Leaching Process Applied to Fluorescent Lamps of Different Brands to Obtain Rare-Earth Elements: A case study in Peru

J. Valerio[1], M. Quintana[1], H. Rivera[1], Agnieszka Hojenska[2], Anna Łukowiak[2], J. M. Rodriguez[1]
[1]Center for the Development of Advanced Materials and Nanotechnology, Universidad Nacional de Ingeniería, Av. Túpac Amaru 210, Lima, Peru
[2]Institute of Low Temperature and Structure Research, ul. Okólna 2, 50-422 Wrocław Poland

Abstract*— In this work, the results in the various stages of rare-earth recycling from Phillips branded fluorescent lamps compared with generic products are presented. Energy Dispersive X-Ray Fluorescence, Energy Dispersive Spectroscopy, and Inductively Coupled Plasma Mass Spectrometry was used to characterize the products. The results show that the rare-earth elements present in the material before recycling are: cerium (Ce), europium (Eu), lanthanum (La), terbium (Tb), and yttrium (Y). Besides, Phillips brand fluorescent lamps have a higher percentage of rare-earth by mass than generic ones. After characterizing the fluorescent raw powder, the multi-stage acid leaching method was used as a working method for recycling, obtaining the complete extraction of yttrium as a relevant result.

Keywords*— Recycling, rare-earth, fluorescent lamps.

1. INTRODUCTION

The rare-earth metals (REM) are a set of 17 metals, 15 lanthanides, while the last two are yttrium (Y) and scandium (Sc). These elements are called "rare-earth", because they are mainly not found in pure form and are present in small quantities, with only a few deposits in the world.

The triply ionized REM ions, except for lutetium (Z = 71), are optically active due to their peculiar electronic configuration. This property found in REMs has allowed in recent decades important advances in various high-tech applications such as green energy, fuel-efficient vehicles, development of high-performance lasers, emitting screens, and fluorescent lamps [1,2].

Currently, our dependence on these materials along with a shortage of supply has forced a search for alternative routes for the production and supply of REM [3]. To counteract this dependency, several European countries have implemented REM recycling, through the recycling of electronic devices and fluorescent lamps being the ones of greatest interest, due to the high consumption of these products in society and the great impact that they generate when thrown into the environment. [4].

Recovery of rare-earth elements from fluorescent lamps. In lamps' composition, one can find compounds such as mercury vapor, an inert gas, oxides, and phosphors; the latter consisting of rare-earth with a 3+ charge, mostly [5]. The Ce^(3+), Eu^(3+), Tb^(3+) ions together with yttrium and lanthanum are used for the generation of white light from ultraviolet (UV) radiation from mercury (Hg) produced inside compact fluorescent lamps by potential difference [6].

Fluorescent lamps are generally made up of a primer, a filament cap and a ballast that is coupled to a discharge tube whose interior is coated with fluorescent powder. The operation of this apparatus consists of making an alternating current flow that reaches the ballast, the latter controls the flow of electricity and directs it towards the filaments. When current flows through the filament, it generates an increase in its temperature that causes a spark with which the electric arc ignites and ionizes the Hg gas contained inside the discharge tube. The gas once ionized emits UV radiation that interacts with the fluorescent powder, finally emitting white light.

In Peru, it is a common practice that after the useful life of fluorescent lamps, they are discarded as common garbage, this being an error because some components inside, such as Hg [7], are harmful to the environment and the living beings. There are also others, such as rare-earth, that are toxic, but have great commercial value [8], highlighting here the importance of recycling. In

this context. various works on the emission of white light from fluorescent dust have been produced and reported [9, 10], but few works report the composition of these dust and their subsequent recycling process [11–13].

In the present work, a study was carried out to find the rare-earth elements and quantify their content in the generic (Low-cost in the market) and Phillips brand fluorescent lamps available in Peru to later recycle them. The favorable results of this work will help us to have economic alternatives through the circular economy, benefiting the population and the environment.

2. EXPERIMENTAL PROCEDURE

A. Fluorescent Powder Characterization

Four groups of raw materials (fluorescent lamps with the power of 28, 36, and 40W) were as follows: new generic (GN), new Phillips brand (PN), used generic (GU), and used Phillips brand (PU). The goal of the studies was to compare the percentage of rare-earth that each group of lamps had.

