

# Dissolution of uranium mixed oxides: The role of oxygen vacancies vs the redox reactions



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## ABSTRACT

While uranium-based mixed oxides are interesting materials for several concepts of nuclear reactors, the effects of trivalent elements in the fluorite structure and the redox reactions at the solid/solution interface during the dissolution of such compounds remain widely unknown. In order to underline the influence of those parameters, various dissolution experiments were carried out on different compositions (i.e.  $U_{0.75}Ce_{0.25}O_2$ ,  $U_{0.75}Th_{0.25}O_2$ ,  $Th_{0.75}Nd_{0.25}O_{1.875}$  and  $U_{0.75}Ln_{0.25}O_{1.875}$  with  $Ln = Nd, Gd$ ). These tests were performed on sintered pellets in nitric acid solutions (from  $10^{-2}$  M to 4 M) at different temperatures ( $22^\circ\text{C}$ – $90^\circ\text{C}$ ) under dynamic conditions. Therefore, a multiparametric study of the dissolution kinetics was then achieved in order to determine the partial order of dissolution reaction regarding to  $H_3O^+$  activity and the activation energy. The obtained results gave evidence of the strong dependency of the dissolution rate with the nitric acid concentration. In fact, for concentrations higher than 2 M, the dissolution process is almost controlled by the oxidation of U(IV) to U(VI). On the contrary the effect of oxygen vacancies became predominant for acid concentrations lower than 0.5 M. Under these conditions, the systems containing trivalent elements exhibited the lowest chemical durability. The partial order of the reaction regarding to the  $H_3O^+$  activity reached  $n = 2.1$  for  $U_{0.75}Th_{0.25}O_2$  and was found to be constant over the entire acidity range. A variation of the partial order of the dissolution reaction regarding to  $H_3O^+$  was observed along the nitric acid concentration range for  $U_{0.75}Ln_{0.25}O_{1.875}$  solid solutions, that underlines the predominance of different controlling reactions in the dissolution mechanism: surface-controlling reaction involving  $H_3O^+$  at low pH (i.e.  $n < 1$ ) for  $C_{HNO_3} \leq 0.5$  M, and uranium oxidation (i.e.  $n > 1$ ) for  $C_{HNO_3} \geq 1$  M.

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## 1. Introduction

Mixed actinide dioxides are currently used as fuels in Pressurized Water Reactors (PWR, including Gen III reactors) and also stand as preferential candidates for several Gen IV concepts including Sodium-cooled Fast Reactor (SFR) or Gas-cooled Fast Reactor (GFR) (Hoffelner, 2005). Moreover, the reprocessing of minor actinides into mixed-oxide fuels or in  $UO_2$ -based blankets surrounding the core is often considered (Tommasi et al., 1995). It is thus necessary to obtain insights about the different mechanisms of dissolution concerning these compounds. In addition, the chemical durability of such compounds must be also evaluated under the chemical conditions encountered in the vicinity of direct disposal

repository settings, because several countries have chosen the “open cycle” option (Hedman et al., 2002; Rosborg and Werme, 2008).

Although, the dissolution of urania ( $UO_2$ ) is rather well described in literature either under anoxic or oxidic conditions, there is a growing interests on  $ThO_2$ ,  $CeO_2$  and associated solid solutions dissolution (Claparede et al., 2011a, 2011b; Horlait et al., 2011; Akabori and Shiratori, 1994; Greiling and Lieser, 1984; Hubert et al., 2001). Therefore, the role of several physico-chemical parameters was recently investigated, either related to the dissolution medium (temperature, pH, complexing agent) (Claparede et al., 2011b), or related to the structural properties of the solid solution (oxygen vacancies, crystal defects) (Claparede et al., 2011a; Horlait et al., 2011) and to the microstructure (cation distribution, pellet density, grain size). Such studies suggest the existence of surface controlling phenomena at the solid/liquid interface for several kinds of solid solutions (Heisbourg et al., 2004, 2003). Indeed, the partial order related to the proton activity ( $0 < n < 1$ ), as well as the activation energy ( $50$ – $80$   $\text{kJ mol}^{-1}$ ) were found to be too high to

