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Basic studies on the kinetics and mechanism of the rapid dissolution reaction of plutonium dioxide under reducing conditions in acidic media

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Abstract

Dissolution of PuO_2 in aqueous solutions is a notoriously difficult task. Until the 1980s few dissolution processes existed except those based on the use of highly corrosive solutions consisting of nitric and hydrofluoric acids at boiling temperature. Thermodynamics calculations suggest that PuO_2 dissolution can be achieved under strong oxidizing or reducing conditions, however. Basic results dealing with the reductive dissolution reaction of PuO_2 with Cr^{II} in sulphuric acid media are presented herein. Simple heterogeneous kinetics modelling is proposed and satisfactorily accounts for the reaction rates observed under various physicochemical conditions. The electron transfer mechanism was investigated by applying ^{18}O-labelling techniques, which provided striking evidence of the pure heterogeneous nature of the electron transfer reaction.

1. Introduction

It is old news among chemists working in the nuclear industry that plutonium dioxide is among the metallic oxides most difficult to dissolve in acidic media, particularly oxide that has been heated to high temperatures. However, since many industrial processes devoted to plutonium recovery are based on hydrometallurgical concepts, the dissolution of PuO_2 in aqueous solutions remains one of the major steps necessary (1) for recycling substandard PuO_2 produced in fuel-reprocessing plants and (2) for treating Pu-bearing solid wastes containing refractory plutonium oxide particles and generated by nuclear facilities as well as many research laboratories.

Until the 1980s the main method applied world wide for dissolving PuO_2 was based on the treatment of the oxide with nitric and hydrofluoric acid mixtures at boiling temperature under reflux. Such a method suffers two main drawbacks, however: on one hand, the reaction is very slow, especially for high temperature fired oxides with low specific surface area; on the other hand, highly corrosive solutions are generated owing to the presence of fluoride ions, which raises the problems of safe effluent management.

To overcome such difficulties, new concepts based on redox reactions were developed, since PuO_2 can also dissolve in aqueous solutions as oxidized or reduced forms (*i.e.* respectively Pu^{VI} and Pu^{III}). The first results dealing with the oxidative dissolution of PuO_2 using Ce^{IV} ions as oxidizing species were reported by Wilson in 1961 [1]. However, basic research providing a better understanding of the reaction thanks to the calculation of thermodynamic data on the redox properties of PuO_2 was published by Ryan and Bray in the early 1980s [2]. This work clearly demonstrated that PuO_2 dissolves in acidic media under the action of strong oxidants such as Ce^{IV}, Co^{III} or Ag^{II} and showed the way to catalysed electrolytic plutonium oxide dissolution (CEPOD) processes [3, 4].

Studies inspired by such results were carried out in France in the fall of 1981, especially using electrochemically generated Ag^{II} ions as a catalyst, which leads to the use of limited amounts of oxidant in the dissolution liquor [5–8]. Industrial facilities were designed, especially at the reprocessing plant of La Hague (Normandy), which currently permit very fast dissolution of highly refractory PuO_2 at room temperature. Unfortunately, such a process is not very efficient for treating PuO_2-bearing wastes consisting of organic matrices such as cellulosic or rubber materials. Indeed, competitive reactions of the oxidant with the reducing matrix are observed, which require very long times for total PuO_2 dissolution as well as large amounts of electricity.

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These two drawbacks can be overcome by using reducing species in non-oxidizing acidic media, in which case no competitive reactions of the reductant with the matrix are observed and the total dissolution of refractory PuO_2 can thus be achieved more efficiently. Empirical results describing the reducing dissolution of PuO_2 using hydriodic acid solutions were published many years ago, especially for analytical applications [9]. However, no basic study was published on the kinetics or mechanism of this reducing process. In the early 1990s Berger calculated thermodynamic data dealing with the overall redox properties of actinide dioxides and validated the concept of reductive PuO_2 dissolution from a thermodynamics viewpoint [10]. Indeed, the standard redox potentials published by Berger confirmed the data reported by Ryan and Bray on the oxidative process and provided similar information on the PuO_2 reductive dissolution reaction.

