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THE POSSIBILITY OF RARE METAL RECOVERY FROM WHITE LED BULBS

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Abstract: White LED bulbs – dominant in lighting technology – can become a significant secondary source for the recovery of valuable rare metals, if a proper extractive metallurgical technology is developed. We have found an efficient way to separate the "phosphors" (phosphor coated LED chips) from the metallic base shells in dilute sodium carbonate and calcium hydroxide solutions. The leaching reactions of the separated phosphors was studied thermodynamically and the process was examined experimentally. The contained base metals and rare earth elements could be efficiently leached in 1 M HCl acid in 1 h, only Ga and In showed inert behavior toward acid solubilization. The separation of the valuable components has been devised by standard hydrometallurgical techniques.

Keywords: LED lighting, recycling rare earth metals, recovery

INTRODUCTION

The electric lighting is indirectly responsible for ~5% of the total CO_2 emission. [1] Thus the traditional – not energy efficient – tungsten-based incandescent light bulbs are being phased out all over the world. In some countries their marketing is completely prohibited. [2] On the other hand, the application of light emitting diode (LED) technology is increasing rapidly. These light bulbs offer much longer lifetime, significantly reduced energy consumption while producing the same amount of light as the incandescent bulbs. [2] Moreover, the energy loss in the form of infrared light is also negligible in the case of LEDs. Based on estimations, approximately 95% of the lighting market will be dominated by LED light sources by 2025. [3]

However, LED light bulbs require some critical raw materials, such as rare-earths, indium and gallium. The most common white light producing LED technology applies an indium-gallium-nitride semiconductor chip on a sapphire substrate, which directly emits blue light in the 440–470 nm range. The chip is enveloped in a

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material called phosphor that converts this primary radiation into a warmer tone, which the human eye perceives as white light. The phosphor used for this technique is most often yttrium aluminium garnet doped with cerium, $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce). Other versions such as $(Y,Gd)_3Al_5O_{12}:Ce^{3+}$, (YGAG:Ce), $(Y,Tb)_3Al_5O_{12}:Ce^{3+}$ (YTAG:Ce), $Y_3(Al,Ga)_5O_{12}:Ce^{3+}$, (YAGG:Ce), $Y_3Al_5O_{12}:Ce^{3+},Pr^{3+}$, (YAG:Ce,Pr), $Lu_3Al_5O_{12}:Ce^{3+}$ (LAG:Ce) and BOSE $(Ca,Sr,Ba)_2SiO_4:Eu^{2+}$ and CASN ($CaAlSiN_3:Eu^{2+}$) are applied also in LEDs. [4], [5], [6] A light source of 1 mm^2 surface area with two LED chips contains ~3 μg Ce or Eu, while elements like Y, Lu, or Gd – which form the basic matrix of the phosphor – are present in higher amounts (approx. 90–200 μg). Moreover ~17–30 μg Ga and In can be found in such a chip. Noble metals like Au (~200 μg) – used as current conductor filaments – can also be found in the LEDs. [7] The recycling of LED waste is not yet practiced, mainly because of the implied novelty. However, the LED industry is expanding rapidly, thus a large supply of these waste materials can be expected in the near future.

1. CHARACTERIZATION AND PREPARATION OF THE RAW MATERIAL

The aim of this work was to examine LED waste materials – gathered from residential applications – in order to assess their metal value and gain fundamental data which can aid the development of a recycling method. The complex structure of a LED bulb makes its recycling difficult, thus before a metallurgical procedure can be developed, their general structure and composition must be explored. The examined LED bulbs of different structural designs and the mechanically removed LED units – including the attached motherboard strips or plates - are shown in *Figure 1*. In the case of the bulb in *Figure 1a*, the electric components are originally attached to the motherboard, however they were removed before the LED unit was taken to the processing steps.

Figure 1
The examined LED bulbs (a–c) and the removed LED units (d)

Unlike incandescent bulbs, LEDs use printed circuit boards, two or more capacitors and coils, which further increase their value as these components can contain Cu, Sn and Ta in not negligible quantities. The mechanically detached LED units containing

the light emitting seeds were examined under the microscope, as shown in *Figure 2*. In general, the LED units consist of the yellow phosphor seed, the LED chip *(Figure 2c)*, the metallic container tray *(Figure 2b)*, the motherboard strip or plate *(Figure 1d)* and the soldering butts at the terminals of the metallic trays *(Figure 1a, b)*. These LED units constitute the principal parts which generate the light upon receiving the proper voltage. The surface of the aluminium- or plastic-based multi-layered motherboard is covered with a non-conductive organic sealing or paint, underneath there are current conductor layers made of isolated copper foils. The container trays of the LED units are attached to these conducting layers.

