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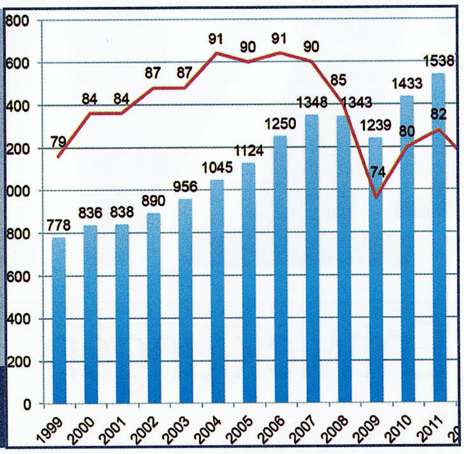

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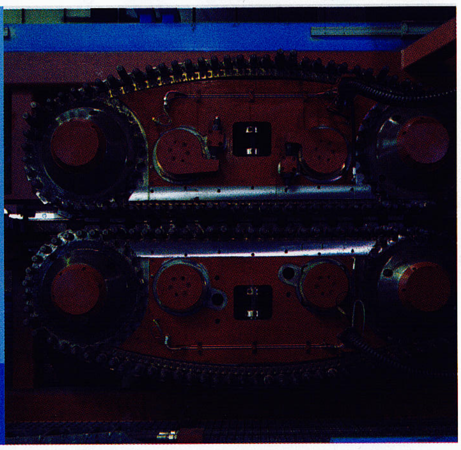

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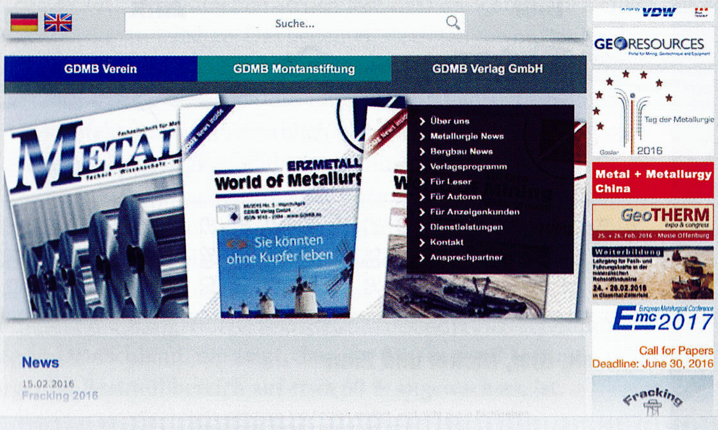

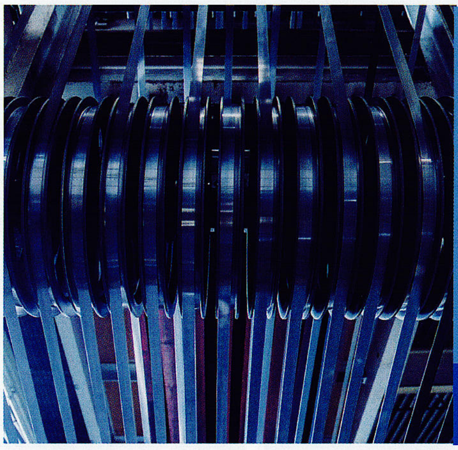

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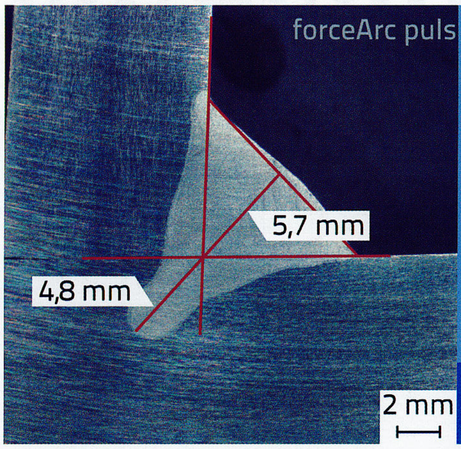

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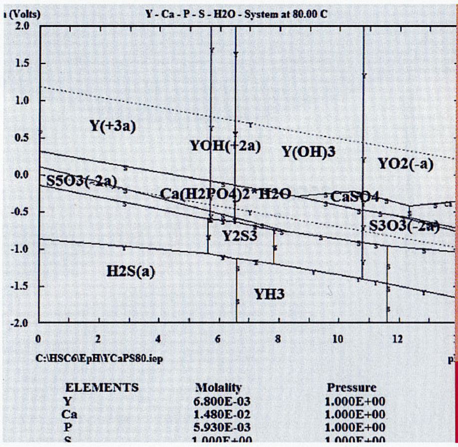

