

KINETICS OF YTTRIUM DISSOLUTION FROM WASTE CERAMIC DUST

Srećko R. Stopić^a, Bernd G. Friedrich^b
RWTH Aachen University, Faculty of Georesources
and Materials Engineering, IME Process Metallurgy
and Metal Recycling, Aachen, Germany
^a e-mail: sstopic@ime-aachen.de,
ORCID iD: <http://orcid.org/0000-0002-1752-5378>
^b e-mail: bfriedrich@ime-aachen.de

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Summary:

Yttrium is a silvery transition metal and has similar chemical properties to lanthanoids. Because of this similarity, yttrium belongs to rare earth elements. Yttrium and yttrium oxide are mostly used in fluorescent lamps, production of electrodes, in electronic filters, lasers, superconductors and as additives in various materials to improve their properties. Yttrium is mainly recovered from the minerals monazite [(Ce,La,Th,Nd,Y)PO₄] and xenotime YPO₄. The presence of radioactive elements such as thorium and uranium in the ore makes it difficult to separate yttrium oxide from primary raw materials. Environmental regulations are getting stricter every year, thus increasing the risk of lacking the supply of rare earths. Therefore, recovery of yttrium oxide from secondary sources such as red mud, coatings from ceramic industry and phosphors is extremely important. The main aim of this study is to examine the yttrium dissolution kinetics from waste ceramic dust using hydrochloric acid.

Key words: *yttrium, recycling, hydrometallurgy, ceramics.*

Introduction

Yttrium is always found with rare earth elements in minerals. Rare earth metals are increasingly establishing themselves as crucial industrial materials, with unique applications in numerous fields (Kim

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and Osseo-Asare, 2012, pp.67-78). The feasibility of using yttrium oxide as a crucial material or a coating for induction melting of titanium is widely used in metallurgy. The native source of yttrium can be found in hard rocks and placer sands. Hard rock deposits are mined by open pit and underground methods. The aim of physical beneficiation is increasing the necessary mineral content by exploiting some physical processes. During physical beneficiation, accompanying minerals such as ilmenite, rutile, zircon, magnetite, and quartz are separated, which results in the formation of a concentrate with an increased content of rare earth elements. During a chemical treatment of a concentrate, rare earths are separated from impurities, especially thorium and uranium from minerals. This is accomplished by attacking minerals with some leaching agents. The process parameters such as temperature, pressure, chemical type and concentration of the leaching agent differ in accordance with the mineral type. In monazite applications, sodium hydroxide and sulfuric acid are mostly used as leaching agents. In the dissolution process, rare earth elements and thorium are precipitated in the hydroxide and sulfate forms. In the alkali application, the formed rare hydroxides are dissolved in the next step with either hydrochloric or nitric acid where thorium is not soluble (Sung-Don, 2010, pp.70-76). Cold water is used to dissolve rare earth sulfates in an acid treatment. The dissolution of xenotime is similar to monazite digestion. It requires more concentrated leaching agents and higher process conditions. During the subsequent separation, individual rare earth elements are separated from their mixtures. Fractional crystallization and solvent extraction (Amaral and Morais, 2010, pp.498-503) are mostly used for this separation.

Yttrium is generally recovered from monazite or xenotime minerals via an acid and an alkaline route as shown in Figure 1.

A full process for the recovery of rare earth elements from a composite ore containing rare earth elements, including a monazite mineral group and an apatite mineral, contains the pre-leaching of the composite ore with an acid in order to substantially dissolve the apatite mineral into the leach liquor and precipitate rare earth elements from the pre-leach liquor (Mackowski et al, 2009, US Patent 0272230 A1). An analysis of a combined hydro-pyrometallurgical route for the processing of ores resulting in the production of rare earth elements was investigated using the Chuktukon ores in East Siberia in Russia (Kuzmin et al., 2012, pp.1-16). The main aim of this work by Kuzmin was to develop methods of unlocking rare earth elements in refractory ores and to study some methods for their further chemical processing.

