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Behavior of thorium–uranium (IV) phosphate–diphosphate sintered samples during leaching tests.

Part I – Kinetic study

N. Dacheux [a,*], N. Clavier [a], J. Ritt [b]

[a] Groupe de Radiochimie, Institut de Physique Nucléaire, Bât.100, Université Paris-Sud-11, 91406 Orsay, France
[b] IRSN, Laboratoire de Radiochimie, BP 17, 92262 Fontenay aux Roses, France

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Abstract

The dissolution of β-TUPD sintered samples was examined in various conditions of pH, temperature, concentrations of anions in the leachate and leaching flow rates. All the normalized dissolution rates were in the range 10^{-7} to 10^{-4} g m^{-2} day^{-1} even in very aggressive media, showing the good resistance of these ceramics to aqueous alteration. The first part of this paper describes several parameters exhibiting a significant influence on the normalized dissolution rate of the pellets prepared. Both the partial order relative to the proton concentration ($n = 0.39$–0.41) and the apparent activation energy ($E_{app} = 49$ kJ mol^{-1}) were found in good agreement with the data reported for powdered samples showing that the sintering process does not degrade the chemical durability of the ceramics. Moreover, due to the high thermodynamical constant of complexation of phosphate species for tetravalent uranium and thorium, the influence of other ligands such as nitrate, chloride or sulphate on the normalized dissolution rates was limited. Near the equilibrium, the increasing of the leaching time, the temperature or the leachate acidity led to the thorium precipitation at the surface of the pellets either in static or in dynamic conditions. Consequently, the dissolution became clearly incongruent and controlled by saturation processes which are described in the second part of this paper.

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1. Introduction

In order to answer to several points mentioned in the French law relative to the radioactive waste management and, as instance, to the immobilization of actinides and fission products in the field of an underground repository [1], a French research group called NOMADE was constituted. One of the aim of the study was to examine several ceramics for the final disposal of minor actinides (Np, Am, Cm) or plutonium excess with weight loadings up to 10 wt%, exhibiting good sintering properties, low normalized dissolution rates during dissolution and good resistance to irradiation [2]. In this context, the chemistry of uranium and thorium

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[*] Corresponding author. Tel.: +33 1 69 15 73 46; fax: + 33 1 69 15 71 50.

E-mail address: dacheux@ipno.in2p3.fr (N. Dacheux).

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phosphates was completely reexamined considering some interesting properties of these materials for such an application [3–7].

Based on the previous properties, four matrices were selected [8]. Zirconolite ($CaZrTi_2O_7$) [2], britholites $Ca_{10-x}Nd_x(PO_4)_{6-x}(SiO_4)_xF_2$ [9], monazites $M^{III}PO_4$/brabantites $N^{II}M^{IV}(PO_4)_2$ solid solutions [10–13] and Thorium Phosphate-Diphosphate, β-$Th_4(PO_4)_4P_2O_7$ (β-TPD) [4] with derivative β-TPD/monazite composites were chosen [14]. In this objective, β-TPD was first prepared for the efficient and specific conditioning of large amounts of tetravalent actinides (up to 47.6 wt% for uranium) [15–17], leading to the formation of associated solid solutions β-$Th_{4-x}U_x(PO_4)_4P_2O_7$ (β-TUPD), β-$Th_{4-x}Np_x(PO_4)_4P_2O_7$ (β-TNpPD) and β-$Th_{4-x}Pu_x(PO_4)_4P_2O_7$ (β-TPuPD) and small amounts of trivalent actinides (<0.5 wt%) [18].

One of the main damages which could affect the host matrix consists of the infiltrations of underground water which could induce the release of the radionuclides then their migration to the biosphere. In this context, the chemical durability of these materials was extensively examined. All the leaching tests devoted to the study of the chemical durability of the powdered materials already led to conclude to the high resistance of β-TPD (and associated solid solutions) to aqueous alteration. In this field, the dissolution of β-TPD, doped or not with trivalent actinides such as ^{241}Am or ^{244}Cm, and of associated β-TPuPD solid solutions was examined from a kinetic point of view as a function of the pH [19], the temperature and the concentration of phosphate ions of the leachate [20,21]. Some preliminary results on the dissolution of β-TUPD powdered samples were also discussed [21].

β-TPD and associated β-TUPD solid solutions were prepared as sintered pellets (with a relative density of 90–99% of that calculated from crystallographic data) using a two-step procedure based on a room-temperature uniaxial pressing at 200–800 MPa then a heat treatment at 1250 °C for 5–30 h, depending on the chemical way of preparation considered [22,23]. More recently, the homogeneity of the final ceramics was significantly improved by using a new way of preparation based on the precipitation of initial low-temperature crystallized precursors, $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ (Thorium Phosphate–HydrogenPhosphate Hydrate, TPHPH) [24] and $Th_{2-x/2}U_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$ (TUPHPH) solid solutions [25]. Their high reactivity allowed to prepare dense pellets for shorter times of calcination, with associated higher relative densities (92–99% of the calculated density) and better final homogeneity [23]. The associated very low solubility reported for these precursors ($K_{S,0} \approx 10^{-67}$) [18,19] allowed to consider the quantitative decontamination of low and high level radioactive liquid waste containing actinides (Th, U, Np, Pu) through a decontamination/precipitation – immobilization chemical process [26,27].

However, the sintering process developed could degrade significantly the chemical durability of the materials due to the formation, as instance, of minor phases (usually mainly localized at the surface of the samples) or poorly crystallized zones. The aim of this paper mainly concerns the better knowledge of the successive steps of the dissolution mechanism of β-TUPD sintered samples and the evaluation of the consequences of the sintering process on their chemical durability. The first part of this paper is focused on the kinetic aspect of the dissolution of β-TUPD solid solutions while the second one is essentially dedicated to the study of the saturation processes involved near the equilibrium then to the characterization of the neoformed phases.

2. Experimental

2.1. Preparation and characterization of the β-TUPD sintered samples

β-TUPD sintered samples with several x values were prepared by wet chemistry methods [23] from low-temperature crystallized precursors through a two-step procedure including an uniaxial pressing at room temperature (200–500 MPa) then a heat treatment for 10 h at 1250 °C under inert atmosphere to avoid the oxidation of uranium (IV) into uranyl ions [25]. Among these precursors, crystallized TUPHPH solid solutions were prepared by precipitation of a mixture containing tetravalent uranium chloride ($C_U = 1.1$–1.5 M), thorium chloride ($C_{Th} = 0.7$–1.0 M) concentrated solutions and 5 M phosphoric acid [25].

The samples were extensively characterized by Electron Probe MicroAnalyses (EPMA) using a Cameca SX 50 apparatus with an acceleration voltage of 15 kV and a current of 10 nA considering $SmPO_4$ (K_α ray of phosphorus), ThO_2 (M_α ray of thorium) and UO_2 (M_β ray of uranium) as calibration standards. The counting time was fixed to 10–30 s while the size of the spot was evaluated to