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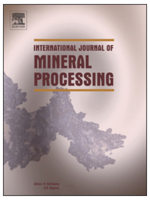

Leaching of yttrium from cathode ray tube fluorescent powder: Kinetic study and empirical models

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ABSTRACT

In this paper, leaching kinetics of yttrium from cathode ray tubes in sulphuric acid and hydrogen peroxide solution was investigated. It was found that hydrogen peroxide concentration, followed by temperature, has the greatest influence on leaching rate. Leaching rate is clearly enhanced by the increase in H_2O_2 concentration. The leaching process without hydrogen peroxide follows the kinetic model controlled by the chemical regime, whereas in presence of H_2O_2 it follows the kinetic model controlled by diffusion through the product layer. The apparent activation energy was determined to be 40.0 kJ/mol and 90.3 kJ/mol with and without hydrogen peroxide in solution, respectively. Moreover, the experimental data were used to describe empirical mathematical models in order to predict the yttrium extraction as a function of sulphuric acid concentration, hydrogen peroxide concentration, temperature and time. From the analysis of the results and models, the optimal conditions to maximize the extraction of yttrium were inferred: 40 °C, 10%vol hydrogen peroxide, 15 min of reaction with 15%wt/vol pulp density, or alternatively at higher temperature (80 °C) 15%wt/vol pulp density, 120–180 min with 0% or 5%vol hydrogen peroxide in solution. Hence, yttrium is easily leached from CRTs powder at low temperature (40 °C) with higher concentration of hydrogen peroxide, or by means of higher temperature (80 °C) and lower concentration, even null, of hydrogen peroxide.

1. Introduction

Yttrium is one of the most important rare earth elements used for many applications, for instance as phosphor in fluorescent lamps, but also to create cubic zirconia jewels, in fighter jet engines, as laser in industrial, medical, graphic technologies, in electronic components for missile defense systems and others (Innocenzi et al., 2014). One of the main secondary sources for yttrium is represented by cathode ray tubes (CRTs) from TVs and computers. Although such devices were fully replaced by new technologies like LCDs and LED screens, there is still a huge amount that is being wasted by people and therefore need to be treated. These wastes contain valuable materials and hazardous elements and pose danger to the environment and health if inappropriately managed (Nnrom et al., 2011). A CRT unit usually contains about 63.2%wt of screen glass, 24% of cone glass, 12% of ferrous materials, 0.4% of getter plus electron gun, 0.4% of ceramic seal and 0.04% of fluorescent powder (Méar et al., 2006). In CRT and TV monitors around 0.4 kg and 1 kg of lead oxide is present, respectively. In such glasses, barium is often found, whereas the fluorescent powder contains many elements such as yttrium, europium and cadmium sulphide (Menad, 1999). Yttrium is contained in the red phosphor of colored television tubes. These phosphors also contain europium in lower concentration with respect to yttrium. The first red phosphor, $YVO_4{:}Eu^{3+}$, was replaced by $Y_2O_2S{:}Eu^{3+}$ due to the increased brightness of the latter phosphor (Binnemans et al., 2013; Bredol et al., 1994). European Union (EU) introduced some directives in order to regulate the management of electronic wastes at the European level. The European directives related to waste from electrical and electronic equipment (WEEE) are the Directive 2002/96/EC, the Directive on the Restriction of Hazardous Substances (RoHS) (Directive 2002/95/EC), and more recently the Directive 2012/19/EU that encourages the recycling of waste and set the recycling standard to achieve in the future. The aims of those directives are mainly two: to increase the recovery rate and reduce the quantity of these wastes disposed of in landfills or incinerated. As regards CRTs, the recycling limit is fixed to 70% including the recovery of plastics, glass and metals such as copper and other precious metals like Y (Nnrom et al., 2011). Considering the intrinsic economic value, the recovery of yttrium from CRTs and other types of waste is very attractive. In our previous review (Innocenzi et al., 2014) the main processes for recovery of yttrium from WEEE were summarized, whereas other interesting processes can be found in Binnemans et al. (2013). Typical treatments include physical operations to separate glass, metals and fluorescent materials; afterward, glass and metals can be recovered, refined and put on the market. The fluorescent powder was treated to recover rare earths by a sequence of operations as solvent extraction,

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Table 1
Full factorial plan defined to describe the effect of sulphuric acid, hydrogen peroxide concentration and time on leaching yields.

