



Recovery of Eu and Y from Waste Fluorescent Lamps

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Abstract

Eu and Y were extracted from waste fluorescent lamps containing ~0.3% Eu and 7% Y by acidic leaching, hydrolytic precipitation and/or solvent extraction. The leaching tests showed that about 90% Eu and 95% Y were leached in 3M HCl or 3M HNO₃ at 80°C, liquid to solid ratio 10:1 in 30 min. Leaching in H₂SO₄ provided lower Eu and Y extraction efficiency. Only around 85% Eu and 80% Y were extracted at temperatures higher than 70°C. Eu and Y started precipitating simultaneously at pH 1.5 and the precipitation completed at ~ pH 2. Solvent extraction of Eu and Y from sulfate solutions using D2EHPA is strongly influenced by solution pH. At pH 1.4 about 80% Eu and 100% Y were extracted while at pH 1.16 only 25% Eu was extracted together with 90% Y.

Key words: rare earth metals, waste fluorescent lamps, leaching kinetics, precipitation, solvent extraction

Introduction

The world production and consumption of rare earth metals is estimated at about 1.23.105 t per year (Naumov, 2008). The metals are increasingly used in modern technologies. For examples neodymium and dysprosium are irreplaceable in permanent supermagnets, which can operate even at high temperature; Tb, Ho, Er, Tm, and Yb function as activators in laser crystals; some rare earth metals are used as powerful deoxidation agents; a yttrium isotope is used in radiology and in treatment of joint inflammation (Murphy et al., 2008; Gumpelet et al., 1975). About 15% of rare earth metals were used in phosphor powders, which provide most of the light produced by fluorescent lamps and metal halide lamps (Naumov, 2008). The main phosphors and their main characteristics are listed in Table 1 (Phosphor technology product list, 2016).

In the Czech republic 7818 t of waste lamps were collected, corresponding to about 15 mill lamp pieces in 2014 (The year book, 2014). The phosphor powders are separated from the waste lamps in the company Eko-vuk Pribram but are not processed in order to recover the rare earth metals.

The waste phosphors were processed usually by leaching, followed by refining, solvent extraction and precipitation. Europium and yttrium oxides are dissolved quite well in H₂SO₄, HCl and HNO₃ but H₂SO₄ provided more selective leaching due to a removal of most Ca and Sr (Takahashi et al., 2001). About 92% of Y and 98% Eu were extracted in 1,5 M H₂SO₄ at 70°C for 3 h. Precipitation of rare earth metals from

solution has not been reported, only few works were carried out, using oxidation of Ce³⁺ to Ce⁴⁺ or reduction Eu³⁺ to Eu²⁺ (Otsuki, 2007). Europium and yttrium were selectively separated using liquid-liquid solvent extraction, mostly to acidic extraction agents especially D2EHPA (Rabie, 2005; Hirashima et al., 1978; Yongqi, 2008; Presto et al, 1996; Geist et al, 1999 and Leopard, 1962). Most of the works concluded in the use of aliphatic solvents, especially ketone, which led to more clear-cut phase separation. For examples Rabie (2005) showed that extraction of 99.9% of yttrium after 5 cycles and 99% of europium after 12 cycles from solution containing 3.51 mol/l Y a 0.19 mol/l Eu were achieved by using 0.05 M D2EHPA in kerosene. Hirashima (1978) showed that distribution ratio between organic phase containing 0.5 M D2EHPA and inorganic phase with concentration of REE³⁺ in range 0.02–0,05 mol/l decreased with decreasing pH.

The main objectives of this work is to study leaching behaviors of europium and yttrium from waste phosphors from discarded fluorescent lamps collected in the Czech republic in different acidic media and their separation from selected leaching liquors by hydrolytic precipitation and liquid-liquid solvent extraction.

Experimental

Materials

Phosphor samples were obtained from Ekovuk Pribram a.s. The fine fraction separated in a cyclone was used for the work. The chemical and mineralogical composition of the samples is illustrated in Table 2 and Table 3, respectively.

