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# ARTICLE

## Dissolution of thorium dioxide in aqueous solution by using thermochemical conversion

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ThO<sub>2</sub> is one of the candidates for thorium fuels since the ThO<sub>2</sub> fuel has a higher melting point, higher thermal conductivity, and higher chemical stability. The dissolution of ThO<sub>2</sub> in aqueous solution is required, if the aqueous reprocessing process is used for the reprocessing of spent ThO<sub>2</sub> fuel. However, ThO<sub>2</sub> is difficult to dissolve in aqueous solution because of its chemical stability. Thus, we proposed to use the thermochemical conversion method to convert ThO<sub>2</sub> into soluble compounds to promote the dissolution of ThO<sub>2</sub>. The experimental conditions for the thermochemical conversion method are heating at 400°C for 12 h, heating at 400°C for 4 h, heating at 300°C for 12 h, and heating at 300°C for 4 h. We confirmed that ThO<sub>2</sub> can be dissolved in aqueous solution by pretreatment using thermochemical reaction with carbon halides, such as CCl<sub>3</sub>CCl<sub>3</sub> or CBr<sub>4</sub>. The optimal experimental condition is heating at 300°C for 12 h.

Keywords: thoria; halogenation; thorium cycle; radiopharmaceutical isotope; secular equilibrium; Th series

## 1. Introduction

<sup>232</sup>Th can be converted by neutron capture into <sup>233</sup>U, a fissile isotope of uranium that does not exist in nature. When a thermal neutron is absorbed by this isotope, the number of neutrons produced is sufficiently larger than 2.0 to permit breeding in a thermal nuclear reactor [1]. Only one natural fissile isotope, <sup>235</sup>U, accounts for 0.7% of the uranium element. The most abundant isotope in uranium is 99.2% fertile isotope <sup>238</sup>U. Although <sup>238</sup>U is not a fissile isotope, <sup>238</sup>U can also generate a fissile isotope <sup>239</sup>Pu by neutron capture. Therefore, the current reactor nuclear fuel is based on these three isotopes: <sup>235</sup>U, <sup>238</sup>U, and <sup>232</sup>Th [2]. The current nuclear power plants are basically uranium-based fuel. Due to the rising demand for energy and the reduction of uranium resources, there is an increasing interest in improving the utilization of uranium resources and developing thorium-based fuel [3]. Studies have shown that natural thorium (<sup>232</sup>Th) cannot be used as nuclear fuel alone, and it needs to be supplied or mixed with fission sources (such as <sup>235</sup>U, <sup>239</sup>Pu) or neutron sources (such as spallation neutrons from ADS). Most natural thorium resources exist in the form of ThO<sub>2</sub>. The material properties of thorium mixed oxide (Th-MOX) fuel are more reliable and effective than conventional uranium and plutonium mixed oxide fuel. Because ThO<sub>2</sub> has a higher melting point, higher thermal conductivity, resistance against radiation damage, and higher chemical stability. The properties of Th-MOX fuel vary with the content of ThO<sub>2</sub>[4-7]. Thorium-based fuel greatly reduces weapon-grade materials and long-lived minor actinides in spent fuel than uranium-based fuel. Besides, Th-MOX fuel can be loaded into existing nuclear reactors, such as pressurized light, boiling, and heavy water reactors. Thorium molten salt reactor(TMSR) is designed to utilize thorium-based and hybrid nuclear fuel. There are two types of fuel for TMSR: liquid fuel and solid fuel. The liquid fuel dissolved the fuel in salt (LiF-BeF<sub>2</sub>-UF<sub>4</sub>-ThF<sub>4</sub>), and the solid fuel is TRISO-type nuclear fuel. Compared with other reactors, the advantage of TMSR is that weapon-grade materials and long-lived actinides will be burned during operation. In addition, it has a strong negative Doppler reactivity coefficient, which means that once the reactor core temperature rises, the nuclear fission rate will decrease [3,5,8-10]. However, there is a problem with the chemical stability of ThO<sub>2</sub>. Because the liquid fuel of TMSR is fluoride salt, it is necessary to dissolve ThO<sub>2</sub> in salt. In addition, if ThO<sub>2</sub> is used as the nuclear fuel, the spent ThO<sub>2</sub> fuel is treated by the aqueous reprocessing process, and the dissolution of ThO<sub>2</sub> in the aqueous solution is necessary.

