AVAILABLE METHODS USED FOR RECOVERY OF THE RARE EARTH METALS FROM SPENT FLUORESCENT LAMP - REVIEW

SATERNUS Mariola[1], WILLNER Joanna[1], FORNALCZYK Agnieszka[1], ŚWIĘCICKA Zofia[2]

[1]Silesian University of Technology, Gliwice, Poland, EU
[2]Mining Institute, Katowice, Poland, EU

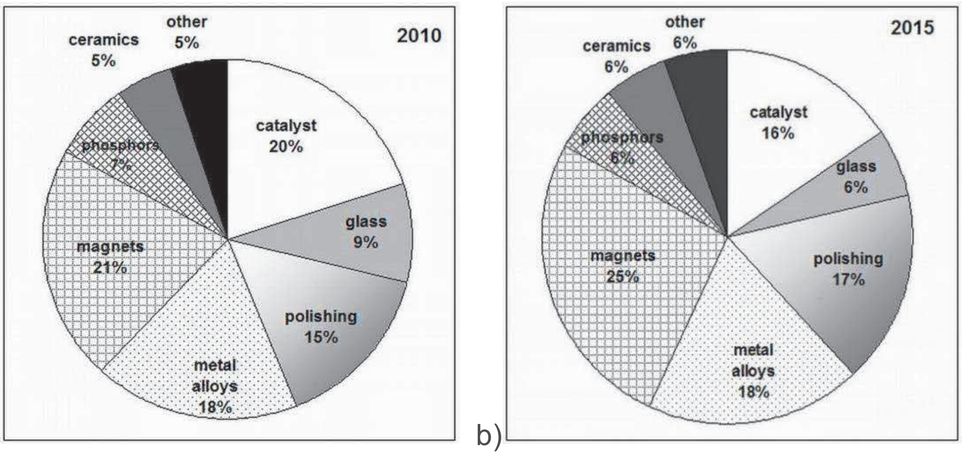
Abstract

From year to year the demand for rare earth metals is constantly growing. Majority of these metals find application in permanent magnets, lamp phosphors, catalyst and rechargeable batteries. The production of such metals in 2016 was 126 000 tones and China was the leading producer (84%). In the last years China limited the supplies of these products; therefore it is really important to be more absorbed in recycling of spent products containing rare earth metals. Today the researchers focus on recycling of rare earth metals from their three applications: permanent magnets, nickel metal hydride batteries and lamp phosphors. The article presents review of available methods of recovery the rare earth metals but only from the fluorescent lamps (monochrome and trichromatic phosphors - red, blue and green). Mentioned methods based mainly on hydrometallurgical processes such as leaching and pyrometallurgical methods like alkali fusion; purification approaches were also shortly discussed.

Keywords: Fluorescent lamp, rare earth metals, recovery, recycling of spent products

1. INTRODUCTION

Rare earth metals have a more significant meaning in today's life. They are used as a component in phosphors, lasers, magnets, batteries, magnetic refrigeration, high temperature superconductivity, safe storage and transport of hydrogen, catalyst, polishing powders, glass additives, metallurgy, ceramics and many others. What is more for common people it is really important to know that such devices as smart phones, digital camera, computer hard disks, fluorescent and light emitting diode (LED) lights, flat screen TV, computer monitors do not exist without rare earth metals. **Figure 1** shows the percentage world demand by application for rare earth metals in 2010 and 2015. The slight insignificant decrease of rare earth metals application in light technologies are due the fact that LED technologies (the most popular today) relies in less measure on rare earth metals. On the contrary application of rare earth metals in NiMH batteries used in electric vehicles or magnets should be increasing. It is estimated that the consumption of rare earth metals should be in 2020 about 150 000 tones [2].



a) b)

Figure 1 Percentage world demand for rare earth metals in: a) 2010, b) 2015 [1]

The production of metals in 2016 was 126 000 tones and to the leading producers belong China (84%), Australia (11%) and Russia (2%) (see **Figure 2**). Apart from China small mines are working in India, Brazil, Malaysia and Russia. In the last years China limited the supplies of these products; as a result new mine production in Australia (Mount Weld) and the USA (Mountain Pass, California) has begun [5]. Technologies of obtaining the rare earth metals from minerals are complicated, time-consuming, energy consuming and producing many wastes; therefore it is really important to be more absorbed in recycling of spent products containing rare earth metals.