The fluorescent dust from each lamp was recovered inside a fume hood with the help of a spatula; this was done with great caution due to the mercury vapor given off by these lamps. The samples of each group were homogenized and then divided into two containers, which were: GN-1, GN-2, PN-1, PN-2, GU-1, GN-2, PU-1, and PU-2.

Once the fluorescent powder of each group was obtained, its composition was characterized by an Energy-dispersive X-ray Fluorescence spectrometer (EDXRF) from PANalytical B.V., model Epsilon 5, and X-ray Energy Dispersion Spectroscopy (EDS) Bruker from an SEM SU 8230 Hitachi.

B. Fluorescent Powder Leaching Methodology

The work carried out by Eduafo and coworkers [4] was taken as a guide to using a methodology that allows yttrium and europium to be extracted from disused fluorescent lamps (GU-1). The procedure consists of recovering the fluorescent dust from each lamp inside a container with distilled water and under a hood. With the powders obtained after decantation, the acid leaching process was used, using HCl, in multi-stages under agitation and constant temperature. The flow chart for the methodology is shown in Figure 1.

In each leaching stage, yttrium and europium were dissolved different concentrations., on the precipitate side, this contained the other remaining compounds of the fluorescent powder. The step to follow was to decant the mixtures, with which a liquid solution and a solid were obtained. Finally, we proceeded to add oxalic acid to the solution to **precipitate yttrium and europium** in the form of oxides and, on the part of the solid, we proceeded with the steps shown in Figure 1.

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In the process of staged leaching, a small amount of liquid was separated, and together with the residues that were obtained, they were characterized by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) from Thermo Scientific, model iCAP 7000.

3. RESULTS

A. Data obtained for the chemical composition in each sample of fluorescent powder

The samples of each group were obtained from the fluorescent powder of 51 fluorescent lamps of different characteristics (28, 36, and 40W lamps were taken interchangeably), where for each lamp 2g of said powder was extracted. The semi-quantitative compositional data for each sample, obtained by ray fluorescence are shown in Tables 1-4.

B. Data obtained at each leaching stage for fluorescent powders

The rare-earth of yttrium and europium were recovered from one of the used generic lamp fluorescent powders (GU-1). This powder was separated into three samples with the same amount of mass. Before and after each leaching stage, prewash (Pw), first leach (1st leach) and second

leach (2nd leach), the quantity of elements was determined by ICP-OES analysis. The obtained results are shown in Tables 5-8.

After the process of the second leaching, a precipitate is also obtained that was called residue (Res). These residues found in each sample were analyzed by the ICP-OES and also by the EDS. The data obtained are presented in Table 9 and 10.

4. DISCUSSIONS

The measurements carried out gave, as a result, the chemical composition of powders from fluorescent lamps. With these data, we can compare the percentages of the rare-earth present, Ce, Eu, La, Tb, and Y; for each dust group, the total percentages of rare-earth in NG lamps are about 2,9% to 3,5% and for PN lamps 46,4% to 50,3%. With these data it is mentioned that generic lamps have a lower percentage of rare-earth compared to Phillips brand lamps, reaching a composition of one-tenth of the latter. As well as, it is highlighted that the rare-earth with the highest percentage by mass in each group is yttrium.

Regarding new and used fluorescent lamps, we can mention that the used ones have a lesser amount of rare-earth due to the reactions that are generated by the wear that occurs inside the discharge tube. These rare-earth losses are around 20% to 30% and 90% to 98% for the Phillips and generic brand lamps respectively, losing in large quantities these elements of the generic lamps, while to the Phillips lamps loss was up to 30% maximum. In addition, an important detail in all groups of fluorescent powders is the removal of Hg, with the extraction in distilled water being a safe procedure for its removal in fluorescent powders.

Whereas the results with regard to the RMS and the amount of REM that could be retrieved from GU samples, where their content in the powder is very low. They show the data from the rare-earth recycling process, obtained by the ICP-OES team, which gives us information about the stages and their results when removing Eu and Y. From this information, we can highlight that the pre-washing and first leaching process extracts with success to these items. From the second leaching stage, Eu and Y were extracted, but not in the same proportions as the previous stages.At this stage as well, we can mention that La, Tb, and Ce can be removed, but in small quantities.

