# An introduction to head-end in reprocessing

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# SUMMARY

The Plutonium and Uranium Reduction EXtraction process (PUREX), is the most widely used process to reprocess Spent Nuclear Fuel (SNF). Head-end constitutes the second step of the PUREX process. This review article provides an in-depth description of the whole head-end process from a mechanical and chemical perspective.

## **1. INTRODUCTION**

In a world where technology is constantly advancing, it is extremely important to find new technologies and improve the existing ones to produce safer, cleaner and more efficient energy. Nuclear energy has been used for over 70 years to produce energy worldwide and currently, constitutes, the second (26.4%) most used energy source in Europe according to "Eurostat". The Plutonium and Uranium Reduction EXtraction process (PUREX) can be used in nuclear to reprocess and recycle spent nuclear fuel (SNF) and improve the sustainability of the nuclear fuel cycle that is needed around the nuclear reactors themselves. The PUREX process recycles SNF from, inter alia, Light Water Reactors (LWRs), Pressurized Heavy-water reactors (PHWRs), Boiling Water Reactors (BWRs), advanced gas-cooled reactors (AGRs), firstgeneration Magnox reactors and fast reactors (FRs) to recover valuable materials (e.g. U and Pu) that can be reused as fuels for current or future reactors. Additionally, recycling of SNF helps to reduce the high-level waste consigned to geological disposal and the long-lived radioactivity (heat generating isotopes) associated with it. Aqueous reprocessing based on the PUREX process has been performed industrially for decades. There are currently five operative reprocessing plants in the world handling two fuels from two types of reactor (LWR and PHWR). LWR fuel is reprocessed at UP3 and UP2-800 in La Hague (France), and Mayak (Russia). Kalpakkam and Tarapur (India) reprocess fuels from pressurized PHWR. Additionally, Rokkasho-mura (Japan) is still under construction but will treat LWRs fuel.

PUREX is based on the separation of uranium and plutonium from nitric acid solutions using tri-butyl phosphate (TBP) in kerosene (OK). PUREX reprocessing can be broken down into four main steps: 1) fuel receipt and storage, 2) head-end, 3) separation (PUREX) and 4) waste treatment. A simplified version of the process is shown in Figure 1. Fuel receipt and storage involves receiving and storing the fuel in a pond for a period of time until it cools. Then, the head-end process starts. Head-end includes: 1) exposing the fuel by removing cladding or, shearing (chopping up) of the fuel, 2) the dissolution of the Spent Nuclear Fuel (SNF) in nitric acid, 3) off-gas treatment, 4) conditioning the solution and 5) clarifying the dissolver solution, prior to solvent extraction. Detailed descriptions of solvent extraction and waste treatment can be found elsewhere and the reader is directed to [1].

The first step of the head-end process involves the dismantling and shearing of the SNF to transform fuel assemblies into small pieces. The shearing and dissolution processes release and produce off-gases, which are treated via the Dissolver Off-Gas (DOG) system. The major gases released include iodine (129I) and krypton (85Kr), as well as small amounts of tritium (3H), 14C, NOx and other gases. Then, in the second step, the exposed fuel undergoes acid dissolution in HNO, at high concentrations (4 - 9 M) and elevated temperatures (60 - 90 °C). The aim is to completely dissolve all the elements found in SNF. However, some remain as insoluble solids in the dissolver product liquor (DPL) under these conditions. These are known as insoluble fission products (IFPs). The presence of IFPs causes problems in the downstream separation steps, which are based on homogeneous liquid-liquid extraction. The fuel clarification (or removal of IFP) is usually carried out mechanically with the

help of centrifuges. Further reprocessing processes may use centrifugal contactors (CCs), which are expected to be more sensitive to the presence of entrained particulate. This review supports consideration of the application of CCs for the highly active cycle, which may require improved clarification efficiency. This review paper focuses on the head-end process. It provides



Figure 1: Diagram of a PUREX process detailing head-end steps

a general review that explains the head-end process from start to end from both mechanical and chemical perspectives. This paper: 1) explains how the head-end process works, 2) provides information about the physical and chemical characteristics of SNF, 3) explains dissolution fuels from different reactors and compositions (UO<sub>2</sub> and MOx) and 4) gives information about the physical and chemical characteristics of the IFPs produced after the dissolution.

## 1.1. Nuclear Fuel

The current main Nuclear Fuel (NF) rod consists of pellets (made of UO<sub>2</sub> for LWR) or Mixed uranium plutonium diOxide (MOx) stacked in a chemically resistant metal tube (or cladding) that is closed from both ends. The cladding prevents the corrosion of the fuel and the release of FP. The rods are arranged together in fuel assemblies with different arrays with the help of grid spacers that ally the rods. Pressurized Water Reactors (PWR) have 13x14, 14x14, 15x15, 15x16, 16x16, and 17x17 fuel rod arrays. Boiling Water Reactors (BWR) have 6x6, 7x7, 8x8, 9x9, 10x10, and 11x11 fuel rod arrays [2]. Table 1 shows the main physical characteristics of the assembly, fuel rods and pellets of two 15x15 Babcock & Wilcox assemblies used for PWR [2]. Current assembly models, use Zircaloy cladding due to its low neutron absorption and its corrosion resistance. The cladding is secured with pressurised helium gas to avoid a collapse in the defueled region. BWR and AGRs use Stainless Steel (SS) cladding.