Tab. 1 Main phosphors and their characteristics

Tab. 1. Główne fosforany i ich charakterystyka

Composition	Particle size [μm]	Wave length [nm]
Y ₂ O ₃ :Eu	2.5	611
Y ₂ O ₂ S:Eu	3.5	627
ZnO:Zn	3.5	505
Y ₃ (Al,Ga) ₅ O ₁₂ :Eu	4.0	543
Gd ₂ O ₂ S:Tb	3.5	544
SrGa ₂ S ₄ :Eu	4.0	535
ZnS:Ag	3.5	450
SrGa ₂ S ₄ :Ce	4.0	415
Y ₂ SiO ₅ :Ce	3.5	400

Tab. 2 Chemical composition of waste phosphors by XRF analysis

Tab. 2 Skład chemiczny odpadowych fosforanów – analiza XRF

Element [%]								
Fraction	Hg	Sr	Y	Eu	Ca	P	Si	Na
cyklone	0.04	8.44	6.82	0.33	42.60	17.96	0.80	0.30

Tab. 3 Mineralogical composition of waste phosphors

Tab. 3 Skład mineralny odpadowych fosforanów

Ref. code	Score	Chemical formula	Presence
01-084-1997	73	Ca ₅ (PO ₄) ₃ F _{.94} Cl _{0.1}	Strong
00-051-0424	49	Ni _{2.4} Sr _{18.6} (PO ₄) ₁₄	Weak
00-050-1744	52	Sr ₅ F(PO ₄) ₃	Weak
00-025-1011	57	(Y _{0.95} Eu _{0.05}) ₂ O ₃	Weak

1.5M H₂SO₄, 3 M HNO₃ and 3 M HCl leaching solutions were prepared from concentrated acids of analytical grade and used for leaching experiments without further treatment. D2EHPA and PRIMENE JM-T were used as the extraction agents, which were dissolved in kerosene at required concentrations. 2–10% wt/wt NaOH and 10% wt/wt NH₄ OH solutions were used as the precipitation agents.

Experimental procedure

The leaching experiments were carried out in a 1-L glass reactor fitted with a condenser and a thermometer, heated with a mantle controlled by a regulator and agitated with a mechanical stirrer. The liquid to solid ratios were 10:1 and 15:1 and leaching was performed at temperature ranging from 20 to 80°C. Samples were collected at selected time intervals and filtered off. Solid phase was analyzed for mineralogical composition and chemical attack, and the liquor analyzed for rare earth metals concentration. After the reaction mixtures were cooled to the laboratory temperature, the products were separated by filtration, washed and dried at 90°C in an air oven.

Precipitation experiments were carried out in a 500ml beaker with a magnetic stirrer at room temperature. Solution pH and redox potential were recorded using pH meter ORION 525A+.

Solvent extraction experiments were carried out by a rotary device from StuartScientific, model ROTATOR DRIVE STR4. Test tubes of volumes from 15 to 45 ml were used. The organic and inorganic solutions of ratio 1:1 were mixed at room temperature. The extraction efficiencies were determined at selected time intervals and under different concentration of D2EHPA.

Analysis

Solution and solid samples from alkali decomposition and magnetite formation were analysed using a GBC atomic absorption spectrophotometer (model GBC 932 plus) to determine metals composition. Mineralogical analysis was undertaken with X-ray diffraction (PANalytical's X'Pert PRO) using Cu radiation and surface analysis was undertaken with a Scanning Electron Microscope (Hitachi S4700).

Results and discussion

The leaching kinetics of Eu and Y from waste phosphors in H₂SO₄ medium at different liquid to solid ratio at 70°C is shown in Fig. 1. The results show that Eu and Y were dissolved very fast in the first 30 minutes and then the dissolution slowed down and reached the steady state after 90 minutes. The liquid to solid ratio (l:s) did not influence the extraction efficiency of Eu significant-