Test	A	B	C	Response
Treatment	H_2SO_4 (M)	H_2O_2 (%)	t (min)	Leaching yield
1	0.5	0	90	2.23%
a	3.5	0	90	9.58%
b	0.5	5	90	54.20%
ab	3.5	5	90	39.90%
c	0.5	0	180	3.10%
ac	3.5	0	180	14.70%
bc	0.5	5	180	47.30%
abc	3.5	5	180	50.00%

supercritical solvent extraction, selective precipitation, ion-exchange and others.

Dexpert Ghys et al. (2009) studied a process to recover metals from fluorescent materials by thermo-chemical treatments. The powder contained Al film (16%wt), doped zinc sulphide (49%wt), europium-yttrium oxysulphide (32%wt) and residual impurities, or metallic dopants and silicates. The results showed that handling of the screens and pretreatments were important, as the silicate impurities from the glass' screen could react with Y and Eu at 1200 °C and prevent the further recovery of the red phosphors Y_2O_3:Eu^{3+}.

The main hydrometallurgical processes for yttrium recovery from fluorescent powder include: leaching with acids to dissolve metals and separation by selective precipitation or solvent extraction with further chemical treatments. The dissolution can be preceded with pretreatments like roasting with sodium hydroxide or ammonia chloride, followed by leaching with sulphuric acid (Tedjar et al., 2010; Lee et al., 2009; Resende and Morais, 2010; Pan et al., 2013). After leaching, sodium hydroxide or potassium hydroxide can be added in the leach liquor to precipitate Y and Eu (Tedjar et al., 2010). In the process described by Lee et al. (2009), the powder was mixed with sodium hydroxide and treated with ultrasounds for 30 min to obtain a soaking effect and separate aluminum. After that, H_2SO_4 solution (36 N) was added into the filtered solution to precipitate and recover aluminum. Sulphuric acid (12 N) was added to the filtered residues containing Eu, Y and Zn, thus ultrasonic treatment was applied for 120 min at 70 °C to soak out the whole amount of Eu and Y and 57% of Zn; Zn was recovered by the addition of thioacetamide in a water tank at a constant temperature for 7 days; instead, Eu and Y hydroxides were recovered by precipitation with NaOH at pH 4.

In their work, Pan et al. (2013) described a hydrometallurgical process that includes roasting with ammonia chloride, leaching with water and purification with sodium sulphide. Precipitation with oxalic acid and calcination at high temperature lead to the recovery of high-grade yttrium. The recovery rate of Y and Eu was 92.1% and 90.4%, respectively. The content of Y and Eu in the final product was 98.10% and 96.30%, respectively.

In our previous works (De Michelis et al., 2011; Innocenzi et al., 2013a, 2013b) some hydrometallurgical treatments to recover yttrium from fluorescent materials were described. The research activities developed in the ambit of the two HydroWEEE projects (Beolchini et al., 2013) were carried out in lab- and pilot-scale and the results of the experiments allowed to set-up a process that includes leaching with sulphuric acid and hydrogen peroxide, a purification stage to remove metals like zinc, and final precipitation by oxalic acid. The composition of the hydrated rare earth oxalate was about 88% for CRTs with around 70% of total recovery rate.

As already written above, many scientific works described methods to recover yttrium from CRTs; however, the dissolution patterns and kinetics of this rare earth element was never investigated, as authors mainly focused on set-up of the best conditions for maximization of the extraction and purity of the final product. In the present manuscript, particular attention was given to the leaching stage of fluorescent

Table 2
XRF analysis of the initial cathode ray tubes material (*ICP analysis).

Element	Mg	Al	Si	P	S	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
%	2.00	1.28	11.41	0.03	7.22	0.003	1.35	0.01	0.01	0.38	0.36	0.82	0.09	0.003	0.004

Element	Zn	Ga	As	Se	Br	Sr	Zr	Mo	Ag	Cd	Y*	Eu*	Tb*	La*	Ca*
%	24.60	0.01	0.02	0.002	0.001	1.64	0.20	0.03	0.01	0.12	14.73	0.88	0.013	0.001	0.002