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Dissolution of sintered thorium dioxide in phosphoric acid using autoclave and microwave methods with detection by gamma spectrometry

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ABSTRACT

A quantitative and fast method of dissolution of refractory thoria (ThO_2) was developed for the determination of thorium (Th) in a given sample. The dissolution of sintered ThO_2 powder, microspheres and pellets using 88% phosphoric acid was investigated. The conditions of quantitative dissolution of ThO_2 microspheres were optimized by conventional heating in autoclave and also by microwave heating. 100 mg of sintered ThO_2 microspheres were dissolved in 8 g of phosphoric acid in an autoclave, and heating at 170 °C for 3 h, in comparison to 5 g of phosphoric acid by microwave heating (375 W) at 220 °C for 1 h. Dissolution studies on the powder form of sintered ThO_2 were also performed. 1 g of sintered ThO_2 powder could be dissolved in 6.5 g of phosphoric acid in autoclave heating at 170 °C for 1 h. Strong complexing of $(PO_4)^{3-}$ with Th^{4+} may be the influencing factor for quantitative dissolution of ThO_2.

1. Introduction

^{232}Th is a fertile radionuclide which leads to the formation of ^{233}U by thermal neutron capture. The feasibility of thoria based reactors is being investigated for reduced production of radionuclides such as minor actinides [1], its potential of burning weapon grade plutonium [2] and its excellent resistance to aqueous corrosion [3,4] etc.

With the advent of Th fuel technology, rapid radiometric methods for the determination of Th have to be developed which need quantitative and fast dissolution of refractory thoria. In our laboratory, samples of nuclear grade ThO_2 microspheres, powders and pellets are received for the determination of thorium. Due to non-uniform geometry of solid samples and nonavailability of solid thorium standards, non-destructive radiometric determination of thorium is difficult. Conventionally, determination of thorium is performed by EDTA complexometric titration [5]. Though this method is precise (relative standard deviation ~0.5%), it does not tolerate other complexing anions such as fluorides, carbonates etc., which are used for dissolution of refractory ThO_2 [6].

The EDTA complexometric titration method requires quantitative dissolution of solid ThO_2 samples. ThO_2 is a high temperature (fusion temperature — 3360 °C) refractory material. Thorium being a monovalent, chemically stable element, ThO_2 dissolution is generally achieved by using conc. HNO_3 with HF [7]. Several hours required for this dissolution can be reduced to 1–2 h by using microwave assisted dissolution [8]. The mechanism of dissolution of refractory material by microwave energy [9,10] is found to be superior to conventional heating [11,12]. It is desirable to eliminate the use of hazardous HF if other reagents can be used for quantitative dissolution of ThO_2. Therefore, systematic studies were performed for the dissolution of ThO_2 using complexing reagents such as formic acid and ammonium carbonate with conc. HNO_3 [6]. Though the reagents were suitable for dissolution of 50–100 mg of ThO_2, the reactions were found to lead to strong effervescence with higher amounts [13].

Thorium attacked by phosphoric acid (H_3PO_4) is historically well-known [7]. Recently, there have been many investigations on use of H_3PO_4 for immobilization of spent nuclear fuel using thorium phosphate diphosphate (TPD: $Th_4\{PO\}_4P_2O_7$) matrix [14–18]. Therefore, dissolution of sintered ThO_2 using strong (88%) H_3PO_4 was investigated. The studies were performed using conventional heating in autoclave as well as by microwave heating. Since the strong complexing of $(PO_4)^{3-}$ with Th^{4+} interferes in the complexometric determination of Th by EDTA, the yields of Th dissolved were determined by using radiometric method [19]. In this paper, studies on dissolution of sintered ThO_2 in strong H_3PO_4 are presented using a gamma spectrometric method for the determination of thorium in thorium phosphate solutions.

2. Experimental

2.1. Reagents

ThO_2 microspheres prepared by internal gelation process [20] and sintered at 1700 °C, ThO_2 powder and ThO_2 pellet sintered at 1700 °C were used for dissolution studies. The dissolution medium was 88% A.R. grade H_3PO_4. H_3PO_4 (88%) being very viscous, all the additions of H_3PO_4 were done on weight basis with 1 mL weighing 1.75 g.

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2.2. Instruments

2.2.1. Autoclave

An indigeneous autoclave with 250 mL pressure SS-316 pot was used for dissolution studies. Maximum working pressure of this autoclave is 60 bar and maximum working temperature is 300 °C. The sample was resistively heated at a programmed rate. A RTD PT-100, 3 wire temperature sensor with high accuracy (±0.4°) and linearity was housed in a thermowell reaching near to the sample. Digital temperature indicator showed the temperature of the sample during heating. The sample temperature was controlled by a PID temperature controller within ±1 K. The temperature controller gives variable heating signals depending on the set point and the proportional band of the controller.

2.2.2. Microwave system

Microwave reaction system "Multiwave 3000" supplied by Anton Par, Austria was used. It has an installed power of 1700 W delivered through 2 magnetrons of 850 W each, with an output power of 1400 W. Rotor is of 8 SXF 100 type to accommodate 8 high pressure vessels made of ceramic and PTFE-TFM (100 mL). The rotor upper plate contains a unique, hydraulic pressure sensor for simultaneous measurement of all vessels with wireless data transmission to the oven. The 8-vessel rotor is designed for high pressure reactions to be performed at 300 °C and 120 bar for several hours. Temperature measurement is achieved by means of a remote IR sensor beneath the lower outer surface of the vessels.