To gain a better understanding of the kinetics and mechanism of the reducing dissolution reaction of PuO_2, basic studies were performed at Fontenay-aux-Roses (France) [11–13]. Cr^{II} ions were selected as reducing agent owing to the chromium inner-sphere coordination properties that permit the study of the electron transfer mechanism, as will be shown below. The main results obtained in this research programme are briefly presented in this paper.

2. Results and discussion

2.1. *Thermodynamics*

As stated previously, Ryan and Bray [2] were the first to publish thermodynamic data dealing with the standard redox potential of the $Pu^{VI}/PuO_2(s)$ couple. Similar information was published about 10 years later by Berger for $PuO_2(s)/Pu^{III}$ and other common Pu oxidation states [10]. This work also included systematic calculations for light actinides (*i.e.* from U to Am). Standard potentials corresponding to various redox couples involving actinide dioxides are therefore available, which is of course necessary for predicting AnO_2 oxidation–reduction behaviour in aqueous solutions.

The data presented in Table 1 clearly indicate that the reducing dissolution of PuO_2 requires the use of potentials lower than 0.67 V *vs.* the standard hydrogen electrode (SHE). From a thermodynamics point of view, many redox couples match this requirement (*e.g.* I^0/I^-, U^{VI}/U^{IV}, V^{IV}/V^{III}, Ti^{IV}/Ti^{III}, Ti^{III}/Ti^{II}, V^{III}/V^{II}, Cr^{III}/Cr^{II}, U^{IV}/U^{III}, etc.). The corresponding reductants react with PuO_2; kinetically speaking, however, major differences exist between these reagents, which must be kept in mind when selecting the reducing agent.

Among those available, U^{IV} and Cr^{II} can also be used as probes for studying the electron transfer mechanism owing to their very particular coordination properties, as Taube reported in the 1950s [14]. Of course, the selection of U^{IV} might obviously be a good choice for nuclear applications. However, the low dissolution rates observed with U^{IV} were not satisfactory from an experimental point of view. In contrast, the higher rates observed when divalent chromium reacts with PuO_2 were more convenient and Cr^{II} was thus selected as reducing agent for performing the experiments presented below.

TABLE 1. Thermodynamic data for various PuO_2 redox couples [10]

Half-reaction	ΔG° (kJ mol^{-1})	E° (V(SHE))
$PuO_2(s) \longrightarrow Pu^{3+}(aq)$	−64.96 (±4.00)	0.67 (±0.04)
$PuO_2(s) \longrightarrow Pu^{4+}(aq)$	32.04 (±4.00)	–
$PuO_2(s) \longrightarrow PuO_2^{+}(aq)$	138.27 (±9.79)	1.43 (±0.10)
$PuO_2(s) \longrightarrow PuO_2^{2+}(aq)$	236.19 (±15.40)	1.22 (±0.06)

2.2. *Kinetics*

The determination of reaction mechanisms generally implies kinetics studies, the aim of which is to formulate an empirical rate equation that satisfactorily accounts for the reaction rate observed under various physicochemical conditions. Indeed, chemical kinetics is helpful for better understanding the overall reaction mechanism and identifying the reaction-limiting step under particular experimental conditions.

Owing to the use of Cr^{II} as strong reductant (the standard redox potential of the Cr^{III}/Cr^{II} couple is −0.41 V(SHE)), the reaction investigated was mainly performed in sulphuric acid solutions under a nitrogen atmosphere and is written as follows:

$$PuO_2(s) + Cr^{II}(aq) + 4H^+(aq) \longrightarrow Pu^{III}(aq) + Cr^{III}(aq) + 2H_2O(l) \quad (1)$$

Preliminary measurements were performed to characterize the PuO_2 samples used throughout this research programme. Among these characterizations, the PuO_2 specific surface area was determined using the Brunauer–Emmett–Teller (BET) method with nitrogen as adsorbed gas [15]. The particle size distribution was also determined by applying classical particle-counting techniques (Coulter Counter) [16]. Moreover, as shown in Fig. 1, scanning electron micrographs were taken and surprisingly revealed truncated octahedral particles, which led to a very simple geometric modelling of PuO_2 powder on the assumption of cubic particles and permitted us to apply a classical kinetics model based on isotropic reactivity [17].

