residue (NoM+). Sono-leaching conditions: 3 hours at pH 3.

The CRT powder shows similar tendencies, although REE remain to a lesser degree (Figure 6). An appreciable quantity of Ce was lost to the pyrophosphate solution, probably due to its great affinity for pyrophosphate and ends up in the magnetic solid. As in the monazite case, the great majority of phosphate was removed from the original material.



Figure 6. Phosphate ion (P) and REE remaining in the non-magnetic CRT residue (NoM+). Sono-leaching conditions: 3 hours at pH 3.

As a final remark regarding temperature control, given the at most marginal improvement selectivity and phosphate removal, the extra expense that would be required to maintain a constant temperature might not be justified. However, the wear on the ultrasound equipment at the higher temperature (especially of the titanium tip) and the operation at elevated solid to liquid ratios will decisively determine the need for cooling.

3.3. Recovery of REE from the Non-magnetic Residue (NOM+)

As it was determined in the previous section, the resulting non-magnetic residues (NoM+) contained most of the REE, despite the almost complete removal of the phosphate ion. The fact that the REE did not dissolve into the pyrophosphate solution shows that their recovery requires stronger leaching conditions, such as elevated concentrations of inorganic acids, longer times and/or higher temperatures, although these measures could lead to larger energy expenditures and the introduction of more contaminants in this second leaching solution [15]. In any event, to confirm this premise, several leaching tests were performed on the monazite non-magnetic residue (NoM+) to determine their efficiency in the dissolution of the REEs. Firstly, two samples of the NoM+ was subjected to a 24hour leach at room temperature in contact with 1 M HCl or 1 M H_2SO_4 , respectively. The results, shown as the percentage of each element leached, are presented in Table 6, indicating that sulfuric acid is more effective than nitric acid.

Table 6. Dissolution of the REEs contained in the non-magnetic residue (NoM+).Sono-leaching pretreatment conditions: 3 hours at pH 3.

	% Y	% Dy	% Nd	% Tb	% La
$1 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	43.5	31.8	32.6	23.1	15.1
1 M HNO ₃	30.1	27.2	11.9	12.3	3.9

4. CONCLUSIONS

Sono-leaching in pyrophosphate solution, with metallic iron, is an efficient method to remove the phosphate ion from monazite and CRT powder, concentrating it in a separate, magnetic solid; this solid can be easily separated from the non-magnetic residue. In both starting materials, the majority of the REE remains in the non-magnetic leach residue, with a minimum phosphate content. Furthermore, since only small amounts of phosphate stays in the pyrophosphate leach liquor, which would probably permit its direct reuse in subsequent leach cycles and/or allow processing of larger quantities of these wastes with the same volume of liquid. After the sono-leaching stage, the REE may be leached with sulfuric or nitric acid, although the former is apparently more efficient.

In conclusion, sonic pretreatment with the addition of metallic iron is constitute low-cost technique to decrease the refractory characteristics of CRT powder and monazite, assisting in the economic recovery of REE.

REFERENCES

- [1] U.S. Geological Survey (USGS), Mineral Commodity Summaries, January 2022
- [2] Gupta, C.K. & Krishnamurthy, N. (2004). Extractive Metallurgy of Rare Earths. CRC Press, New York.

- [3] Kim, E.-Y. & Osseo-Asare, K. (2012). Aqueous stability of thorium and rare earth metals in monazite hydrometallurgy: Eh-pH diagrams for the systems Th-, Ce-, La-, Nd- (PO₄)-(SO₄)-H₂O at 25 °C. *Hydrometallurgy* 113–114, 67–78. doi:10.1016/j.hydromet.2011.12.007
- [4] Panda, R., Kumari, A., Jha, M.K., Hait, J., Kumar, V., Kumar, J.R. & Lee, J.Y. (2014). Leaching of rare earth metals (REMs) from Korean monazite concentrate. *J. Ind. Eng. Chem.* 20, 2035–2042. doi:10.1016/j.jiec.2013.09.028
- [5] Lucas, J., Lucas, P., Le Mercier, T., Rollat, A. & Davenport, W. (2015). Rare Earths: Science, Technology, Production and Use. Elsevier, Amsterdam, pp. 51–55.
- [6] Lapidus, G.T. & Doyle, F.M. (2015), "Selective Thorium and Uranium Extraction from Monazite: II. Approaches to Enhance the Removal of Radioactive Contaminants", *Hydrometallurgy*, 155, 161-167. doi:10.1016/j.hydromet.2015.03.015
- [7] Alvarado Hernández, L., Lapidus, G. T., & González, F. (2019). Recovery of rare earths from waste cathode ray tube (CRT) phosphor powder with organic and inorganic ligands. *Waste Management*, 95, 53-58. doi: 10.1016/j.wasman.2019.05.057
- [8] Berry, L., Galvin, J., Agarwal, V. & Safarzadeh, M.S. (2017). Alkali pug bake process for the decomposition of monazite concentrates, *Minerals Engineering 109*, 32-41. doi:10.1016/j.mineng.2017.02.007
- [9] Hielscher Ultrasonics GmbH (2022), <u>https://www.hielscher.com/es/information-about-sonochemistry.htm</u>
- [10] Jiang F, Chen YQ, Ju SH, Zhu QY, Zhang LB, Peng JH, Wang, XM & Miller, JD (2018). Ultrasoundassisted leaching of cobalt and lithium from spent lithium-ion batteries. *Ultrason Sonochem.* 48, 88–95. doi: 10.1016/j.ultsonch.2018.05.019
- [11] Luque-García, J., & Luque de Castro, M. (2003). Ultrasound: a powerful tool for leaching. *Trends in Analytical Chemistry*, 22(1), 41-47. doi:10.1016/S0165-9936(03)00102-X
- [12] Palomino Resendiz, RL, Bolarín Miró, AM, Tenorio, FN, Sánchez De Jesús, F, Cortés Escobedo, CA & Ammar, S (2016), Sonochemical assisted synthesis of SrFe12O19 nanoparticles, *Ultrason Sonochem*, 29, 470-475. doi:10.1016/j.ultsonch.2015.10.023
- [13] Toache-Pérez, A.D., Bolarín-Miró, A.M., Sánchez-De Jesús, F. & Lapidus, G.T. (2020). Facile method for the selective recovery of Gd and Pr from LCD screen wastes using ultrasound-assisted leaching. *Sustainable Environment Research*, 30, 20. doi: 10.1186/s42834-020-00060-w
- [14] NIST (2004), NIST Critically Selected Stability Constants of Metal Complexes Database, 46, version 8.0, compiled by R. M. Smith, A. E. Martell and R. J. Motekaitis, May 2004
- [15] Tunsun, C., Petranikova, M., Gergorić, M., Ekberg, C., & Retegan, T. (2015). Reclaiming rare earth elements from end-of-life products: A review of the perspectives. *Hydrometallurgy*, 156, 239-258. doi: 10.1016/j.hydromet.2015.06.007