In addition to the above, the samples of Residues 1, 2 and 3 were characterized by the ICP-OES and EDS equipment, results obtained from the first characterization, with an yttrium removal of less than 10ppm. The EDS analysis, on the other hand, confirms what was exposed by the ICP-OES tests, since no trace of yttrium was found in the composition of Residues 1, 2 and 3.

5. CONCLUSIONS

To conclude for recycling of rare-earth elements in Peru, the fluorescent lamps analyzed contain 5 elements belonging to rare-earth, which are: Ce, Eu, La, Tb and Y. Of these elements, Y is the one with the highest percentage by mass, reaching 1.1%, 16, 9%, 0.03% and 14.4% in the GN, PN, GU and PU groups, respectively.

Eduafo's method of recycling europium and yttrium by acidic leaching in fluorescent powder results in a suitable process for recycling yttrium, but inefficient for recycling the other rare-earth found in the generic fluorescent composition. Therefore, it is necessary to improve the multistage leaching method by varying parameters such as the type of acid, the pH, and the stirring temperature; establishing a work methodology in which selective recycling of fluorescent dust can be carried out.

Besides, in the Phillips brand fluorescent lamps, it is concluded that they are more suitable for a circular economy at an industrial level, due to the larger number of rare-earth that they possess and the lower loss of rare-earth that they experience when wearing out these lamps.

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TABLE CAPTION

Table 1. Elements composition of fluorescent powder samples from new generic lamps (GN-1,2).

Sample	**GN-1**	**GN-2**
Ca **(%)**	35.9 ± 4.4	36.2 ± 4.218
Mn **(%)**	1.8 ± 0.1	1.8 ± 0.132
Zn **(ppm)**	884 ± 57	667 ± 46
Sr **(ppm)**	1295 ± 49	1268 ± 48
Y (%)	**1.10 ± 0.04**	**1.06 ± 0.04**
Sb **(%)**	2.9 ± 0.2	3.0 ± 0.2
Ba (%)	<0.5	<0.5
La (%)	**<0.5**	**<0.5**
Ce (%)	**1.0 ± 0.1**	**0.6 ± 0.05**
Eu (%)	**1.1 ± 0.1**	**0.9 ± 0.05**
Tb (%)	**0.3 ± 0.06**	**0.3 ± 0.02**
Hg **(ppm)**	754 ± 65	IWF
Pb **(ppm)**	93 ± 15	107 ± 10
Matrix **(%)**	P3O12F=53.9	P3O12F=47.85

Table 2. Elements composition of fluorescent powder samples from new Phillips lamps (PN-1,2).

Sample	**PN-1**	**PN-2**
Sr **(ppm)**	8219 ± 328	10674 ± 407
Y (%)	**16.9 ± 0.5**	**16.3 ± 0.5**
Ba (%)	7.8 ± 0.4	6.3 ± 0.3
La (%)	**IWF***	**IWF**
Ce (%)	**8.0 ± 0.2**	**7.6 ± 0.2**
Eu (%)	**6.1 ± 0.2**	**6.6 ± 0.2**
Tb (%)	**5.7 ± 0.2**	**5.9 ± 0.2**
Hg **(ppm)**	1592 ± 99	2604 ± 104
Pb **(ppm)**	745 ± 60	297 ± 28
Matrix **(%)**	MgAll0O17=19.9	Mg2Al16O27=24.2

* IWF = It wasn't found.

Table 3. Elements composition of fluorescent powder samples from used generic lamps (GU-1,2).

Sample	**GU-1**	**GU-2**
Ca **(%)**	34.2 ± 3.21	37.3 ± 3.0
Mn **(ppm)**	2.2 ± 0.09	2.6 ± 0.1
Sr **(ppm)**	893 ± 39	2192 ± 78
Y (ppm)	**300 ± 13**	**400 ± 15**
Sb **(%)**	11.6 ± 0.8	3.1 ± 0.4
Ba **(%)**	< 0.5	< 0.5
La (%)	**IWF**	**IWF**
Ce (%)	**IWF**	**IWF**
Eu (%)	**IWF**	**IWF**
Tb (%)	**IWF**	**IWF**
Hg **(ppm)**	6944 ± 299	6153 ± 145
Pb **(ppm)**	154 ± 14	96 ± 7
Matrix **(%)**	P6O25H2=51.3	P3O13F=56.0

Table 4. Elements composition of fluorescent powder samples from used Phillips lamps (PU-1,2).