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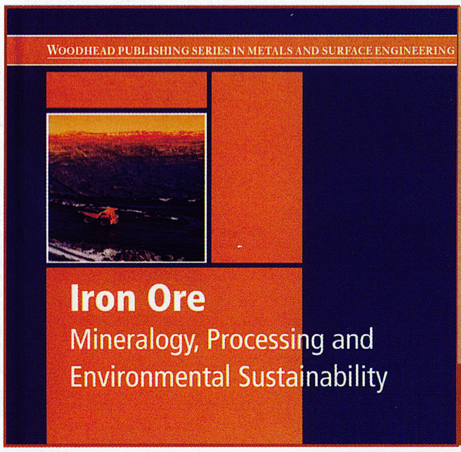

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Thermodynamic Study of Hydrometallurgical Treatment of Waste Containing Rare Earth Elements

Kochmanova, A.; Miskufova, A.; Palencar, M.; Horvathova, H. (1)

The paper is focused on the characteristics of rare earth elements, their occurrence, use and application. A special type of electric and electronic waste – fluorescent lamps (FL) is known as a potential source of yttrium and other rare earth elements. This work includes an overview of spent fluorescent lamps treatment processes according to several authors. Due to the character and amount of waste the most appropriate method is hydrometallurgy. The paper describes thermodynamic aspects of yttrium leaching from FL in basic solutions (sulfuric acid, hydrochloric acid and sodium hydroxide). The chemical reactions for leaching of yttrium oxide as well as main impurities (calcium and phosphor compounds) in selected media have been proposed. The leaching systems and behavior of individual species during leaching at elevated temperatures by calculated E-pH diagrams were also described. Sulphuric and hydrochloric acids seems to be the most appropriate for phosphor treatment.

Rare earth elements (REE) are a group of 17 metal elements, which includes 15 lanthanides and another two metals with similar chemical and physical characteristics, scandium and yttrium [1]. According to the atomic mass values they are divided into two groups: light REE (lanthanum - europium) and heavy REE (gadolinium - lutecium and yttrium) [1, 2].

REE are found in oxide, carbonates and silicates form in the nature. The most famous minerals of REE are bastnäsite (Ce, La, Y) CO_3F, monazite $(Ce, La, Th, Nd, Y)_4PO_4$ and xenotime YPO_4 [3]. According to The U.S. Geological Survey – USGS, the estimated total world reserves of REE are 114 million tons. Almost 50 % of this reserves are in China´s deposites [4].

Rare earth elements are used in many applications, for example phosphors, permanent magnets, catalysts in cars, hybrid engines, metal alloys, ceramics etc. [5].

It is estimated only 1 % of REE containing wastes are recycled nowadays, which represents only a small part of what could be reused. For example, rare earth elements used in fluorescent lamps and hard discs can be obtained and reused [6]. Although recycling REE is a huge challenge, but recycling of these elements can cover almost 40 % of global demand [7]. REE demand increased nowadays, the recycling of these elements is one of priorities of European Union. The European Union extended the list of 14 critical raw materials in terms of their availability for Europe (which included the REE) in 2014 to 20 raw materials. REE were divided to light and heavy REE in this list (yttrium belongs to heavy REE), which are on the top of this list [5].

Fluorescent lamps (FL) seem to be a very important waste material for recycling and REE recovery. Only mercury, glass and aluminum parts of FL were recycled in the past. Recently, the treatment of fluorescent powder from FL is of special interest.

FL is gas discharge lamps that use mercury vapors for conversion of electrical energy into radiation energy. The inside of the tube is coated with a thin layer of triband luminescent powder containing REE, which absorbs the UV energy causing visible light [8]. Composition of fluorescent lamps is shown in Fig. 1.

Fluorescent lamps are made in various shapes and sizes. The phosphor content in standard 40 W lamps is about 4-6 g, which represents 2 % of FL´s mass. The luminescent layer consist of red (55 %), green (35 %) and blue (10 %) components and it is a rich source of many REE (Eu, Y, Tb, Ce). FL consist of Al, Si, P, Ca in high concentrations and Ba, Sr, Mg, Mn, Sb, Cl, F, Hg, Pb, Cd in low concentrations [9]. The chemical composition of phosphor is shown in table 1.