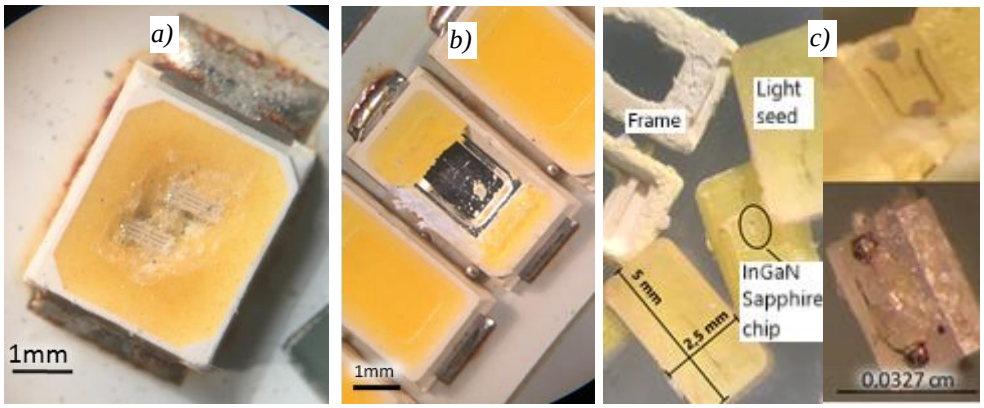

Figure 2

Two LED units removed from the motherboard strips (a, b), separated phosphors (c) and the LED chip physically separated from the phosphor coating (d)

The LED chip is laid on a metallic tray – confirmed to be of silver plated steel – and enveloped in the phosphor, which is fixed in a plastic/ceramic frame. The current is conducted from the terminals of the LED unit to the chip through the phosphor via a gold filament. One such LED unit can contain one or multiple LED chips.

Each different type of the collected LED bulbs was dismantled and the major components determined. Results are shown in *Table 1*. The bulbs contain large amounts of plastic/ceramic or glass components, requiring a complex treatment.

Table 1

The distribution of the individual components of the LED bulbs in mass-%

Type	LED units	E. circuit	Steel base	Glass	Plastic/ceramic
Figure 1*a*)	8.97	7.48	3.17	–	80.4
Figure 1*b*)	32.33	5.11	3.41	–	59.13
Figure 1*c*)	13.12	6.59	1.23	64.08	14.6

We have examined the total metal content of the LED units – as attached to the motherboard pieces – by leaching in 12 M HCl, 15 M HNO_3 and aqua regia, respectively at boiling temperatures. The solutions were analysed by microwave plasma emission spectroscopy (MPOES). The highest extracted amounts by any of the lixiviant media were accepted as the representative metal contents. The base metal content of the LED units, as dissolved by aqua regia at boiling temperature, can be seen in *Figure 3*.

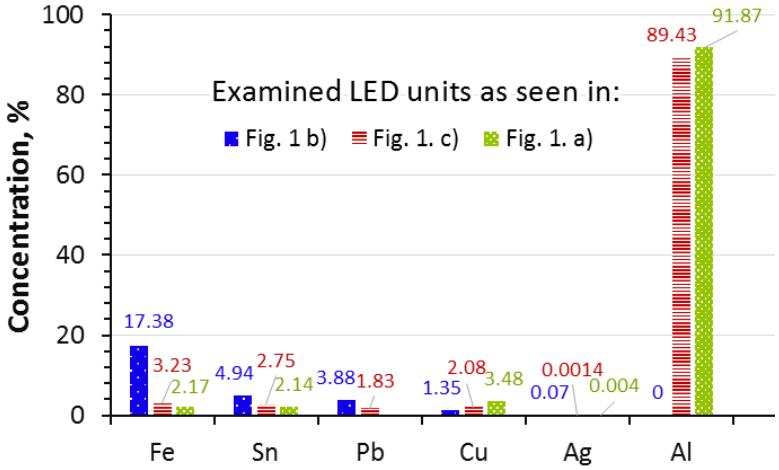

Figure 3

Dissolved base metal content of the examined LED units (aqua regia: 10 cm^3/g)

Aside from Al – which is the motherboard material of the LED units in more durable LED bulbs – the concentrations of Fe, Sn, Pb and Cu are also significant. The prices of these metals strongly depend on their respective purity. Thus Sn and Cu recovery could contribute to the economic incentive for recycling. Moreover, the removal of heavy metals such as Pb could also be beneficial for environmental protection. While iron carries relatively little value neither is toxic, a complex recycling technology could provide some valuable iron compounds too.

