Processes and technologies for the recycling of spent fluorescent lamps

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The growing industrial application of rare earth metals led to great interest in the new technologies for the recycling and recovery of REEs from diverse sources. This work reviews the various methods for the recycling of spent fluorescent lamps. The spent fluorescent lamps are potential source of important rare earth elements (REEs) such as: yttrium, terbium, europium, lanthanum and cerium. The characteristics of REEs properties and construction of typical fluorescent lamps is described. The work compares also current technologies which can be utilized for an efficient recovery of REEs from phosphors powders coming from spent fluorescent lamps. The work is especially focused on the hydrometallurgical and pyrometallurgical processes. It was concluded that hydrometallurgical processes are especially useful for the recovery of REEs from spent fluorescent lamps. Moreover, the methods used for recycling of REEs are identical or very similar to those utilized for the raw ores processing.

Keywords: fluorescent lamps, recycling, rare earth elements, hydrometallurgical process, pyrometallurgical process, solvent extraction, leaching.

INTRODUCTION

One of the most important applications of rare earth metals (REEs) is the production of luminescent materials (phosphors) which are used as components of the fluorescent lamps. There are two types of lamps that are commonly used nowadays: lamps containing mercury (so called fluorescent lamps) and lamps without mercury (incandescent lamps and halogen/dichroic lamps)[1]. There are various kinds of commercial light sources containing mercury, including cathode fluorescent lamps (CCFLs), ultraviolet (UV) lamps and high pressure mercury lamps (SHPs). The CCFLs are components of liquid crystal display tv-sets (LCD TV), LCD monitors and scanners[2]. All fluorescent lamps contain mercury, which is one of the most toxic elements and therefore belongs to hazardous substances. Development of recycling was driven by environmental and economical benefits. The European Union, under Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (EEE) prohibited the use of these substances in electrical and electronic equipment. In case of compact fluorescent lamps (CFLs) concentration of mercury should not exceed 5 mg per lamp. The management of spent CFLs is regulated by Directive 2002/96/EC on electrical and electronic equipment, and waste management (WEEE) [3,4]. The spent fluorescent lamps can be treated by means of mechanical, thermal and chemical processes. Several technologies for the recycling of lamp waste have been proposed[5–11].

This paper reviews hydrometallurgical and pyrometallurgical technologies applied for the efficient recovery of REEs from phosphors powders. In the first part of review, the characteristic and application of REEs as well as structure of typical fluorescent lamps is discussed. In the second part, the overview of studies concerning of REEs recovery from fluorescent lamps is described.

THE RARE EARTH METALS

The rare earth metals are comprising of 14 lanthanides (cerium to lutetium), lanthanum, yttrium and scandium. The REEs are divided in two groups: the light group (the cerium group) and the heavy REEs (yttrium group). Due to their specific properties, these metals are used in various applications, like lighter flints, glass polishing, phosphors, lasers, magnets, batteries, high-temperature superconductors. The rare earth phosphors are used as the components in fluorescent lamps, having no substitutes. Europium is used in cathode-ray tubes and liquid-crystal displays, erbium – in laser repeaters for fiber-optic cables; cerium oxide is the only polishing agent for glass used in the production of mirrors, eyeglasses, and precision lenses. Neodymium, samarium, gadolinium and dysprosium are applied in the production of small, lightweight and high-strength magnets that allow miniaturization of many electrical and electronic components[3]. According to the recent data it can be stated that four rare earth elements (i.e. cerium, lanthanum, neodymium, and yttrium) represent almost 90% of the global production. Recycling and/or reuse of these metals is possible, but difficult. The other rare earth elements are usually utilized in much lower quantities, and for that reason the recycling would be complex and challenging, especially due to problems associated with the removal of the rare earths from the products[12].