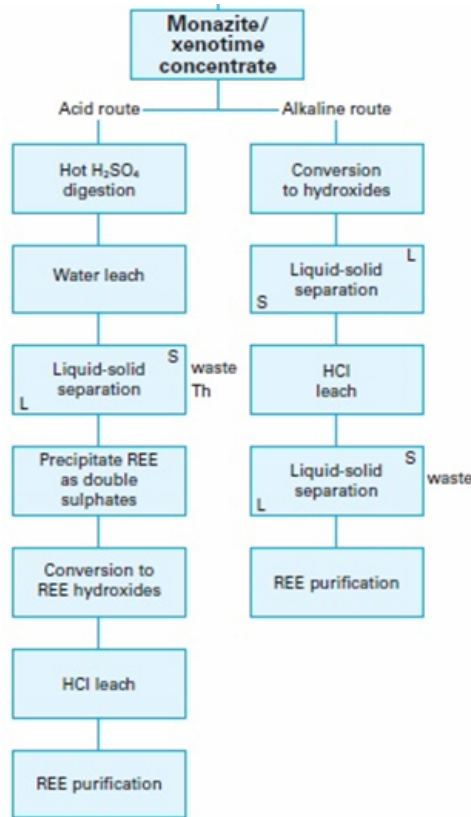


Figure 1 – Flow diagram of the dissolution of monazite and xenotime
 Рус. 1 – Диаграмма процесса растворения моноцита и ксенотима
 Slika 1 – Dijagram toka rastvaranja monazita i ksenotima

The precipitation of a cleaned solution with oxalic acid and the thermal decomposition of a formed metal oxalate after filtration with its previous drying represent the final steps in the production of rare earth oxides (Ibrahim and El-Hussaini, 2007, pp.11-17).

The importance of yttrium and other rare earth elements is increasing in the transition to green economy because of their essential role in permanent magnets, lamp phosphors, catalysts, rechargeable batteries, etc. Due to the fact that China presently produces more than 90% of the global REE output and has an increasingly tight export quota, the rest of the world is in the risk of lacking REE supply. Because of the absence of economical and/or operational primary deposits on their territories, many European countries have to be included into the recycling of REEs from pre-consumer scrap, industrial residues and REE-containing End-of-Life products. Despite considerable, mostly lab-

scale research effort to recycle REEs, less than 1% of REEs were recycled by 2011. This is mainly due to inefficient collection, technological problems and, especially, a lack of incentives. A drastic improvement in the recycling of REEs is, therefore, an absolute demand. This can only be realized by developing efficient, fully integrated recycling routes, which can take advantage of the rich REE recycling literature. In Table 1, secondary materials for REEs are listed (Binnemans, 2013, pp.1-22.)

Table 1 – REE-containing streams for recycling
 Tabela 1 – Vrste otpada kao izvori retke zemlje za recikliranje
 Таблица 1 – Виды отходов как источник сырья для рециклирования

Materials stream & application	REEs	Present / future contribution
1. Preconsumer production scrap and residues		
REE containing residues arising during metal production/recycling	All REEs	Increasing
Postsmelter and Electric Arc Furnace residues	Ce, La, critical REEs	Future levels depend on End-of-Life presmelter recycling
Industrial residues (phosphogypsum, red mud, etc.)	All REEs	Relatively stable
2. End-of-Life products containing		
Phosphors	Eu, Tb, Y (Ce, Gd, La)	
Fluorescent lamps (straight/curved)	Eu, Tb, Y (Ce, Gd, La)	Relatively stable
Compact fluorescent lamps (CFLs)	Eu, Tb, Y (Ce, Gd, La)	Increasing
LEDs	Ce, Y	Increasing
LCD Backlights	Eu, Tb, Y (Ce, Gd, La)	Relatively stable
Plasma Screens	Eu, Tb, Y (Ce, Gd, La)	Relatively stable
Cathode-ray tubes (CRTs)	Eu, Y	Sharply decreasing
CRT phosphors, fluid, glass polishing powders, optical glass, cracking catalysts,	All REEs	
3. Landfilled REEs containing residues		
Industrial residues (phosphogypsum, red mud, etc.)	All REEs	Depending on a residue type