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correspond to pure diffusion controlled reactions and too low to be associated to the direct break of covalent bonds and the subsequent detachment of elements from the solid to the solution (Rose, 1991; De Pablo et al., 1999; Terra et al., 2003). These results suggest the existence of a three steps control of the dissolution mechanism. It involves first the adsorption of aqueous species from the solution, reaction of adsorbed species between themselves or with atoms at the solid surface, then the release of the elements from the solid to the solution. The effect of incorporation of trivalent element in the fluorite structure on the dissolution kinetics of cerium and thorium-based oxides was also evaluated (Horlait et al., 2012a, 2012b). The chemical durability of  $Ce_{1-x}Ln_xO_{2-x/2}$  or  $Th_{1-x}Ln_xO_{2-x/2}$  oxides was found to decrease strongly with the increasing lanthanide element content as a result of the material weakening (the chemical durability being decreased by one order of magnitude each 9% of trivalent element incorporated in the fluorite structure).

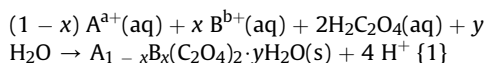
Unlike thoria, ceria and associated solid solutions, the dissolution of urania is highly sensitive to the redox conditions setting in the solution due to the oxidation of U(IV) to U(VI). This oxidation affects strongly the chemical durability of  $UO_2$  compared to the  $ThO_2$  and  $CeO_2$  systems. Thus, the normalized dissolution rate of  $UO_2$  in oxidizing media is six to eight orders of magnitude higher than that of  $ThO_2$  and  $CeO_2$ . However, the impact of the lanthanide element incorporation and the subsequent formation of oxygen vacancies on the dissolution mechanism of uranium-based oxides remain widely unknown.

The aim of this work is thus to evaluate the impact of the structural properties (occurrence of oxygen vacancies) on the kinetics of dissolution and/or leaching for selected model compounds which could exhibit redox reactions:  $U_{0.75}Ce_{0.25}O_2$ ,  $U_{0.75}Th_{0.25}O_2$ , and  $U_{0.75}Ln_{0.25}O_{1.875}$  (with  $Ln = Nd, Gd$ ). Such study should allow us to quantify the particular contribution of uranium oxidation (from the comparison between the behaviour of  $U_{0.75}Ce_{0.25}O_2$  and  $U_{0.75}Th_{0.25}O_2$  with that of  $Th_{0.75}Ce_{0.25}O_2$ ) and of the presence of crystal defects associated to the presence of oxygen vacancies in  $An^{IV}/Ln^{III}$  solid solutions (from the direct comparison of the behaviour of  $Th_{0.75}Ce_{0.25}O_2$  and  $Th_{0.75}Nd_{0.25}O_{1.875}$  with that of  $U_{0.75}Ln_{0.25}O_{1.875}$ ).

## 2. Material and methods

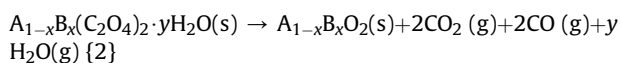
### 2.1. Preparation and characterization of the solids

All the studied oxides were prepared by the conversion of their corresponding oxalate precursors (Hubert et al., 2001; Arab-Chapelet et al., 2007). The initial oxalate precursors (1 g) were synthesized by mixing the cationic solutions with the calculated ratio of elements (in hydrochloric media) and the oxalic acid solution (1 M, large excess) at room temperature, under stirring (Claparede, 2011). Then, the precipitation of the oxalate precursor occurred immediately with a high yield according to the following chemical reactions:



The obtained powders were washed with deionized water and ethanol, filtered or centrifuged then dried overnight in an oven at 90 °C.

