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Dissolution kinetics of CeO_2 powders with different morphologies and analogy to PuO_2 dissolution

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ABSTRACT

Several CeO_2 powders with different morphologies were synthetized thanks to four different processes (two at the laboratory by sol-gel and oxalic routes and two commercial powders). These powders were divided into five batches each and calcined at several temperatures. Thus, twenty different powders were made, each possessing different structural or morphological properties. After a thorough characterization of the 20 powders, this work is dedicated to the study of their dissolution in nitric acid using the same experimental conditions to exhibit the morphology effect on dissolution kinetics. Significant differences in dissolution kinetics were observed meaning that the morphology of the powders was found to be a key parameter that has to be considered in studies of dissolution kinetics. The effect of the morphological parameters on dissolution kinetics was quantified and a kinetics law was established and then, applied with success to PuO_2 dissolution.

1. Introduction

Nuclear fuel used in pressurized water reactors consists of UO_2 (UOX) or (U,PuO_2) (MOX). Once discharged from the reactor, the spent fuel in which minor actinides (Am, Np, Cm) and fission products (from Ge to REE) have accumulated, still contains mostly uranium and plutonium (96% of the spent UOX metals as an oxide form). Treatment of the spent UOX fuel using PUREX hydrometallurgical processes, involving nitric dissolution and liquid/liquid extraction, allows the recycling of these two valuable elements as MOX fuel (Poinssot and Boullis, 2012; Poinssot et al., 2012; Clark et al., 2011; Paiva and Malik, 2004; Sarsfield, 2015). If nitric dissolution of spent UOX fuel is almost complete with only a very low quantity of remaining solid (recovery rate > 99.9%) (Treatment and Recycling of Spent Nuclear Fuel – Actinide Partitioning – Application to Waste Management, Monographie DEN, Editions Le Moniteur, France, 2008), the residues can be much important for MOX fuel. These residues are mainly composed of fission products and Pu-rich $(U,Pu)O_2$. The quantity and the Pu content of the latter is highly dependent on the initial Pu content of the MOX fuel, the burnup conditions and the method of preparation of the mixed oxide (Treatment and Recycling of Spent Nuclear Fuel – Actinide Partitioning – Application to Waste Management, Monographie DEN, Editions Le Moniteur, France, 2008; Ikeuchi et al., 2012; Carrott et al., 2012). The treatment of un-irradiated non-certified MOX is also a complementary issue to assess (Madic et al., 1992) as PuO_2 grains may be found in such materials increasing the amount of dissolution residues. Indeed, PuO_2 is very refractive to nitric dissolution exhibiting very low dissolution kinetics, particularly when sintered at high temperatures (Clark et al., 2011; Treatment and Recycling of Spent Nuclear Fuel – Actinide Partitioning – Application to Waste Management, Monographie DEN, Editions Le Moniteur, France, 2008; Madic et al., 1992; Nikitina et al., 1997a,b; Ryan and Bray, 1980; Bourgeois, 2000; Kleykamp, 1985; Kleykamp, 1999). The most common way to dissolve PuO_2 is to add a catalytic amount of fluorohydric acid to use F^- surface complexation (Clark et al., 2011; Madic et al., 1992; Nikitina et al., 1997a,b; Ryan and Bray, 1980; Berger, 1990; Gué et al., 1993; Takeuchi et al., 1971). If such solution is widely used at the laboratory scale, it suffers from some drawbacks such as the corrosion of equipment and effluent management that limits its use at industrial scale. Oxidative dissolution with the help of strong oxidant cations (Ce(IV) Ag(II), …) is another option (Clark et al., 2011; Nikitina et al., 1997a,b; Ryan and Bray, 1980; Machuron-Mandard and Madic, 1994; Bourges et al., 1986; Gelis et al., 2011; Ivanov and Nikitina, 1995a,b; Ivanov et al., 1995; Chiba et al., 1995; Horner et al., 1977a; Gombert et al., 2006) that has been implemented at La Hague plant (Normandy, France) for unirradiated non-certified PuO_2 with an electro-chemical regeneration of the oxidant cations in order to limit their required amount. If very fast dissolution rates are reached using this method, an over consumption of

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Ag(II) is observed in the presence of some fission products that would limit its use in case of the dissolution of irradiated MOX. The management of the effluents and generated products (e.g. volatile RuO_4) would also have to be considered. Therefore this method would only be implemented on dissolution residues after a first dissolution step in sole nitric acid. A full understanding of the impact of fuel characteristics and nitric dissolution parameters is then needed to dimension the first step of the MOX dissolution process. If some previous studies deals with the impact of the Pu content on $(U,Pu)O_2$ nitric dissolution kinetics (Uriarte and Rainey, 1965; Vollath and Wedemeyer, 1985), none of these studies consider the effect of the morphology except a normalization to the specific surface area. However, geochemical studies show differences between specific surface area and reactive surface area without the suggestion of a formula linking these two surfaces (Beckingham et al., n.d.; Fournier et al., 2017). Then, prior to determine more precisely the influence of Pu content of the mixed oxide on its dissolution kinetics the determination of morphologic effects appears to be a first priority.

Cerium oxide has many similarities with plutonium oxide, notably in terms of its crystalline structure (Kim et al., 2008) but also on some chemical properties (Joret, 1995). Although the kinetics of dissolution of cerium and plutonium oxides may not be exactly the same, the cerium is a non-radioactive element and so its manipulation is less restrictive than the plutonium one, which can only be handled in a glove box. Cerium oxide is well-known as a good non-radioactive analogue for dissolution of plutonium dioxide studies (Beaudoux et al., 2015; Beaudoux et al., 2016; Tyagi et al., 2002; Gaillard et al., 2014). Several research studies are already dealing with the dissolution of CeO_2 pellets in nitric acid weakly concentrated (Stennett et al., 2013; Horlait et al., 2012). These authors concluded to a refractory dissolution of CeO_2 materials in this media as it is the case for PuO_2. Therefore, CeO_2 was chosen in this study as a surrogate of PuO_2 to determine the morphology effects on dissolution kinetics.

