

# INTEGRATED FLOW SHEET FOR THE RECOVERY OF RARE EARTHS FROM CRTs AND LAMP PHOSPHOR WASTE

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In this paper we describe the recovery of rare-earth elements (REEs) from spent lamp phosphors and cathode-ray tube (CRT) phosphors through a combination of different techniques, namely pyrometallurgical, hydrometallurgical and solvometallurgical processes. The results presented here are part of the experimental activity carried out within WP1 of the REMAGHIC project (EU H2020 SPIRE 2015, Grant Agreement N°680629), which focuses on the recovery of REEs and magnesium from secondary sources to produce new high-performance and low-cost REE-Mg alloys for the automotive, aeronautic and biomedical sector.<sup>1</sup>

CRT powder is rich in yttrium and europium which are present as yttrium europium oxysulphide ( $Y_2O_2S:Eu^{3+}$ , red phosphor). Zinc is also present in the powder as zinc sulfide (ZnS, as host matrix of the green and blue phosphors). In order to avoid  $H_2S$  release during the leaching step, the CRT powder was treated through several pyro-treatment processes. By roasting, ZnS is transformed into ZnO (oxidising and sulphating roasting) or volatilized as  $ZnCl_2$  (chloridising roasting). The laboratory tests concluded that oxidising roasting at 850 °C gives the best performance without the need of any added reagent in the process. During the trials performed, XRD analysis on the products obtained at different furnace residence time showed the formation of yttrium europium oxysulphate at early stages; this compound decomposed into yttrium and europium oxides at longer times.<sup>2</sup> However roasting for extended time generated also yttrium and zinc compounds based on silicates and oxysilicates that may reduce the performance in further leaching process. In order to optimise the process and to increase roasted material production for research purpose, the oxidising roasting treatment was scaled up from a laboratory muffle furnace to a continuous pilot rotary tubular furnace (up to 5 Kg/h production).

The possibility to selectively remove zinc from the roasted CRT phosphors was investigated by employing acetic acid as leaching agent in the solvometallurgical process. The leaching tests were performed on samples roasted at different furnace residence time (1h, 7h and 24h). Several operative parameters (such as lixiviant concentration, contact time, liquid/solid ratio and temperature) were varied in order to define the optimal operative conditions in terms of high Zn leaching efficiency combined with low coextraction of Y and Eu. REEs recovery from the leaching residue

was then studied by employing both inorganic (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) and organic acids (methanesulfonic and triflic acid) and the best operative conditions were defined as well. Y and Eu recovery from the leach liquor was finally performed through precipitation with oxalic acid followed by calcination, which gives a mixed REE oxide. REEs recovery from lamp phosphor waste type can be performed by leaching with mineral acids giving high recovery yields (>95%) for some REEs. However, it was experimentally proven that Ce, La and Tb recovery yields were below 20%. This can be explained because of the fact that phosphate compounds are not easily leached by acids. In order to improve those REEs leaching, a pyrometallurgical treatment based on roasting the waste with Na<sub>2</sub>CO<sub>3</sub> at about 900 °C was studied. The target of the roasting is to convert REE phosphates into REOs which are more easily leachable. Temperature, Na<sub>2</sub>CO<sub>3</sub> to lamp phosphor waste ratio and residence time were evaluated at several laboratory furnace roasting tests until reaching recovery yields above 99% for all REEs when acid leaching was later applied.

Y/Eu separation from a mixed REEs oxide obtained by a hydrometallurgical process was studied by solvent extraction with several ionic liquids, such as Cyphos IL 101 thiocyanate and Aliquat 336 thiocyanate. Preliminary tests were performed on synthetic chloride solutions, in order to define the best operative conditions. The investigated process parameters were the equilibrium time, pH, temperature, chloride and thiocyanate concentration. The optimal conditions were then employed for the treatment of the real lamp phosphor leachate. The treatment of the Tb-rich residue was investigated as well. This step involves the attack of the very resistant phosphate and aluminate phosphors (LAP, CAT, BAM phosphors). The recovery of La, Ce and Tb from this residue was tested by using strong organic acids as lixiviants. REEs recovery from the leachate was investigated through solvent extraction with D2EHPA followed by precipitation with oxalic acid. Preliminary tests were first performed on synthetic LAP phosphor; once the optimal conditions were defined, they were applied on a real lamp phosphor residue.

## References

1. Project website: <http://www.remaghic-project.eu/>
2. M. Leskelä and T. Leskelä, "Thermal stability of rare earth oxysulfide solid solution in air", *Thermochim. Acta*, **48**, 43-50 (1981).