One of the major challenges in the processing of used phosphors for the extraction of rare earths lies in a large number of different compounds and their individual chemical properties such as solubility in an aqueous phase (Poscher, 2013, pp.1217-1222). The summary of this

work showed that the hydrochloric leaching of a screened luminophore powder followed by the precipitation of a contaminated RE oxalate, converting the mixture into their oxides and subsequent refinement in order to dissolve most of the alkali metal oxides leads to a RE concentrate which could be applied as a new raw material for the subsequent process steps of refining.

The dissolution of non-ferrous metals from ores into a solution during high pressure leaching in an autoclave was described in detail (Author, 2011, pp.29-44.) for some nonferrous metals such as nickel and cobalt. A hydrometallurgical treatment has a lot of advantages compared to a pyrometallurgical treatment.

In this work, a dissolution of yttrium from waste ceramic dust under atmospheric and high pressure was studied in detail. The influence of different process parameters such as leaching temperature and time, concentration of hydrochloric acid and operating pressure was analyzed. The main aim is to study the kinetics of yttrium dissolution with hydrochloric acid in the temperature range from 20°C to 70°C at atmospheric pressure.

Experimental Work

Material

Ceramic materials remain from a knock-off of cast parts containing a high amount (up to 15 %) of yttrium oxide from the upper layers of shells. The elements such as titanium, aluminium, and iron are regarded as impurities in these waste materials.



Figure 2 – The waste ceramic dust
Рис. 2 – Отходная керамическая пыль
Slika 2 – Odpadni keramički prah

The chemical composition of the waste ceramic dust studied in this work amounts to (in %): 1.34 Y; 0.56 Fe₂O₃, 0.5 TiO₂; 0.48 SiO₂; and 97.12 Al₂O₃. This fine dust fraction was approx. below 250 µm.

Experimental Procedure

Leaching tests were performed under a) atmospheric pressure in a glass reactor at 20°C, 45°C and 70°C and b) high pressure in an autoclave at 150°C (pressure about 5 x10⁵ Pa) using hydrochloric acid. The temperature was controlled within ± 1 °C by a temperature control system which controlled a water cooling system as well (see Figure 3).

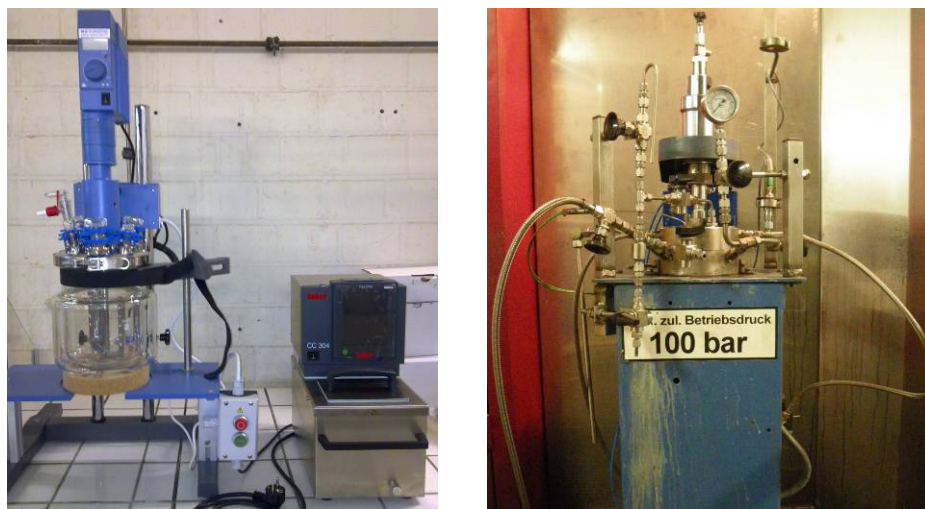


Figure 3 – a) a glass reactor b) an autoclave
 Рус. 3 – а) стеклянный реактор б) автоклав
 Slika 3 – a) stakleni reaktor b) autoklav