2.2.3. HPGe detector

HPGe detector supplied by Eurisys, France with 40% efficiency relative to a 3"×3" NaI(Tl) detector and a resolution of 2.1 keV (FWHM) at 1408 keV of ^{152}Eu was used for non-destructive gamma spectrometric analysis. The detector was coupled to a PC based 4K multichannel analyzer.

2.3. Procedure

2.3.1. Dissolution studies in autoclave

Weighed amounts (~100 mg) of sintered ThO_2 were taken in five different quartz beakers. To each beaker, ~8 g of 88% H_3PO_4 was added. Each beaker was heated up to a certain temperature; i.e. 100 °C, 150 °C, 160 °C and 170 °C for different times.

Weighed amounts (~100 mg) of sintered ThO_2 were taken in six different quartz beakers. To each beaker, ~8 g of 88% H_3PO_4 was added. Each beaker was heated at 170 °C for different times.

About 1 g of sintered ThO_2 powder, ~100 mg of sintered ThO_2 microspheres and ~17 g of sintered ThO_2 pellet were heated separately, at 170 °C with ~6.5 g of 88% H_3PO_4 for 1 h.

2.3.2. Dissolution studies in microwave system

Weighed amounts (~100 mg) of sintered ThO_2 microspheres were taken and mixed with different amounts of 88% H_3PO_4. The microwave energy was supplied at 425 W and 375 W for 60 min.

Weighed amounts (~100 mg) of sintered ThO_2 microspheres were taken and mixed with ~5.2 g of 88% H_3PO_4 with different volumes of distilled water. The microwave energy was supplied at 375 W for 60 min.

2.3.3. Determination of % yield of dissolved Th

In all the studies, the % yield of dissolved Th was determined by high resolution gamma spectrometry monitoring 911.4 keV gamma of ^{228}Ac [19] which is a daughter product of ^{232}Th.

3. Results and discussions

With the advent of thorium fuel technology, various forms of thoria such as ThO_2 powder, ThO_2 microspheres and ThO_2 pellet were investigated for their dissolution behavior. Even mixed oxide fuels like $(Th,U)O_2$, $(Th,Pu)O_2$ and $(Th,U,Pu)O_2$ are also being studied. Pure ThO_2 cannot be dissolved in nitric acid; but even a small fraction of uranium in $(Th,U)O_2$ yields a certain solubility [21]. Dissolution of sintered ThO_2 in conc. HNO_3 is extremely slow and it is thermodynamically unfavorable [22]. Sintering increases the density of material and it becomes less prone to dissolution [23]. Considering these challenges, we selected sintered (1700 °C) ThO_2 microspheres for dissolution studies.

Single oxidation state (+4) exhibited by thorium in aqueous solutions makes it non-amenable to oxidative–reductive dissolution techniques. Therefore, HF is used with nitric acid for endothermic dissolution of thoria [7]. Presence of fluoride is undesirable due to its corrosive nature [24]. Use of complexing reagents such as formic acid and ammonium carbonate was found to be unsuitable with higher amounts of thoria. Therefore, we decided to study use of concentrated (88%) H_3PO_4 as a dissolvent.

The initial autoclave studies showed that ~100 mg of sintered ThO_2 microspheres did not appreciably dissolve in ~8 g of 88% H_3PO_4 at 100 °C. Since boiling point of 88% H_3PO_4 is in the range 153–158 °C, it was decided to study dissolution pattern above boiling point of 88% H_3PO_4 in a closed system under pressure. The results are shown in Table 1. These studies established that ~100 mg of sintered ThO_2 microspheres quantitatively dissolved in ~8 g of 88% H_3PO_4 at 170 °C. To confirm the results, ~100 mg of sintered ThO_2 microspheres with 88% H_3PO_4 in autoclave was subjected to heating at 170 °C for different length of time. The %yield of dissolved thorium is shown in Table 2. The results showed that for maximum dissolution of ThO_2 in the autoclave, the minimum temperature required is 170 °C and isothermal heating at this temperature is for a minimum of 3 h at a pressure of 1.4 bar. These experiments also confirmed that dissolution of thoria is a highly endothermic reaction as reported by many authors [8,24].

To study the effect of surface properties of materials on their dissolution, sintered ThO_2 microspheres, sintered ThO_2 powder and sintered ThO_2 pellet of different amounts were subjected to dissolution in autoclave. The results of % yields of dissolved ThO_2 are given in Table 3. From this table, it can be seen that dissolution of powdered ThO_2 is quantitative in contrast to that of microspheres or pellet. This observation shows that dissolution of ThO_2 increases with increase in surface area of the material [23,24] and the large surface area makes the material more susceptible to attack by dissolvent. Hence from this study, it is clear that for dissolution of sintered ThO_2, energy of activation$_{Powder}$<energy of activation$_{Microsphere}$<energy of activation$_{Pellet}$ [23].

Microwave heating technique has its unique advantages such as fast processing time, less consumption of reagents and adaptability to glove-box/hotcell [8]. ~100 mg of sintered ThO_2 microspheres was subjected to microwave radiation at parameters shown in Tables 4 and 5. Effect of high temperature on containers can be seen clearly. %

Table 1
Dissolution of sintered ThO_2 microspheres using H_3PO_4 at different temperatures and for different times in an autoclave.

Weight of ThO_2 (g)	Weight of H_3PO_4 (g)	Temperature (°C)	Time (min)	Th dissolved (%)
0.1013	8.0253	100	60	Negligible
0.1057	8.0321	100	180	10±0.20
0.0944	8.0394	150	120	25±0.05
0.0934	8.0451	160	120	51±0.09
0.1020	8.0413	170	180	98±2.00