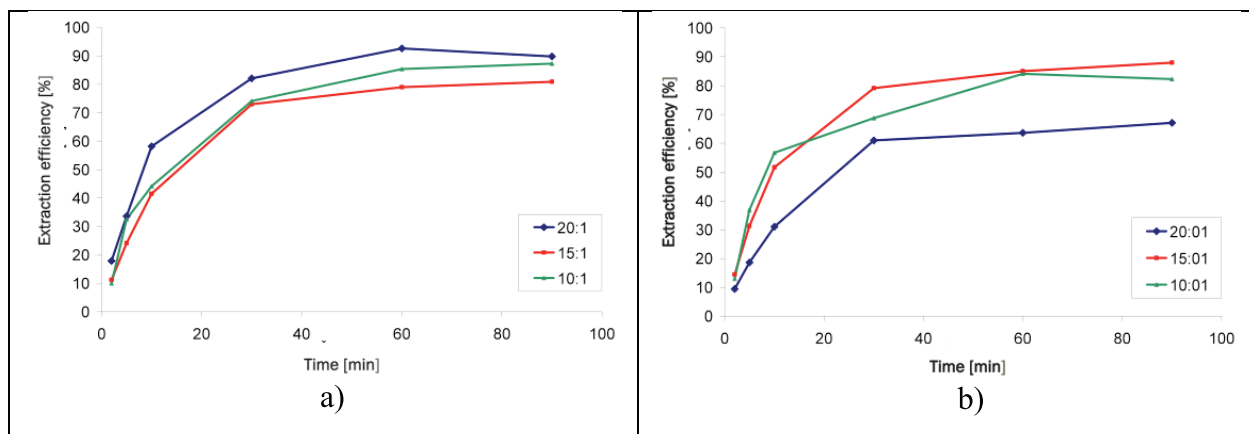


Fig. 1 Dependence of extraction efficiency of a)Eu and b)Y on leaching time : 1.5M H₂SO₄, 70°C, different l:s

Rys. 1. Zależność współczynnika ekstrakcji dla: a) Eu i b) Y od czasu ługowania: 1.5M H₂SO₄, 70°C, dla różnych wartości l:s

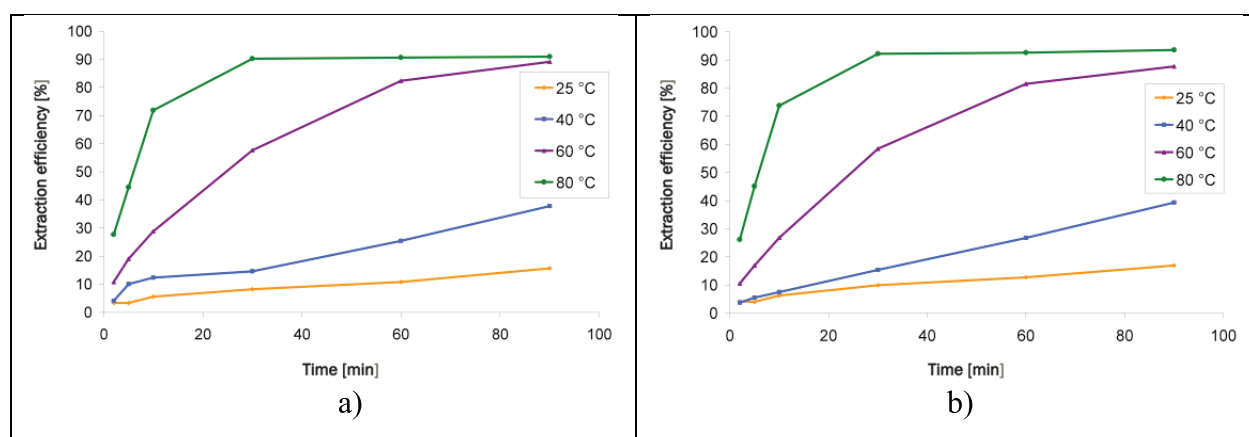


Fig. 2 Dependence of extraction efficiency of a)Eu and b)Y on leaching time : 3M HNO₃, different temperatures, l:s 10:1

Rys. 2. Zależność współczynnika ekstrakcji dla: a) Eu i b) Y od czasu ługowania: 3M HNO₃, różne temperatury, l:s 10:1

ly. The yttrium extraction at l:s 20:1 was the lowest, at only 60%. The optimal l:s ratio is evidently 10:1, which also provided the most concentrated leach liquor.

Fig. 2 and Fig. 3 show that leaching temperature influenced the extraction of Eu and Y significantly. With increasing temperature the extraction of Eu and Y increased very fast. Almost all Eu and Y were dissolved after 30 minutes in both 3M HNO₃ and 3M HCl. At room temperature only about 10% of Eu and Y were extracted into solution after 90 minutes of leaching. On the other hand consumption of HNO₃ and HCl was much higher than that of H₂SO₄ due to high calcium content in phosphors.