FLUORESCENT LAMPS CHARACTERISTICS

The fluorescent lamps are gas discharge lamps which use mercury vapors to produce light[3]. Part of mercury introduced into a lamp is used to produce visible light and the other part of this metal interacts with the phosphor powder and the glass matrix[4]. The typical lamp consists of a glass tube filled with an inert gas (argon, neon, krypton and/or xenon) at low pressure (3 mbar) and mercury vapor at low partial pressure. Cathodes made of either tungsten or stainless steel are assembled on the ends of the lamp[1]. The inside of the tube is coated with a layer of phosphors powder. The composition of the phosphors powder is responsible for the light's color and intensity[3]. Rare earth elements have been widely used as luminescent materials. The characteristics of phosphor materials are shown in Table 1[8]. Table 2[13] displays the amount of various REEs in phosphors materials. Rare

Table 1. Characteristics of phosphor materials[8]

Type	Simplified formula	Density [g · cm^{-3}]	Median size, d$_{50}$ [μm]
White	3Ca$_3$(PO$_4$)$_2$Ca(F,Cl)$_2$:Sb, Mn	3.07	13.42
Red	(Y,Eu)$_2$O$_3$	5.12	4.72
Green	(La, Ce,Tb)(P,B)O$_4$	5.23	3.72
Blue	(Sr,Ca,Ba,Eu)$_{10}$(PO$_4$)$_6$Cl$_2$	4.34	5.18

Table 2. Composition of the recovered and fresh phosphors[13].

Component	Content [wt%]		Component	Content [wt%]	
	Fresh phosphors	Recovered phosphors		Fresh phosphors	Recovered phosphors
CaO	50.9	49.5	Gd$_2$O$_3$	0.20	–
P$_2$O$_5$	35.7	34.9	Tb$_4$O$_7$	0.20	0.16
Y$_2$O$_3$	3.28	3.09	Eu$_2$O$_3$	0.18	0.19
F	2.48	2.43	SiO$_2$	0.14	1.88
Al$_2$O$_3$	1.21	1.16	ZnO	0.10	0.02
SrO	1.14	1.13	Fe$_2$O$_3$	0.05	0.12
Sb$_2$O$_3$	1.04	0.91	Na$_2$O	0.05	0.33
MnO	0.80	0.82	SO$_3$	0.04	0.06
La$_2$O$_3$	0.79	0.97	HgO	0.03	–
C	0.63	0.70	GeO$_2$	0.02	0.02
BaO	0.54	0.83	PbO	–	0.23
Cl	0.50	0.44	MgO	–	0.09

Table 3. Chemical composition of the spent optical glass[14]

Component	La$_2$O$_3$	Y$_2$O$_3$	Gd$_2$O$_3$	ZrO$_2$	ZnO	Nb$_2$O$_5$	Sb$_2$O$_3$	BaO	B$_2$O$_3$	SiO$_2$	Others
Content [wt.%]	43.1	9.37	4.60	6.48	0.25	3.30	0.13	1.25	24.5	6.25	0.77

earths elements, such as lanthanum are also present in spent optical glasses. For a comparison, Table 3 presents chemical composition of the spent optical glasses[14]. Recently, a large number of luminescent materials based on rare earth ions or rare earth host lattices have been invented. Until 1980s, mainly halophosphate with 1–2% antimony and manganese Ca$_5$(PO$_4$)$_3$(F,Cl):(Sb,Mn)(halophosphate, CHP) was used in fluorescent lamps for general lighting purposes. In this case, the UV radiation, generated by the Hg discharge, is absorbed by Sb^{3+} and partly transferred to Mn^{2+}. The combination of a blue (Sb^{3+}) and yellow (Mn^{2+}) emission band results in white light. Nowadays, rare earth phosphors are important components of fluorescent lamps. For example, BaMgAl$_{10}$O$_{17}$ doped with Eu^{2+} (BAM) is used as a blue emitting phosphor in high quality fluorescent lamps. The photons are absorbed and emitted by the Eu^{2+} ions, due to a 4f→5d and a 5d→4f optical transition, respectively. The red emission in these lamps is generated by Y$_2$O$_3$:Eu. All green emitting Tb^{3+} phosphors rely on optical absorption on Ce^{3+} ions, followed by energy transfer to the emitting Tb^{3+} ions. LaPO$_4$:Ce^{3+},Tb^{3+}; (Ce,Tb)MgAl$_{11}$O$_9$ and (Ce,Gd,Tb)MgB$_5$O$_{10}$ are examples of green phosphors that can be used[13].