On a different subject, since <sup>225</sup>Ac and its daughter nuclide can emit four alpha particles, which is very harmful to cancer cells, it has become a promising  $\alpha$ -therapeutic radiopharmaceutical isotope. Despite consistently growing interest in the use of <sup>225</sup>Ac as an alpha-emitting radiolabel for targeted molecular therapies of human disease, the output of <sup>225</sup>Ac is too small to support large clinical trials

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of multiple radiopharmaceutical candidates, which limits the development of <sup>225</sup>Ac as an alpha-emitting therapeutic radionuclide for RPT(Radiopharmaceutical) [11-13]. <sup>225</sup>Ac is on the Np decay series, if we want to obtain <sup>225</sup>Ac, we can radiate a nuclide on another decay series and then transform it to nuclides on the Np series. We proposed that the radioactive isotope of the <sup>232</sup>Th decay series be used to obtain <sup>225</sup>Ac. For this method, the dissolution of ThO<sub>2</sub> is also required.

However, ThO<sub>2</sub> is chemically too stable to dissolve in acid or alkaline aqueous solutions. In order to improve the dissolution rate of ThO<sub>2</sub>, the most widely used method is to use 13 M HNO<sub>3</sub> containing 0.02-0.05 M HF and 0.1 M  $Al(NO_3)_3$  to dissolve ThO<sub>2</sub>. HF is used to catalyze the dissolution of ThO<sub>2</sub> in nitric acid, while Al(NO<sub>3</sub>)<sub>3</sub> is used to prevent corrosion of HF acid and precipitation of thorium fluoride. However, the dissolution rate of ThO<sub>2</sub> using this method is still low, and due to the use of HF, special corrosion-resistant containers are required, and a large amount of HNO3 will be lost in the dissolution process because NOx gas will be generated, which will cause harm to the environment [14-15]. The methods for dissolving ThO<sub>2</sub> also include:1. ammonium sulfate and ThO<sub>2</sub> reacting at high temperatures to generate soluble thorium salt; 2. ThO<sub>2</sub> dissolving in concentrated trifluoromethanesulfonic acid solution under reflux condition; 3. heating ThO<sub>2</sub> with 88% phosphoric acid at a certain temperature [16-17].

We proposed a new method to increase the dissolution rate of ThO<sub>2</sub> by reacting halides with ThO<sub>2</sub> to generate thorium halides. Because the carbon atom can combine with the oxygen atom in ThO<sub>2</sub> to form carbon oxygen compound, which does not affect the experiment, the carbon halides (CCl<sub>4</sub>, CCl<sub>3</sub>CCl<sub>3</sub>, CBr<sub>4</sub>) were selected. These carbon halides are easily soluble in organic solvents, such as ethanol, so ethanol can be used to remove excess reagents. In addition, according to the literature [18], AlBr<sub>3</sub> can generate ThBr<sub>4</sub> at a lower temperature with ThO<sub>2</sub> because of its high reactivity. Hence, we also chose AlBr<sub>3</sub> and ThO<sub>2</sub> to react to compare which of the four reagents is better.

The theory of the new method is that ThO<sub>2</sub> and halides undergo a chemical reaction under heating conditions to generate soluble thorium halides. The name of this new method is the thermochemical conversion method. Hence, the heating temperature and time are very important. Due the radioactive nature of ThO<sub>2</sub>, conducting to thermochemical conversion experiments directly with ThO<sub>2</sub> will generate a significant amount of radioactive waste. Therefore, we need an analogue with a similar structure and properties to ThO<sub>2</sub> for simulation experiments. Because cerium dioxide (CeO<sub>2</sub>) and ThO<sub>2</sub> have the same fluorite structure and very similar microstructures, and CeO<sub>2</sub> always appears to simulate tetravalent actinide oxides, we used CeO<sub>2</sub> to do simulation experiments to explore the best reaction conditions [19,20]. In the present work, the dissolution of ThO<sub>2</sub> and CeO<sub>2</sub> into aqueous solution by using the thermochemical conversion to thorium halides and cerium halides were studied.

