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Effect of the microstructural morphology on UO_2 powders

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Abstract

Several UO_2 powders with different morphologies were synthesized and characterized. Three different morphologies were synthesized thanks to sol gel process (big heap of about 200 μm wide consisting of sintered crystallites) on the one hand, and to oxalic precipitations (one square platelet morphology and one hexagonal stick morphology) on the other hand. Significant differences in dissolution kinetics were observed. Therefore, the morphology of the powders was found to be a key parameter that has to be considered in studies of UO_2 dissolution kinetics. The second part of the study consists in dissolving in nitric acid in the same operating conditions three UO_2 powders having different crystallites sizes. It was shown that dissolution kinetics is dependent on the morphology but also on the powder stoichiometry.

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1. Introduction

The dissolution of spent nuclear fuel in nitric acid is one of the main steps of nuclear fuel recycling by hydrometallurgical process. For this purpose, it is useful to fully understand and quantify the impact of fuel characteristics on uranium dioxide dissolution kinetics. In this study, a focus on the impact of the oxide morphology on dissolution kinetics was done. Morphology is a general term whose influence on dissolution kinetics of UO_2 is not well referenced in the scientific literature. Some questions remain unanswered: what are the relevant parameters to be used to define the morphology versus its influence on the dissolution kinetics? Agglomerate size, grain size,

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form that could be expressed as a wide/length ratio, specific surface area? Some studies have already been realized¹ determining nitric acid attack takes place at the grain boundaries. This paper presents our contribution done recently in the Atalante facility at CEA Marcoule to understand the phenomena occurring during the dissolution of actinide oxides in nitric acid.

2. Experimental section

2.1. Synthesis of powders

As the aim of this study is to elucidate the effect of the morphology of the powder on its dissolution, different synthesis routes had to be used to make different UO_2 samples exhibiting different morphologies. In all cases, concentration, purity and oxidation of monometallic solutions were determined by UV-visible spectroscopy.

2.1.1. Oxalic route

The oxalic conversion is usually reported to synthesize actinide oxides^{2,3}. This process is based on an oxalic precipitation followed by a calcination step under controlled atmosphere. In this study, UO_2 is obtained by uranium (IV) oxalic precipitation. In details, uranium (IV) solution was prepared by catalytic reduction of uranium (VI) nitrate by H_2 on a Pt/Si support. Hydrazinium nitrate (N_2H_5^+) was used as an anti-nitrous agent to stabilize the uranium to the oxidation states +IV. The uranium precipitate was obtained by mixing oxalic acid and the U(IV) nitrate solution.

2.1.1.1. Platelet morphology

Concentrations were fixed in order to reach in the precipitator a final concentration of nitric acid equal to 2M and an oxalic excess. Under this conditions, tetravalent actinides form an oxalate of formula $\text{An}^{\text{IV}}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}^4$. This oxalate has a monoclinic structure and crystallizes as agglomerate square-plates⁵. Obtained-precipitate was filtered off and rinsed with a water/ethanol mixture (10/90) before being air dried.

2.1.1.2. Hexagonal morphology

Hexagonal stick morphology can be obtained with the synthesis of another oxalate: $\text{U}_2\text{M}_2(\text{C}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$ (with $\text{M}^+ = \text{H}_3\text{O}^+, \text{N}_2\text{H}_5^+$). To obtain this oxalate rather than the first one giving a platelet morphology, concentration of oxalic acid was increased while amount of nitric acid decreased. The concentration of hydrazinium nitrate was fixed and equal to approximately 0.25 mol.L^{-1} . The so obtained-precipitate was filtered off and rinsed with a water/ethanol mixture (10/90) before being air dried.

2.1.2. Sol-gel route

Articles referring to the sol-gel method deal with the synthesis of microspheres.^{6,7} In this work, to synthesize powders, protocol was modified as follows. A 1.7 M U(+VI) monometallic nitrate solution was obtained through dissolution of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ in pure water. This metal nitrate solution was mixed with urea ($\text{CO}(\text{NH}_2)_2$) and HMTA (hexamethylenetetramine) solution at low temperature ($\sim 5^\circ\text{C}$). Urea acts as a complexing agent of U(VI) preventing from premature precipitation of this cation when HMTA is added. The $[\text{urea}] / [\text{U}]$ and $[\text{HMTA}] / [\text{U}]$ used ratios were respectively 1.74 and 1.71. Once urea and HMTA were dissolved into the cold uranyl solution, the solution was stirred and heated at 80°C . HMTA was decomposed at high temperature causing an increase in pH and hydrolysis of uranium. In a few minutes, the solution gelled. At room temperature, this gel was washed with NH_4OH allowing the elimination of the remaining organic matter provided by the reagents. The washed gel was dried at 250°C for 20 hours to obtain an UO_3 and to remove residual ammonium nitrate and moisture.

2.1.3. Heat treatments

Heat treatments were performed for all precursors (oxalate and UO_3) up to 1127K with a rate of 20 K.min^{-1} . Compounds were maintained to this temperature for 90 min then cooled down to room temperature. Different calcination atmospheres were used in order to obtain in all cases UO_2 powders. So-obtained oxalate characteristic of platelets morphology powder was then divided into three batches: one was calcined under Ar/H_2 (96/4) reducing

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