By so doing, the advancement of the dissolution reaction or the dissolution yield α can easily be calculated

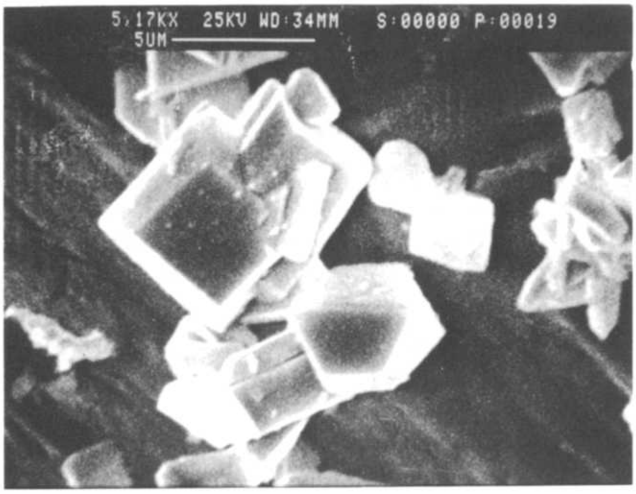

Fig. 1. Scanning electron micrograph of PuO_2 particles showing truncated octahedral shape (PuO_2 fired at 750 °C) (magnification, ×5170).

from

$$\alpha = 1 - \int_{kt}^{a_{\max}} f_g(a) F(a, t) \mathrm{d}a \qquad (2)$$

where a corresponds to the PuO_2 particle size ($a_{\max}$ is the largest PuO_2 particle size), k is the interface progression rate constant, $f_g(a)$ represents the PuO_2 particle size distribution function and $F(a, t)$ depends on the geometrical grain form and its change with time t.

For spherical particles, for example, the size parameter a is the radius of the sphere. As mentioned earlier, the particle size distribution function $f_g(a)$ was determined in a separate experiment with a Coulter Counter device, which also permitted us to estimate the largest PuO_2 particle size parameter $a_{\max}$. $F(a, t)$ is a power function of time, of the rate constant and of the particle symmetry (particle shape) and size parameters. A comprehensive treatment of this model may be found in the book by Delmon [17].

Figure 2 shows an example of experimental and computed particle size distributions corresponding to a PuO_2 sample fired at 850 °C. The log–normal function selected for size distribution modelling satisfactorily fits with the experimental data and permits us to calculate α in a very simple way thanks to eqn. (2):

$$f_g(a) = \frac{1}{a\sigma(2\pi)^{1/2}} \exp\left(- \frac{\frac{1}{2}(\ln a - m)^2}{\sigma^2} \right) \qquad (3)$$

where m and σ are constant parameters of the distribution.

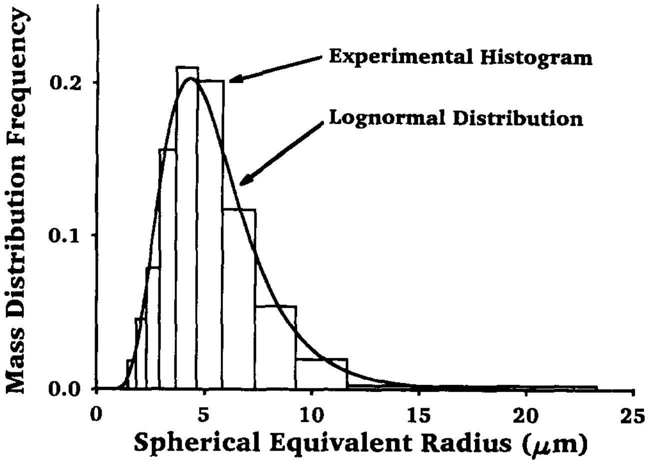

Fig. 2. Particle size distribution of PuO_2 (PuO_2 fired at 850 °C).