Agitation was provided by a motor-driven impeller. A certain amount of waste dust was mixed with a pre-calculated amount of deionised water. The slurry was then heated up to a predetermined temperature under continuous agitation. Upon temperature stabilisation, a certain amount of different concentration of hydrochloric acid was injected into the reactor under atmospheric and high pressure. Using the sampling system, 20 ml of liquid was periodically withdrawn through a dip tube and then rapidly cooled. After the end of the experiments, the solutions aliquots were filtered and analysed, aiming at Y, Fe, Al and Ti by inductively coupled plasma ICP spectrophotometry and X-ray fluoroscency.

Results

The influence of different experimental parameters such as the leaching time, the leaching temperature and the concentration of hydrochloric acid on yttrium dissolution were investigated. The obtained results between 20°C and 150°C were shown in Figure 4 and Figure 5:

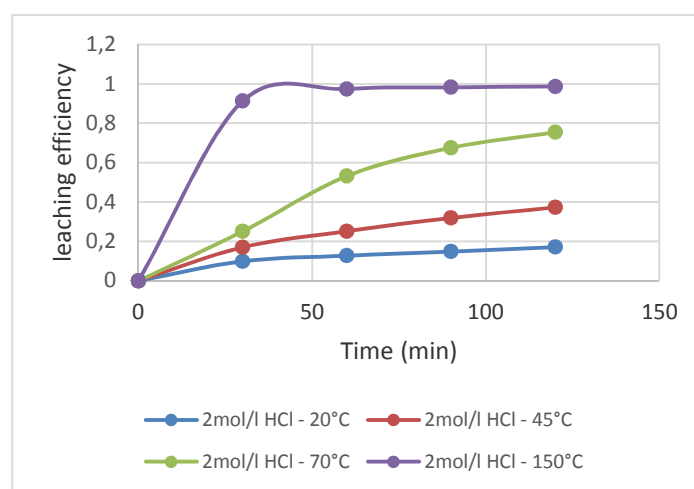


Figure 4 – Influence of temperature and time on the yttrium dissolution
 Рус. 4 – Влияние температуры и времени на процесс растворение иттрия
 Slika 4 – Uticaj temperature i vremena na rastvaranje itrijuma

The minimum efficiency of yttrium dissolution is found at room temperature. An increase of leaching time to 120 min and temperature from 20°C to 150°C using 2M HCl solution leads to an increased leaching efficiency of yttrium up to 98.6 %. At 70°C and under atmospheric pressure, the leaching efficiency amounts to about 80 % in 120 min. An increase of the concentration of hydrochloric acid from 0.5 mol/L to 2.0 mol/L leads to an increased yttrium dissolution efficiency.

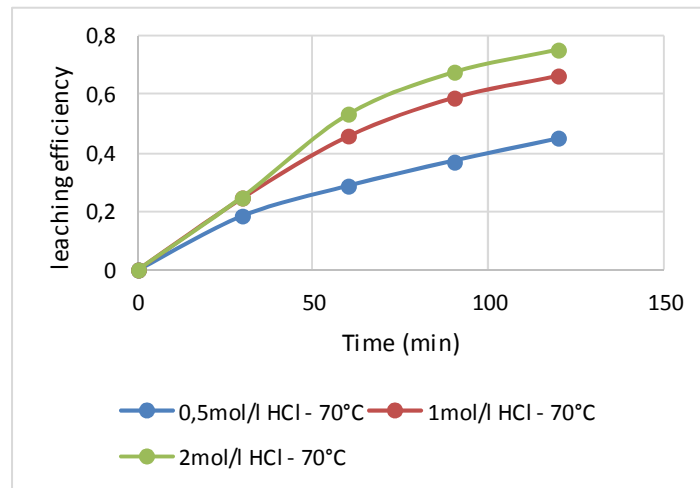


Figure 5 – Influence of the concentration of hydrochloric acid on yttrium dissolution
 Рус. 5 – Влияние концентрации соляной кислоты на процесс растворения иттрия
 Slika 5 – Uticaj koncentracije hlorovodonične kiseline na rastvaranje itrijuma

Under the same conditions, the dissolution of iron with hydrochloric acid is very high at 70°C for all used concentrations.