RECOVERY OF RARE EARTH METALS FROM SPENT FLUORESCENT LAMPS

Recycling processes of spent fluorescent lamps commonly involve lamp crushing under water to avoid air pollution from mercury vapour. Hydrometallurgical and pyrometallurgical studies indicate that many methods could be applied to recovery of REEs from different wastes[6, 12]. The pyrometallurgical recovery processes for spent lamps usually consist of the following basic steps: feed preparation, blending and pelletizing, reduction, melting and casting[6]. Pyrometallurgy processes are using high temperatures. At such conditions rare earths can

be oxidized easily, what makes the recovery complicated. Moreover, volatile organic compounds (VOCs) and/or dioxins are generated and this fact creates additional environmental problem[12]. Rabah[6] reported a combined pyro-hydrometallurgical method to recover pure metals from spent fluorescent lamps. Spent lamps were decapped under water containing 35% acetone to achieve safe capture of mercury vapour. Cleaned glass tubes were cut using a rotating diamond disc to a standard shorter length. Aluminium and copper–nickel alloys in the separated metallic parts were recovered using suitable flux to decrease metal losses going to slag. Pure aluminium was recovered by melting at 800ºC under sodium chloride/carbon flux for 20 min. Standard nickel–copper alloys with less than 0.1% tin were prepared by melting at 1250ºC using a sodium borate/carbon flux. De-tinning of the molten nickel–copper alloy was carried out using oxygen gas. Subsequently, tin was recovered by reducing tin oxide using carbon or hydrogen gas at 650–700ºC. Different valuable chloride salts were also obtained of good quality[6]. However, these pyrometallurgical operations are energy consuming, some emission of dust and gases is also expected and moreover they are not versatile compared to hydrometallurgical processes. Hydrometallurgy shows benefits compared with pyrometallurgical techniques such as low cost requirements, possible recovery of leachants and decrease of air pollution[15]. Hydrometallurgy processes use strong acidic or basic solutions to dissolve selectively and then precipitate metals of interest from a preprocessed powder form. The specific used process depends on the metal to be recovered and options include solvent extraction, leaching, and selective precipitation[12]. Many patented processes have already been developed, mainly for treatment of spent lamps[3, 16–18]. One of them is the recovery of rare earth metals from fluorescent lamps in a multistage process. The individual process steps are: mechanical separation of coarse components, separation of the halophosphate,

leaching of mainly yttrium and europium oxides using inorganic or organic acids, extraction of rare earth metal ions from solutions and final treatment. The REEs can be precipitated from the solutions obtained in the various process steps either with oxalic acid as oxalates or with ammonia as basic salts. Subsequently the oxalates are heated to form oxides[16].

Acid leaching of metal ions contained in the phosphors powders of spent fluorescent lamps, is a very important chemical process in the treatment of these waste. Different conditions (leaching agent concentration, temperature, solid/liquid ratio, stirring intensity, etc.) were investigated. Nitric acid, hydrochloric acid, sulphuric acid were used in leaching of phosphors powders. The inorganic acids proved to be efficient leaching agents, extracting more than 80% rare earth metal[10]. For example, the leaching of phosphors powders with HCl followed by precipitation with ammonia/oxalic acid has been studied. The optimum leaching conditions were as follows: HCl concentration 4M, solid/liquid ratio 100 g/l, stirring at 600 rpm, temperature of 60°C, 1 h. 89.9% of the total
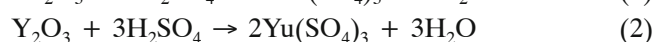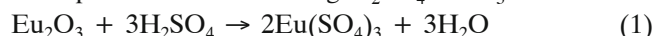
rare earth metals were leached, yttrium accounting for 96.3%[3]. For comparison, leaching of rare earths from the spent optical glass is very difficult using inorganic acids, such as: hydrochloric acid, nitric acid and sulphuric acid. However, it is possible to convert them to REEs hydroxides with sodium hydroxide under proper conditions, and the resulting hydroxides are very easily dissolved in inorganic acids[14].

