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Perspectives for the recovery of rare earths from end-of-life fluorescent lamps

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Abstract: This vision paper discusses the advantages and disadvantages of the three main options for the recycling of rare-earth elements from end-of-life fluorescent lamps: (1) direct re-use of the lamp phosphor mixture; (2) separation of the lamp phosphor mixture into the different phosphor components; (3) recovery of the rare-earth content. An overview is given of commercial activities in Europe in the domain of recycling of materials from end-of-life fluorescent lamps and the recovery of rare earths from these lamps. The collection of end-of-life fluorescent lamps is currently driven by a legal framework that prohibited the release of mercury to the environment. The contaminations of the lamp phosphor powders by mercury and by small glass particles of crushed fluorescent lamps are limiting factors in the recycling process. Research should be directed to an advanced clean-up of the reclaimed lamp phosphor fraction, and in particular to the removal of mercury and glass fragments. The recovery of rare earths from the lamp phosphors could be facilitated by taking advantage of the differences in resistance of the different lamp phosphors by chemical attack by inorganic acids and bases.

Keywords: balance problem; fluorescence lamps; lamp phosphors; lanthanides; rare-earth elements; recycling; urban mining

The efficient use of natural resources is mandatory in a sustainable, circular economy. This is only possible by the re-use and recycling of materials from end-of-life consumer goods. Whereas high recycling rates are being achieved for base metals such as iron, aluminum and copper, as well as for precious metals (gold, silver, platinum-group metals), the recycling rates of the rare-earth elements (REEs) are still very low (<1%)[1–3]. These low recycling rates can be attributed to different factors, such as technological difficulties, low toxicities of the REEs, and, until recently, low prices and lack of incentives. The technological issues of the recycling of rare earths can be understood by the fact that the rare earths are often minor components of complex materials in consumer goods[4]. For instance, a mobile phone contains less than 1 g of rare earths, mainly under the form of neodymium-iron- boron magnets. The flow sheets of the presently used pyrometallurgical processes for the recycling of metals, such as Umicore's recycling plant at Hoboken, near Antwerp in Belgium, have not been specifically designed for the recovery of rare earths, and consequently, the rare earths are lost to the oxide slags[5,6]. Given the complexity of REE-containing consumer goods, it is recommended that research efforts for the development of recycling schemes of rare earths do not adopt a general approach to the recovery of rare earths, but they must follow a product-centric approach[5]. This means that independent recycling technologies have to be developed for the different main applications of rare earths: devices containing permanent magnets, nickel metal hydride batteries and lamp phosphors. Recently, reviews on the recycling of rare earths have been published[7–9]. These give a state-of-the-art overview of the scientific and patent literature about this subject.

The aim of this paper is to discuss the perspectives for the recovery of rare earths from lamp phosphors. Three different approaches for recycling of rare earths from end-of-life fluorescent lamps and compact fluorescent lamps (energy-saving lamps) are considered: (1) direct re-use of the lamp phosphor mixture; (2) separation of the lamp phosphor mixture into the different phosphor components; (3) recovery of the REE content. Commercial activities are highlighted, with emphasis on the situation in Europe. Finally, suggestions for further developments are made.

1 Composition of lamp phosphor mixtures

On average, a compact fluorescent lamp consists of glass (88 wt.%), metals (5 wt.%), plastic (4 wt.%), lamp phosphor powder (3 wt.%) and mercury (0.005 wt.%). The composition of the lamp phosphor fraction obtained after crushing and sieving of the compact fluorescent lamps is: halophosphate phosphor (45 wt.%), fine glass particles and silica (20 wt.%–30 wt.%), alumina (12 wt.%), rare-earth phosphors (10 wt.% to 20 wt.%) and a

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residual fraction (5 wt.%). Alumina (Al_2O_3) and silica (SiO_2) are used in the barrier layer. The barrier layer is present between the phosphor layer and the glass tube. Its main function is to protect the glass envelope against attack by mercury vapor, and thus preventing mercury depletion of the lamp and reduction of the lumen output of the lamp. The barrier layer also improves the efficiency of the lamp by reflecting back the UV light that passes through the phosphor layer to the glass layer.

