

## Effects of mechanical activation on the kinetics of terbium leaching from waste phosphors using hydrochloric acid

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**Abstract:** The effect of mechanical activation (MA) on the kinetics of terbium (Tb) leaching from waste phosphors using hydrochloric acid was investigated. Leaching kinetics, such as apparent reaction rate, activation energy and reaction order, were determined using the shrinking-core model and the Arrhenius equation. Results obtained from experiments with different concentrations of HCl and under different leaching temperatures were used for the determinations. The impacts of factors such as rotational speed, HCl concentration and leaching temperature on the leaching rate of Tb were also discussed. The results showed that MA could dramatically increase the leaching rate of Tb from waste phosphors, and the apparent reaction rate ( $k_{ap}$ ) of leaching was accelerated as well. For inactivated waste phosphors, the apparent activation energy ( $E_{ap}$ ) was  $52.82 \pm 3.95$  kJ/mol, indicating that the rate-controlling step of the leaching process was the chemical reaction. The  $E_{ap}$  dropped to  $25.96 \pm 3.90$  kJ/mol and  $10.96 \pm 2.79$  kJ/mol when the waste phosphors were mechanically activated at rotational speeds of 400 and 600 r/min, respectively; the leaching process transformed to a hybrid (chemical-reaction and diffusion) control process, and even a reagent-diffusion (through the product layer) control process. The apparent reaction order for Tb leaching from 400 r/min-activated waste phosphors was  $2.49 \pm 0.11$ , and it decreased to  $1.16 \pm 0.17$  when the rotational speed of 600 r/min was used. Kinetics results indicated that MA could make Tb leaching occur spontaneously, and the activation intensity of waste phosphors was strengthened with higher rotational speed.

**Keywords:** terbium; mechanical activation; waste phosphors; leaching kinetics; hydrochloric acid; rare earths

Phosphor plays an essential role in fluorescent lamps (FLs), transferring the electricity into visible light, and accounts for 2 wt.%–3 wt.% of an FL<sup>[1,2]</sup>. Phosphor is one of the major applications of rare earth elements (REEs). It consumes approximately 100%, 85%, and 77%, respectively, of the amounts of europium (Eu), terbium (Tb) and yttrium (Y) used in all REE application fields, and also uses small proportions of cerium (Ce) and lanthanum (La)<sup>[3]</sup>. Recovering REEs from wastes is a promising method for the sustainability of REEs and has attracted increasing attention from researchers all over the world<sup>[4,5]</sup>. In fact, there is a much higher percentage of rare earth elements (REEs) in phosphors than in naturally occurring REE ores. Specifically, REEs account for more than 23 wt.% of phosphors in FLs<sup>[6–8]</sup>, while the minimum industrial-grade levels of primary REE ores and ion-adsorption REE ores are 1.5%–2.0% and 0.06%–0.15%, respectively<sup>[9]</sup>; less than 1/10 and 1/150 of their contents in phosphors. Besides, it was estimated that about 4.46 billion units of FLs, or about 0.66 million metric tons in weight, entered the waste stream in mainland China in 2016<sup>[10]</sup>. The environmentally sound management of waste FLs could contribute to sustainable

utilisation of REEs in phosphors<sup>[11–13]</sup>.

Extensive work has been carried out on the recovery of REEs from phosphors in FLs<sup>[14,15]</sup>. So far, however, the highest extraction rate that has been obtained for Tb, the highest-value REE in waste phosphors<sup>[16]</sup>, is 7%<sup>[15]</sup>, whether by supercritical liquid extraction<sup>[17]</sup> or hydrometallurgy<sup>[2,6,18–20]</sup>. Although pyrometallurgy approaches<sup>[7,21–25]</sup> might be more effective, they have the disadvantages of high energy consumption (because of the high operational temperatures required). As for molten decomposition and leaching, they consume massive amounts of alkali material and acids. The application of electrometallurgical<sup>[26]</sup> methods to recover REEs from waste phosphors is also hindered by the shortcomings of high energy consumption during electrolytic reduction, molten salt-assisted halogenation processes, and the use of chlorine gas. Only a very limited proportion (< 1%) of REEs are recycled from wastes all over the world<sup>[27]</sup>. Therefore, a low-energy-consumption method that can achieve a high recovery rate of REEs, especially Tb, from waste phosphors, would be highly desirable.

Mechanical activation (MA) has been successfully applied in the fields of mineral processing, and chemical

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and materials engineering<sup>[28]</sup>, and has also exhibited promising application potential for recovering metals from various types of waste<sup>[29,30]</sup>, such as lead (Pb) from waste cathode ray tube (CRT) glass<sup>[31,32]</sup>, gold (Au) from gold-containing waste<sup>[33]</sup>, and copper (Cu) from waste printed circuit boards<sup>[34]</sup>.

