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Dissolution of uranium dioxide in nitric acid media: what do we know?

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Abstract. This article draws a state of knowledge of the dissolution of uranium dioxide in nitric acid media. The chemistry of the reaction is first investigated, and two reactions appear as most suitable to describe the mechanism, leading to the formation of monoxide and dioxide nitrogen as reaction by-products, while the oxidation mechanism is shown to happen before solubilization. The solid aspect of the reaction is also investigated: manufacturing conditions have an impact on dissolution kinetics, and the non-uniform attack at the surface of the solid results in the appearing of pits and cracks. Last, the existence of an autocatalytic mechanism is questioned. The second part of this article presents a compilation of the impacts of several physico-chemical parameters on the dissolution rates. Even though these measurements have been undertaken under a broad variety of conditions, and that the rate determining step of the reaction is usually not specified, general trends are drawn from these results. Finally, it appears that several key points of knowledge still have to be clarified concerning the dissolution of uranium dioxide in nitric acid media, and that the macroscopic scale which has been used in most studies is probably not suitable.

1 Introduction

Recycling has been chosen for decades by several countries for treating their spent nuclear fuel. This way of treatment has been demonstrated to be environmentally efficient, by allowing a maximum use of the energetical potential of uranium [1].

Several processes have been developed for recycling nuclear spent fuels, most of them being based on hydrometallurgy. Among these hydrometallurgical processes, the PUREX process is the most used at industrial scale, enabling the separation and recovery of uranium and plutonium from spent nuclear fuels [2,3]. In this process, as in most of the other hydrometallurgical processes, the head-end step consists in dissolving uranium dioxide based spent nuclear fuels (UOX) in a hot concentrated nitric acid medium.

Given that UOX spent fuels still contain about 96% of uranium dioxide [4], it is the dissolution of this element which mainly governs the dissolution of the overall fuel.

Due to its importance, the dissolution of spent nuclear fuels in nitric acid media has been widely studied during the past decades. But surprisingly, the number of articles dealing specifically with the dissolution of uranium dioxide in nitric acid media appears to be pretty small in comparison to its importance in the process, and most of the articles which can be found in the literature mainly focus on the dissolution rates of this material, or only on a part of the mechanism taking place. The ability of uranium dioxide to easily dissolve when contacted with nitric acid is probably one of the reasons, with the complexity of the phenomena involved, why little interest has been devoted to understanding the mechanisms of this reaction. However, the kinetics of this reaction define the size, and then the cost, of the process installation for a given production rate. More specifically in the nuclear field, they also influence the hold-up of nuclear products in the head-end step, and thus the criticality issues.

Another problem is that the studies reported in the literature have been realized under a broad variety of conditions. For example, solids are usually made by sintering, but the condition of this sintering varies from a study to another, just as the geometrical characteristics of

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the resulting solids (spheres, pellets, powders). As a result, the mechanisms taking place remain poorly understood. It appears that this lack of knowledge limits the capability to develop efficient models of the dissolution process, and that any change in the operating conditions for industrial dissolution is complicated to predict.

This paper presents a compilation of the most relevant studies on the dissolution of uranium dioxide in nitric acid media. Despite the difficulties mentioned above, the cross referencing enables to make a state of the art of the understanding of this reaction according to literature, to draw conclusions on some parts of the mechanism, and finally, to enlight the gaps which still need to be filled concerning the understanding of the mechanisms and the kinetics of this reaction.

2 Reaction of uranium dioxide with nitric acid

The reaction of uranium dioxide UO_2 with nitric acid HNO_3 leads to the formation of soluble salts of uranyl nitrate of formula $\text{UO}_2(\text{NO}_3)_2$. During this reaction, uranium is oxidized from the degree +IV to +VI, leading to the common designation of oxidative dissolution for this reaction. While UO_2 is oxidized by nitric acid, this reaction is accompanied by the formation of nitric acid reduction by-products.

It must also be pointed out that all these studies have been realised with reaction by-products accumulation in the bulk, which must be taken into account regarding the potential autocatalytic characteristic of the dissolution of uranium dioxide in nitric acid media (the autocatalytic characteristic will be detailed later in this article).

2.1 Proposed reaction equations

A literature survey shows that at least eight different stoichiometric equations, summarized in [5,6], are proposed to describe the balance of the reaction (Eqs. (1)–(8)).

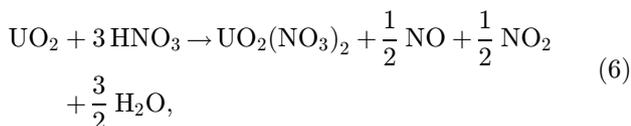
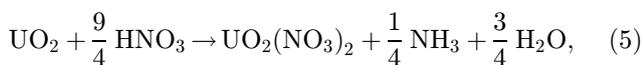
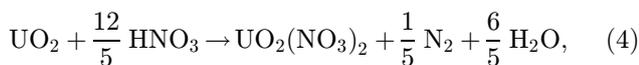
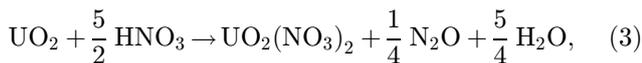
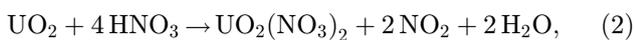
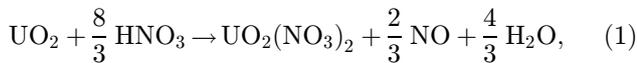
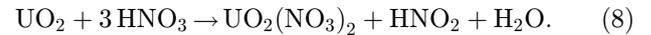
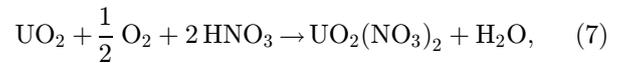


Table 1. Methods used by Hermann [5] for dissolution off-gases analysis.

Analyzed species	Method	Result
N_2	Gas chromatography	Not detected
NH_4^+	Measured in the dissolution solution	Not detected
NO	Chemiluminescence and IR-Spectroscopy	Detected
NO_2	Chemiluminescence	Detected
N_2O	IR-Spectroscopy	Detected



Looking closer at these equations, one can make the following comments:

- equation (6) is a linear combination of equations (1) and (2),
- equations (6) and (8) are related by the equilibrium presented in equation (9) [7].



Many studies have been realized in order to determine which of these reactions are really taking place during dissolution.