Sample	**PU-1**	**PU-2**
Ca **(%)**	IWF	IWF
Mn **(ppm)**	IWF	IWF
Sr **(ppm)**	9186 ± 0.04	8666 ± 500
Y (%)	**14.4 ± 0.6**	**11.3 ± 0.5**
Sb **(%)**	IWF	IWF
Ba **(%)**	6.3 ± 0.4	5.3 ± 0.3
La (%)	**10.0 ± 0.4**	**13.8 ± 0.5**
Ce (%)	**15.1 ± 0.6**	**12.6 ± 0.4**
Eu (%)	**5.1 ± 0.2**	**4.0 ± 0.2**
Tb (%)	**5.7 ± 0.3**	**4.7 ± 0.2**
Hg **(ppm)**	4347 ± 248	1338 ± 73
Pb **(ppm)**	684 ± 89	175 ± 36
Matrix **(%)**	MgAl16O27 < 2.7	MgAl16O27 <2.7

Table 5. Elements composition of fluorescent powder samples from used generic lamps (GU-1).

Elements	Resulted	Unit
Al	8.059±0.3	**%**
Ca	39.44±2.0	**%**
P	16.30±1.0	**%**
Si	5.237±0.3	**%**
Ce	**0.114±0.006**	**%**
Eu	**241.7±12.0**	**ppm**
La	**0.258±0.01**	**%**
Tb	**539.0±30.0**	**ppm**
Y	**0.159±0.01**	**%**

Table 6. Elements composition of the samples of the prewash solution (Pw).

Elements	Pw-1 (ppm)	Pw-2 (ppm)	Pw-3 (ppm)
Al	264.6±13.0	138.7±7.0	223.9±10.0
Ca	1.262±0.06 **(%)**	1.327±0.1 **(%)**	1.308±0.1 **(%)**
P	0.518±0.03 **(%)**	0.559±0.03 **(%)**	0.538±0.03 **(%)**
Si	314.6±16.0	267.0±13.0	220.0±10.0
Ce	**< 1.0**	**< 1.0**	**< 1.0**
Eu	**6.7±0.3**	**2.6±0.1**	**8.0±0.4**
La	**< 1.0**	**< 1.0**	**3.0±0.15**
Tb	**< 1.0**	**< 1.0**	**< 1.0**
Y	**60.0±3.0**	**80.0±4. 0**	**200.0±10.0**

Table 7. Elements composition of the solutions in the first leaching (1st leach).

Elements	1°leach-1 (ppm)	1° leach-2 (ppm)	1° leach-3 (ppm)
Al	42.92±2.0	119.6±6.0	94.46±5.0
Ca	857.9±3.0	804.2±40.0	84.94±4.0
P	430.4±20.0	428.1±20.0	265.5±13.0
Si	14.55±1.0	33.22±2.0	432.2±20.0
Ce	**< 1.0**	**< 1.0**	**2.5±0.1**
Eu	**2.6±0.1**	**11.8±0.6**	**6.7±0.3**
La	**2.0**	**< 1.0**	**3.5±0.2**
Tb	**< 1.0**	**< 1.0**	**1.6±0.1**
Y	**55.0±3.0**	**267.2±13.0**	**130.0±6.5**

Table 8. Elements composition of the solutions in the second leaching (2nd leach).

Elements	2° leach -1 (ppm)	2° leach -2 (ppm)	2° leach -3 (ppm)
Al	14.2±1.0	65.29±3.0	31.24±2.0
Ca	23.34±1.2	24.31±1.0	20.71±1.0
P	13.83±1.0	18.06±1.0	13.61±1.0
Si	20.0±1.0	8.957±0.5	6.92±0.3
Ce	**< 1.0**	**6.0±0.3**	**3.2±0.2**
Eu	**< 1.0**	**1.5±0.1**	**0.5±0.02**
La	**2.9±0.1**	**12.0±0.6**	**6.7±0.3**

Tb	**< 1.0**	**3.3±0.2**	**2.0±0.1**
Y	**3.0±0.15**	**30.0±1.5**	**10.0±0.5**

Table 9. Elements composition of the samples of the residues in the IPC-MS equipment (Res).