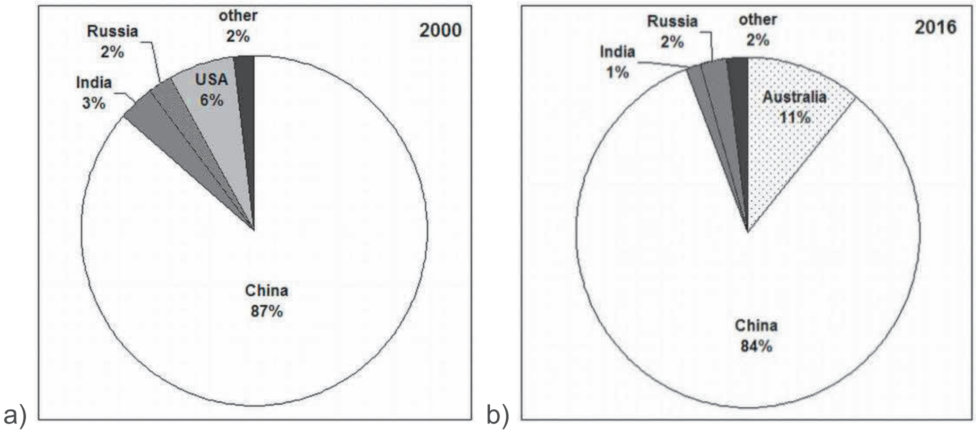


Figure 2 Production of rare earth metals by different countries in: a) 2000, b) 2016 [3, 4]

2. RARE EARTH METALS USED IN FLUORESCENT LAMPS

There are different kinds of lamps (see **Figure 3**), however LEDs technology increasingly replace light bulbs, halogen lamps, fluorescent lamps because of longer lifespan (40 000 hours), high quality of continuous warm and pleasant light, more energy-saving and environmental-friendly technology [6, 7]; therefore in the nearest future among others compact fluorescent lamp will be for sure recycled. Rare earth metals used in fluorescent lamp concentrated in phosphors which main aim is to convert the lamp`s ultraviolet radiation into visible light (see **Figure 4**), phosphors influence also the lamp ability to reproduce all colors in natural way and having the color temperature of the generated light [8]. Typical fluorescent lamp consist of 88% glass, 5% metals, 4% plastic, 3% phosphor powder and mercury (about 0.005%) [9]. In lamps are used five different phosphors: green $LaPO_4:Ce^{3+},Tb^{3+}$ (LAP), $(Gd,Mg)B_5O_{12}:Ce^{3+},Tb^{3+}$ (CBT), $(Ce,Tb)MgAl_{11}O_{19}$ (CAT), blue $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) and red $Y_2O_3:Eu^{3+}$ (YOX).