2.2 Study of gas emitted during dissolution

Except for equations (7) and (8), proposed equations involve the formation of gaseous species. Many studies focus on the analysis of emitted gas during dissolution of uranium dioxide in nitric acid, in order to identify the species constituting them, and to try to discriminate between some of the proposed equations.

2.2.1 Identification of the species contained in the gas

Herrmann [5] has analyzed the composition of cooled dissolution off-gases using various methods: these methods and associated results are reported in Table 1.

Given the sensitivity of the methods used for the detection, N_2 and NH_3 have not been detected. On the other hand, the presence of NO , NO_2 , and N_2O is confirmed by the author.

Glatz et al. [8] have used a similar experimental system to that of Hermann, but they endeavored minimizing the contact duration between the off-gases and the dissolution medium by depositing the uranium dioxide pellet on a glass frit. A helium flow is applied, which dilutes and removes quickly the off-gases from the dissolution medium, thus avoiding any chemical reaction between the off-gases and the medium. They have confirmed the presence of NO and NO_2 , but N_2O is not detected in this study.

Table 2. Produced NO_x quantity and NO/NO_2 ratio for various nitric acid concentrations.

Reference	Pellet's weight (g)	[HNO_3] (mol l^{-1})	Temperature ($^{\circ}\text{C}$)	Quantity and composition of collected NO_x		
				Total quantity (10^{-3} mol)	NO	NO_2
[9]	1.0195	3.4	100	2.673	86%	14%
	1.005	4.5		2.599	84%	16%
	0.9904	6.7		2.718	75%	25%
	1.0057	8.1		3.642	45%	55%
	0.9406	12.5		4.956	18%	82%
[8]	1.22	6	80	126 ml g^{-1} of dissolved material	34%	66%

Sakurai et al. [9] have analyzed the off-gases after trapping in a liquid-nitrogen trap. The presence of NO and NO_2 was confirmed, but they do not detect N_2O in their IR-spectra. This result is also confirmed by the study of Sakurai et al. [10] on the off-gases emitted during the dissolution of irradiated uranium dioxide pellets in nitric acid.

The off-gases analysis conducted in these three works show beyond any doubt that the off-gases emitted during dissolution of UO_2 in nitric acid are a mix of NO and NO_2 . This result makes sense with that of Pogorelko and Ustinov [11], who have observed a reduction in the quantity of off-gases produced during dissolution with urea addition (urea reacts with NO_x species). Nevertheless, these studies do not agree on the presence or not of N_2O in the off-gases.

Comparison of the IR-spectra to the *NIST Chemistry WebBook* IR-spectra of water and detected NO_x species in the dissolution off-gases shows that N_2O has an absorption band at about 2300 cm^{-1} , which is not disturbed by the presence of water nor other nitrogen oxides. It can be seen on Sakurai's spectra that this absorption band is absent. Hermann [5] and Glatz et al. [8] do not give the spectra they obtained, making the same comparison impossible. Given the strong oxidizing property of the nitric acid media in these studies, it is unlikely that N_2O results of a reaction between the dissolution medium and the off-gases. Thus, the detection by Hermann [5] of N_2O in the off-gases may find its origin in the difference in the experimental procedures: Herrmann sent the off-gases through a condenser before analyzing it, while Sakurai et al. [9] used a liquid-nitrogen trap to recover it before analysis. Glatz et al. [8] also placed a condenser between the IR analyser and the dissolution reactor, but the fact that the off-gases are diluted with helium before flowing through it could result in the absence of recombination reactions. Thus, it seems that N_2O is not produced during dissolution of uranium dioxide in nitric acid media, and that the reason of its detection by Hermann [5] remains unclear and could be attributed to the experimental procedure she used.

It can be concluded from the review of literature that the only off-gases observed during UO_2 dissolution are NO and NO_2 , thus ruling out equations (3)–(5). Nevertheless, it must be pointed out that, even in the studies which tried to

Table 3. Produced NO_x quantity and NO/NO_2 ratio for various nitric acid concentrations per UO_2 dissolve quantity [9].

Pellet's weight (g)	[HNO_3] (mol l^{-1})	NO_x/UO_2	NO/UO_2	NO_2/UO_2
1.0195	3.4	0.71	0.64	0.07
1.005	4.5	0.70	0.62	0.08
0.9904	6.7	0.74	0.61	0.13
1.0057	8.1	0.98	0.54	0.43
0.9406	12.5	1.42	0.36	1.06

minimize it, the collected off-gases have been transported through the bulk, which is a chemical reaction grey zone. It is possible that during this transport, fast chemical reaction occurs between the off-gases and the dissolution solution before analysis: it is therefore likely that the detected off-gases in these studies result of the chemical equilibria between the dissolution solution and the gaseous species actually produced by the dissolution reaction. However studying these off-gases directly after their production at the solid/liquid interface is a difficult problem.

2.2.2 Influence of nitric acid concentration on off-gases composition

Many authors have pointed out an evolution of the NO/NO_2 ratio depending on the concentration in nitric acid of the dissolution solution [5,8,9,12].

Glatz et al. [8] and Sakurai et al. [9] have measured the quantity of degased NO_x during the dissolution of UO_2 pellets under various nitric acid concentrations. Table 2 presents the results they obtained, and Table 3 contains the reworked results of Sakurai et al. per UO_2 dissolved quantity. Two points are emphasized by these results:

- Increasing the concentration of nitric acid or the temperature of the solution results in an increase of the quantity of NO_x produced per mole of dissolved UO_2 .
- The NO/NO_2 ratio evolves to an NO_2 enrichment of the produced gas with an increase of the concentration of nitric acid.

Table 4. List of predominance domains found in literature.

Reference	[12,15]	[2]
Reaction 1 (Eq. (1))	$[\text{HNO}_3] < 10 \text{ mol l}^{-1}$	$[\text{HNO}_3] < 3 \text{ mol l}^{-1}$
Reaction 2 (Eq. (2))	$[\text{HNO}_3] > 10 \text{ mol l}^{-1}$	$[\text{HNO}_3] > 8 \text{ mol l}^{-1}$

It must also be pointed out that in the studies of Glatz et al. [8], two types of pellets were dissolved. Due to probable triuranium octoxide impurities remaining in one of the two pellets, the results collected in this paper only deal with the pellet sintered from pure uranium dioxide powder.

Two hypotheses exist to explain these observations.