The five most common rare-earth phosphors in fluorescent lamps are the red phosphor $Y_2O_3:Eu^{3+}$ (YOX), the green phosphors $LaPO_4:Ce^{3+},Tb^{3+}$ (LAP), $GdMgB_5O_{10}:Ce^{3+},Tb^{3+}$ (CBT), $(Ce,Tb)MgAl_{11}O_{19}$ (CAT) and the blue phosphor $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM)[10,11]. A less common blue phosphor is the chloroapatite $(Sr,Ca,Ba,Mg)_5(PO_4)_3Cl:Eu^{2+}$. Many older fluorescent lamps, as well as lamps that have recently been produced by some non-Chinese lamp manufacturers contain the halophosphate phosphor $(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2:Sb^{3+},Mn^{2+}$, which is a broad-band white emitter. This halophosphate phosphor is often mixed with $Y_2O_3:Eu^{3+}$ to obtain a good color-rendering. The halophosphate phosphor does not contain any REEs and is therefore of low intrinsic value for recyclers. On the other hand, $Y_2O_3:Eu^{3+}$ has the highest intrinsic value, because it contains large concentrations of yttrium and europium, and represents the main REE-containing phosphor in the recycled phosphor fraction (up to about 20 wt.%).

2 Direct re-use of lamp phosphor mixtures

The recovery of lamp phosphors from end-of-life fluorescent lamps for direct re-use in new fluorescent lamps is an obvious recycling route. This route comprises separation of the powder fraction from the glass, metal and plastic fractions of the end-of-life fluorescent lamps. This route seems to be straightforward and is appealing from the point of view of the limited need for chemicals in the different process steps (or the need to use no chemicals at all). However, there are several technological issues associated with this processing route: (1) This approach is applicable only to one type of lamp, because different manufacturers are using different types of phosphor blends, and one single manufacturer may even use different phosphor blends; (2) Collection of one combined mixed lamp phosphor fraction from end-of-life fluorescent lamps will result in an inferior end product, which few lamp manufacturers are willing to use; (3) Another technological issue is the recovery of the phosphor powders from the lamps. The removal of the phosphor powder is relatively straightforward for linear tube fluorescent lamps: the end caps are cut off and the phosphor powder can be easily blown out of the glass tube by a pressurized air stream and, ultimately, collected. For other fluorescent lamps (non-linear tube fluorescent lamps and compact fluorescent lamps), crushing of the lamps is required, followed by a sieving step. This sieving process can be done in a dry or a wet way. It is evident that the lamp phosphor powder reports to be the finest sieving fraction. However, the lamp phosphor powder collected via this process is heavily contaminated by glass dust and very fine glass particles. The glass fraction can be up to 50% of the collected powder fraction. It is very difficult, if not impossible, to separate these small glass particles from the phosphor particles. It must be realized that even the lamp phosphor fraction recovered from linear tube fluorescent lamps is contaminated by components of the binder material, which consists mainly of alumina[7]. During the operational lifetime of the lamp, the phosphors can deteriorate due to the long-term exposure to high-energy UV radiation and the impact of gas molecules and ions. All these events can create defects in the crystal structure of the host material of the phosphor. Moreover, the phosphor powder gets contaminated by mercury. It has been shown that a larger part of the mercury present in a fluorescent lamp accumulates in the lamp phosphor over time. All these issues make that direct re-use of lamp phosphors from end-of-life fluorescent lamps is not recommended, especially not from lamps other than the linear tube fluorescent lamps.

Ingenious methods have been developed for the sorting of collected end-of-life tube fluorescent lamps in different classes of lamps with the same lamp phosphor mixture, based on recording of the fluorescent spectrum of the phosphor coating of the lamps. The lamps are enlightened for a short time (this can be done even by the presence of an external AC electrical field) and the fluorescence spectrum is captured by a fast spectrofluorimeter. Each lamp phosphor mixture has its characteristic emission spectrum and this spectrum can serve as a fingerprint for the composition of the lamp phosphor mixture. The spectrum allows identifying the different phosphor components and their relative abundance in the phosphor mixture. Such a process was developed by the Belgian waste-processing company Indaver, in close collaboration with Philips Lighting, in order to recycle the phosphors from Philips' linear tube fluorescent lamps.

3 Separation of phosphor mixtures in individual components

In order to overcome the problem that different lamp manufacturers are using different lamp phosphor mixtures, the recycled lamp phosphor fraction could be separated into the different components. It can also be tried to separate the fine glass particles from the phosphor powder. Just as in the case of the direct re-use of the lamp phosphors, this method is appealing, because it does not involve dissolution of the phosphor powder and further chemical processing of the dissolved rare-earth content, so that a limited amount of waste is generated. This method could