In parallel with this, since the 1980s, CeO_2 is used in the automotive pollution control. It has become so broad to evolve the most important application of the rare earth oxides (Kaspar et al., 1999).The automotive catalytic converters are composed of a stainless steel casing incorporating a honeycomb ceramic monolith which allows the conversion of harmful and toxic gases into environmentally inert substances. This ceramic is recovered after a washcoating process by cerium-based oxide combined with platinum group metal (e.g. Pt, Rh, Pd). This process is responsible for the catalytic function of the converters (Math and Manjunath, 2016). The rising demand for more efficient catalytic converters coupled with the economic and demographic development of emerging countries have continuously increased the price of these metals. Recycling such materials appears nowadays as an economically viable alternative. Selective or simultaneous dissolution of cerium-based oxides appears in consequence as a promising alternative strategy in order to recover selectively rare earth and platinoids (Rumpold and Antrekowitsch, 2012; Bleiwas, 2013). Currently, cerium recycling is not performed for catalysts recovered from automotive industry. However, each automotive catalytic converter may contain up to 80 g of cerium oxide (Patent CN 101362091 A, 2009). There is therefore a major interest in studying the dissolution of CeO_2 for this industry. Several research studies have already been carried out on Ce and platinoids recovery processes by ultrasound-assisted dissolution (Beaudoux et al., 2015; Beaudoux et al., 2016).

In a first part, a study using ceria will be conducted to eliminate morphological parameters having an insignificant influence on dissolution rates and a kinetics law is established. In a last part, validation tests on plutonium dioxide will be presented to perfect the demonstration of the influence of morphological characteristics on the dissolution kinetics of the actinide oxides of fluorine structure.

This paper presents our contribution done recently in Atalante facility at CEA Marcoule to understand the phenomena occurring during the dissolution of ceria in nitric acid and its application to the dissolution of actinide oxides.

2. Experimental section

2.1. Synthesis of materials

2.1.1. CeO_2 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 CeO_2 samples exhibiting different morphologies. In all cases, concentration and purity of monometallic solutions were determined by ICP-AES.

2.1.1.1. Oxalic route. The oxalic conversion is usually reported to synthetize actinide oxides (Grandjean et al., 2009; Hingant et al., 2011; Abraham et al., 2014; Grandjean et al., 2005). This process is based on an oxalic precipitation followed by a calcination step under controlled atmosphere. In this study, CeO_2 is obtained by cerium (III) oxalic precipitation. In details, cerium (III) solution was prepared by dissolving cerium nitrate hexahydrate (Sigma-Aldrich ref 202991, 2017) in water. The cerium precipitate was obtained by mixing oxalic acid and the Ce(III) solution. Concentrations were fixed in order to reach in the precipitator a final concentration of nitric acid equal to $1\,mol{\cdot}L^{-1}$ and an oxalic excess of $0.20\,mol{\cdot}L^{-1}$. In this conditions, oxalic precipitation of trivalent cerium leads to an oxalate of formula $Ce_2(C_2O_4)_3{\cdot}10H_2O$, exhibiting a monoclinic structure and crystallizing as stick agglomerates (Ivanov, 1970; Ollendorff and Weigel, 1969; Tamain et al., 2013). The so-obtained precipitate was filtered off and rinsed with a water/ethanol mixture (10/90) before being air dried and calcined under air atmosphere.

2.1.1.2. Sol-gel route. Articles referring to the sol-gel method deal with the synthesis of microspheres (Vaidya, 2008; Jeong et al., 2005). In this paper, to synthesize powders, protocols were modified as follows. A 2.08 M Ce(III) monometallic nitrate solution was obtained through dissolution of cerium nitrate hexahydrate in pure water. This cerium nitrate solution was mixed with HMTA (hexamethylenetetramine) solution at low temperature (~5 °C). The ratio [HMTA]/[Ce] used was equal to 2.0 (https://www.alfa.com/en/catalog/044662/, 2017). Once HMTA was dissolved into the cold nitrate solution, the solution was stirred and heated at 80 °C. HMTA decomposed at high temperature leading to an increase in pH and hydrolysis of cerium. In a few minutes, solution turned to a gel. At room temperature, this gel was washed with 2 M NH_4OH allowing the elimination of the remaining organic matter provided by the reagents. The washed gel was dried at 250 °C for 20 h to remove residual ammonium nitrate and moisture. The dried gel was then calcined under air atmosphere according to the process describe in Section 2.1.1.4.

2.1.1.3. Other powders. Two additional commercial powders were used for this study. There is little information concerning the synthesis of the commercial powders. The powder Ref 44662 (https://www.alfa.com/en/catalog/044662/, 2017) would have been prepared by sol-gel route while powder Ref 11328 (https://www.alfa.com/fr/catalog/011328/, 2017) would come from a rare-earth element separation process (cerium, samarium, neodymium and praseodymium). The manufacturer supplying these powders does not wish to give more details concerning the processes for obtaining these powders.

2.1.1.4. Thermal treatments. In order to have as many morphologies as possible (size and shape of the crystallites and agglomerates, porosity, specific surface area), each of the four powders (two commercial ones, an ex-oxalate and an ex-sol-gel) was separated into five batches each in order to carry out different thermal treatments ranging from 600 °C to 1600 °C with a ramp of $20\,°C{\cdot}min^{-1}$. Compounds were maintained at the target temperature for 90 min then cooled down to room temperature. Following their thermal treatments, the different powder batches were characterized to determine their morphology in