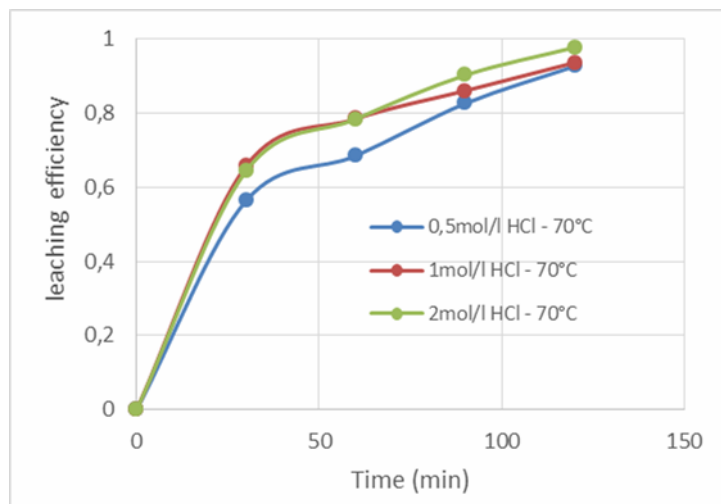


Figure 6 – Influence of the concentration of hydrochloric acid on iron dissolution at 70°C
 Рус. 6 – Влияние концентрации соляной кислоты на процесс растворения железа при температуре выше 70°C
 Slika 6 – Uticaj koncentracije hlorovodonične kiseline na rastvaranje gvožđa na temperaturi od 70°C

We assumed that the chemical reaction at the phase boundary solid-liquid is the limiting step. The solid phase is yttrium oxide on aluminium oxide as a matrix. Therefore, a kinetic analysis of the dissolution process of waste dust was performed using the next mathematical model.

$$1 - (1-X)^{1/3} = k t \quad (1)$$

Where:

X – Leaching efficiency of yttrium dissolution (between 0 and 1)

k – Rate constant, min^{-1}

t – Leaching time (min).

A graphical representation of the experimental data of the leaching processes in the coordinate system which corresponds to the chemical rate control for spherical particles is shown in Figure 7:

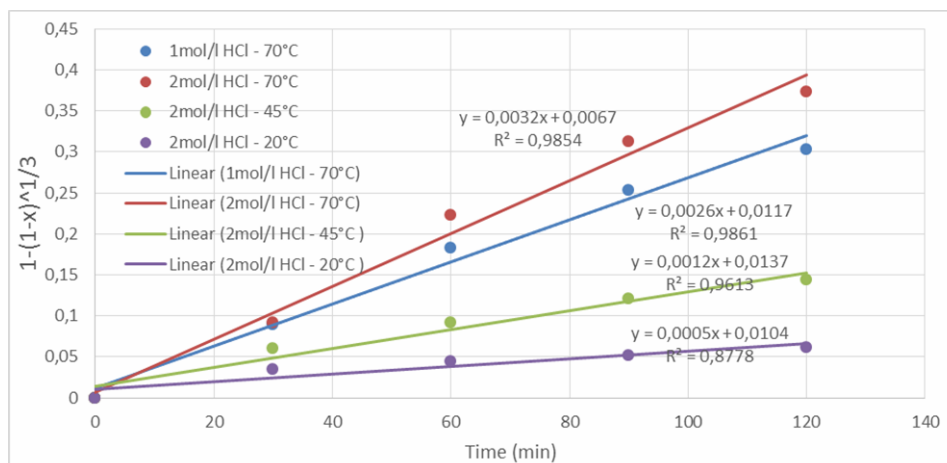
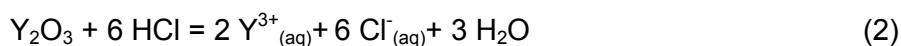


