

ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 39

no. 3

pp. 107 - 114

2013



PL ISSN 2083-4772

DOI: 10.2478/aep-2013-0023

© Copyright by Polish Academy of Sciences and Institute of Environmental Engineering of the Polish Academy of Sciences,
Zabrze, Poland 2013

THE RECOVERY OF YTTRIUM AND EUROPIUM COMPOUNDS
FROM WASTE MATERIALS

STEFAN GÓRALCZYK*, ELŻBIETA UZUNOW*

Instytut Mechanizacji Budownictwa i Górnictwa Skalnego
ul. Racjonalizacji 6/8, 02-673 Warszawa

*e-mail: s.goralczyk@imbigs.pl, e.uzunow@imbigs.pl

Keywords: Recovery, yttrium, europium, waste materials.

Abstract: Rare earth metals including yttrium and europium are one of several critical raw materials, the use of which ensures the development of the so-called high technology. The possibility of their recovery in Europe is limited practically only to secondary materials such as phosphogypsum and electronic waste.

The article presents the results of our research concerning the development of recovery technology of yttrium and europium from luminophore CRT used lamps. It describes the principle of separation of elements and the test results of cleaning the concentrate. It was shown that the costs of preparing the concentrate according to the proposed technology are lower than the phosphogypsum processing technology and the composition of the resulting product does not contain hazardous substances.

INTRODUCTION

The ongoing economic crisis in Europe largely highlighted the importance of security of supply for the modern European economy. It turned out that the sourcing of raw materials is becoming one of the critical threats and is all the greater as the more modern industry becomes.

Modern technologies and products are often based on specific raw materials, whose importance has grown almost exponentially over the past 50 years, such as the technologies using elements and compounds of rare earths. The problem of satisfying the needs of the Polish economy in the rare earths has long been indicated [1], and after the years the problem of their deficit is back on a larger scale, as a problem of the entire EU. Observing the activities undertaken in the past and at present we cannot help noting that there are still no effective technologies which treat waste products as a renewable source of critical raw materials. On the basis of realized and described in the article own works, we believe that the recovery of critical raw materials such as yttrium and europium compounds from discarded electronic products is possible and economically justified.

ASSUMPTIONS OF RECOVERY TECHNOLOGY OF YTTRIUM AND EUROPIUM COMPOUNDS

The study which aimed to develop recovery technology of yttrium and europium compounds [2] was due to a combination of measures needed to dispose of hazardous waste, such as worn tubes with simultaneous recovery of valuable critical raw materials.

CRT classification as a hazardous waste results from the presence of cathode luminophores inside the cathode – ray tubes. The cathode luminophores are based on cadmium and zinc sulphide as well as on oxysulphide of yttrium and europium additionally mixed with other impurities such as a vast number of aluminum powder and iron oxide. Accordingly, the disposal of the CRT process was proposed, which involves the simultaneous execution of the following tasks:

1. Separation and disposal of hazardous luminescence waste from discarded cathode and transformation into the safe waste, suitable for storage in accordance with the applicable law on waste.
2. The combination of the disposal of waste with the recovery of rare earth compounds such as yttrium and europium of the above mentioned waste.

In this perspective, the recovery technology of rare earth compounds is an integral part of the whole process of waste treatment and conversion of luminescence. The basis of the presented technology is a method based on mechanical separation, selective leaching and precipitation of rare earth compounds concentrate [2]. The specific conditions of particular processes are defined in the above mentioned patent description. A diagram of a hazardous waste disposal technology, combining technological operations required for its disposal and for recovery of yttrium and europium compounds is shown in Figure 1.

As it is clear from the proposed scheme, the starting material for the implementation of recovery technology of yttrium and europium compounds is acidic solution, which arises from the operation of waste luminophore stabilization using nitric acid.

This solution is formed on the basis of 5 mol/dm³ nitric acid solution and the filtrate is recycled to the circulation of the acid, wherein the amount of nitric acid has also been completed to 5 mol/dm³.

Such actions allow for:

- recovery of yttrium and europium, which remain in the filtrates after acid precipitation of oxalate yttrium-europium,
- reduction of the amount of nitric acid necessary for stabilizing hazardous waste,
- reducing the total amount of waste to neutralize.