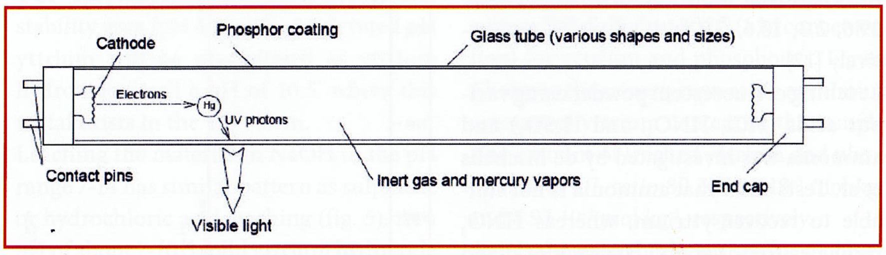

Fig. 1: Schematic representation and operation principle of fluorescent lamp [8]

The recycling process of spent FL depends on lamp´s shape. The first step in the linear fluorescent lamps treatment is cutting the ends and then the phosphor is blown out. Compact fluorescent lamps recycling is more problematic. During recycling, lamps are crushed and the various materials are separated under a continuous vacuum filtration process. The glass, aluminium and mercury can be useed in other products but the usage of phosphor powder is not resolved yet [9, 10].

Due to rich content of REE in FL they seem to be interesting compensation of raw sources for REE recovery. Research in

Phosphor	Chemical formula	Element content [%]							
		O	Y	Eu	Al	Mg	Ba	Ce	Tb
Red	Y_2O_3:Eu^{3+}	17.5	67.2	6.5					
Green	$CeMgAl_{10}O_{17}$:Tb^{3+}	42.6			31.3	5.7		9.5	5.3
Blue	$BaMgAl_{10}O_{17}$:Eu^{2+}	42.3		1.9	32.4	2.7	12.4		

Tab.1: Chemical composition of fluorescent powder [9]

luminescent layer treatment is focused on hydrometallurgy because of waste character. Many studies were interested in leaching of phosphor in various acids, resp. in mixture of acids. Leaching the phosphor mixture of H_2SO_4/HNO_3 was also investigated by Rabah. Autoclave digestion of the powder in the acid mixture for 4 h at 125 °C and 5 MPa dissolved 96.4 % of yttrium and 92.8 % of europium. Sulphate salts of Eu and Y were converted to thiocyanate. Trimethyl-benzylammonium chloride solvent was used to selectively extract Eu and Y from the thiocyanate solution. The metal loaded in the organic solvent was recovered by tri-n-butyl phosphate (TBP) in 1 M HNO_3 to produce nitrate salts of Eu and Y. Europium nitrate was separated from yttrium nitrate by dissolving in ethyl alcohol [11].

Shimizu et al. extracted REE from luminescent material in waste FL using supercritical carbon dioxide (SF-CO_2), which contains tri-n-butyl phosphate complexes with HNO_3 and H_2O. Using this complex, extraction efficiencies for Y and Eu increased to over 99 % after the static extraction for 120 min at 15 MPa, 333 K. The determined Y, Eu, La, Ce and Tb in the employed luminescent material were 29.6, 2.3, 10.6, 5.0 and 2.6 wt. %, respectively [12].

Leaching of fluorescent powder using various acids (HCl, HNO_3, and H_2SO_4) and ammonia was investigated by de Michelis et al. Tests show that ammonia is not suitable to recover yttrium, whereas HNO_3 produces toxic vapors. Hydrochloric and sulphuric acid leaching systems give similar results in terms of yttrium extraction yield. The greatest extraction of yttrium was obtained by 20 % w/v S/L ratio, 4 N H_2SO_4 and 90 °C. From this solution yttrium oxalate (80 %) can be obtained by precipitation with oxalic acid [13].

Wang et al. were investigated REE recovery too. The results show that: rare earth trichromatic phosphors contains Y, Eu, Ce, Tb and La, rare earth oxide content is as high as 27.94 %. In the experiments, it is found that the rate of rare earth leaching reached almost 90 % when the optimum process conditions were: 4.0 mol·l^{-1} HCl, pH of 8.0, S/L ratio of 100 g^{-1}, 60 °C and reaction time of 1 h. REE yield reached 94.98 % when the process conditions were of 33.70 g·L^{-1} ammonia, 6.25 g·L^{-1} oxalic acid, aging time of 3 h [14].