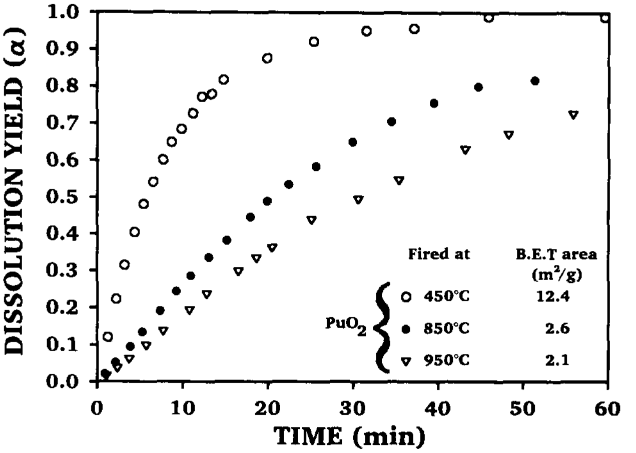

Fig. 3. Examples of influence of oxide surface area on dissolution kinetics ($[Cr^{II}]_{t=0} = 0.1$ M; $[H_2SO_4] = 1$ M; $T = 49.0 \pm 0.5$ °C; oxide mass 271 mg; volume of solution, 124 ml).

It must be pointed out that no significant change was observed in the size distributions when the samples were fired at various temperatures between 450 and 1050 °C. Consequently, the log–normal distribution was applied to every sample used throughout this study, the distribution parameters being adjusted for each sample.

This isotropic reactivity model was used to determine the rate constant k under various experimental conditions. The main physicochemical parameters investigated are the stirring rate of the PuO_2 suspension, the concentration of the reductant, the concentration of the reaction products, the reaction interface area, the temperature, the proton concentration and the hydrogen sulphate ion concentration.

As an example, experimental dissolution curves obtained for PuO_2 powders with various specific surface areas due to different firing temperatures are plotted in Fig. 3. These curves clearly illustrate the increase in the dissolution rate resulting from an increase in the interface area.

The empirical rate equation can be formulated in two different but equivalent ways. The first formulation corresponds to a macroscopic equation with a rate expressed in moles of PuO_2 per second and is written as

$$\nu = 1.8\times 10^4 A[\mathrm{H}^+]^{0.4\pm 0.1}\exp\left(\frac{(-65\pm 5)\times 10^3}{RT}\right) \tag{4}$$

where ν is the dissolution rate (in moles of PuO_2 per second), A (m^2) is the PuO_2 BET surface area measured with nitrogen, $[H^+]$ (mol l^{-1}) corresponds to the proton concentration, R is the molar gas constant (SI units) and T (K) is the absolute temperature.

The kinetics equation can also be expressed in terms of the interface linear progression rate as

$$k = 8.4[\mathrm{H}^+]^{0.4\pm 0.1}\exp\left(\frac{(-65\pm 5)\times 10^3}{RT}\right) \tag{5}$$

where k (m s^{-1}) is the linear progression rate and the other parameters are the same as those defined for eqn. (4).

Equations (4) and (5) were determined with proton concentrations ranging from 0.02 to 1 mol l^{-1} and temperatures varying between 35 and 65 °C, which permitted us to collect samples conveniently for plutonium concentration analysis and dissolution yield calculation. However, the validity limits of these equations for proton concentration and temperature were not investigated further.

The above-presented equations are only valid for fluidized PuO_2 suspensions with $[Cr^{II}]$ higher than 0.05 M. Under such conditions the reductant transportation to the reaction interface, which is controlled by molecular motion processes through the diffusion layer, is probably rapid owing to the high concentration gradient existing between the oxide surface and the bulk solution. Consequently, the chromous ion transportation cannot be considered as the rate-determining step of the reaction, which is a plausible explanation of why no influence of the reductant concentration on the overall dissolution rate was observed. Likewise, the reaction rate does not depend on the hydrogen sulphate ion concentration if it ranges from 0.1 to 1.2 mol l^{-1}. However, this observation only indicates that such ions do not take part in the rate-determining step of the reaction.