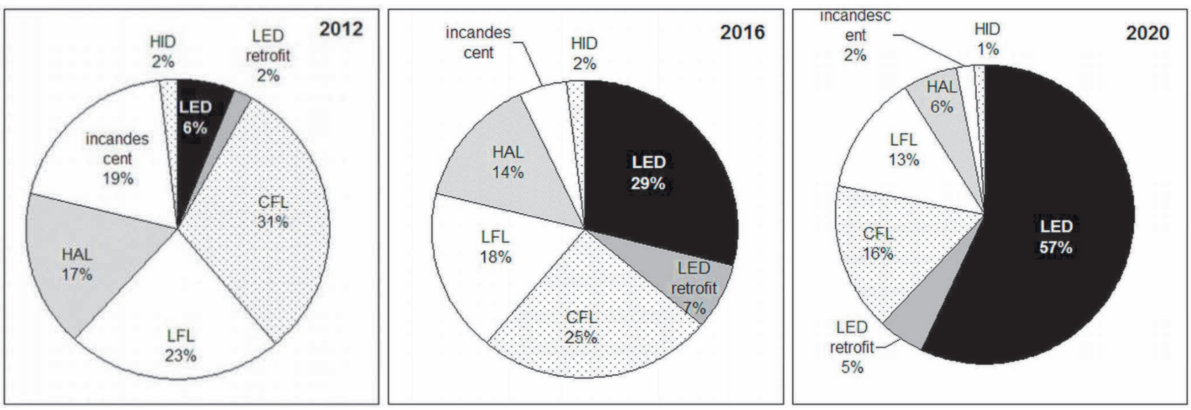


Figure 3 Predicted values in year 2020 of global market considering different lightning technology: CFL - Compact Fluorescent Lamp, LFL - Linear Fluorescent Lamp, HAL - Halogen lamp, HID - High-intensity discharge lamp, LED - Light Emitting Diodes comparing with year 2012 and 2016 [6, 7]

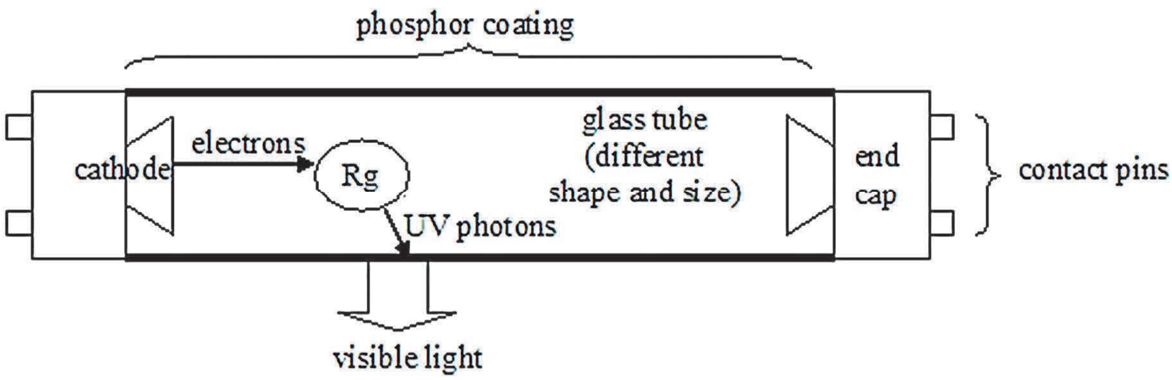


Figure 4 The view and principle of working the fluorescent lamp [10]

Typical tricolor phosphor composition taking into account the metals is the following: 46.9-51.2% Y (Y_2O_3), 3.9-4.4% Eu (Eu_2O_3), 4.1-5.3% Ce (CeO_2), 2.2-2.6% Tb (Tb_4O_7), 29.9-35.9% Al (Al_2O_3), 2.7-4.0% Mg (MgO) and 2.1-3.2% Ba (BaO) [8]. **Table 1** shows the the main rare earth metals dominating in tricolor phosphors.

Table 1 Main rare earth metals dominating in tricolor phosphors [10]

Phosphor	Chemical formula	% Y_2O_3	%Eu_2O_3	%CeO_2	%Tb_4O_7
red	$Y_2O_3:Eu^{3+}$ (LAP)	85.3-93.0	6.8-7.6	-	-
green	(Ce,Tb)$MgAl_{11}O_{19}$ (CAT)	-	-	11.5-15	6.2-7.4
blue	$BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM)	-	2.0-2.2	-	-

To sum up, fluorescent lamp phosphors taking into account rare earth metals are a prime candidate for recycling because lamps can be collected in large amounts (used widely in industry and business), in the nearest future they will be replaced by LEDs lamp, and additionally they contain mercury which is treated as a danger substance for which recycling infrastructure exist [11].