As a result, this process was carried out to give a concentrate of yttrium and europium compounds of compositions presented in Table 1.

THE STUDY OF CONCENTRATE YTTRIUM AND EUROPIUM, AND THE RESULTS

The study included the following range:

- the quantity of recovered concentrate yttrium-europium,
- yttrium and europium content in the concentrate,
- impurity content of heavy metals,

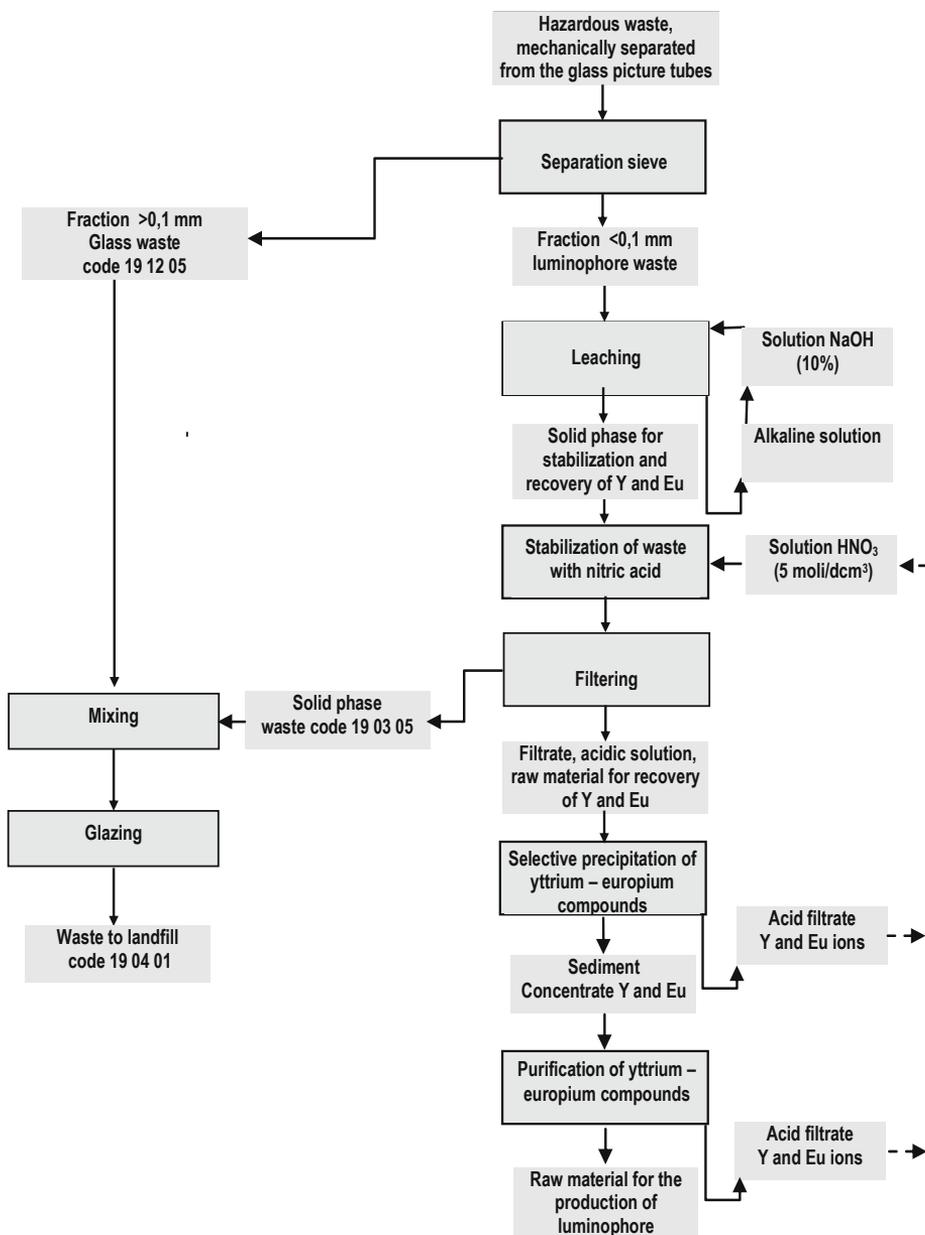


Fig.1. Diagram of disposal technology of luminophore waste, combining disposal and recovery of yttrium and europium compounds

- impact on the recovery efficiency of rare earth compounds by reversing into the process the sour solutions which remain after the precipitation of poorly soluble compounds of yttrium-europium.

