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## Recovery of yttrium from deep-sea mud<sup>☆</sup>

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### ABSTRACT

Deep-sea mud rich in rare earth yttrium has received lots of attention from the international community as a new resource for Y. A novel process, which mainly includes acid leaching, solvent extraction, and oxalic acid precipitation-roasting, is proposed for recovery of Y from deep-sea mud. A series of experiments were conducted to inspect the impacts of various factors during the process and the optimum conditions were determined. The results show that the Y of deep-sea mud totally exists in apatite minerals which can be decomposed by hydrochloric acid and sulfuric acid solution. The highest leaching efficiency of Y is 94.53% using hydrochloric acid and 84.38% using sulfuric acid under the conditions of H<sup>+</sup> concentration 2.0 mol/L, leaching time 60 min, liquid–solid ratio 4:1 and room temperature 25 °C (only in case of sulfuric acid, when using hydrochloric acid, the leaching temperature should be 60 °C). Because of the much lower leaching temperature, sulfuric acid leaching is preferred. The counter current extraction and stripping tests were simulated by a cascade centrifugal extraction tank device. Using 10 vol% P204, 15 vol% TBP and 75 vol% sulfonated kerosene as extractant, 98.79% Y<sup>3+</sup> and 42.60% Fe<sup>3+</sup> are extracted from sulfuric acid leaching liquor (adjusted to pH = 2.0) after seven-stage counter current extraction with O/A ratio of 1:1 at room temperature, while other metals ions such as Al<sup>3+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Mn<sup>2+</sup> are almost not extracted. The Y<sup>3+</sup> in loaded organic can be selectively stripped using 50 g/L sulfuric acid solution and the stripping efficiency reaches 99.86% after seven-stage counter current stripping with O/A ratio of 10:1 at room temperature, while only 2.26% co-extracted Fe<sup>3+</sup> is stripped. The Y<sup>3+</sup> of loaded strip liquor can be precipitated by oxalic acid to further separate Y<sup>3+</sup> and Fe<sup>3+</sup>. The precipitation efficiency of Y<sup>3+</sup> in loaded strip liquor can be 98.56% while Fe<sup>3+</sup> is not precipitated under the conditions of oxalic acid solution concentration 200 g/L, quality ratio of oxalic acid to Y of 2, and precipitation time 0.5 h. And the precipitate was roasted at 850 °C for 3 h to obtain the oxide of Y in which the purity of Y<sub>2</sub>O<sub>3</sub>/REO is 79.02% and the contents of major non-rare earth impurities are less than 0.21%. Over the whole process included acid leaching, solvent extraction, and oxalic acid precipitation-roasting, the yttrium yield is 82.04%.

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### 1. Introduction

Yttrium is playing an increasingly important role in fields of national defense, aviation and advanced manufacturing owing to its technological and strategic applications. The demand for Y has

increased significantly during these years. With the expansion of demand, the resources for Y on the land have been exhausted and deep-sea rare earth resources are gradually receiving attention.

Japan is one of the most active countries in the survey of deep-sea rare earths. In 2013, Japanese researcher Kon et al.<sup>1</sup> found that the concentration of rare earth in the shallow sediment about 3 m below the seafloor 5600 m deep and 200 km south of the South Bird Island could reach 0.66%, which was the highest in the world, and the total rare earth reserves was about 6.8 million tons equivalent to Japan's 227-year domestic consumption. In the same year, Japanese researcher Yasukawa et al.<sup>2</sup> once again announced the discovery of seabed mud containing high concentrations of rare earths on the seabed of the eastern Indian Ocean, and the rare

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earth-bearing mudstorms with a quite high concentration existed in 75–120 m below the seafloor about 5600 m deep. In recent years, the abundance of Y and low radioactive elements in the deep-sea mud under north Pacific Ocean, southeast Pacific Ocean and east Indian Ocean has been confirmed by analytical studies in several countries, which was expected to be the future resources for Y.<sup>1–8</sup> However, though a considerable amount of theory and characterization researches on Y from deep-sea mud has been reported, the recovery of Y started relatively backward and relative reports were rarely seen.

The survey showed that Y in deep-sea mud was mainly present in the form of phosphate and totally occurred in apatite minerals.<sup>19</sup> The occurrence status of Y in deep-sea mud was much similar to that in phosphate concentrate on land,<sup>10</sup> which means that process researches on recovery of Y from phosphate concentrate ores on land could give us some reference. Some researches<sup>11–14</sup> carried out researches on acid leaching of apatite in phosphate concentrate and the results showed that the Y in apatite could be leached out and relatively high leaching efficiency could be obtained by adjusting to a acidity ratio when using sulfuric acid or hydrochloric acid as leaching agent. Some other researchers<sup>15–18</sup> investigated the solvent extraction process of Y in acid leaching liquor, and the results showed that the Y could be selectively extracted and enriched using phosphate ester extractants such as P204, P507. Meanwhile, Zhang et al.<sup>19</sup> used oxalic acid to precipitate Y from the leaching liquor and then roasted precipitate to obtain a oxide concentrate of Y with content of 1.87%.