The first one assesses a progressive change in the predominant dissolution reaction: Shabbir and Robins [12] claim that the reactions presented in equations (1) and (2) happened simultaneously. But, depending on the nitric acid concentration of the dissolution solution, one will predominate over the other. They propose the concentration of 16 molal in the bulk (about 10 mol l^{-1}) as the concentration at which the change in predominant mechanism occurs. This concentration corresponds to the concentration at which Taylor et al. [13,14] have observed a change in the evolution of dissolution kinetics when nitric acid concentration increases, which they also attribute to a change in the dissolution mechanism.

Various domains of predominance can be found in literature, and are summarized in Table 4.

However, as mentioned earlier, it should be noticed that these concentrations refer to concentrations in the bulk, and thus do not reflect the concentrations of the solution in near contact with the solid.

The second hypothesis introduces an equilibrium between nitric acid and NO_x species: Sakurai et al. [9] claim that the only dissolution reaction taking place is represented by equation (1), and that the observed NO and NO_2 mixture results of the equilibrium existing between these two species in nitric acid solutions.

Sicsic [7] has made a review of literature on these equilibria, showing that two mechanisms can take place, depending on phases under consideration, and nitric acid concentration (Eqs. (10) and (11)):

– For $[\text{HNO}_3] < 6.7 \text{ mol l}^{-1}$:



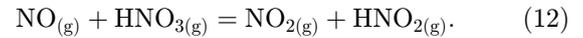
– For $[\text{HNO}_3] > 13 \text{ mol l}^{-1}$:



The equilibrium presented in equation (11) refers to the over-head gas phase and gases contained in the solution either as nucleated gases of dissolved gases, in which case the equilibrium must be modified taking into account the solubilities.

For intermediate concentrations, the two reactions would occur simultaneously, which could be represented by the sum of equations (10) and (11), as shown in

equation (12).



Sakurai et al. [9] do not consider that concentration and phase have an impact on the reaction equation: they only refer to equation (11). This hypothesis being supported by Lefers [16] who explains that nitrous acid is unstable, and rapidly decomposes into nitric acid solutions according to equation (13).



It must be pointed out that the stoichiometric coefficients of equations (1), (2) and (11) make any demonstration based on the analysis of produced NO and NO_2 quantities impossible.

The existence of the equilibrium presented in equation (11) is demonstrated by Sakurai et al. [9] by the analysis of off-gases obtained by bubbling NO and NO_2 , diluted with nitrogen, through nitric acid solutions. The quantity and average flow rate of the bubbled gases were the same as those of the corresponding UO_2 pellet dissolution (Tab. 5).

Whether the gas is NO or NO_2 , a mixture of both is obtained after bubbling through the nitric acid solution. In the case of NO, the NO/ NO_2 ratio always fits the one observed in the case of UO_2 dissolution, whatever nitric acid concentration in the solution. Contrary to NO, when NO_2 is bubbled through the solution, the NO/ NO_2 ratio is found to be different, from the one obtained when UO_2 is dissolved, for the highest acidities. For these acidities, NO_2 is present in higher proportions. Decreasing NO_2 rate (and increasing the bubbling time, to keep the same quantity of NO_2 bubbled) induces a lower ratio of NO_2 , meaning that the difference in the NO/ NO_2 ratios is due to a too short residence time for equilibrium to establish.

It seems complicated to conclude on the sole existence of equation (1) with these results. Studies at higher acidities (in domains where Eq. (2) is supposed to predominate), would have been necessary. Nevertheless, the effect of temperature and nitric acid concentration on the NO/ NO_2 ratio shown in Table 2, combined to the fact that even at an acidity of 6.7 mol l^{-1} , the reaction leading to the formation of NO remains predominant, seem to indicate that NO is produced by the dissolution reaction, and seriously question the existence of a dissolution chemical reaction resulting in the formation of only NO_2 .

2.2.3 Conclusion on dissolution off-gases studies

The study of dissolution off-gases reveals that previously realized works have focused on the analysis of the off-gases flowing out of the dissolution solution. The numerous equilibria existing between these species and nitric acid make any interpretation tricky: the observed off-gases are more likely an image of the dissolution products modulated

Table 5. Comparison between the composition of produced NO_x during UO_2 pellets dissolution and by bubbling of pure NO and NO_2 through nitric acid solutions [9].

HNO_3 (mol l^{-1})	Mass of the UO_2 pellet or NO_x content of bubbled gas	Quantity and composition of collected NO_x		
		Total quantity (mol)	NO	NO_2
3.4	UO_2 1.0195 g	2.673×10^{-3}	86%	14%
	NO 25%	2.476×10^{-3}	86%	14%
	NO_2 46%	5.805×10^{-3}	87%	13%
4.5	UO_2 1.0050 g	2.599×10^{-3}	84%	16%
	NO 25%	2.917×10^{-3}	85%	15%
	NO_2 47%	7.153×10^{-3}	84%	16%
6.7	UO_2 0.9904 g	2.718×10^{-3}	75%	25%
	NO 25%	2.917×10^{-3}	73%	27%
	NO_2 48%	7.367×10^{-3}	54%	46%
	NO_2 5%	2.420×10^{-3}	70%	30%

by equilibria taking place between the generation of these products at the solid/liquid interface, and the analysis of the off-gases after they flowed through the solution. It would be required to study these species at a much more local scale to be able to conclude on this point. In absence of such studies, the following conclusions are made, with all the previously detailed reservations:

- The only off-gases detected during the dissolution of UO_2 in nitric acid are NO and NO_2 . Equations (3)–(5) can be ruled out.
- Even if the work realized by Sakurai et al. [9] is not sufficient enough to establish beyond reasonable doubt that only NO is produced, the formation of NO_2 by dissolution of UO_2 in nitric acid is questionable, and complementary work would be required on this point.
- Equation (7) can also be ruled out: judging from the of NO_x collected, this reaction, even if it would occur, is negligible.

2.3 Study of nitrous acid concentration during the reaction

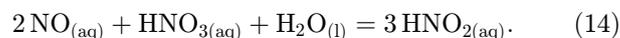
As shown in equation (8), another considered reaction involves the production of nitrous acid as nitric acid reduction product. This possibility has been studied by Fukasawa et al. [17]. The authors have carried out UO_2 pellets dissolution using a silicon film at the solution surface. This film removes the liquid/gas interface, thus preserving nitrous acid in solution by blocking the degradation reaction occurring at this interface (Eq. (9)).