The valuable rare metals are contained in the usually yellow colored phosphor seeds fixed in the metallic container trays and thus attached by soldering to the motherboard. The complete dissolution of the solder butts and the partial dissolution of the Ag layer on the metallic container trays result in the separation of the phosphor seeds with the LED chip remaining enclosed. The liberated phosphor seeds (of less than 2.5 mm diameter) were separated from the large pieces of the mixed residue by sieving and were subjected to crushing and grinding in a mortar. The obtained powder was than leached in aqua regia at boiling temperatures. The rare earth content could be accessed partly also directly by the preliminary leaching of the LED units. The remaining part was leached subsequently from the separated phosphor seeds after fine grinding. The results obtained by the consecutive leaching steps are presented in *Figure 4*.

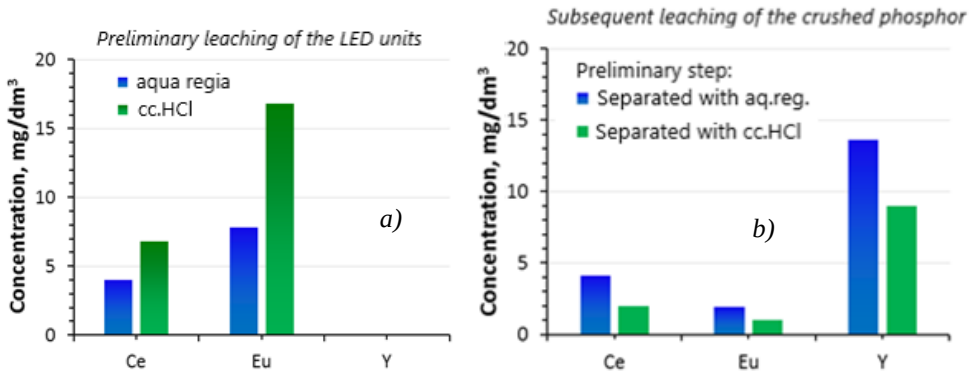

Figure 4

Relative amounts of rare metals dissolved directly from the LED units (a) and from the separated and crushed phosphor with aqua regia (b.) (20 g LED units, or 1.84 g phosphor seeds removed, 40 cm³ solution, 350 rpm, 2 h boiling)

As shown by the comparison of *Figures 4a* and *4b*, most of Ce and Eu has dissolved from the phosphor during the preliminary liberating step applying strong acids. However, all the Y remained to be dissolved in the subsequent leaching of the separated and crushed phosphor seeds. The $Y_3Al_5O_{12}$ is composed of two oxides with high thermodynamic stability, thus it is hard to dissolve. On the other hand, the solution from the first leaching step infiltrated the phosphor, thus some of the Ce and Eu may have been carried over physically entrapped in the phosphor to the subsequent leaching step. This mechanism explains why the impurity levels shown in *Figure 5* were found relatively high in the leachate of the crushed phosphor.

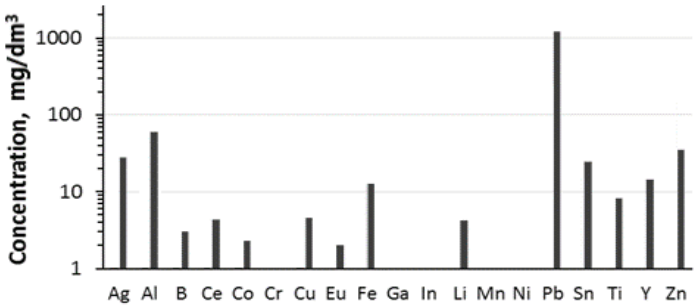

Figure 5

The metal concentration of the aqua regia solution obtained from the leaching of the phosphors previously separated from The LED units with cc. HCl (1.84 g phosphor seeds, 40 cm³ solution, 350 rpm, 2 h boiling)

After leaching, the solution was cooled and the poorly soluble Pb salts crystallized inside the phosphor. Moreover, during leaching the solution quickly becomes saturated in $PbCl_2$, thus the crystallization can occur even during the leaching. The com-

plex composition and the high impurity content would make the economically feasible rare metal recovery difficult. Thus to selectively solubilize the rare metals, the phosphor and LED chip must be preliminarily separated from the panel and the base of the LED unit, while avoiding the dissolution of the base and rare metal content.