Based on the above research foundation, a novel completed recovery process of Y from deep-sea mud sample was investigated to obtain the highest yield and enrichment ratio of Y, which includes acid leaching, solvent extraction, and oxalic acid precipitation-roasting. A series of experiments were conducted to inspect the impacts of various factors during this process to determine the optimum conditions.

## 2. Experimental

### 2.1. Materials

The columnar deep-sea mud sample named REGC010 was collected by Guangzhou Marine Geological Survey from central Pacific Ocean (the sampling location is shown in Fig. 1) and then air-dried and crashed (size of  $-45\ \mu\text{m}$  accounts for 100%) for subsequent experiments. P204 (purity of 95%), TBP (chemically Pure) and sulfonated kerosene (technical grade) were provided from Shanghai Laiyashi Chemical Company. Sulfuric acid (analytical reagent), hydrochloric acid (analytical reagent), sodium carbonate (analytical reagent) and oxalic acid (analytical reagent) were provided from Nanjing Chemical Reagent Company.



Fig. 1. The sampling location of REGC010.

### 2.2. Methods

The leaching experiments were carried out in a device as shown in Fig. 2. The dried deep-sea mud and acid solution were put into a 500 mL three-necked flask (provided from Beijing BOMEX Glass Company) immersed in a temperature controlled water bath (provided from Changzhou Aohua Instrument Company). The beginning and ending of the leaching reaction was controlled by a stirring apparatus (provided from Changzhou Aohua Instrument Company). The experimental conditions including acid concentration, temperature, liquid–solid ratio and time were investigated using hydrochloric acid and sulfuric acid as leaching agent respectively. The leaching efficiency of Y in each experiment was calculated by the following Eq. (1).

$$E_1 = \frac{[Y]_{a0} V_{a0}}{C_Y S} \times 100\% \quad (1)$$

[Y]<sub>a0</sub>: Concentration of Y in leaching liquor, mg/L; V<sub>a0</sub>: Volume of leaching liquor, L; C<sub>Y</sub>: Concentration of Y in deep-sea mud sample, ppm; S: Weight of deep-sea mud sample put into leaching reaction, kg.

The single-stage extraction and stripping experiments were carried out in a 125 mL separating funnel (provided by Beijing BOMEX Glass Company) immersed in a constant temperature oscillator (provided by Jiangsu Maipulong Instrument Manufacturing Company). To determine the extraction distribution isotherms, the organic system was contacted with leaching liquor at O/A ratios of 1:1, 1:2, 1:3 and 1:5. To determine the stripping distribution isotherms, the loaded organic system was contacted with stripping agent solution at O/A ratios of 1:1, 2:1, 5:1, 10:1, 15:1, and 20:1. The multistage counter current extraction and stripping experiments were simulated in a cascade centrifugal extraction tank device (provided by Beijing Institute of Extractive Applied Technology). The extraction efficiency could be calculated by the following Eq. (2). The concentrations of loaded organic solutions were calculated by subtraction method as Eq. (3) and the stripping efficiency could be calculated by the following Eq. (4).

$$E_2 = \frac{[Me]_{a1} V_{a1}}{[Me]_{o1} V_{o1}} \times 100\% \quad (2)$$

[Me]<sub>a1</sub>: Concentrations in raffinate, mg/L; V<sub>a1</sub>: Volume of raffinate, L; [Me]<sub>o1</sub>: Concentrations in leaching liquor put into extraction reaction, mg/L; V<sub>o1</sub>: Volume of leaching liquor put into extraction reaction, L.

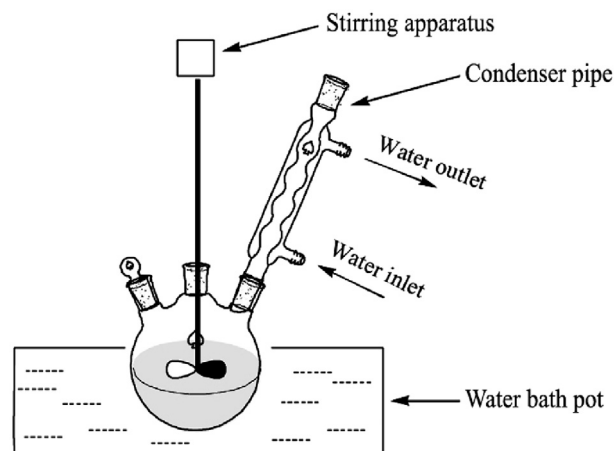


Fig. 2. Leaching experiment device.

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