The process of Cathode Ray Tube (CRT) and fluorescent lamps powder recycling is described in the study of Innocenzi et al. They used three kinds of phosphor: CRT, FL and their mixture. Leaching experiments were carried out in 2 M sulphuric acid (hydrogen peroxide was added in case of CRT and MIX powder), S/L ratio of 20 and temperature 70 °C. Next steps included purification of the leach liquors using sodium hydroxide and sodium sulfide, precipitation of yttrium using oxalic acid (10 %) and calcinations (600 °C) of oxalates for production of yttrium oxide. The recoveries of yttrium oxide were about 95 %, 55 % and 65 % for CRT, lamps, and MIX powders, respectively [15].

Various leaching medium (hydrochloric, sulphuric, nitric acid and ammonia) were investigated to recover REE to the solution. Instead of, high pressure extraction was investigated. Sulphuric acid seems to be the most effectively, because of achieved yields over 90 %. Leaching was carried out at elevated temperatures. Precipitation by oxalic acid and solvent extraction by TBP was studied to recover yttrium and europium from solution.

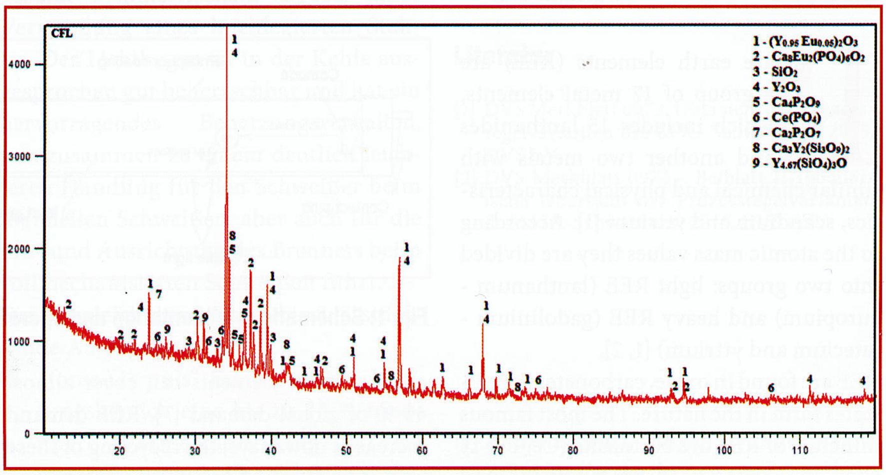

Fig. 2: XRD pattern of phosphor from fluorescent lamps

In the current research, there is only a little information about behavior of phosphorus and calcium during leaching the phosphor and REE precipitation from solution. It also hasn't been documented thermodynamic aspects that affect the operation of the process of REE leaching. This work focuses on the description of the process of leaching of yttrium from a thermodynamic point of view.

Element	Y	Eu	Ca	Fe	Si	Al	RH [%]	LOI [%]
Content [%]	4.85	0.31	4.75	0.48	7.26	0.19	0.011	2.22

Tab. 2: Chemical composition of fluorescent powder from spent fluorescent lamps

Experimental

Material and methods

Demercurised phosphor powder was sieved on the sieve with mesh size 1 mm and quartered to prepare a representative sample. A sample of FL powder was analysed for elements as well as the phase composition by Varian AA24+ (tab. 2) and XRD analyzer Phillips Panalytical Xpert Pro.

XRD diffraction phase analysis (by use of software HighScore Plus) established probable phases which may be present in the phosphor (fig. 2). The phase composition of the input material showed the presence of oxides $(Y_{0.95}Eu_{0.05})_2O_3$, Y_2O_3, SiO_2 and phosphates $Ca_8Eu_2(PO_4)_6O_2$, $Ca_4P_2O_9$.

Results and discussion

A thermodynamics study was conducted in this paper to obtain information about leaching of yttrium in various leaching media (H_2SO_4, HCl and NaOH). Calculations of ΔG° for chemical reactions were performed with the HSC Chemistry 6.1. Performed analysis indicated presence of yttrium in oxide form. Potential chemical reactions of yttrium oxide (under standard condition) leaching and standard Gibbs energy change for the various temperatures are shown in table 3.