The authors have observed an increase of HNO_2 concentration in the solution proportional to the increase of uranyl nitrate in the solution when the film of silicon oil is added. A titration of the solution after complete dissolution of the pellets has shown a consumption of three moles of nitric acid for one dissolved mole of UO_2 . The authors conclude that the occurring dissolution reaction is the one presented in equation (8).

This experiment has been reproduced by dissolving copper in nitric acid with a film of silicon oil. It appeared that an important amount of NO_x bubbles

formed at the solid/liquid interface, even when a silicon oil film was added. It does not seem realistic that such a quantity of off-gases could be generated by the sole nitrous acid decomposition at the interface, judging from the lower acidity at the interface compared to that of the solution [18,19], and from the low surface area of gas/liquid interfaces existing at the surface of the solid (these interfaces are required for the nitrous acid decomposition reaction to occur, equation (9)).

Thus, it seems that HNO_2 is not a direct by-product of UO_2 dissolution reaction. The increase in HNO_2 concentration with the addition of a silicon oil film can probably be explained by the fact that this film keeps the generated NO_x in contact with the solution, increasing HNO_2 concentration (see Eqs. (10)–(13)). Sicsic [7] has pointed out the existence of the equilibrium presented in equation (14) (the equilibrium constant being 4×10^2 at 25°C). Considering equation (1) and (14), one can find one mole of HNO_2 produced, and three moles of HNO_3 consumed for the dissolution of one mole of UO_2 .



2.4 Oxidation mechanism of uranium dioxide by nitric acid

Many oxidation mechanisms have been proposed in the literature. Fournier [6] has made a synthesis of these mechanisms, which can be sorted in two categories:

- mechanisms where uranium dioxide is solubilized before being oxidized,
- mechanisms where uranium dioxide is oxidized in the solid, and then moved into the solution.

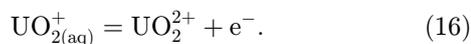
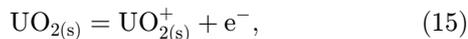
The hypothesis of an oxidation after solubilization has been supported by Shabbir and Robins [12,20]. The mechanism involves a first step where UO_2 is turned into U^{4+} .

On the other hand, Hermann [5] has led analysis showing the absence of formation of U^{4+} during dissolution of UO_2 . Another work by Ikeda et al. [21],

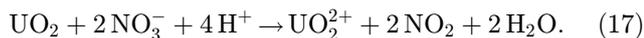
which consisted in dissolving isotopically pure $U^{17}O_2$, followed by ^{17}O NMR analysis of the solution, has shown that U–O bonds do not break during dissolution. It is demonstrated by these two studies that the oxidation of UO_2 happens most probably before any solubilization as U^{4+} ion.

The exact oxidation mechanism remains poorly understood: is it a two-electrons transfer mechanism, or is there formation of U(+V) as an intermediate, the mechanism being in this case a single-electron transfer?

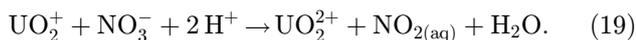
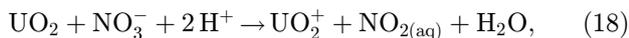
Berger [22] proposes a single-electron transfer mechanism, as shown in equations (15) and (16):



Ikeda et al. [21] do not decide between the two possible ways of electron transfer, and propose one mechanism for both cases. Equation (17) presents the proposed mechanism for a two-electron transfer mechanism, which is presented as the most likely.



In the event that the UO_2^+ oxidation reaction rates to UO_2^{2+} are much faster than that of the disproportionation reaction of UO_2^+ and the rate of oxygen exchange between UO_2^+ and water is slow, the authors also consider a single-electron transfer mechanism presented in equations (18) and (19).



Nevertheless, the lack of data concerning the different rates mentioned earlier makes this last mechanism hypothetical.

2.5 Conclusion on the reaction of uranium dioxide with nitric acid

This first part has focused on the studies realized to understand the chemical reaction of uranium dioxide with nitric acid. These studies have demonstrated that only two off-gases are produced during dissolution: nitrogen monoxide NO and dioxide NO_2 .

A doubt remains on the origin of these two gases: are they both produced by the dissolution reaction, or is nitrogen dioxide a result of equilibria existing between nitric acid and nitrogen monoxide? In any case, even if the study of Sakurai et al. [9] is not sufficient to decide clearly on this point, it shows that if both off-gases are considered to be produced by the dissolution reaction, the predominance domain of equation (10) should be revised, and is likely to be more extended than expected. Thus, the main reaction occurring would be represented by the mass-balance equation presented in equation (1).

The oxidation mechanism of uranium dioxide, which turns U(+IV) into U(+VI), does not involve the U=O bonds rupture, and likely happens in the solid phase. For now, it is not possible to decide between one or two electron transfer mechanisms.

3 Solid side of the dissolution reaction

3.1 Overview of solid properties

Uranium dioxide dense pellets are commonly obtained by sintering at high temperature (1973–2023 K) under reductive atmosphere (dry Ar/ H_2 5%) of raw pellets mainly composed of overstoichiometric $UO_{2+\delta}$ and few weight percent of U_3O_8 . In this case, U_3O_8 is used as an inorganic (i.e. radiolysis-proof) performer. During the sintering thermal treatment between 773 K and 873 K [23,24], this oxide is reduced to UO_2 . Since the theoretical density of UO_2 is 10.97 and that of U_3O_8 8.38 [25], a volume contraction of around 24% of the initial U_3O_8 grains occurs, generating an additional porosity. The latter yields to pellet final densities of around 95% TD (theoretical density), which allows fuel mechanical accommodations during irradiation.

After sintering, monophasic and stoichiometric $UO_{2.00}$ is formed presenting a cubic fluorite-like structure with space group Fm-3m (No. 225). The use of UO_2 and U_3O_8 grades ensures that neither additional phases nor significant quantities of impurities are present. Pellets have homogeneous microstructure generally composed of large grains ($\sim 10 \mu m$) associated by grain boundaries. A grain is considered as a crystallite with only one single crystallographic orientation whereas the grain boundary ensures the transition between two grains presenting different crystallographic orientations. As a consequence, grains boundaries generally have lower crystallographic orders and due to/because of their thickness (few nanometers) can be considered as two-dimension defects. The residual porosity is not preferentially located in the bulk or in the grain boundaries and is mainly closed.

Greiling and Lieser [26] have noted that manufacturing conditions of the powders they used for their dissolution experiments have an impact on dissolution kinetics.