From Fig. 4 it is evident that Eu and Y cannot be selectively separated by hydrolytic precipitation using NaOH solution. The precipitation curves for both metals are almost the same and at ~pH 2 all Eu and Y were precipitated. Similar precipitation behaviors were observed with NH₄OH.

Extraction efficiency of Eu and Y from leaching liquors in DE2PHA is higher than in PRIMERE-JM. At

concentration of DE2PHA of 0.7 mol/l almost 90% of Eu was extracted together with about 30% of Y. With decreasing concentration of DE2PHA the extraction efficiency of Eu decreased more rapidly than that of Y. In contrary at concentration of PRIMENE-JM of 0.7 mol/l only 50% of Eu was extracted together with 10% of Y. On the other hand PRIMENE-JM provides more selective extraction of Eu. At concentration of PRIMENE-JM of 0.2 mol/l, around 20% of Eu was extracted into organic phase while Y remained in aqueous phase. This means all Eu can be selectively separated from Y after 2 extraction cycles.

Conclusions

(1) The best leaching conditions are as followed: 3M HCl, 80°C, l:s = 10:1. Under these leaching conditions about 91 % Eu and 97 % Y were extracted after 30 minutes of leaching.

(2) Hydrolytic precipitation is not suitable for selective separation of Eu and Y.

(3) Both DE2HPHA and PRIMERE-JM are effective for separation of Eu and Y but PRIMENE-JM pro-

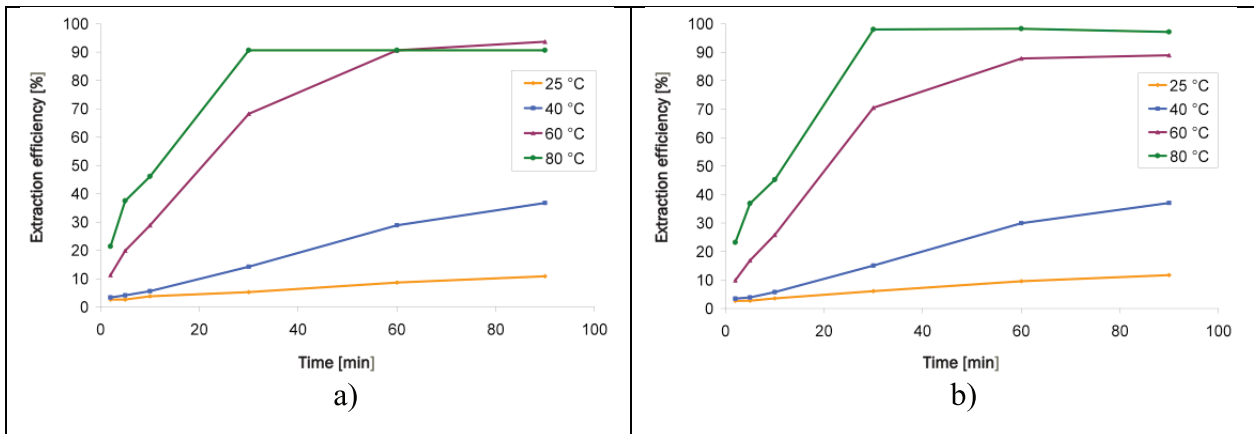


Fig. 3 Dependence of extraction efficiency of a)Eu and b)Y on leaching time : 3M HCl, different temperatures, l:s 10:1
 Rys. 3 Zależność współczynnika ekstrakcji od: a) Eu i b) Y od czasu ługowania: 3M HCl, różne temperatury, l:s 10:1