3. AVAILABLE METHODS OF RECYCLING SPENT FLUORESCENT LAMPS

Today recovery of precious and critical metals from waste materials is really important [12-14]. Rare earth metals become today treated as critical metals, therefore there are many different approaches what to do with spent fluorescent lamp; they for sure are discarded or stockpiled. It is estimated that by 2020 the stockpiled phosphor waste will contain about 25 000 tones of rare earth metals [15]. **Table 2** shows the potential for rare earth metals from magnets, batteries and phosphors in 2020. Presented estimation shows that recycling process of rare earth metals could essentially improve the state of overall rare earth metals, mainly in regions where the primary metals are not produced.

It is possible to use for recycling lamp phosphors physical separation methods such as magnetic separation, flotation or centrifugation - they enable to reuse the phosphors; however high purity requirements and deterioration of the phosphors powders during their lifetimes are the barriers for industrially application of the physical separation methods. Additionally these methods can be used only to one type one fluorescent lamp - different lamps use different phosphor powders [16].

Figure 5 shows typical scheme of recycling process. Firstly, physical processes like dismantling, crushing, segregation are used to sort waste fluorescent lamp into different materials (glass, phosphors, metals, mercury); then phosphors are treated chemically to separate rare earth metals - see **Table 3**.

Table 2 Recycling potential for rare earth metals from magnets, batteries and phosphors in 2020 [16]

Application	Average lifetime	Estimated values of metals, tones	Estimated scrap of metals, tones	Pessimistic	Optimistic
				Scenario, amount of recycled metals	
Magnets	15 years	300 000	20 000	3 300 tones	6 600 tones
Ni-M-H batteries	10 years	50 000	5 000	1 000 tones	1 750 tones
Lamp phosphor	6 years	25 000	4 167	1 333 tones	2 333 tones

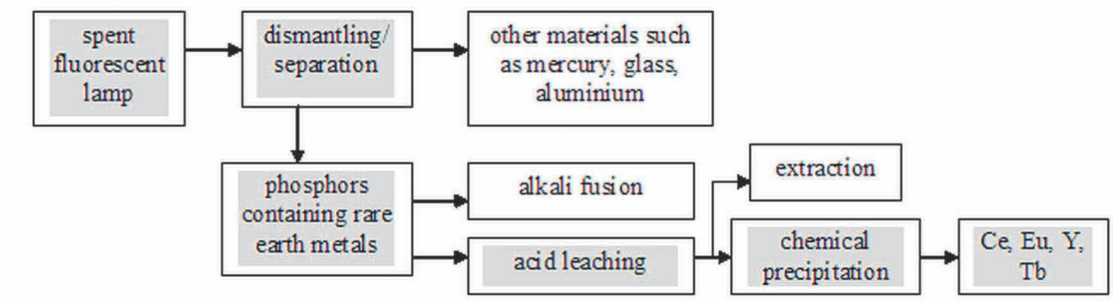


Figure 5 The scheme of recycling process of rare earth metals [10]

Table 3 Characteristics of pretreatment or physical processes and chemical treatment used in recycling rare earth metals [7, 10, 14, 17-25]