Table 1 shows the obtained results:

Table 1. Content of impurities in chosen ordinary metals samples of the concentrate obtained in the recovery operation of rare earth compounds with acidic solutions

No.	Test sample	The amount of received concentrate with 100 ml of solution [g]	The content of recovered rare-earth [mg/g concentrate]		The content of heavy metal contamination (mg metal / g of concentrate)					
			Y	Eu	Cu	Fe	Ni	Zn	Cd	Cr
1	Concentrate obtained without the use of acid filtrates	0.6289	530.7	38.7	0.126	4.95	0.069	1.53	1.577	0.050
2	Concentrate obtained by combining technologies of waste disposal and recovery of rare earths	0.7559	527.7	40.1	0.186	18.32	0.08	25.0	0.541	0.060

Using for stabilization waste in addition to pure nitric acid solution as the filtrate remaining after precipitation of the operation of yttrium and europium compounds resulted in approximately 20% increase in the amount of concentrate received. The resulting concentrate of yttrium and europium compounds contained 67% by weight of yttrium oxide and 4.64 wt% of europium oxide per Y_2O_3 and Eu_2O_3 .

There was also a negative phenomenon, namely the increase in the level of pollution of concentrate with heavy metals, especially iron compounds. This is due to the fact that recycled materials undergoing the process of acidic solutions contain non-precipitated addition of rare earth metal ions as well as all other contaminants from the first implementation of this operation. So it is obvious that the secondary use of acid filtrates is limited, and that beyond a certain level of pollution the filtrates should be periodically disposed.

The presented in Figure 1 diagram of luminophore waste disposal process can provide a conclusion that the process forms both acidic and alkaline filtrate, and therefore the most preferred way to neutralize them is their neutralization.

Dissolved heavy metal compounds are located mainly in the acidic waste water, which in neutral solution precipitates as a sediment, while the neutralization of acidic and alkaline sewage allows removing most of the aluminum ions in the form of insoluble deposits. For this process to occur efficiently, before neutralization small amount of sulphuric acid was introduced to the filtrates.

As a result, the neutralization solution was obtained at pH around 7 and settlements. In order to verify the effectiveness of such a method of mutual utilization of aggressive

post-reaction solutions heavy metal content in the filtrate from the acid neutralization was examined, in the solution obtained by the neutralization of acid and alkaline filtrates and in the sediment. The results are shown in Table 2.

Table 2. The contents of selected heavy metals in the filtrate acid prior to disposal and neutralization of waste products

No.	Test sample	The content of heavy metal contamination				
		Cu	Ni	Zn	Cd	Cr
1	Acid filtrate	16.64 mg/l	23.90 mg/l	1292 mg/l	99.26 mg/l	5.53 mg l
2	Solution after neutralization	0.728 mg/l	2.439 mg/l	2.530 mg/l	0.755 mg/l	0.120 mg/l
3	Permissible water pollution by heavy metals	0.5 mg/l	0.5 mg/l	1.5 mg/l	0.05 mg/l	0.5 mg/l
4	The precipitate	0.046% by weight	0.085% by weight	4.53% by weight	0.46% by weight	0.0055% by weight

As it is clear from the results of research, the neutralization of alkaline and acid solutions significantly reduces the amount of heavy metals in solution to precipitate as sediment.

Under the current rules this sediment is dangerous and as such should be collected, stabilized and transferred to the storage of hazardous waste in landfills. In order to complete stabilization of the sludge it is preferred to use the vitrification operations together with the fraction of the previously separate glass dust with the code 19 12 05, the resulting product is safe for the environment and can be safely stored as hazardous waste code 19 04 01.