2. SEPARATION AND PREPARATION OF THE PHOSPHOR SEEDS

The valuable rare earth metals are concentrated in the phosphor seeds contained in the LED units. A selective removal of the phosphor layer – including the LED chip – from the LED unit and the attached motherboard can be achieved by boiling the units in a mildly alkaline medium. The examined agents were Na_2CO_3, $Ca(OH)_2$, and water. The best results were obtained with saturated $Ca(OH)_2$ solutions, but with a longer time, the dilute Na_2CO_3 solution was also efficient. Results are shown in *Figure 6*.

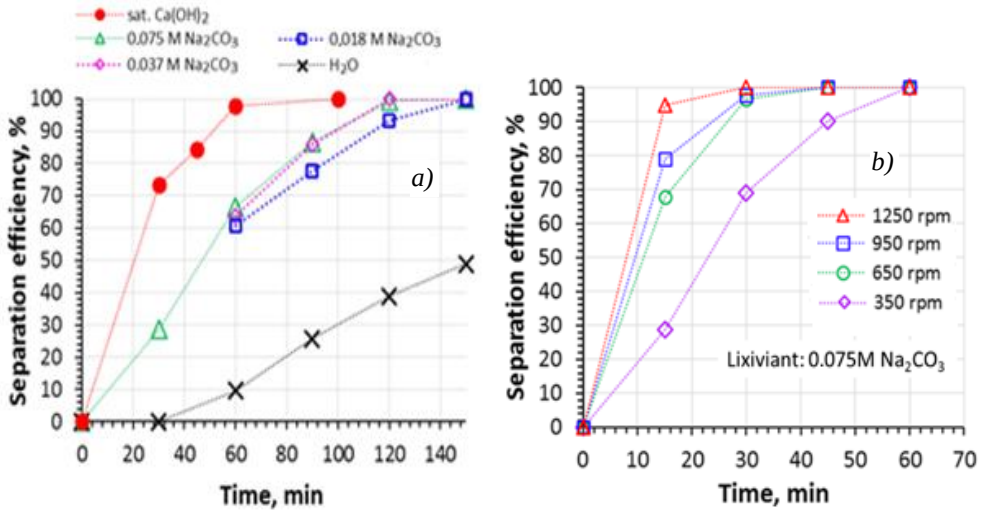

Figure 6
Separation efficiencies of the phosphor seeds in different media (a); the effect of stirring speed on the separation efficiency (b)

Applying pure water assures only rather low separation efficiencies. In contrast, saturated $Ca(OH)_2$ solutions seems to be the most effective at separating the phosphor, followed by the dilute Na_2CO_3. It must be noted that this separation process has been only tested on used LEDs. Thermal aging processes during usage weakens the structure and bonding between the phosphor and its surroundings. The LED motherboard pieces and the phosphors were separated from each other by sieving. The latter was ground into a fine powder with a ceramic mortar and a pestle. The separation process and the products are shown in *Figure 7*.

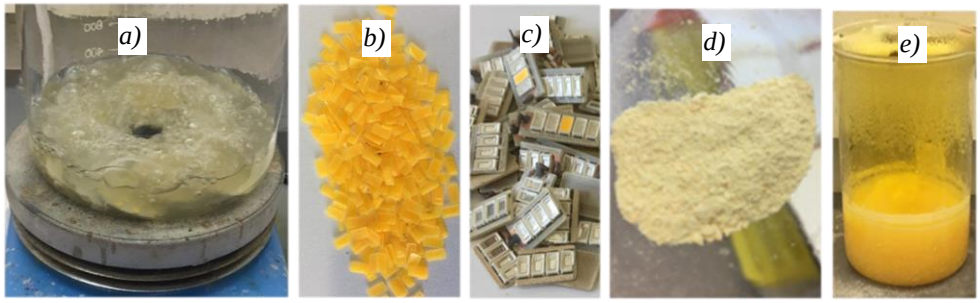

Figure 7

The separation of the phosphor including the LED chip in an alkaline medium (a); the separated phosphor seeds (b); the residue bearing base metals (c); crushing the phosphor (d); leaching of the phosphor powder (e)