Figure 7 – Testing of kinetic model for dissolution of yttrium
 Рус. 7 – Тест кинетической модели растворения иттрия
 Slika 7 – Ispitivanje kinetičkog modela rastvaranja itrijuma

Good linearization exists for all three investigated temperatures. In all three cases, at 20°C, 45°C and 70°C, the straight lines begin from the origin of the coordinate system. The slopes of these lines correspond to the rate constants of the corresponding reactions of yttrium dissolution in hydrochloric acid (Eq. 2).



The reaction rate constants for yttrium dissolution at different temperatures were graphically determined:

$$k_{70^{\circ}\text{C}} = \tan(0,0032) = 5,585 \cdot 10^{-5} \text{ min}^{-1}$$

$$k_{45^{\circ}\text{C}} = \tan(0,0012) = 2,0944 \cdot 10^{-5} \text{ min}^{-1}$$

$$k_{20^{\circ}\text{C}} = \tan(0,0005) = 8,7266 \cdot 10^{-6} \text{ min}^{-1}$$

The statement on the rate-limiting step was further investigated using the Arrhenius plot.

$$k = k_0 \cdot \exp(-E_A/RT) \quad (3)$$

If in k over $1000/T$ is applied, the apparent activation energy E_A can be determined (as shown in Figure 8).

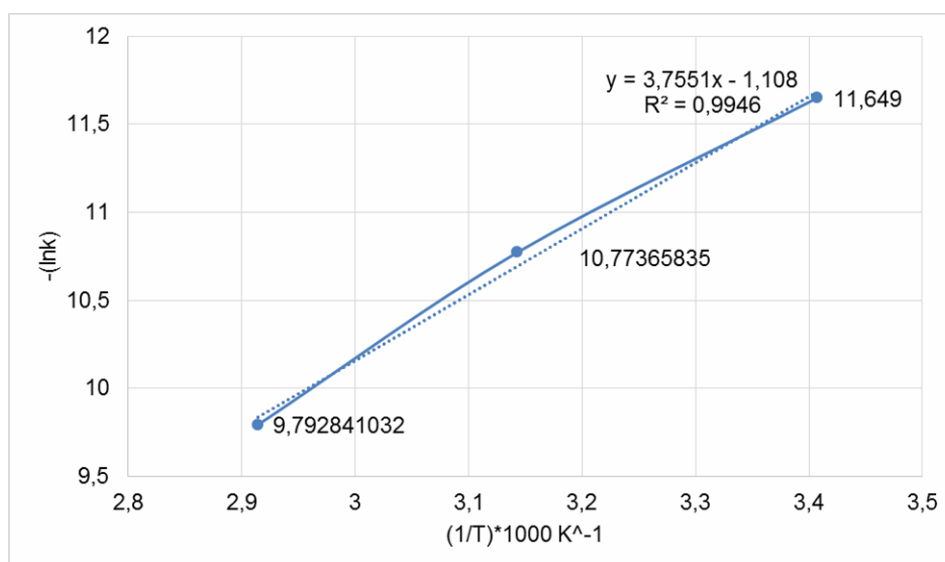


Figure 8 – Arrhenius plot for the dissolution of yttrium with hydrochloric acid between 20°C and 70°C

Рис. 8 – График уравнения Аррениуса для растворения иттрия в соляной кислоте при температуре 20 °С - 70 °С

Slika 8 – Grafički prikaz Arrheniusove jednačine rastvaranja itrijuma u hlorovodoničnoj kiselini na temperaturi između 20°C i 70°C

The calculated activation energy amounts to 31.2 kJ/mol. The dissolution of yttrium as yttrium oxide with hydrochloric acid from aluminum oxide as matrix depends on a reaction at the solid-liquid phase.