### 2. Experimental

## 2.1. Reagents, reaction vessel, analytical instruments

# 2.1.1 Reagents

ThO<sub>2</sub> powder was provided by the Institute for Integrated Radiation and Nuclear Science, Kyoto University. The purity of CeO<sub>2</sub> is 99.5%, AlBr<sub>3</sub> is 99%, CCl<sub>4</sub> is 99.5%, CCl<sub>3</sub>CCl<sub>3</sub> is 98%, and CBr<sub>4</sub> is 98%, all purchased from Wako. All other reagents are solid except for CCl<sub>4</sub>, which is liquid and volatile. The decomposition products of CCl<sub>4</sub>, CCl<sub>3</sub>CCl<sub>3</sub>, and CBr<sub>4</sub> are CO, CO<sub>2</sub>, and halides. The decomposition products of AlBr<sub>3</sub> are halides and metal oxides. The purity of HCl is 35% -37%, and HNO<sub>3</sub> is 60% -61%, both of which are guaranteed reagents and purchased from Wako.

#### 2.1.2 Reaction vessel

The reaction vessel we are using is shown in **Figure 1**. This reaction vessel was purchased from the Swagelok company. Therefore, we named it Swagelok.



Figure 1. Reaction vessel: Swagelok.

### 2.1.3 Analytical instruments

We used ICP-OES (Simultaneous ICP Atomic Emission Spectrometer, ICPE-9800) to detect the filtrate in the CeO<sub>2</sub> experiment and ICP-MS (ICAP6300DUO, manufactured by ThermoFisher Scientific) to detect the filtrate in the ThO<sub>2</sub> experiment.

## 2.2. Experimental procedures

We used ThO<sub>2</sub> and CeO<sub>2</sub> powder for experiments. At first, 0.1 g of CeO<sub>2</sub> or ThO<sub>2</sub> and 1 g of halide were added to the Swagelok capsule made of stainless steel 316. The Swagelok was tightened and placed in the heating furnace, and the heating temperature and heating time were set according to the experimental conditions. The thermochemical conversions were carried out at 400°C for 12 h, 400°C for 4 h, 300°C for 12 h and 300°C for 4 h respectively. After heating, waited for the Swagelok to cool down, open and place it in a beaker, and added 30ml of 11.33 M HCl or 13.14 M HNO<sub>3</sub> to the beaker. Soaked it at room temperature for one hour and then filtered it. Cleaned the beaker and Swagelok with 20 ml H<sub>2</sub>O and then filtered the water. The obtained filtrate is measured by ICP-OES and ICP-MS.



Figure 2. Dissolution rate of CeO<sub>2</sub> by using thermochemical conversion.

### 3. Results and discussion

The dissolution rate can be calculated according to Formula 1 below and ICP-OES or ICP-MS results.

$$\begin{aligned} Dissolution \ rate\% &= \\ \frac{Mass \ of \ cerium \ ion \ or \ thorium \ ion \ in \ filtrate}{Mass \ of \ XO_2 \cdot \left(\frac{Relative \ atomic \ mass \ of \ XO_2}{Relative \ atomic \ mass \ of \ XO_2}\right)} \cdot 100\% \end{aligned}$$

$$(1)$$

Where the mass of  $XO_2$  refers to the mass of  $CeO_2$  or  $ThO_2$  added to Swagelok.

According to the results calculated by Formula 1, Figure 2 is drawn as follows. There are four kinds of reagents and CeO<sub>2</sub> reactions, respectively, and then there are eight experimental conditions. The horizontal axis is the eight experimental conditions, and the vertical axis is the dissolution rate.