After leaching waste fluorescent lamps using inorganic acids, solvent extraction is the most adequate process to provide an efficient purification. Actually, the solvent extraction plays an important role as a separation and concentration method. Many investigations have been conducted on the separation of REEs ions by solvent extraction processes[6–38]. The pH, acid concentration, ionic strength and concentration of the metal ions in the aqueous phase influence the extraction efficiency and the selectivity of the process. Different compounds were utilized to earth metal ions extraction from the model leach liquor of phosphors powder. Table 4 gathers chosen extraction systems, which were investigated for separation
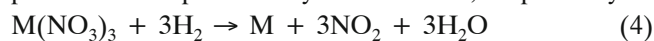
Table 4. Extraction systems applied for the separation of rare earth metal ions

Metal ions	Extractants	Ref.
La(III), Eu(III), Lu(III)	bis(4-acyl-5-hydroxypyrazoles)	[19]
La(III), Gd(III), Y(III) Yb(III), Sc(III)	mixture of bis(2,4,4-trimethylpentyl)phosphinic acid and *sec*-nonylphenoxy acetic acid	[20]
La(III), Pr(III), Nd(III)	di-2-ethylhexylphosphoric acid (DEHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP))	[21]
La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Y(III)	carboxylic acids such as cekanoic, naphthenic, neo-heptanoic and Versatic 10 in dodecane	[22]
La(III), Pr(III), Nd(III)	8-hydroquinoline with and without 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester	[23]
Th(III)	*p*-phosphorylated calix[4]arene, 5,11,17,23-tetra(diethoxyphosphoryl)-25,26,27,28-tetrapropyloxy-calix[4]arene	[24]
La(III), Pr(III), Nd(III)	Cyanex 272 and its mixture with solvating, cationic and anionic extractants like TBP, TOPO, DOS, Cyanex 301, Versatic-10, Alamine 308, Alamine 336	[25]
La(III), Nd(III)	mixture of two neutral extractants: trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TRPO)	[26]
La(III), Yb(III)	di(2,4,4-trimethylpentyl)phosphinate of methyltrioctylammonium	[27]
La(III), Nd(III), Y(III), Ce((II)	18-crown-6 (18C6)	[28]
La(III), Y(III), Ce(III)	Cyanex 272, Cyanex302 and TBP (HA)	[29]
Tb(III), La(III), Ce(III), Lu(III), Y(III), Er(III), Dy(III), Ho(III)	phosphors solvent (TOPS 99), di-2-ethylhexyl phosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272)	[30]
14 lanthanoids (except Pm(III)) and Y(III)	1-phenyl-3-methyl-4-benzoylpyrazalone-5 (HPMBP, HA), s*ec*-octylphenoxyacetic acid (CA12, H2B2)	[31]
La(III), Ce(III), Nd(III), Y(III), Eu(III)	binary extractants, such as salts of trioctylmethylammonium with dialkylphosphinic, dialkylmonothiophosphinic, dialkyldithiophosphinic acids	[32]
La(III), Gd(III)	Aliquat-336, Amberlite XAD-4	[33]
La(III), Sm(III), Er(III)	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA)	[34]
La(III), Nd(III)	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A)	[35]
La(III), Th(III), Eu(III)	bis(2-ethylhexyl)phosphoric acid using 2-nitrobenzo-18-crown-6	[36]
La(III)	1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) and triisobutylphosphine sulphide (TIBPS)	[37]

of rare earths metal ions[19–37]. Recently, recovery and separation of rare earths metal ions from aqueous solutions was examined using different extractants, i.e. solvating type extractants[6, 7, 26, 27, 30], amine extractants[28, 29, 31, 32], acidic extractants (carboxylic and organophosphorous acids)[21–25, 33–36]. Extractants applied for separation and recovery of REEs from aqueous solutions should be efficient and selective. These properties are one of the most important criterion during development of metals recovery technologies. Up to date, some papers show solvent extraction of REEs using ionic liquids or their mixture in a role of new and efficient extractants. Investigation of metallurgical and hydrometallurgical research indicates that many techniques can be used to improve the recycling processes of spent fluorescent lamps. Rabah et al.[6, 7] reported a combined pyro-hydrometallurgical method recovery of aluminum, nickel-copper alloys, europium and yttrium metals and various salts from spent fluorescent lamps. The rare earth metals and some valuable salts were recovered from the powder coating the inner surface of the glass tubes. The tubes were broken under 30% aqueous acetone to avoid emission of mercury vapor to the atmosphere, and the powder was collected by brushing. The powder contained 1.62% europium oxide, 1.65% yttrium oxide, 34.48% calcium sulphate, 61.52% Ca orthophosphate and 0.65% other metal oxides by weight. Metals present in the powder were pressure leached using H_2SO_4/HNO_3 mixture.