3. RARE METAL DISSOLUTION FROM THE PHOSPHOR SEEDS

The viability of leaching the phosphor has also been examined thermodynamically. The most valuable components are the phosphor matrix itself ($Y_3Al_5O_{12}$) doped with Eu and Ce and the semi-conductor (InGaN) layer on the LED chip. Calculations were carried out using the HSC Chemistry software. The considered aqueous reagents were H_2SO_4, HCl and HNO_3. The standard Gibbs free energy change of the aqueous reactions are plotted as functions of the temperature in *Figure 8.*

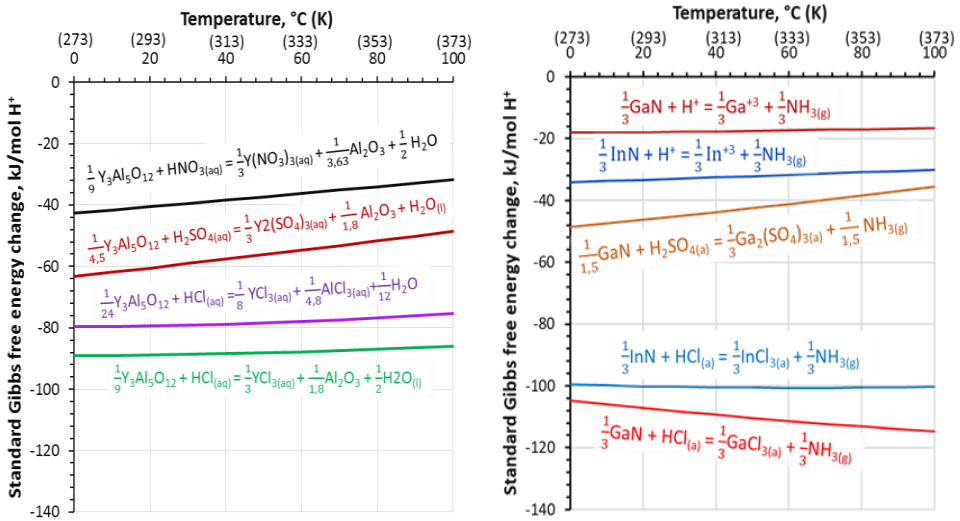

Figure 8

The temperature dependence of the standard Gibbs free energy change accompanying the leaching of the YAG compound (a) and the semiconducting LED material (b) with different solvents

It can be seen, that HCl acid has superior solubilizing power compared to cheaper sulphuric and the strongly oxidizing nitric acid. The relatively largely negative standard Gibbs free energy change of the reactions in aqueous media suggests, that the dissolution of the metals in the InGaN semiconductor chip is feasible. However, the nitrides are known to behave as refractory toward leaching in virtually any kind of aqueous solvents. It could be only effected at elevated pressures and temperatures, or after a thermal conversion via alkaline roasting. [8]. This has been confirmed by our results of the experimental digestion *(Figure 5)* aimed at the complete dissolution of the LED units. This inert nature could be advantages, as the other more soluble components (such as rare earth metals and most impurities) can be dissolved, while the Ga and In remain in the solid residue, thus selective retention can be achieved. It is convenient that the aqueous ions of the rare earth metals can be kept stable at relatively high pH values. *Figure 9* shows the E-pH diagrams of Eu, Ce and Y.