Then, the expected oxide solid solutions were obtained after heating the initial precursors in alumina crucible at 500 °C either under  $Ar/H_2$  atmosphere (for uranium based compounds) or in air for 7 h, according to the following chemical reaction:



The experimental chemical composition for each oxide was then determined by the means of X-ray Energy Dispersive Spectrometry (X-EDS) coupled with the Environmental Scanning Electron Microscope (ESEM) device. Calculations were performed considering at least 10 analyses leading to an average composition ( $x$ ) with an accuracy of  $\pm 0.01$ . Powder X-Ray Diffraction (PXRD) patterns were recorded with the use of the Bruker D8 diffractometer in the Bragg-Brentano geometry from 20° to 120° with a step of 0.01° and a counting time of 1.5 s per step. For all the samples, the determined chemical composition obtained from X-EDS and PXRD refinement agreed well with the expected values according to the quantitative precipitation of actinide and lanthanide elements as oxalate precursors (recovery yield higher than 99%) and also with the formation of homogeneous and single phase samples. Similar results were already reported for  $An(IV)/An(III)$  or  $An(IV)/Ln(III)$  systems (Arab-Chapelet et al., 2007; Claparede, 2011; Horlait, 2011). The specific surface area of the prepared oxide powders, determined from  $N_2$ -adsorption (BET method) using a Micrometric ASAP 2020 apparatus ranged from  $5.0 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$  to  $20.0 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ .

After a thorough characterization of the powders, the samples were compacted into cylindrical pellets of 5–8 mm in diameter through a uniaxial pressing at 200 MPa at room temperature. The obtained green pellets were sintered under reducing atmosphere (for uranium based compounds) or in air at 1550 °C during 8 h in order to reach a high densification rate of at least 92% compared to the calculated density. The main characteristics of the prepared sintered samples are gathered in Table 1.

### 2.2. Dissolution experiments

The dissolution tests were performed using batch experiments at different temperatures in various nitric acid media. For each dissolution experiment, the sintered pellets (same microstructure: relative density, specific surface area, cationic homogeneity, etc.) were contacted with 25 mL of solution in a polytetrafluoroethylene (PTFE) container from few hours to several months. The rate of renewal of the solution,  $q$  ( $\text{mL h}^{-1}$ ) was then adjusted between  $2.5 \text{ mL h}^{-1}$  and  $40 \text{ mL h}^{-1}$  depending on the nature of the studied material and the expected dissolution rate in order to avoid the establishment of saturation processes (Claparede et al., 2011a; Hubert et al., 2001; Heisbourg et al., 2003; De Pablo et al., 1999; Horlait et al., 2012b; Taylor et al., 1963). The dissolution of the solid was then monitored through regular uptakes of the leachate and the analysis by ICP-AES (Spectro Arcos) of the elementary concentrations,  $C_i$  ( $\text{g L}^{-1}$ ).

The normalized weight loss ( $N_L$ ,  $\text{g m}^{-2}$ ) for each element was calculated from the elementary concentrations (Thomas et al., 2000) after normalization by the reactive surface ( $S$ ,  $\text{m}^2$ ) of the solid in contact with the solution and by the mass ratio of the considered element in the solid ( $X_i$ ,  $\text{g g}^{-1}$  calculated as the ratio

**Table 1**

Properties of the sintered pellets of fluorite-type actinide and actinide/lanthanide oxide samples (two duplicates).

Expected chemical formula	$x$ (exp) (from EDS)	100 $\rho_{\text{exp}}/\rho_{\text{cal.}}$ (%) <sup>*</sup>
$U_{0.75}Nd_{0.25}O_{1.875}$	$0.26 \pm 0.01$	$97 \pm 1$ $98 \pm 1$
$U_{0.75}Gd_{0.25}O_{1.875}$	$0.27 \pm 0.01$	$96 \pm 1$ $95 \pm 1$
$U_{0.75}Th_{0.25}O_2$	$0.24 \pm 0.01$	$97 \pm 1$ $95 \pm 1$
$U_{0.75}Ce_{0.25}O_2$	$0.24 \pm 0.01$	$96 \pm 1$ $95 \pm 1$
$Th_{0.75}Nd_{0.25}O_{1.875}$	$0.27 \pm 0.01$	$95 \pm 1$ $94 \pm 1$

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