Inert wastes were largely devoid of harmful heavy metals, but prior to their introduction into groundwater or the soil they must undergo further treatment process, according to the level specified in the regulation of November 29, 2002 (Journal of Laws No. 212, item. in 1799, 2002).

Comparing the requirements of this regulation with the results shown in Table 2, it was found that:

- The content of cadmium is much higher than the permissible level,
- The copper, zinc and nickel are slightly exceeded.

Such wastewater after neutralization cannot therefore be disposed of into drains or the ground, but removing the most aggressive and harmful substances simplifies the process of purification and allows the application of the routine methods (e.g. ion exchange).

CONCLUSIONS

Implementation work on the disposal of hazardous waste, removed from the cathode to the experimental lines of CRT disassembly was conducted on a laboratory scale. It should be recognized that the scale of these operations in industrial practice will not be too large – if you consider the need for disposal of industrial lines of picture tubes with a capacity

of 50 000 units per year, the amount of recycled hazardous waste containing phosphors is not greater than about 100 kg as a way of removing CRT and disposal of these luminescent layer technology was developed by IMBiGS designed [2] to mechanically separate hazardous waste disposal so it would mainly contain harmful substances, without undue burden.

Thus, the results obtained in the course of laboratory work carried out can be the basis for forecasting the effects which may be achieved after the implementation. On the basis of preliminary work the material balance was established:

1. To dispose of 1 kg hazardous waste (removed mechanically from about 5 mg of dismantled cathode ray tubes) there were used about:
 - 1.2 l concentrated nitric acid,
 - 0.24 kg sodium hydroxide
 - 4l deionized water
2. For recovery and purification of yttrium and europium compounds isolated from 1 kg of neutralized hazardous waste there were used about:
 - 0.060 kg oxalic acid
 - 0.040 l concentrated nitric acid
 - 0.5 l deionized water
3. In the course of the above operation there are formed:
 - about 5 liters of water, pH 7, pre-treated with heavy metals,
 - around 0.36 kg of hazardous waste, in the form of precipitates of sparingly soluble metal compounds.
4. The amount of recovered compounds of yttrium and europium from 1 kg of hazardous waste is approximately 0.012 kg.

Presented above recovery process of rare earth compounds is an integral part of hazardous waste treatment technologies. Hazardous waste, in accordance with regulations, has been removed from discarded cathode ray tubes during its dismantling.

The main ecological effect of the developed technology is a significant reduction in the amount of hazardous waste for storage – several hundred tones (used tubes) gives off only a few kilograms of hazardous substances (sediment precipitated during neutralization treatment).

The final environmental effect, as defined by the operation of an experimental line for recycling picture tubes, with a capacity of about 50,000 units per year results from waste reduction through the following actions:

- a. segregation – from 500 Mg per year separate worn on devices have been divided into:
 - glass, about 350 Mg
 - metals – about 75 Mg
 - electronic waste, approximately 50 Mg
- b. economic-use of waste as a result of segregation can be used as a segregated transmitted to a collection point of the following recyclable materials:
 - 300 Mg of glass
 - 50 g of metal
- c. change in category of hazardous waste: 500 Mg of hazardous waste code 16 02 13 was converted into non-hazardous waste codes: 19 12 05 19 12 03 16 02 16

- d. disposal of old CRT is the reduction of the volume of waste deposited in landfills – each year about 6,000 m³.

Presenting the above disposal of cathode ray tubes connected to the recovery of yttrium and europium compounds one should draw attention to the projected low cost of these operations, in comparison with the recovery of these elements with other industrial waste, e.g. phosphogypsum.

Comparing the two processes of recovery of yttrium and europium compounds from these two types of recyclable materials provides the following facts:

1. Out of 1 ton of phosphogypsum it can be obtained a concentrate of rare earth compounds, in which europium is about 4 g, 3 g of yttrium [3–8]. Receipt of this concentrate, inter alia, requires the use of chemical treatment with sulfuric acid 10% of the total waste phosphogypsum and then the separation of concentrates on individual rare earth elements, which is one of the most difficult processes in chemistry.
2. Out of the 1 ton of cathode ray tubes it can be obtained a concentrate which contains about 2.4 g of yttrium and europium mixture. Although the amount of the mixture is less than from a ton of phosphogypsum, but to receive it is not necessary to chemically treat a whole ton of cathode ray tubes, but only 0.24 kilograms mechanically separated phosphor waste.