Thermodynamics study shows that leaching reactions proceed according to the equations toward the production of products in the case of all selected media. How-

Chemical reaction	Temperature [°C]	ΔG° [kJ]
$Y_2O_3 + 3H_2SO_4 \rightarrow 2Y^{+3}_{(a)} + 3SO_4{}^{2-}{}_{(a)} + 3H_2O$	20	-433.200
	40	-416.715
	60	-398.832
	80	-379.689
$Y_2O_3 + 6H^+_{(a)} + 2Cl^-_{(a)} \rightarrow 2YCl^{+2}_{(a)} + 3H_2O$	20	-295.985
	40	-288.552
	60	-282.306
	80	-277.210
$Y_2O_3 + 2OH^-_{(a)} \rightarrow 2YO^{-2}_{(a)} + H_2O$	20	-7.951
	40	-11.152
	60	-13.897
	80	-16.259

Tab. 3: The values of the standard Gibbs energy changes of reactions leaching of yttrium selected temperatures and media

ever, in the case of NaOH, ΔG° is in the range of -40 to 40 kJ, when it is not clearly established that the reaction is carried out or it isn´t in such conditions. Reaction of yttrium oxide with sulphuric acid is thermodynamically preferable to hydrochloric acid within researched temperature range.

Based on thermodynamic study E-pH diagrams for selected systems were constructed. the behavior of yttrium and yttrium species during leaching (at different pH and potentials) is showed at the diagrams. Based on previous study and literature survey E-pH diagrams at 80 °C have been constructed. In construction of diagrams the maximum amount of yttrium content in the sample was considered. In this case the maximum amount of leached yttrium at S/L ratio 80 represents 6.8 10^{-3} mol·kg^{-1}.

As it is shown in fig. 3, in the system of Y-S-H_2O at 80 °C, the trivalent Y is stable in solution within a range of water stability area to pH about 5.5. At elevated pH up to 7, yttrium occurs in solution in YOH^{2+} form, and at pH above than 7, yttrium begins to precipitate as yttrium hydroxide. In the pH range 10.5-14 yttrium is in solution in the YO^{2-} form. In the case of HCl at temperature of 80 °C (fig. 4), yttrium is presented as YCl^{2+} specie in the solution within the water stability area (pH about 7). At elevated pH yttrium will be precipitated as yttrium hydroxide, until a pH of 10.5, where this metal exists in the YO^{2-} form.

Leaching the material in NaOH in the pH range 7-14 has similar pattern as sulphuric or hydrochloric acid leaching (fig. 5). At a pH of about 7-10.5 solid yttrium hydroxide is precipitated and at pH 10.5-14 yttrium is presented in YO^{2-} anion form. Trivalent cation form of yttrium is presented in the solution within the water stability area to pH 5.5. However, this pH value cannot be achieved without the addition of acid during the leaching in NaOH solution.

When we expect Y^{3+} specie in the solution, it is necessary to choose sulphuric acid as leaching media. In case of sulphuric acid leaching medium is used, other elements, without yttrium, are usually leached from spent fluorescent lamps. These elements have an important influence on yttrium leaching and it is necessary to examine the behaviour of these elements (especially calcium and phosphorus).

Due to yttrium leaching from spent fluorescent lamps is a very complex and heterogeneous system, a lot of potential reactions can proceed there as it is shown by equation given in tab. 4. It is clear from tab.4, that in the presence of calcium and phosphorus in the leaching solutions (in case of sulphuric acid), calcium sulphate, yttrium phosphate or calcium phosphate can create. Moreover, these species can start to precipitate during leaching depending on their concentrations and solubilities what complicates the process.

Figure 6 a shows the E-pH diagram of the system Y-P-S-H_2O at 80 °C (1 M concentration) for yttrium and phosphorus. Figure 6 b shows the same system at the maximum amount of yttrium content in the sample. The amount of leached yttrium and phosphorus at S/L ratio 80 is 6.80 10^{-3} mol·kg^{-1} and 5.93 10^{-3} mol·kg^{-1}, respectively.