In fact, eqn. (4) shows that the dissolution rate is proportional to the interface area A and that an increase in the proton concentration leads to an increase in the reaction rate to the power of 0.4 ± 0.1. The latter empirical relationship certainly reflects the protonation of the oxide surface prior to the electron transfer reaction. Unfortunately, no satisfactory explanation was provided to account for such a proton partial kinetics order. Nevertheless, the value determined is consistent with many results dealing with other metallic oxide dissolution reactions in acidic media [18]. The temperature is also among the parameters having significant influence on the dissolution kinetics. The classical Arrhenius relation was applied and permitted us to determine an activation energy of 65 ± 5 kJ mol^{-1}, which suggests that the rate-determining step is not diffusion controlled but more probably chemically limited.

As an example of the use of the isotropic linear reactivity model, Fig. 4 provides a comparison of experimental data with the curves computed with the aid of eqns. (2), (3) and (5) under two different temperature conditions (*i.e.* at 52 and 65 °C for PuO_2 with a BET specific area of 1.24 m^2 g^{-1}). Much of the explanation for the differences observed between the experimental measurements and the model rests with the uncertainty in parameters such as the activation energy, the proton partial kinetics order and the largest particle size parameter. Nevertheless, these curves clearly indicate that the model proposed is satisfactorily validated by experiment and permits us to make good kinetics predictions.

2.3. Electron transfer mechanism

As mentioned earlier, Taube's work was epoch making owing to his introduction of new methods to investigate redox reaction mechanisms. Thus experimental procedures developed in the 1950s permit us in some cases to provide undisputed evidence of the formation of bridging groups between oxidant and reductant prior to the electron transfer reaction.

For metallic oxides the existence of hydroxyl groups at the solid–liquid interface, resulting from proton equilibria involving in part oxygen atoms initially present at the oxide surface, is well established [19]. Moreover, it is well known that adsorption equilibria and ligand exchange reactions occur between aqueous ion species

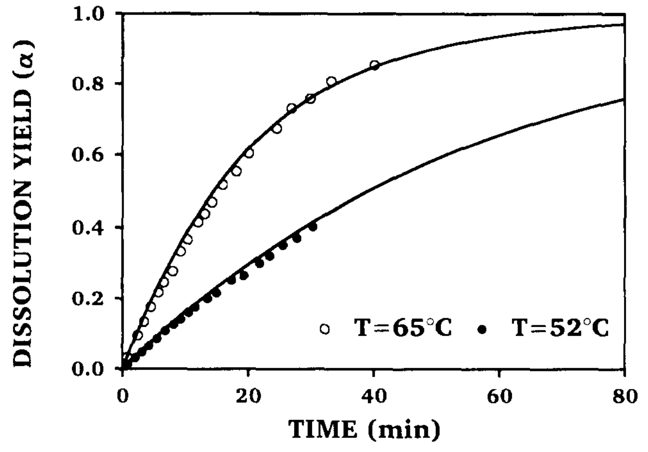

Fig. 4. Experimental and computed PuO_2 dissolution curves ($[Cr^{II}]_{t=0}=0.1$ M; $[H_2SO_4]=1$ M; oxide mass 271 mg; volume of solution, 124 ml).

in solution and such hydroxyl sites, which can lead to adsorbed inner-sphere coordination structures [20].

Consequently, the behaviour of the oxygen atoms initially present in the oxide during the dissolution reaction is of great interest and can be investigated by applying Taube's concepts. Among the procedures reported, one is based on the use of Cr^{II} ions as reducing agent owing to the fast and slow ligand exchange rates observed for Cr^{II} and Cr^{III} aqueous ion species respectively. Thus it is possible, by performing the reductive dissolution of PuO_2 consisting of natural isotope composition oxygen (*i.e.* $^{16}O/^{18}O = 99.762/0.200$ at.%) in an acidic medium enriched with ^{18}O under the action of Cr^{II}, to determine whether oxygen atoms from the oxide have been transferred to the Cr^{III} species to become oxygen atoms of its inner-sphere water molecules.

The oxygen isotope composition of the water molecules constituting the inner coordination sphere of Cr^{III} ions was determined using the method published by Taube [14]. The procedure adopted is briefly presented below.