In our previous study, we found that the leaching rate of Tb, as well as four other REEs (Ce, Eu, La, and Y), from waste phosphors, can be dramatically accelerated with the assistance of MA after process optimization<sup>[16]</sup>. The obtained results indicated that an MA operation would lead to physical disintegration along with the formation of active surfaces, as well as changes in the physicochemical properties of the particles. Meanwhile, MA is also an effective method of damaging and destroying the particle structures and increasing the reactivity of the waste phosphors compounds. After mechanical activation, leaching rates of Tb, Ce and La increased to more than 90% under the optimized condition; they were merely around 1.5% when the phosphors were inactivated. Besides, the leaching rate of Eu and Y increased from 80% and 85% to more than 90% and 95% after activation, respectively. An initial calculation of the cost of MA enhanced leaching of REEs was conducted based on the data obtained during experiments of laboratory scale. The cost for MA and leaching was approximately 5.2 USD, while the value of REEs in waste phosphors (1 kg) was about 14.4 USD. Thus, MA is a promising method for recovering REEs from waste phosphors.

Studies by other researchers have pointed out that the fundamental kinetic behavior of a number of critical processes can be affected by MA<sup>[35,36]</sup>. According to investigations on leaching kinetics and the mechanisms of various mechanically activated materials such as galena<sup>[37]</sup>, pyrrhotite<sup>[38]</sup>, kaolin residue<sup>[39]</sup>, and hemimorphite<sup>[40]</sup>, the reaction rate of leaching processes can be substantially enhanced by MA, and the rate-controlling step can be changed as well. However, the effects of MA on the leaching kinetics of inactivated and activated waste phosphors have rarely been studied.

In this study, the hydrochloric acid leaching kinetics of inactivated and activated waste phosphors with an emphasis on the leaching of Tb (accounts about 79% of the total value of REEs in waste phosphors relatively) was systematically investigated. The aim was to enhance the application of previously proposed recovery approaches on a larger scale and contribute to a sustainable utilization of REE resources from waste phosphors.

## 1 Experimental

### 1.1 Raw materials and reagents

The original raw material used for the experiments in this study was provided by Beijing Eco-Island Science

and Technology Co., Ltd.. It was a mixture of waste phosphors and cullet, and represented the output fraction containing waste phosphors from a waste FL treatment plant using a dry route. A sieving operation using a 300-mesh (48  $\mu\text{m}$ ) screen was conducted in the laboratory to remove most of the cullet in the original raw material. No more than 0.1% of Tb in the original raw material was lost through sieving. The fraction with reduced cullet content was dried at 105 °C for 24 h and stored as raw waste phosphors (inactivated waste phosphors) for the experiments. Reagents for the experiments were purchased from Beijing Chemical Works. All reagents were of analytical grade and used without further purification.

### 1.2 Mechanical activation operation and acid leaching

Mechanical activation of waste phosphors was carried out using a planetary ball-mill apparatus (P-7, Fritsch, Germany) under an ambient atmosphere. In each batch of activation, 5 $\pm$ 0.01 g of the waste phosphors was weighed and mixed with 7 zirconia balls (15 mm in diameter) in a zirconia pot (40 mm in inner diameter, 45 mL inner volume). During the activation operation, the mill was set to run and pause alternatively at a 15 min interval to avoid the accumulation of generated heat. All activated samples were subjected to hydrochloric acid leaching within 12 h after mechanical activation.

Hydrochloric acid leaching of inactivated and activated waste phosphors was conducted with water-bath heating and magnetic stirring. One gram of the solid sample was agitated into a 120 mL (liquid/solid ratio-120 mL/g) pre-heated HCl solution for leaching. Temperatures and HCl concentrations were set in the ranges of 323–363 K and 0.2–1 mol/L, respectively. Vacuum filtration with a cellulose acetate membrane (0.45  $\mu\text{m}$ ) was conducted for liquid-solid separation after leaching.

### 1.3 Characterization and determination of samples

Aqueous samples were analyzed using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES: IRIS Intrepid II XSP, ThermoFisher), supplemented with ICP-MS (X Series 2, ThermoFisher) when necessary. The recovery of Standard-Addition in 6 independent tests was in the range of 95%–105%. The elemental composition of waste phosphors was tested with X-ray fluorescence (XRF, XRF-1800, Shimadzu, Japan). A more accurate content of Tb in waste phosphors was determined through microwave-assisted digestion with aqua regia.

The leaching rate of Tb was calculated from the Eq.

$$\alpha = \frac{c_{\text{Tb}} \times R_{\text{L/S}}}{1000 \times W_{\text{Tb}}} \times 100\% \quad (1)$$

where  $\alpha$  is the leaching rate of Tb,  $R_{\text{L/S}}$  is the liquid-solid ratio of leaching process (mL/g),  $c_{\text{Tb}}$  is the concentration

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