In the case of sintered solids, manufacturing conditions will have an impact on solid's consolidation and density, these two parameters having in turn an impact on pellets' dissolution kinetics, as shown by Taylor et al. [13] and Uriarte and Rainey [27].

3.2 Preferential attack sites

Studies realized by Briggs [28, 29] and Shabbir and Robbins [30] have revealed that dissolution kinetics vary with crystallographic orientation of the surface exposed to the solution: grains with crystallographic orientation (1 1 1) parallel to the surface show slower dissolution kinetics than those with crystallographic orientation (1 0 0) parallel to the surface. This seems to be in agreement with the results of Castell et al. [31] and Muggelberg et al. [32,33] who have studied the (1 0 0), (1 1 0) and (1 1 1) surface of uranium dioxide, and who have found that the (1 0 0) surface is probably less stable than the other ones due to a higher surface energy.

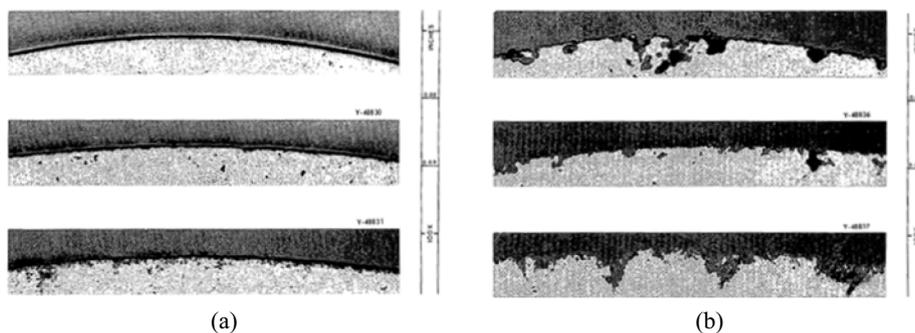


Fig. 1. Metallographic sections of UO_2 pellets before (a) and after (b) dissolution [27].

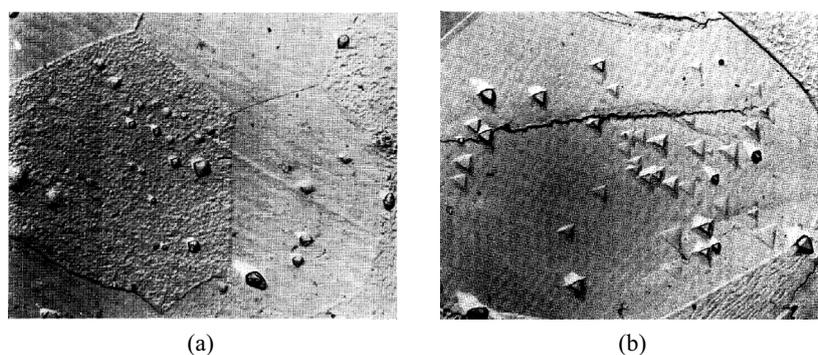


Fig. 2. Electron micrograph of polycrystalline UO_2 attacked by 37 molal nitric acid [30].

These works, as well as those of Uriarte and Rainey [27], Kim et al. [34] and Zhao and Chen [35–37], let also appear preferential attack sites:

- Grain boundaries, which can be explained by the fact that these areas are poorly crystallized, with lower cohesion energy (Fig. 1). This probably makes these areas more apt for dissolution.
- Other very located sites on the surface of the grains (Fig. 2). The origin of these pits remains unknown.

The attack and development of the surface and number of these sites lead to an increase of the specific surface area and thus probably, but not necessarily, of the reactive surface of the solids in the first part of dissolution, as measured by Taylor et al. [13,14], Fukasawa and Ozawa [38], and Fournier [6]. It is observed that the specific surface area can grow up to a factor of 4, and that the maximum development is measured when 20–40% of the solid is dissolved. After this first period, the specific surface area decreases to zero due to the consumption of the solid.

However, the issue of internal mass transport makes the relation between reactive surface and specific surface area complicated to establish [39,40], and no study has yet demonstrated a convincing relationship between reactive surface and specific surface area.

4 An autocatalyzed reaction?

A particularity of the dissolution reaction of UO_2 in nitric acid media is the supposed existence of an autocatalytic reaction, which means that one of the products of the dissolution reaction would act as a catalyst. This

assessment is nowadays commonly accepted, even though neither the species involved nor the mechanisms have been formally identified.

4.1 Observations in favor of the existence of an autocatalytic reaction

Many experimental observations reported in the literature support the assessment of an autocatalytic mechanism.

Wada et al. [41] have studied the effect of UV irradiation on the dissolution of uranium dioxide powders in nitric acid solutions. In their blank tests (without UV irradiation), and all else being equal, the measured dissolution rates are multiplied by almost ten when the amount of uranium dioxide powder dissolved increased from 10 to 100 mg.

4.1.1 Effect of mixing

Shabbir and Robins [12,20], Taylor et al. [13,14], Delwaille [19] and Zhao and Chen [35–37] have reported that increasing mixing for batch dissolution, or input flow for continuous dissolution, results in a decrease in dissolution kinetics (Fig. 3).

This effect is against what one would intuitively expect, i.e. that increasing mixing or input flow results in lowering the thickness of the diffusion layer, increasing reactants' mass transport and dissolution kinetics. But, if there were an autocatalytic reaction, increasing mass transport would also result in lowering the concentration of products at the solid/liquid interface, including potential catalytic species.

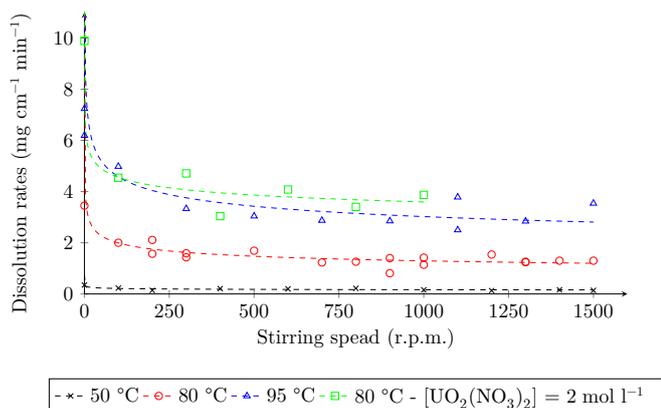


Fig. 3. Effect of stirring speed on the dissolution rates of uranium dioxide pellets in $[\text{HNO}_3] = 6 \text{ mol l}^{-1}$ [13].

