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Dissolution Study of Thorium-Uranium Oxides in Aqueous Triflic Acid Solutions

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Abstract

The dissolution of sintered mixed oxides of thorium with uranium in various concentrations of trifluoromethanesulfonic (triflic) acid solutions was investigated under reflux conditions to evaluate the suitability of the method. Various fragment sizes (1.00 mm < x < 7.30 mm) of sintered $(Th,U)O_2$ and simulated high-burnup nuclear fuel (SIMFUEL) were almost completely dissolved in a few hours, which implies that triflic acid could be used as an alternative to the common dissolution method, involving nitric acid-hydrofluoric acid mixture. The influence of acid concentration, composition of the solids, and reaction time on the dissolution yield of Th and U ions was studied using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The dissolution rate was found to depend upon the triflic acid concentration and size of the solid fragments, with near complete dissolution for the smallest fragments occurring in boiling 87% w/w triflic acid. The formation of Th and U ions in solution appears to occur at the same rate as the triflic acid simultaneously reacts with the constituent oxides as evidenced by the results of a constant U/Th concentration ratio with the progress of the dissolution.

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Keywords: Dissolution kinetics; Triflic acid; Thorium-Uranium oxides; Nuclear fuel; Sintered mixed oxides

1. Introduction

Thorium dioxide, also known as thoria, is of great interest for its potential use in nuclear energy applications[1]. However, implementation of thorium fuel cycle processes still has significant challenges[1,2]. Several researchers have

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argued that the barrier to the potential development of thorium-based oxide fuels lies in the development of reprocessing steps and subsequent refabrication[2]. The most viable method for reprocessing spent thorium-based fuels, the THORium - uranium EXtraction (THOREX) process, does not have an efficient method of dissolution of sintered thorium oxides. Of the metallic oxides, thorium dioxide, especially sintered ThO_2, is the most difficult to dissolve in acidic media. The complete dissolution of the ThO_2 matrix is one of the major steps necessary in extracting ^{233}U and other valuable radionuclides from the spent thorium-based nuclear fuels. At present, most thorium-containing oxides are dissolved in a mixture of nitric acid and hydrofluoric acid[3]. The main disadvantages of this approach are that it has low dissolution rates and requires special containers due to the great corrosiveness of hydrofluoric acid. Moreover, the dissolution process propagates the loss of a considerable amount of HNO_3 because of volatilisation as NO_x gases, which are hazardous to the environment, and often cause corrosion of various pieces of process equipment. Therefore, it is desired to develop a robust and cleaner dissolution process so as to achieve the maximum utilization of thorium resources.

A method for dissolving ThO_2 with concentrated trifluoromethanesulfonic (triflic) acid solution was suggested by Lyczko and co-workers[4], with an objective to increase the rate of dissolution, reduce corrosion and reduce the amount of waste generated. In this process, ThO_2 powder (sintered at 1200 °C for 30 hours) is dissolved in concentrated triflic acid under reflux conditions. Their experimental results showed a substantial increase in the rate of dissolution for ThO_2 in triflic acid compared to that of the nitric acid-HF mixture. The study also indicates that concentrated triflic acid can be used as an effective solvent for Th-based nuclear fuel dissolution. Recently in our laboratory, we used triflic acid to dissolve sintered thorium-uranium mixed oxides (sintered at 1700 °C for 6 hours). Our interest was to further study the chemical dissolution of sintered $(Th,U)O_2$ and simulated high-burnup nuclear fuel (SIMFUEL) in order to establish the best conditions and parameters that can provide dissolution rates acceptable for a plant-scale process. Here, we describe the results of our experiments on the dissolution of UO_2 powder, ThO_2 powder, sintered $(Th,U)O_2$ and SIMFUEL fragments in triflic acid solutions. The influence of acid concentration, composition of the solids and reaction time on the dissolution yield of thorium and uranium ions were investigated using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS).

2. Experimental

2.1. Materials

Trifluoromethanesulfonic "triflic" acid (CF_3SO_3H, Sigma-Aldrich®, 98% w/w, Lot #MKBK5422V) was used as received. The required stock solution of triflic acid was prepared using deionized water under atmospheric conditions in a fume hood. As this is a strong, corrosive and fuming acid, the triflic acid solution with concentration of 87% w/w was obtained by carefully adding 300 g of triflic acid to 40.8 mL water in a glass container. Triflic acid stock solution was standardized by titration against tris (hydroxymethyl) aminomethane (THAM, Alfa Aesar certified ACS, 99.8 – 100.1%, Lot #B01Z051), to an estimated accuracy of ± 0.2%. Additional solutions with concentrations of 74% w/w and 63% w/w were made by dilution of the prepared stock solution using deionized water. Deionized water (resistivity 17.4 MΩ·cm at 25 °C) was used to prepare all the solutions.

Samples of unirradiated UO_2 powder, unirradiated ThO_2 powder, unirradiated $(Th,U)O_2$ sintered solid solutions and SIMFUEL were obtained from the Fuel Development Branch at Canadian Nuclear Laboratories (CNL). The UO_2 powder used in these experiments was ceramic grade UO_2 containing natural U, i.e., 0.7% ^{235}U. Thoria powder was obtained from Rhodia Terres Rares (99.99%, Batch #9815301). The average particle size of the ThO_2 powder as indicated on the certificate of analysis was 1.5 µm. Fragmented material ($1.0\ mm < x < 7.3\ mm$) was obtained from three kinds of $(Th,U)O_2$ pellet samples: unirradiated $(Th,U)O_2$ pellets with 1.5% UO_2 in ThO_2, unirradiated $(Th,U)O_2$ pellets with 13% UO_2 in ThO_2, and SIMFUEL pellet corresponding to burn-up of 43 GWd/t. The $(Th,U)O_2$ pellets were made by mixing ThO_2 and UO_2 powders, followed by cold pressing and sintering at around 1700 °C for 6 hours. The SIMFUEL pellet was prepared by co-grinding ThO_2 and UO_2 with the oxides of 11 stable elements representing the non-volatile fission products in high-burnup nuclear fuel. The $(Th,U)O_2$ with 1.5% UO_2 and SIMFUEL pellets had densities of 9.69 $g \cdot cm^{-3}$ and 9.38 $g \cdot cm^{-3}$, respectively. The initial colour of the fragments obtained from the pellets varied from white to black depending on the UO_2 content in the $(Th,U)O_2$. Weights of the solids were measured to 0.0001 g using a calibrated Quintix®- Sartorius YDK03 analytical balance.