$$Eu_2O_3 + 3H_2SO_4 \rightarrow 2Eu(SO_4)_3 + 3H_2O \qquad (1)$$

$$Y_2O_3 + 3H_2SO_4 \rightarrow 2Yu(SO_4)_3 + 3H_2O \qquad (2)$$

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4 \qquad (3)$$

The autoclave digestion of the powder in the acid mixture for 4 h at 125°C and 5 MPa resulted in dissolving 96.4% of the yttrium and 92.8% of the europium. The obtained mixture of sulphate salts of europium and yttrium was subsequently converted to thiocyanate at low temperature. Extraction of Eu(III) and Y(III) ions from the thiocyanate solution attained its maximum at 80°C using tri-*n*-butyl phosphate (TBP) in 1 M HNO_3. Thermal reduction using hydrogen gas at 850°C and 1575°C produced europium and yttrium metals, respectively.

$$M(NO_3)_3 + 3H_2 \rightarrow M + 3NO_2 + 3H_2O \qquad (4)$$

TBP is one of the most known and widely applied extractants in separation process of REEs. This is kind of neutral extractant which was used also in the separation of actinides. TBP can be also used as modifier of solvent extraction which reduce the possibility of third phase formation.

Hirajima et al.[8, 9] showed the separation of low-density calcium halo-phosphate phosphors from high density rare earth-activated phosphors through dense-medium centrifugation. A sink product assaying 48.6% of rare earth-activated phosphors could be recovered from waste phosphor materials pre-treated with $5 \cdot 10^{-5}$ mol/dm³ of sodium oleate (NaOl) surfactant. For example, the yield, grade and recovery of rare earth-activated phosphors in the sink product were 21.3, 38.7 and 97.3%, respectively.

Michelis et al.[10] described recovery of yttrium from fluorescent lamp powder from dismantling of spent fluorescent tubes. Metals were leached by using different acids (HNO_3, HCl, H_2SO_4) and ammonia solutions. The investigations showed that ammonia solutions was not

suitable to recover yttrium, whereas HNO_3 produces toxic vapours. On the other hand, HCl and H_2SO_4 were suitable as solvents. The highest extraction of yttrium was obtained by 20% w/v S/L ratio, 4N H_2SO_4 concentration at 90°C. Yttrium and calcium yields were nearly 85 and 5%, respectively. Yttrium can be subsequently recovered from liquor leach by precipitation as a pure yttrium oxalate *n*-hydrate (99% grade) by using the stoichiometric amount of oxalic acid. A block diagram of this process for the recovery of yttrium from spent fluorescent lamps is shown in Figure 1.
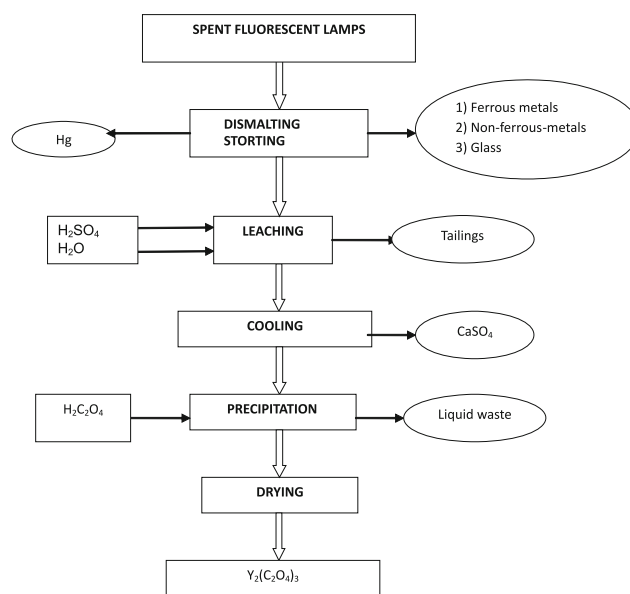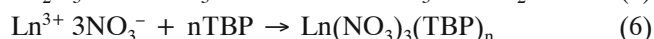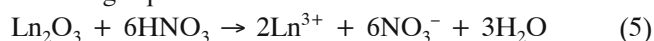

Figure 1. Flow sheet of the process for the recovery of yttrium from spent fluorescent lamps (adapted from[10])