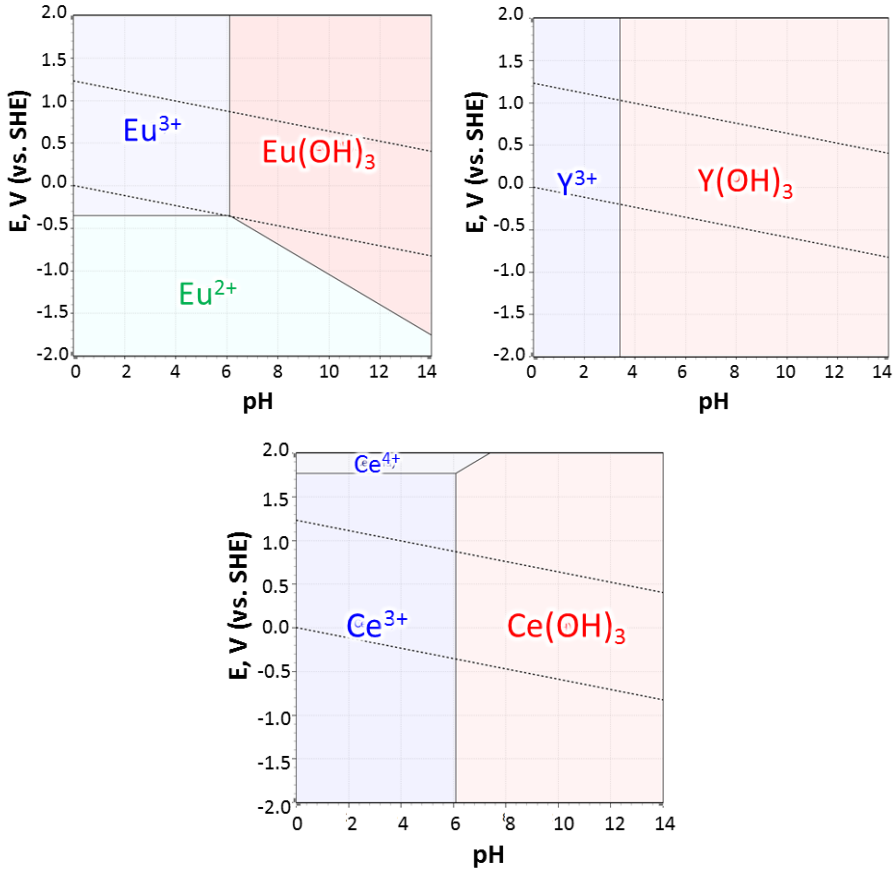

Figure 9
The E-pH diagrams of Eu, Ce, Y (25 °C, dissolved metal: 1 mol/dm³)

One of the main challenges in extracting pure rare earth metals is their very similar chemical behaviour. While Y is not one of the lanthanides, still it is chemically similar to this group. The Pourbaix-diagrams suggest that the hydrolysis of Y can be expected at lower pH. However, the activity conditions may alter the predominance limits of the indicated ions. Based on the published stability constants of the respective hydroxides, [9] we have calculated and plotted the pH dependence of the equilibrium Ce^{3+}, Eu^{3+};Y^{3+} ion concentration. This is presented in *Figure 10*.

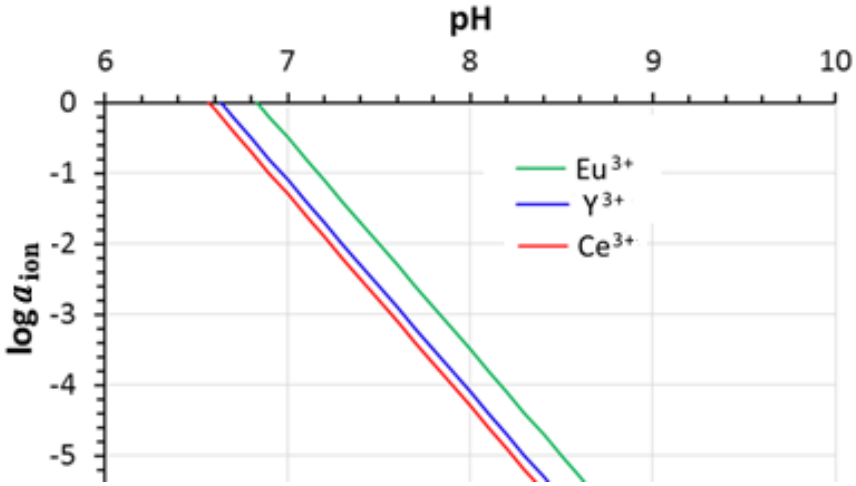

Figure 10

The equilibrium activities of dissolved rare earth metal ions as functions of the pH

Based on the equilibrium curves, the hydrolysis of the phosphor components can only be expected above pH 6. Thus close to neutral conditions could be applied at the end of the leaching step. This would significantly reduce the Fe(III) and Al concentration in the leachate.