As it is shown at the diagrams (fig. 6), phosphorus content in spent fluorescent lamps

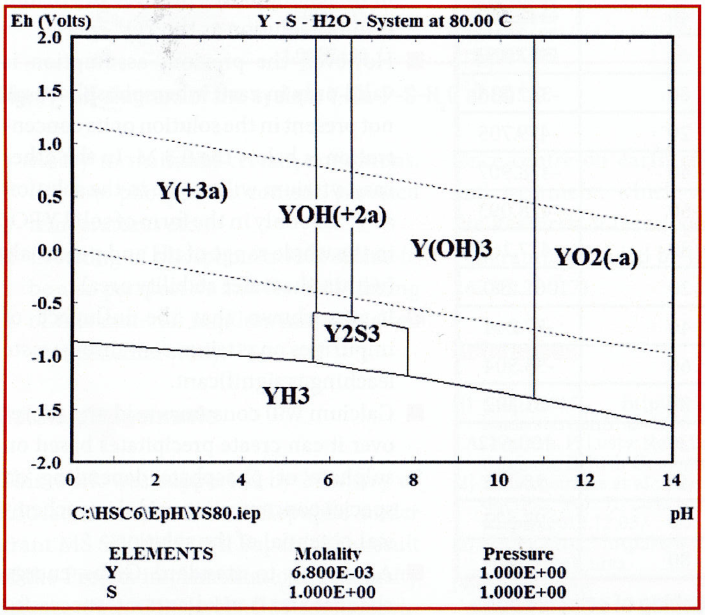

Fig. 3: E-pH diagram of the system Y-S-H_2O at 80 °C

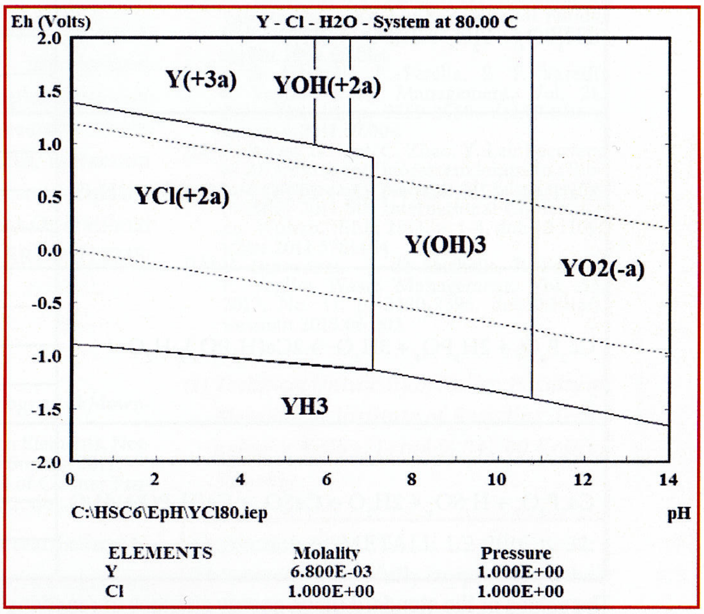

Fig. 4: E-pH diagram of the system Y-Cl-H_2O at 80 °C

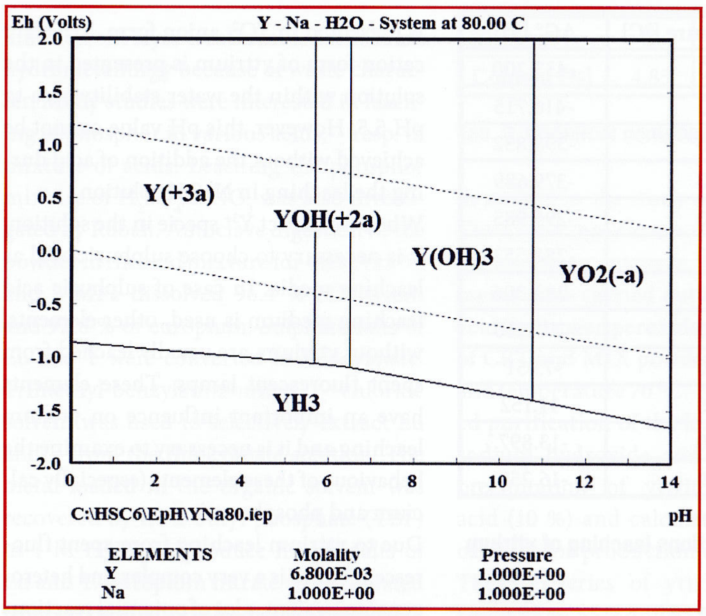

Fig. 5: E-pH diagram of the system Y-Na-H_2O at 80 °C

has significant influence on yttrium leaching. In the case of 0.3 M phosphorus is in the solution, Y^{3+} stability area starts to create at pH=0. It means, when the phosphorus content is very low (below 0.3 M), yttrium cation will occur in the solution, but still at very aggressive acid conditions (low pH value). At the same time, with decreasing concentration of phosphorus, trivalent yttrium cation stability area is increasing.