It can be seen from Figure 2 that under the same heating time and temperature, the effect of HCl is better than that of HNO<sub>3</sub> for CCl<sub>4</sub>, CCl<sub>3</sub>CCl<sub>3</sub>, and CBr<sub>4</sub>. For CCl<sub>4</sub>, the change in heating time and temperature has little effect on the dissolution rate of the sample soaked in HCl. On the contrary, for AlBr<sub>3</sub>, the effect of HNO<sub>3</sub> is better than that of HCl, and the change of heating time and temperature has little effect on the dissolution rate of samples soaked in HNO<sub>3</sub>. The solubility of the reaction products generated by the reaction of CeO<sub>2</sub> and AlBr<sub>3</sub> in HNO<sub>3</sub> is higher than that in HCl, which is opposite to the results of the other three reagents. I think it should be caused by the different reaction products. The decomposition products of CCl<sub>4</sub>, CCl<sub>3</sub>CCl<sub>3</sub>, and CBr<sub>4</sub> are CO, CO<sub>2</sub>, and halides. Therefore, CeO<sub>2</sub> reacts with these three reagents to produce cerium halides. The decomposition products of AlBr3 are halides and metal oxides; hence, the reaction product of CeO<sub>2</sub> and AlBr<sub>3</sub> may be CeAlO<sub>3</sub>. During the experiment, I found that reddish-brown gas was generated when the reaction products of CeO<sub>2</sub> and AlBr<sub>3</sub> were immersed in HNO<sub>3</sub>. It should be that the reaction products reacted with HNO<sub>3</sub> to generate NO<sub>2</sub>, which may be the reason why the solubility of the reaction products of CeO<sub>2</sub> and AlBr<sub>3</sub> in HNO<sub>3</sub> is higher than that of HCl [18,21]. On the whole, under the same reagent, the influence of acid type on sample dissolution rate is greater than that of heating time and temperature. From the overall effect, the effect of CCl<sub>4</sub> is relatively stable, however, CCl<sub>4</sub> is regulated and highly volatile. In addition, we found that the dissolution rate of samples heated at 300°C for 12h, whether soaked in HCl or HNO<sub>3</sub>, was relatively stable and high. Therefore, CCl<sub>3</sub>CCl<sub>3</sub>, CBr<sub>4</sub>, and AlBr<sub>3</sub> reagents were selected to react with ThO<sub>2</sub>. The experimental condition was heating at 300°C for 12 h.

The following **Figure 3** shows the results of the  $ThO_2$  experiment. The lowest dissolution rate is 70%. It also can be seen that CBr<sub>4</sub> has the best effect. Whether HCl or HNO<sub>3</sub> is used to dissolve the reaction products, the dissolution rate is more than 90%. CBr<sub>4</sub> performs better than CCl<sub>3</sub>CCl<sub>3</sub>, which may be because the lattice energy of ThBr<sub>4</sub> is smaller than that of ThCl<sub>4</sub>. Because the lattice energy is directly proportional to the charge of anions and cations, and inversely proportional to the distance between anions and cations. The cation and anion charges of ThBr<sub>4</sub> and ThCl<sub>4</sub> are the same, but the distance between the cation and anion of ThBr<sub>4</sub> is greater than that of ThCl<sub>4</sub>. The smaller the lattice energy, the greater the solubility [22].



Figure 3. Results of three reagents and ThO<sub>2</sub> heated at 300 °C for 12h respectively and then dissolved in HCl or HNO<sub>3</sub>.

### 4. Conclusions

We confirmed that the  $ThO_2$  can be dissolved by a pretreatment using the thermochemical conversion. Dissolution rates of both CeO<sub>2</sub> and ThO<sub>2</sub> in HCl are generally higher than in HNO<sub>3</sub>. We obtained high dissolution rates by thermochemical reaction of ThO<sub>2</sub> with CCl<sub>3</sub>CCl<sub>3</sub> and CBr<sub>4</sub>.

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