The separation of the phosphor seeds in alkaline media results in low impurity levels in further steps of rare earth recovery, as practically no reaction took place during the preliminary leaching. Besides the rare earth metals, the recovery of noble metals (Au, Ag) could also become important, as Au constitutes ~0,6% and Ag ~0,2% of the total weight of the phosphor. It would be beneficial if the rare metals and other impurities could be dissolved from the residue without the dissolution of the noble metals. As the thermodynamic study suggest, HCl can be a suitable solvent. Therefore, further leaching experiments were carried out at 60 °C using 1 M HCl with 350 1/min stirring speed. The relative recovery rates are plotted in Fig. 11 as compared to the values obtained by a virtually complete digestion with aqua regia at boiling temperatures for 3 hours. Dopant materials (Eu, Ce) can be dissolved from the YAG matrix much faster than Y, which is possibly due to the higher stability of the YAG double oxide. Thus if Y dissolution is desired, longer time and higher temperatures are required.

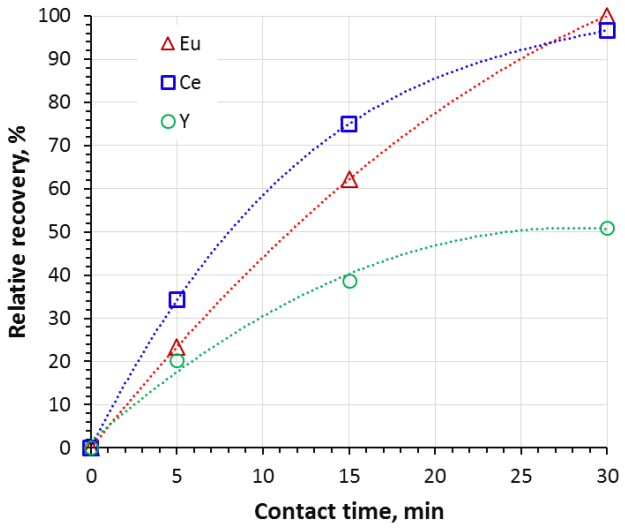

Figure 11

Relative recoveries of the rare earth metals from the phosphor powder by leaching with 1 M HCl at 60 °C, as compared to the total metal content determined by aqua regia leaching at boiling temperature

CONCLUSIONS

The end-life white LEDs were examined physically, it was found that the LED motherboard and panel contains significant amounts of metallic aluminium and copper, while further values (Pb, Sn) can be found in the solder. The LED units hold the phosphor and the LED chip itself, which contains rare earth metals along with Ga and In. The physical separation of the phosphor – including the LED chip – was best achieved via slightly alkaline treatment. The fastest separation was achieved with a saturated $Ca(OH)_2$ solution, while 0,075M Na_2CO_3 could produce similar results at longer times. The solubilisation of the separated phosphor and LED chip was first studied thermodynamically, proving that HCl has superior solubilizing power when compared to H_2SO_4 and HNO_3. The stability diagrams showed that neutral leaching could be considered also for a cleaner extraction of the rare metal oxides. Experimental leaching proved, that the rare metals can be leached efficiently from the separated and crushed phosphor seeds in 1 M HCl at 60 °C. If Au is also to be recovered, aqua regia leaching at boiling temperature may be applied.

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REFERENCES

[1] Kitai, A. (2011). *Principles of solar cells, LEDs and diodes. The role of the PN junction*. Mississauga: Wiley.

[2] Held, G. (2009). *Introduction to Light Emitting Diode technology and applications*. Boca Raton: CRC Press.

[3] McKittrick, J. (2013 Oct.). *Solid State Lighting Program: Final Report*. [Online]. Available: https://www.osti.gov/servlets/purl/1113955.

[4] Inamuddin, K. Anish, Abdullah, A. M. (2020). *E-waste Recycling and Management*. Cham, Switzerland: Springer.

[5] Chen, W.-S., Hsu, L.-L., Wang, L.-P. (2018). Recycling the GaN waste from LED industry by pressurized leaching method. *Journal of Metals*, Vol. 8, No. 10, Article number: 861, http://doi.org/10.3390/met8100861.

[6] Sillén, L. G., Martel, A. E., Bjerrum, J. (1964). *Stability constants of metal-ion complexes*. London: Chemical Society.