Elements	Res-1 (%)	Res-2 (%)	Res-3 (%)
Al	6.941±0.3	7.4±0.4	5.451±0.3
Ca	4.272±0.2	4.158±0.2	4.357±0.2
P	0.953±0.05	0.92±0.05	0.741±0.04
Si	3.164±0.2	3.021±0.2	3.269±0.2
Ce	**0.120±0.01**	**0.1±0.005**	**0.103±0.005**
Eu	**203.9±10.0 (ppm)**	**216.6±10.0 (ppm)**	**80.0±4.0 (ppm)**
La	**0.21±0.01**	**0.171±0.01**	**0.176±0.01**
Tb	**0.16±0.01**	**0.138±0.01**	**889.3±45.0 (ppm)**
Y	**< 10.0 (ppm)**	**< 10.0 (ppm)**	**< 10.0 (ppm)**

Table 10. Data measured in the EDS equipment in the sample called Residue 1, 2 and 3.

Elements	Res 1 (%)	Res 2 (%)	Res (%)
La	**9.61 ± 0.20**	**7.23 ± 0.15**	**5.52 ± 0.11**
P	3.65 ± 0.12	2.53 ± 0.09	1.61 ± 0.06
Al	13.51 ± 0.42	16.32 ± 0.47	19.34 ± 0.44
Si	41.12 ± 1.08	46.25 ± 1.13	52.33 ± 1.02
Na	12.14 ± 0.54	12.05 ± 0.50	IWF
Mg	3.62 ± 0.16	2.97 ± 0.13	2.95 ± 0.11
K	0.96 ± 0.05	0.68 ± 0.04	1.44 ± 0.05
Ca	5.11 ± 0.12	6.13 ± 0.13	7.88 ± 0.14
Ba	5.22 ± 0.13	1.86 ± 0.07	6.31 ± 0.12
Ce	**5.06 ± 0.12**	**3.38 ± 0.10**	**2.62 ± 0.07**

FIGURE CAPTION

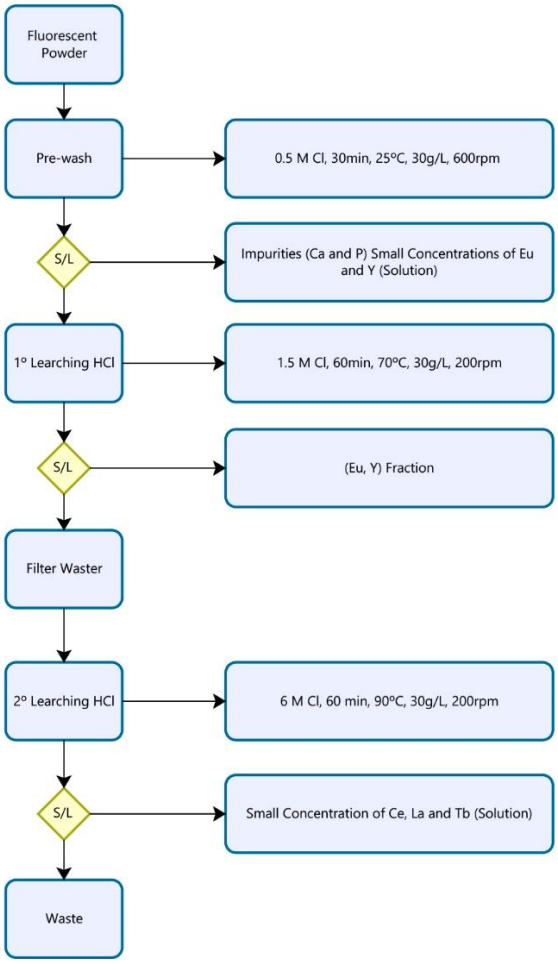

Figure 1. Flow chart of the leaching methodology (based on [4]).