Shimizu et al.[17] reported the extraction of rare earth elements from luminescent material from waste fluorescent lamps using supercritical carbon dioxide (SF-CO₂) containing tri-*n*-butyl phosphate (TBP) complexes with HNO_3 and H_2O. The content of the major elements in the luminescent material was a follows: 29.6% of Y, 10.6% of La, 5.0% of Ce, 2.6% of Tb, 2.3% of Eu. Y and Eu were present as oxides, whereas La and Ce were present as phosphates. It was not possible to identify the structure of Tb. Yttrium and Eu were directly extracted from luminescent material using extraction by SF-CO₂ containing tri-*n*-butyl phosphate (TBP) complexes with HNO_3 and H_2O for 120 min. at 15 MPa, 333K. The extraction efficiencies of Y and Eu were 99.7% and 99.8%, respectively. The dissolution and extraction reactions of lanthanide oxides can be showed by the following equations:

$$Ln_2O_3 + 6HNO_3 \rightarrow 2Ln^{3+} + 6NO_3^- + 3H_2O \qquad (5)$$

$$Ln^{3+} 3NO_3^- + nTBP \rightarrow Ln(NO_3)_3(TBP)_n \qquad (6)$$

Naitou et al.[18] studied recovery of rare earth oxides from a waste rare earth phosphors. This process consisted of a strong HCl leaching at 70°C with hydrogen peroxide (or leaching with only HNO_3 only), followed by precipitation of rare earths by oxalic acid addition.

Several studies have reported the characterization and recovery process of the phosphor powders from the spent fluorescent lamps[5, 19]. The analytical results presented by Raposo at al.[5] showed that the phosphors powder matrix

is a hazardous and polluting material in the waste of spent fluorescent lamps. Mercury concentrations in this type of matrix are much higher than that in new lamps of the same kind, in some cases even 40-fold. The basic difference is that mercury in spent lamps is adsorbed primarily into the phosphors matrix and, to a lesser extent, into glass and other components. In new lamps, mercury predominates as a vapor phase element.

Chang et al.[13] described the physical characteristic, crystal structure and the luminescence properties of the phosphor powders recovered from the spent fluorescent lamps. The experimental results showed that the halo-phosphate contains small amount of rare-earth elements including La, Gd, Tb and Eu, due to the contamination from other phosphors during the recycling process. After the thermal desorption/distillation process at tempera-tures between 300 and 800°C, mercury was effectively removed from the phosphor powder. The composition of the phosphors powders before and after the thermal treatment are showed in Table 2. The recovered pho-sphor can be mixed with the fresh phosphor and used in the fluorescent lamps again[13]. Innocezi et al.[38] showed results of yttrium recovery from fluorescent powder of lamps and cathode ray tubes (CRTs). The process for treating these materials includes the following steps: (1) acid leaching, (2) purification of the leach liquors using sodium hydroxide and sodium sulfide, (3) precipitation of yttrium using oxalic acid, and (4) calcinations of oxa-lates for production of yttrium oxides. The recoveries of yttrium oxide are about 95, 55, and 65% for CRT, lamps, and CRT/lamp mixture powders, respectively. The lower yields obtained during treatments of lamp powders are probably due to the co-precipitation of yttrium toge-ther with other metals contained in the lamps powder. The possibility to treat simultaneously both CRT and lamp powders is very important and interesting from an industrial point of view since it could be possible to run a single plant treating fluorescent powder coming from two different electronic wastes[38].

CONCLUSIONS

Safe disposal of spent fluorescent lamps becomes a se-rious problem due to the presence of toxic mercury and therefore the development of their effective recycling process is very important. What is even more important, some economic benefits can be achieved in recovery of value earth metals with important possible applications in numerous fields. Various techniques utilized in recovery of rare earth metals such as: yttrium, terbium, europium, lanthanum, and other REEs from spent fluorescent lamps have been reviewed. The hydrometallurgical technologies are the main methods which are used to recycle or dispose of the spent lamps. The metals from these wastes can be recovered by leaching using inor-ganic acids. The recovered metal ions are separated by solvent extraction and subsequently are precipitated as salts. Pyrometallurgy processes are the energy consuming technologies. Moreover during smelting, volatile organic compounds (VOCs) and dioxins could be generated. Review demonstrated that the fundamental processes used for recycling of REEs are identical or very similar to those utilized for the raw ores processing.

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