Stage	Characteristics
Pretreatment and physical processes	
Dismantling: end cut/air push method	Method was developed by the MRT Company in 2013 in Holland; equipment from MRT has been imported by the Beijing Eco-island science and technology Co., LTD in China in 2013, additionally Germany WEREC, OS-RAM, BISON and OSIMA companies developed the “end cut/air push” system; this method consist of the following stages: – aluminum caps at two ends of the tube are cut off - caps can be crushed to recover metal, – fluorescent powders containing Hg are blown out by the high-pressure air and collected, – mercury can be recovered with the gas flowing through the active carbon, – non-metallic materials can be used as additives of building materials or as fillers for wastemines.
Crushing	– Wet crushing - operated in liquids like ethanol or acetone to capture the mercury and avoid mercury vapor contamination; method used in the industrial production of fluorescent lamps in some countries (Germany, Finland and Switzerland), – dry crushing - carried out in closed or vacuum environment, metals, glass and phosphors containing Hg are separated, phosphors then are chemically separated and Hg is recovered - many companies (Fluorescent Lamp Recyclers Technologies Inc., Canada; AERC Recycling Solutions, USA; Lampcare, UK) have developed dry crushing equipment, however Japan is leading in this area (Nomura Kohsan).
Chemical treatment	
Acid leaching	Extraction of rare earth metals from waste tricolor phosphors, the most important wet processes, parts of rare earth metals in wastes can be transferred to aqueous liquor in the form of ions, it is possible to use HCl, H_2SO_4 and HNO_3 as a leaching agent; higher leaching efficiency could be obtained by H_2SO_4 leaching, with the increase of temperature, H_2SO_4 concentration and shaking rate; 4M HCl with addition of H_2O_2 (4.4 g/dm^3) is strong leaching agent; YOX is easy soluble in acid after milling; Y and Eu can be recovered during pressure leaching in H_2SO_4/HNO_3 (4 h, 125 °C, 5 MPa).
Alkali fusion	Thermal decomposition of insoluble substances, the main aim is to destruct the structure of the substance and transfer it into soluble substance; this method can effectively destroy the spinel structure of waste fluorescent powders; LAP, BAM and CAT phosphors are heated with solid Na_2CO_3 in 1000 °C; the main factors are: mass ratio of NaOH and the waste phosphors, calcination temperature and time; results showed that (in condition: mass ratio 6:1, 900 °C and reaction time 2 h) leaching efficiency of the rare earth metals (Y, Eu, Ce, and Tb) could reach close to 100%.

After chemical treatment there should be separation of rare earth metals. It can be done by precipitation; however this approach is not the best one when high purity products are required [25]. Separation of rare earth metals ions in solution can be obtained by solvent extraction and ion exchanges - see **Figure 6**. Today a liquid-liquid extraction is one of the most promising methods for such separation. In conventional solvent extraction the use of large amount of volatile organic solvents has been problematic. So, ionic liquids seems to be alternative due to their unique properties like flame resistance and negligible vapor pressure [27].