However, when the phosphorus concentration in the solution is higher than 0.3 M, YPO_4 occurs in whole range of stability of water area excluding presence of Y^{3+} at all, except for areas with pH more than 13, where yttrium is in the solution as YO^{2-} anion form. When phosphorus concentration is decreasing, the range of this area is increasing. Therefore the alkaline leaching of the luminescent layer from spent fluorescent lamps seems to be promising. On the other hand, the higher temperatures and alkaline solution concentrations in the case of alkaline leaching would probably be desired. Whereas, calcium is also leached in sulphuric acid, so it was necessary to examine behavior of this element in thermodynamic study. Figure 7 shows E-pH diagram of the system Y-Ca-P-S-H_2O at 80 °C. The simplified diagram shows that Y^{3+} specie exist in the solution to pH 5.5. At elevated pH to approximately 6.5, the yttrium is still in the solution in ionic form as YOH^{2+} specie. Yttrium exist in the solution in YO^{2-} form in pH range 10.5-14 and precipitates from the solution in hydroxide form in pH range 6.5-10.5. In acidic pH range calcium preferably reacts with phosphorus than sulphur and creates $Ca(H_2PO_4)_2{\cdot}H_2O$ compound at lower potentials (Eh) under the given conditions and element´s concentration ($6.80\ 10^{-3}$ mol·kg^{-1} Y, $5.93\ 10^{-3}$ mol·kg^{-1} P and $1.48\ 10^{-2}$ mol·kg^{-1} Ca).

Chemical reaction	Temperature [°C]	ΔG° [kJ]
$H_2O + Ca_2P_2O_7 + 2H_2SO_4 \rightarrow 2CaSO_4 + 2H_3PO_4$	20	-139.994
	40	-137.180
	60	-135.741
	80	-134.449
$2H_3PO_4 + Y_2O_3 \rightarrow 2YPO_4 + 3H_2O$	20	-339.711
	40	-341.727
	60	-342.353
	80	-342.816
$Ca_2P_2O_7 + 2H_2SO_4 + Y_2O_3 \rightarrow 2YPO_4 + 2CaSO_4 + 2H_2O$	20	-479.705
	40	-478.907
	60	-478.093
	80	-477.264
$Ca_2P_2O_7 + 2H_3PO_4 + 3H_2O \rightarrow 2Ca(H_2PO_4)_2{\cdot}H_2O$	20	-61.290
	40	-59.244
	60	-55.504
	80	-51.302
$Ca_2P_2O_7 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 + Ca(H_2PO_4)_2{\cdot}H_2O$	20	-100.642
	40	-98.212
	60	-95.622
	80	-92.875

The values of the standard Gibbs energy changes of reactions leaching of selected components at selected temperatures

Conclusions

- REE are critical materials for green technologies development (hybrid vehicles, power generation, fluorescent lamps etc.).
- Fluorescent lamps waste is a rich source of REE such as yttrium, europium, lanthanum or cerium.
- Hydrometallurgical treatment of spent FL powder is possible; based on literature survey more than 90 % of REE can be obtained by leaching in sulphuric acid.
- The process of REE leaching in sulphuric acid was studied from thermodynamic point of view. It has been shown that for successful leaching Y and Eu it is necessary to maintain the pH in the acid range, to a value of 5. When this value increases to 10.5, it leads to precipitation of the hydroxides of the REE in the solution. At a pH of 10.5, yttrium is in the solution as the YO^{2-} specie.
- However, the previous assumption is valid only in case, when phosphorus is not present in the solution or its concentration is below the 0.3 M. In the other case, yttrium will not be in the solution as Y^{3+} but only in the form of solid YPO_4 in the whole range of pH and potentials (within the water stability area).
- It was shown that the influence of impurities on yttrium containing waste leaching is significant.
- Calcium will consumes acid and moreover it can create precipitates based on sulphate or phosphate depending on species concentration and electrochemical potential of the solution.
- According to standard Gibbs energy changes and E-pH diagrams, successful yttrium leaching is possible but it is nec-