The only paper reporting a positive impact of mixing is the one of Kumar Gelatar et al. [42], who report that the dissolution kinetics of uranium dioxide are faster under continuous recirculation of the dissolution solution. This observation can probably be explained by the fact that in this particular case, the mixing involved by the recirculation is probably weak, and simply re-introduces catalytic species into the dissolver.

4.1.2 Induction period

At the beginning of dissolution, there is a period of time where observed dissolution kinetics are lower than those expected for a homogeneous attack of the solid. In the hypothesis of an autocatalytic mechanism, this period would correspond to the time required to reach the autocatalytic species' equilibrium concentration, at the solid/liquid interface.

It must be pointed out that this period could also correspond to an increase of the reactive surface area of the solid, but this explanation cannot support the negative effect of mixing on dissolution kinetics. Most probably, combinations of both effects occur.

4.2 Potential autocatalytic species

4.2.1 Nitrous acid

Nitrous acid is the historically supposed autocatalytic species. As early as 1962, Taylor et al. [13,14] presented nitrous acid as a catalyst of UO_2 dissolution reaction. This observation is related to the increase of dissolution kinetics they observed when adding nitrite salts to solution or $\text{Fe}(\text{NO}_3)_3$ reducing to $\text{Fe}(\text{II})$ in the solution, which reacts in its turn with nitric acid leading to nitrous acid. Myasoedov and Kulyako [43] have also carried out experiments with addition of iron(III) nitrate, but they did not study the effect of this salt on the dissolution kinetics of uranium dioxide. Taylor et al. [13,14] and Pogorelko and Ustinov [11] have also reported a decrease of the dissolution kinetics when urea or hydrazine (which act as nitrous scavengers) are added to the solution.

Similar observations are reported by Shabbir and Robins [20], Herrman [5], Pogorelko and Ustinov [11], Nishimura et al. [44], Yasuike et al. [45], Ikeda et al. [32] and Carrott et al. [46].

Nishimura et al. [44] and Kim et al. [34,47] have proposed the mechanism presented in equation (20) to explain the role of nitrous acid. This mechanism was reused by Homma et al. [48], who have claimed that nitrous acid would be produced by the reaction between nitrogen dioxide and water (Eq. (21)). Inoue [49,50] also supports the mechanism presented in equation (20).



It must be pointed out that in the case of a catalyzed reaction, the catalytic species must be returned at the end of the reaction. The "autocatalytic" term used to describe the assessed mechanism is therefore incorrect: nitrous acid should be returned at the end of the reaction, which is not the case in the proposed mechanism.

4.2.2 Uranyl nitrate

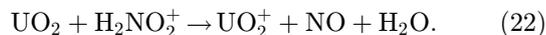
Herrmann [5], Taylor et al. [13,14], Uriarte and Rainey [27], and Homma et al. [48] have done dissolution experiments with uranyl nitrate addition. The authors observed that in the case where uranyl nitrate is added keeping total nitrate concentration constant (which means decreasing nitric acid concentration depending on the quantity of uranyl nitrate added), no impact is observable on dissolution kinetics. On the other hand, if uranyl nitrate is added, and total nitrate concentration increased, there is an acceleration of dissolution kinetics. This last point must be related to the fact that about 80–90% of nitric acid can be replaced by monovalent salts of nitrate with hardly an impact on dissolution kinetics, as reported by Taylor et al. [13] and Uriarte and Rainey [27].

Thus, uranyl nitrate does not seem to be the autocatalytic species.

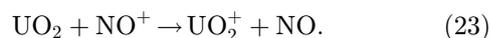
4.2.3 Other considered species

Nitrous acid is a weaker acid and weaker oxidizer than nitric acid. But, its instability in nitric acid solutions makes it in equilibrium with much more reactive species. At least two of these species are found in the literature as potential autocatalytic species

– Nitroacidium ion (H_2NO_2^+) [50]:



– Nitrosonium ion (NO^+) [5]:



The reactivity of these species makes their identification in the solution tricky, and the possibility that they have a role in dissolution reaction remains yet hypothetical.

4.3 Elements against the existence of an autocatalyzed reaction

Two experimental facts disagree with the hypothesis of an autocatalyzed reaction.

4.3.1 The replacement of nitric acid by nitrate salts

As reported earlier in this paper, Taylor et al. [13] and Uriarte and Rainey [27] have undertaken dissolution experiments of UO_2 pellets where part of the nitric acid was replaced by nitrate salts keeping total nitrate concentration constant. It has been observed that about 80–90% of nitric acid could be replaced by an equivalent quantity of monovalent nitrate without impacting dissolution kinetics.

This observation disagrees with the hypothesis of an autocatalyzed reaction, since by modifying the concentration of nitric acid, one also modified the concentration of all the species at equilibrium with it. This means that any by-product of the reduction of nitric acid will see its concentration changed, and if one of them were catalyzing the reaction, a change in its concentration should impact the overall dissolution kinetics, except if the equilibria between the different species are thresholded.

4.3.2 The increase of nitrous acid concentration

Contrary to what has been presented earlier, some authors did not report any impact of nitrous acid or nitrite salts on dissolution kinetics.

Uriarte and Rainey [27] have added sodium nitrite without significant increase in dissolution kinetics. Nevertheless, the authors precise that this addition was made in boiling dissolution solutions, and that the high temperature could accelerate the degradation of the added nitrites. It must also be noted that higher temperatures affect the solubilities of the off-gases produced when nitrites degrade, and that water vapor entrainment could also further lower the off-gases concentrations in solution. These two phenomena could shift the chemical equilibria in favor of nitrites degradation.

Fukasawa et al. [17], in their work with silicon oil films, have noted that the addition of this film resulted in a conservation of nitrous forms in solution. They did not observe any change in dissolution kinetics by increasing by this way the concentration of nitrous acid.

5 Physico-chemical parameters influencing the dissolution rates

This part presents a compilation of the main physico-chemical parameters known for having an impact on the dissolution rates. Nevertheless, it must be pointed out that the results have been obtained using a broad variety of materials (sintering conditions, physical form such as powders, spheres, or pellets), and of dissolution solutions compositions.

This point is although fundamental, for example if one wants to draw conclusions on the chemical mechanisms based on the measurement of dissolution rates. These uncertainties make the conclusions learned from the kinetics measurements uncertain, and are probably responsible for the variety of the results found in the literature, presented below.