These experiments were carried out under a pure nitrogen atmosphere, which permitted us to avoid the very fast oxidation of Cr^{II} by reaction with oxygen. Furthermore, all the solutions were carefully deaerated with nitrogen before use. The solutions were prepared extemporaneously by adding chromous sulphate ($Cr(SO_4) \cdot H_2O$) to a 1 M perchloric acid medium maintained at 90 °C. This medium was preliminarily labelled with $H_2{}^{18}O$ molecules thanks to ^{18}O-enriched water. Plutonium dioxide powder with a specific surface area of 12.35 $m^2\ g^{-1}$ was then put into the solution. The molar ratio of PuO_2 to Cr^{II} was about seven (0.4 mmol of PuO_2 reacted with 0.06 mmol of Cr^{II} in a 500 μl volume). The suspension was stirred vigorously for a few minutes and the very small excess of Cr^{II} was then converted to Cr^{III} by gently bubbling air into the solution. As reported by Ardon and Plane [21] and Zabin and Taube [22], the oxidation of Cr^{II} by oxygen molecules leads to dimeric Cr^{III} species that do not interfere with monomeric Cr^{III} ions resulting from a reaction of Cr^{II} with compounds such as oxides. The Pu^{III} species were then selectively removed by use of ferrocyanide ions and $Cr(H_2O)_6{}^{3+}$ was quantitatively precipitated from the solution as a phosphate ($Cr(H_2O)_6PO_4$) by adding solid sodium phosphate and slowly raising the pH owing to sodium acetate. The precipitate was rinsed afterwards with water and acetone before drying over P_2O_5.

Four of the six hydration water molecules with a statistical oxygen isotope distribution were extracted by heating $Cr(H_2O)_6PO_4$ at 160 °C in a quartz reaction vessel flushed with dry helium gas throughout the calcination. The water was collected in a cold trap maintained at liquid nitrogen temperature, then transferred into a sealed tube containing a mixture of $HgCl_2$ and $Hg(CN)_2$, which permits us to convert the water molecules into carbon dioxide by calcination at 400 °C for 2 h. The CO_2 produced was finally analysed by mass spectrometry, which led to the determination of the oxygen isotope composition.

TABLE 2. Data from ^{18}O-labelling experiments [12]

Experiment	R_{oxide}	$R_{solvent}$	$R_{Cr^{III}}$
1	0.20	39.73	27.2
2	0.20	39.60	30.0
3	0.20	36.88	25.7
Average value	0.20	38.74	27.6

R_{oxide}, $R_{solvent}$ and $R_{Cr^{III}}$ are ^{18}O atomic abundances (at.%) corresponding to PuO_2, solvent and $Cr(H_2O)_6{}^{3+}$ ions respectively.

The experimental data obtained under such conditions are presented in Table 2. From this triplicate experiment the number of oxygen atoms transferred from the oxide surface to the chromium was estimated to be 1.7 ± 0.5. It must be pointed out that such a result provides the earliest striking evidence that the redox reaction is located at the surface of the oxide and is therefore of a purely heterogeneous nature. On the other hand, at least one oxygen atom is transferred from the surface to the reducing species. However, the above-reported average value also indicates that a second reaction path possibly exists with the transfer of two oxygen atoms.

3. Conclusions

Among the research topics available to chemists, the metallic oxide dissolution reactions provide fascinating subjects owing to the pluridisciplinary approach required by the complex reactivity of solid–liquid interfaces. In fact, such a complexity was clearly illustrated by the results briefly presented in this paper.

Two of these results must be emphasized, however. The first is that the heterogeneous kinetics modelling proposed accounts satisfactorily for the dissolution rates measured and does not require difficult computation. The second is that the purely heterogeneous nature of the electron transfer reaction has been demonstrated conclusively in oxygen-labelling experiments. Despite these two major results, it was not really possible to identify the rate-determining step of the reaction, which probably could be due to chemical bond ruptures.

Although the overall reaction mechanism remains unclear and requires to be investigated further, new PuO_2 dissolution methods are currently being studied on the laboratory scale, on the basis of strong electrogenerated reductants in a sulphuric acid medium [23, 24]. The first results obtained are very encouraging and testify to a possible alternative to the oxidizing process for treating PuO_2-bearing wastes.

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