The resulting concentrate of yttrium-europium is cleared by a very simple method of multiple selective crystallization and after such cleaning material may be suitable for the production of new phosphors (e.g. photoluminophores used in the manufacture of energy efficient light sources), without separation of yttrium and europium.

In summary, to obtain a total of 7 g of yttrium and europium with phosphogypsum one should build an industrial plant chemically converting 1 ton of phosphogypsum.

To obtain approximately the same amounts of yttrium and europium from discarded cathode ray tubes one should build a mechanical treatment unit to mechanically process about 3 tons of cathode ray tubes, and the volume of chemical equipment needed for recovery of yttrium and europium is basically the size of the laboratory – allowing chemical treatment of 0.7 kg of luminophore waste. The size of the above mentioned installations and the scale of issues dealing with i.e. waste water management are unparalleled.

REFERENCES

- [1] Kowalczyk, J., & Mazanek, Cz. (1987). *Fizykochemiczne Problemy Metalurgii*, 19, 233–241.
- [2] Uzunow, E., Góralczyk, S., Mazela, A., & Stankiewicz, J., et al.; Poland. Patent P-200095 „Sposób utylizacji kineskopów i/lub monitorów oraz odzyskiwania związków litu i europu z luminoforów otrzymanych z usuniętej warstwy luminescencyjnej utylizowanych kineskopów i/lub monitorów”.
- [3] Wirth, H., Kulczycka, J., Kowalski, Z., Kijkowska, R., Jarosiński, A., & Pawłowska-Kozińska, D. (2005). *Możliwości otrzymywania tlenków metali ziem rzadkich i anhydrytu z fosforu apatytowego. Odzysk odpadów*. Wyd. IGSMiE PAN.
- [4] Kowalski, Z., Kulczycka, J., Góralczyk, M., Koneczna, R., Kijkowska, R., Jarosiński, A., & Cholewa, J. (2005). *Studium wykonalności instalacji do produkcji koncentratów ziem rzadkich i anhydrytu z fosfogipsu apatytowego z bieżącej produkcji i zgromadzonych na hałdzie Z.Ch. Wizów S.A., Kraków: IGSMiE PAN (unpublished)*.
- [5] Jarosiński, A., Kijkowska, R., & Pawłowska-Kozińska, D. et al. (1991). *Przem. Chem.*, 70, 43.
- [6] Kulawik, J., & Mazanek, Cz. (1988). *Ziemie rzadkie w fosfogipsach pochodzenia apatytowego, Monografia*. 74, Kraków: Politechnika Krakowska.

- [7] Kijkowska, R., Kowalczyk, J., Mazanek, C., & Mikołajczyk, T. (1989). *Prace Nauk. Inst. Chemii Nieorg. i Metalurgii. 50. Monografia 28*. Wrocław: Politechnika Wroclawska.
- [8] Kijkowska, R., Kowalczyk, J., Mazanek, C., Mikołajczyk, T., & Pawłowska-Kozińska, D. (1989). *Phosphorus & Potassium*, 163, 22–26.

ODZYSK ZWIĄZKÓW ITRU I EUROPU Z SUROWCÓW ODPADOWYCH

Metale ziem rzadkich, w tym itr i europ należą do tej grupy kilkunastu surowców krytycznych, których stosowanie zapewnia rozwój w obszarze tzw. wysokich technologii. Możliwość ich pozyskiwania w Europie ogranicza się praktycznie do surowców wtórnych, np. fosfogipsów oraz zużytego sprzętu elektronicznego. W artykule przedstawiono wyniki badań autorów dot. opracowania technologii odzysku itru i europu z luminoforu zużytych lamp kineskopowych. Opisano zasady wydzielenia pierwiastków i wyniki badań oczyszczania koncentratu. Wykazano, że koszty otrzymywania koncentratu wg proponowanej technologii są niższe od technologii przeróbki fosfogipsów, a otrzymany produkt nie zawiera substancji niebezpiecznych.