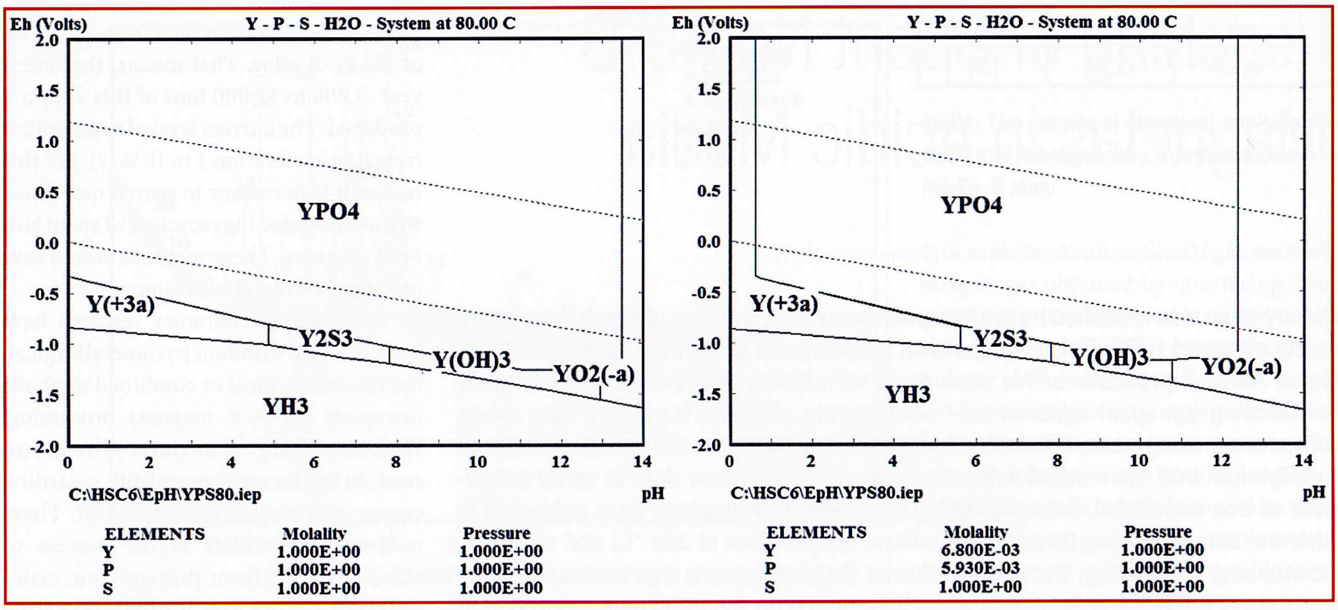

Fig. 6: a) E-pH diagram of the system Y-P-S-H_2O at 80 °C (1 M concentration); b) E-pH diagram of the system Y-P-S-H_2O at 80 °C (variable concentration)

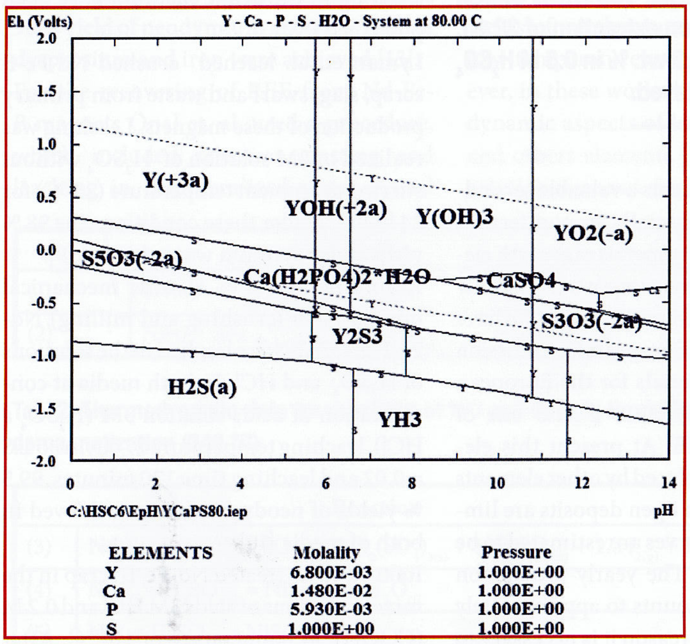

Fig. 7: -pH diagram of the system Y-Ca-P-S-H_2O at 80 °C

essary to maintain certain conditions, e.g. low phosphorus content, elevated temperatures etc.

- Leaching of phosphor in HCl seems to be also perspective and NaOH leaching of this material requires more detailed experimental study.

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