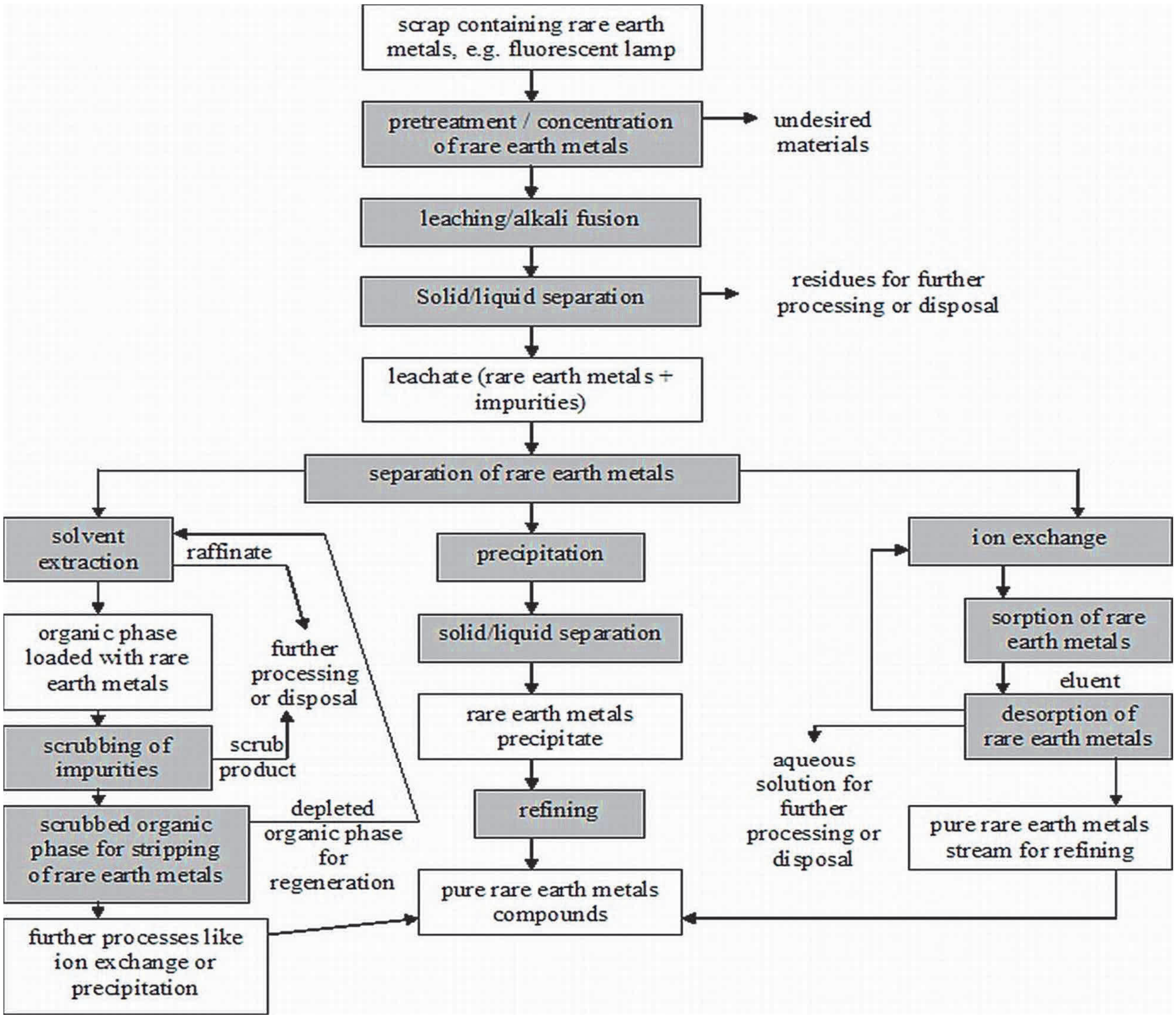


Figure 6 The scheme of different purification processes of rare earth metals [26]

4. CONCLUSIONS

Whereas recycling processes of many waste materials are commonly conducted and know; still there is problem with recovery of rare earth metals. Therefore; today the big environmental challenge has become tens of millions of lamps disposed of each year in Europe and all over the world. Spent lamps are collected, sorted and treated by specialized recycling companies to separate and obtain different components like glass, metal, plastic, mercury. Then phosphor powders should be directed to the plant or process in which the rare earth metals will be separated and purified. Recycling process for lamp phosphors waste for industrial scale is only conducted in one company - Solvay, in 2012 such process was implemented there successfully, it is possible to treat about 2000 tones of phosphor waste powder per year [15, 28]. There are two plants in Saint Fons in which rare earth concentrate is produced; then such concentrate is directed to plant in La Rochelle, where rare earth metals are purified and separated. Recent economic and political changes caused that the recovery of rare earth metals form spent products will be growing from year to year. Fluorescent lamps are in main attention because of they wide use, what ensure their availability.

ACKNOWLEDGEMENTS

Work was supported by Polish Ministry of Science and Higher Education under BK264/RM2/2016.

REFERENCES

[1] HUMPHRIES, M. *Rare Earth Elements: The global supply chain*. Congressional Research Service, 2013.

[2] GAMBOGI, J. *Rare Earths*, USGS, Minerals Yearbook, 2014.

[3] HEDRICK, J. B. *Rare Earths*. USGS, Minerals Yearbook, 2000.

[4] https://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/, 20.02.2017.

[5] *The rare-earth elements, vital to modern technologies and lifestyles*. USGS Mineral Resource Program, 2014.

[6] www.led-professional.com/resources-1/articles/led-lamps-recycling-technology-for-a-circular-economy (10.10. 2016).

[7] SATERNUS, M., WILLNER, J., FORNALCZYK, A., LISIŃSKA, M. Possibilities of recycling LED diodes. *EMC*, 2017, in print.