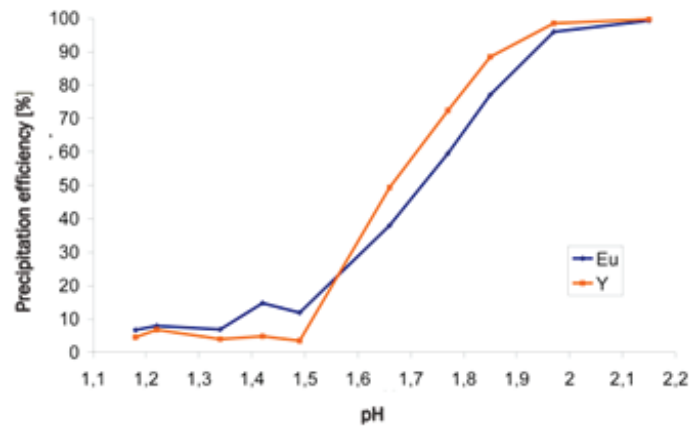


Fig. 4 Dependence of precipitation efficiency of Eu and Y on pH, 10% NaOH
 Rys. 4 Zależność efektywności wytrącania Eu i Y od wskaźnika pH, 10% NaOH

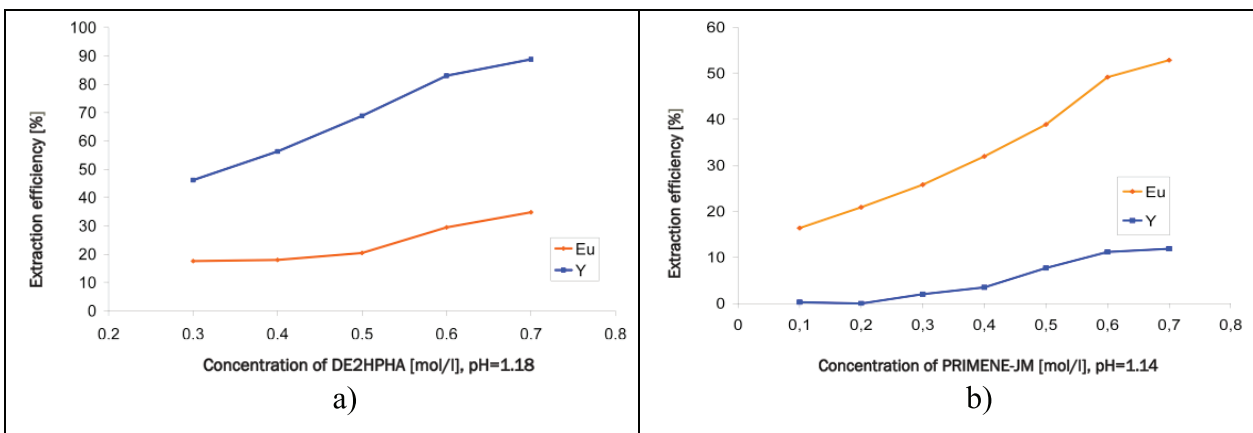


Fig. 5 Extraction behaviors of Eu and Y on concentration of DE2HPA and PRIMENE-JM
 Rys. 5 Zależność ekstrakcji Eu i Y od koncentracji DE2HPA i PRIMENE-JM

vides higher selectivity at concentration lower than 0.2 mol/l but more extraction steps are needed for their complete separation.

Acknowledgement

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Odzysk Eu i Y z odpadów lamp fluorescencyjnych

Eu i Y były odzyskiwane z odpadów lamp fluorescencyjnych zawierających ok 0.3% Eu i 7% Y za pomocą metody ługowania kwaśnego, wytrącania hydrolitycznego i/lub ekstrakcji rozpuszczalnikowej.

Próby ługowania wykazały, że około 90% Eu i 95% Y można wylugować w 3M roztworze HCl lub 3M roztworze HNO₃ w temperaturze 80°C, stosunku fazy ciekłej do stałej 10:1 w czasie 30 min. Ługowanie w H₂SO₄ daje niższy współczynnik odzysku Eu i Y. Jedynie około 85% Eu i 80% Y odzyskano w temperaturze wyższej niż 70°C. Eu i Y zaczęły wytrącać się jednocześnie w pH 1.5, a wytrącanie zakończyło się przy pH około 2. Ekstrakcja rozpuszczalnikowa Eu i Y z roztworów siarczanów z wykorzystaniem D2EHPA zależy silnie od pH roztworu. Przy pH = 1.4 około 80% Eu i 100% Y zostało wydzielone, podczas gdy przy pH = 1.16 wyekstrahowano tylko 25% Eu i 90% Y.

Słowa kluczowe: metale ziem rzdkich, odpady, lampy fluorescencyjne, kinetyka ługowania, wytrącanie, ekstrakcja rozpuszczalnikowa