Conclusions

The present study summarized the influence of different reaction parameters such as leaching temperature, time and concentration of hydrochloric acid on yttrium dissolution from waste ceramic dust. An increase of dissolution time and temperature increases yttrium dissolution. The maximal yttrium dissolution efficiency was obtained using 2M HCl at atmospheric pressure at 70°C (about 80%). An increase of pressure from atmospheric pressure to 0.5 MPA at 150°C leads to the maximum dissolution of yttrium (about 98.6 %). A kinetic analysis revealed that the dissolution of yttrium with hydrochloric acid can be described using a kinetic model based on the reaction at the solid-liquid phase as a limiting step. The calculated activation energy E_A between 20°C and 70°C amounts to 31.2 kJ/mol. The selectivity of the dissolution process regarding the presence of iron will be studied in our future work. Precipitation and solvent extraction will be used in particular for a production of a cleaned solution based on yttrium chloride.

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КИНЕТИКА РАСТВОРЕНИЯ ИТТРИЯ ИЗ ОТХОДНОЙ КЕРАМИЧЕСКОЙ ПЫЛИ

Сречко Р. Стопич, Бернд Г. Фриедрих
Технический университет города Ахен, Институт металлургических процессов и рециклирования металлов, Германия

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Резюме:

Иттрий светло-серебристый редкоземельный металл побочной группы, обладающий аналогичными лантатдоиду химическими свойствами.

Иттрий и оксид иттрия используются в производстве люминесцентных ламп, электродов, электронных фильтров, сверхпроводников и в качестве укрепляющих добавок к различным материалам.

Большая часть иттрия извлекается из его минералов, таких как монациты $[(Ce,La,Th,Nd,Y)PO_4]$ и ксенотимы YPO_4 .

Наличие радиоактивных элементов тория и урана, а также иттрия усложняет процесс получения оксида иттрия из руд и концентратов.

Так как стандарты по охране окружающей среды с каждым днем повышаются, извлечение данных элементов становится рискованным.

Поэтому рециклирование оксида иттрия из вторичных ресурсов, таких как: красный шлак, покрытие для керамики и использованные материалы в производстве люминесцентных ламп имеет большое значение.

Основной целью данной работы является изучение кинетики растворения иттрия с соляной кислотой из отходной керамической пыли.

Ключевые слова: *иттрий, рециклирование, гидрометаллургия, керамика.*

KINETIKA RASTVARANJA ITRIJUMA IZ OTPADNOG KERAMIČKOG PRAHA

Srećko R. Stopić, Bernd G. Friedrich
Tehnički Univerzitet u Ahenu, Institut za procesnu metalurgiju i recikliranje metala, Nemačka

OBLAST: hemijske tehnologije
VRSTA ČLANKA: originalni naučni članak
JEZIK ČLANKA: engleski

Sažetak:

Itrijum je srebrnasti prelazni metal sa hemijskim svojstvima sličnim lantanoidima. Zbog ovih sličnosti itrijum pripada elementima retkih zemalja. Itrijum i itrijumoksid koriste se u fluorescentnim lampama, u proizvodnji elektroda, u elektronskim filterima, superprovodnicima i kao dodatak u različitim materijalima radi poboljšanja njihove stabilnosti. Veliki deo itrijuma dobijen je iz njegovih minerala kao što su monazit [(Ce,La,Th,Nd,Y)PO₄] i ksenotim YPO₄. Prisustvo radioaktivnih elemenata torijuma i urana, zajedno sa itrijumom, predstavlja teškoću u dobijanju itrijumoksida iz ruda i koncentrata. Regulisanje zaštite životne sredine je sve strože i povećava rizik u njihovom snabdevanju. Zbog svega toga recikliranje itrijumoksida iz sekundarnih izvora, kao što su crveni mulj, prevlake u keramici i istrošeni materijali u fluorescentnim lampama, ima veliki značaj. Osnovni cilj ovog rada jeste da prouči kinetiku rastvaranja itrijuma sa hlorovodoničnom kiselinom iz otpadnog praha keramičkih materijala.

Ključne reči: *itrijum, recikliranje, hidrometalurgija, keramika.*

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