[8] RONDA, C. R., JÜSTEL, T., NIKOL, H. Rare earth phosphors: fundamentals and applications. J. *of Alloys and Compounds*, 1998, vol. 275-277, pp. 669-676.

[9] BINNEMANS, K., JONES, P.T. Perspectives for the recovery of rare earths metals from end-of-life fluorescent lamps. *J. of Rare Earths*, 2014, vol. 32, no 3, pp. 195-200.

[10] WU, Y., YIN, X., ZHANG, Q., WANG, W., MU, X. The recycling of rare earths from waste tricolor phosphors in fluorescent lamp: A review of processes and technologies, *Res., Cons. and Recycling*, 2014, vol. 88, pp. 21-31.

[11] MEYER, L., BRAS, B. Rare earth metal recycling, In *2011 IEEE International Symposium*, 2011, pp.1-6.

[12] SATURNUS, M., FORNALCZYK, A., WILLNER, J., KANIA, H. Methods for silver recovery from by-products and spent materials, *Przem. Chem*., 2016, vol. 95, pp. 78-83.

[13] WILLNER, J., FORNALCZYK, A. Electronic scrap as a source of precious metals. *Przem. Chem*., 2011, vol. 90, pp. 1000-1005.

[14] SATURNUS, M., WILLNER, J., FORNALCZYK, A., LISIŃSKA, M. Rare earth metals - receiving and recovery from waste materials. *Przem. Chem*., 2017, in print.

[15] DUPONT, D., BINNEMANS, K. Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of Y_2O_3:Eu^{3+} from lamp phosphor waste. *Green Chem*istry, 2015, vol. 17, pp. 856-868.

[16] BINNEMANS, K., JONES, P. T., BLANPAIN, B., VAN GERVEN, T., YANG, Y., WALTON, A., BUCHERT, M. Recycling of rare earths: a critical review. *J. Cleaner Prod*., 2013, vol. 51, pp. 1-22.

[17] LI H. M. Technology of comprehensive utilization of waste resources of rare earth fluorescent lamp. *Chin. Rare Earths*, 2008, vol. 29, pp. 97-101.

[18] RABAH, M. A. Recovery of aluminium, nickel-copper alloys and some salts from spent fluorescent lamps. *Waste Manage*, 2004, vol. 24, pp. 119-26.

[19] MEI, G. J., XIE, K. F., LI, G. Research progress of harmlessness and reuse of waste fluorescent lamp. *Res. Renew Resour*., 2007, vol. 6, pp. 29-35.

[20] http://www.nomurakohsan.co.jp/business/disposal_fluorescent.html, 20.04.2017.

[21] http://www.lamprecycle.org/commercial-lighting-lamp-recyclers/, 20.04.2017.

[22] https://www.aerc.com/Recycling_Solutions-Lamp_Recycling.php, 20.04.2017.

[23] http://www.wastecare.co.uk/services/lampcare/, 20.04.2017.

[24] DE MICHELIS I., FERELLA, F., VARELLI, E. F., VEGLIÒ, F. Treatment of exhaust fluorescent lamps to recover yttrium: experimental and process analyse. *Waste Manage*, 2011, vol. 31, pp. 2559-2568.

[25] TUNSU, C., PETRANIKOVA, M., EKBERG, C., RETEGAN, T. A hydrometallurgical process for the recovery of rare earth elements from fluorescent lamp waste fractions. *Separation and Purification Technology*, 2016, vol. 161, pp. 172-186.

[26] TUNSU, C., PETRANIKOVA, M., GERGORIĆ, M., EKBERG, C., RETEGAN, T. Reclaiming rare earth elements from end-of-life products: A review of the perspectives for urban mining using hydrometallurgical unit operations. *Hydrometallurgy*, 2015, vol. 156, pp. 239-258.

[27] YANG, F., KUBOTA, F., BABA, Y., KAMILA, N., GOTO, M. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid systém. *J. of Hazardous Materials*, 2013, vol. 254-255, pp. 79-88.

[28] http://www.solvay.com/en/company/innovation/european-life-projects/loop-life-project-objectives.html; 27.04.2017.