5.1 Nitric acid concentration

The impact of nitric acid concentration in the attacking solution has been widely studied in the literature, and conclusions are unanimous: increasing this concentration increases dissolution kinetics.

Taylor et al. [13,14] have reported the increase of dissolution kinetics with nitric acid in the case of unstirred dissolutions. This increase remains constant up to a value, depending on the temperature of the solution, beyond which the increase slows down. Shabbir and Robins [12] have found the same results, and attribute the inflexion of the kinetics increase to a change in the nitric acid reduction mechanism.

Similar results have also been reported by Uriarte and Rayney [27] when dissolving uranium dioxide pellets in boiling nitric acid, and by Hermann [5] and Calaparede et al. [51] but within a smaller range of nitric acid concentrations.

Many authors have taken into account this impact of nitric acid concentration by the mean of equation (24). Table 6 presents a compilation of the different values which have been reported for the partial order of nitric acid n .

$$r = k \times [\text{HNO}_3]^n. \quad (24)$$

5.2 Temperature of the solution

The impact of temperature on the dissolution kinetic has also been widely studied. The assessments are unanimous on its effects [5,13,14], and can be summarized as follow:

- the increase of the temperature results in an increase of the dissolution kinetics up to temperatures around 90–95 °C,
- from 90 to 95 °C to boiling, kinetics keep increasing, but slower than for lower temperatures,
- the reaching of boiling makes kinetics drop. The authors have explained this drop by the solution mixing that boiling involves, but it could also be explained by the effect of temperature on nitrites degradation, gas solubilities and water vapor entrainment, detailed in Section 4.3.2.

Considering that the kinetic constant follows the Arrhenius law (Eq. (25)), Table 7 gives the values of the activation energy reported in the literature.

$$k = A \exp\left(\frac{-E_a}{R T}\right). \quad (25)$$

The fact that calculated activation energy is not constant over the temperature domain indicates that the dissolution of uranium dioxide is not following the

Table 6. Partial order related to nitric acid in the case of equation (25).

Reference	Experimental conditions			n
	[U] (g l ⁻¹)	[HNO ₃] (N)	Temperature (°C)	
[14]	–	2–10 10–14	20–95	2.3–3.3 1
[27]	120–350	2–7 2–12	Boiling Boiling	2.03–2.12 2.3
[45]	–	6–10.6	80	2.3

Table 7. Activation energy values reported by authors.

Reference	Experimental conditions		E_a (kJ mol ⁻¹)
	[HNO ₃] (mol l ⁻¹)	Temperature (°C)	
[5]	4.5–8	60–95	50
[8]	6	50–95	54.8
[14]	2–10 14	20–95 65–95	61.9 ± 5.5 8.3–21
[30]		Wide area with chemical control	67
[35]	8	90 90–110 (Micro-wave heating)	50 71
[36]	8	90–110 (Classical heating) 90–110 (Micro-wave heating)	50 77.4
[37]	4	90–110 (Classical heating)	31.1
[51]	2	40–90	15 ± 1
[52]	8.05 10.28	70–90 60–80	85.2 97.5

Arrhenius law. This could be due to a change in the chemical reaction mechanism with temperature, a change in the mechanism controlling the overall kinetics, or other physico-chemical effects like those induced by boiling on the gas solubilities, or mass-transport phenomena.

5.3 Solid properties

5.3.1 Density and specific surface area of the solid

As shown earlier, the attack of the solid is not uniform. This results in an increase of the solid specific surface area during the earliest stages of dissolution.

This increase has been measured by Taylor et al. [13,14] (Fig. 4), and by Fukasawa and Ozawa [38]. The authors report that the specific surface area can increase by a factor of 4 during dissolution, this maximum being reached when 20–40% of the solid is dissolved.

The density of the solid, which also impacts its specific surface area, has also been studied by Taylor et al. [13] and by Uriarte and Rainey [27]. Despite important disparities in their results, the authors have reported that the decrease

of the density of the solid results in an increase of the dissolution rates. However, it is important to notice once again that no relation between specific surface area and reactive surface has been demonstrated yet.

5.3.2 Role of impurities

The role of some impurities has been studied by Ikeda et al. [53]. The authors have found that the dissolution rates of uranium dioxide powders containing impurities (Al₂O₃, Pd, Rh, Ru or ZrO₂) are significantly faster compared to the dissolution rate of pure uranium dioxide based powders. They have attributed these accelerations to the lower density of the uranium dioxide solids containing Al₂O₃ and ZrO₂ as compared to the density of the pure uranium dioxide solids, without arguing how. The fact that the dissolution rate of the solids containing rhodium is faster than those of the solids incorporating Al₂O₃ and ZrO₂, while all these solids show the same density, indicates that another mechanism, which remains unknown, takes place in this case.

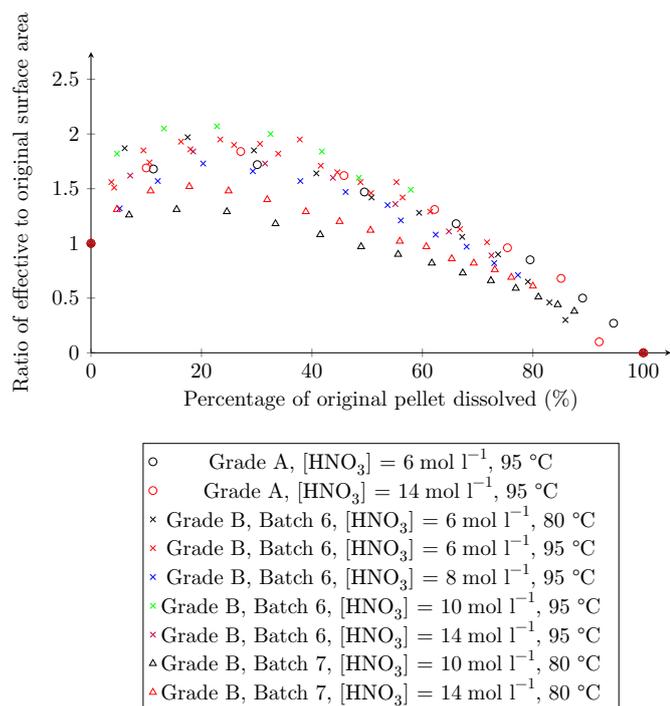


Fig. 4. Evolution of the effective surface area of dissolving pellets under various conditions as a function of the percentage of original pellet dissolved [13].

They have also reported a difference between the densities of the different materials, impure uranium dioxide powders being found to be less dense than pure uranium dioxide ones (93% TD as compare to 95% TD). However, the authors claim that the difference of densities is too small to explain the differences observed for the dissolution rates.

In addition, Tocino et al. [54] have realised dissolution of uranium dioxide pellets containing significant quantities (25%) of lanthanides and actinides (Ce, Gd, Nd, Th), and reported slower dissolution rates than in the case of pure uranium dioxide dissolution. This could indicate that these elements can also have an impact at lower contents.

5.4 Conclusion on the influence of the physico-chemical parameters on the dissolution rates

Despite important variabilities in the results, it can be concluded that the increase of nitric acid concentration and temperature of the dissolution solution results in an increase of the dissolution rates, except when temperature reaches the boiling point: in this case, the dissolution rates brutally drops. In addition, it must be noticed that the effect of the temperature does not fit the Arrhenius law. This could be due to a change in the chemical reaction mechanism, or in other physico-chemical phenomena, and further investigations would be required to conclude clearly on this point.

The characteristics of the solid also play an important role on the dissolution rates, and a relation, which needs to be clarified, exists between the specific surface area of the dissolving solids, probably also impacted by the density of the solid, and the dissolution rates.

Another important point is the fact that most of the studies have not taken interest in the rate controlling mechanism. The primary importance of the knowledge of this mechanism has been widely documented in the literature concerning the kinetics of solid/liquid reactions [39,40,55], and its absence in most of the studies results in the impossibility to know if the measured dissolution rates correspond to the chemical reaction or diffusion kinetics.

Some authors have specified the rate-determining step in their experiment, but their conclusions, even for similar experimental conditions, do not agree. Claparede et al. [51], Desigan et al. [52] and Tocino et al. [54] have found that the activation energy values they have calculated do not correspond to the expected values for a diffusion-controlled processes, and have concluded that the dissolution reaction is likely to take place under chemical control. Nevertheless, this conclusion relies on a serial transport, diffusion and reaction mechanism, which could not take place during uranium dioxide dissolution. Additionally, these conclusions are not in agreement with the observations made by Delwaulle et al. [18,19], who have observed nitric acid concentrations gradients surrounding sintered fragments of uranium dioxide during their dissolution.

The impact of other physico-chemical parameters has been partially studied in the literature, such as the effect of pressure and atmosphere composition by Shabbir and Robins [20]. However, the small number of studies dedicated to the impact of these other parameters makes any discussion on the conclusions they draw too complicated.

Finally, it appears that the knowledge of the rate determining step in these experiments, including the diffusion of the chemical species in the external diffusion layer, is a key element which is most of the time absent, or insufficiently investigated, to draw well-established conclusions.

6 Conclusion

This work has made a state of the art concerning uranium dioxide dissolution in nitric acid solutions. The first conclusion which can be drawn is that this reaction is a complex reactive dissolution reaction, which involves solid, liquid and gaseous species, and a possible autocatalytic reaction. This is complicated by the fact that all these species, and their associated parameters, evolve during the dissolution, and vary from one study to another.

The studies found in the literature have mainly focused on two aspects of this reaction: the understanding of the chemical reaction between uranium dioxide and nitric acid, and the determination of the influence of several physico-chemical parameters of the reaction on the dissolution rates.

Concerning the chemical reaction, it can be seen from the literature that the reaction leads to the production of nitrogen monoxide NO and dioxide NO₂ as by-products, thus making equations (1) and (2) the most likely equations for the mass-balance of the reaction.

The fact that the NO/NO₂ ratio evolves with nitric acid concentration has led to the development of two hypotheses, which are still being debated:

- both reactions take place, but the ratio of one over the other varies with nitric acid concentration,
- equation (1) is the only reaction occurring during dissolution, and the formation of NO₂ is a result of the equilibria between NO and HNO₃ in the solution including their solubilities.

Concerning the mechanism of the oxidation of uranium dioxide, it has been clearly demonstrated that solubilization occurs after oxidation. The electron exchange has not been elucidated yet, and the question of single-electron transfer and two-electrons transfer mechanisms is still open.

Another important aspect of this reaction deals with the solid phase. Dissolution does not occur as a uniform attack, and this leads to important changes in the morphology of the solid, with the appearance of pits and the development of cracks, which imply an increase in the surface of the solid.

The last point concerning the chemical reaction is its supposed autocatalytic property. It has been emphasized that even if this hypothesis is historically and widely accepted in the literature, many elements remain missing on this point: what is exactly the autocatalytic mechanism? Which are the species involved in this mechanism? More work would be required on this subject to clearly elucidate the mechanism of the possible autocatalysis of uranium dioxide dissolution in nitric acid solutions. But the complexity of nitric acid media, which contain many different species related together by multiple equilibria, makes experimental results tricky to analyze, and most of the time, conclusions must be carefully drawn.

The study of the impact of several physico-chemical parameters of the reaction is presented in the second part of this review. Even if the rate determining step of these experiments is not sufficiently known, some conclusions can be drawn based on these results.

The increase of nitric acid concentration and temperature of the dissolution solution results in an increase of the dissolution rates, except near the boiling point, where the dissolution rates brutally drops. This observation is probably due to the increase of the mixing due to the bubbling taking place once the boiling point of the solution is approached. It must also be noticed that the dissolution rates do not follow the Arrhenius law. This could be due to a change in the chemical reaction mechanism, in the rate determining step, or the effect of the temperature on the solubilities of the gas and water vapor entrainment of the dissolved gases.

The characteristics of the solid also play an important role on the dissolution rates. It is commonly accepted that higher specific surface area induces higher dissolution rates, although no formal relation between the reactive surface and the specific surface area of the solid, including the issue of mass-transport, has been demonstrated yet.

To conclude, the compilation of the studies found in the literature has allowed to clarify several points on the dissolution of uranium dioxide in nitric acid media. Nevertheless, this review also enlightens numerous lacks of understanding concerning this reaction. It appears that these can mainly be assigned to the fact that most of the studies have been realised at a macroscopic scale, which is not adapted to the phenomenological complexity and speed of this reaction. Thus, new approaches, enabling to better quantify the contribution of the different phenomena, would be required to better understand the mechanisms of this reaction. This better knowledge of the reaction would enable in turn to improve the dissolution step of the processes used for spent nuclear fuels recycling, but also for other dissolution reactions that imply reaction off-gas and catalysis.

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