Characteristic	Zircaloy assembly	SS Assembly	Unit	
Fuel Rod Positions per Assembly	225	225	-	
Typical Number of Fuel Rods per Assembly	208	204	-	
Rod diameter	1.09	1.07	cm	
Rod length	390.35	321.77	cm	
Active length	360.17	306.07	cm	
Weight per rod	3.18	2.67	kg	
Clad material	Zircaloid-4	SS-304	-	
Clad thickness	0.07	0.04	cm	
Fill Gas Used	Не	Не	-	
Initial Gas Pressure	28.6	2.8	Bar	
Fuel Pellet Material	UO <sub>2</sub>	UO <sub>2</sub>	-	
Fuel Pellet Shape	Dished or Chamfered	Dished or Chamfered	-	
Fuel Pellet Diameter	0.94	0.97	cm	
Fuel Pellet Length	1.10	1.163	cm	
Fuel Pellet Weight per Rod	2.53	N/A	kg	
Open porosity	< 1%	< 1%		
Grain Size	10-14	10-14	μm	
Fuel density theoretical	95%	95%		
Smear Density	9.75	9.75	g/cm <sup>3</sup>	
Spacer Pellet Material	Zircaloy-4	Zircaloy-4		

#### Table 1: Physical description of an assembly from [2]

# 1.2. Composition of Spent Nuclear Fuel (SNF). Physical and chemical characterisation

Spent Nuclear Fuel (SNF) is mainly formed by U and Pu but contains many elements of the Periodic Table as a result of nuclear fission, neutron capture and isotopic decays. Table 2 displays the simulated isotopic composition and concentration in weight (wt%) of SNF legacy from BWR and PWR in German repositories as a result of the Power Plants (PP) closure in 2022 [3]. In order of abundance, SNF consists of U > Pu > Cs > Ru >Am > Tc > Sr > Np > I > Cm > Th > Pa. There are also other minoractinides (MA), lanthanides and Fission Products (FP) at highconcentrations. The constituents of SNF can be found as [4]:

- 1 Fission products dissolved as oxides in the U and Pu matrix (Sr, Th, Zr, Nb, Y, La, Ce, Pr, Nd, Pm and Sm): The concentration of dissolved oxides depends on the oxygen to the metal ratio in the fuel (O/M) [5], as well as, length of the irradiation period and temperature gradients [6].
- 2 Fission gases (Kr, Xe, Br and I),

- 3 Metallic precipitates (Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb and Te) and,
- 4 Oxide precipitates (Rb, Cs, Ba, Zr, Nb, Mo and Te).

Element	SNF (%wt)		
Other MA	1.09 x10 <sup>-9</sup>		
Ра	1.50 x10 <sup>-8</sup>		
Th	3.19 x10 <sup>-7</sup>		
Cm	6.44 x10 <sup>-3</sup>		
I	2.89 x10 <sup>-2</sup>		
Np	6.04 x10 <sup>-2</sup>		
Sr	8.08 x10 <sup>-2</sup>		
Тс	9.03 x10 <sup>-2</sup>		
Am	1.42 x10 <sup>-1</sup>		
Ru	2.72 x10 <sup>-1</sup>		
Cs	2.84 x10 <sup>-1</sup>		
Lanth	1.15		
Pu	1.27		
Other FP	2.12		
U	94.5		

#### Table 2: Elemental composition of SNF from [3]

The composition of the SNF depends on the type of fuel and irradiation history of the reactor [7]. Additional data from the elemental composition of SNF can be found in SCOMPO 2.0 [8-10]. The density of SNF is also dependent on composition. For MOX fuels, density increases with Pu concentration and decreases as the O/M ratio decreases [5].

#### The Head-End process Shearing of SNF

The first step of the head-end process is the shearing of the SNF and its assemblies to expose the fuel. The type of shearing process is specific to the fuel and assembly [11]. Shearing affects the size of the cut SNF and thus the design of the downstream process. The MAGNOX reprocessing plant (UK) uses a slitter wheel to declad, while the THORP reprocessing plant (UK), UP2-800 and UP3 (La Hague, FR) and other reprocessing plants use a hydraulic cutting blade to cut the entire fuel elements from PWR or BWR reactors [12]. The shearing process creates short segments that can undergo acid leaching. Shearing processes are based on two techniques: Single pin (or pellet) shearing or whole-bundle shearing. In both cases, the first step of the shearing process is the removal of non-fuel metal elements at the top and bottom plates or assembly grapher or metal sheet wrappers. Then, the plenum areas of the fuel rod can be cut to remove even more non-fissile material. In whole-bundle shearing, fuel rods, still arranged with the help of the grid spacers, are cut perpendicular to the direction of the rods. The whole bundle is held together by a gag or compaction device, which reduced the pinching of the cladding. The process crushes the fuel pellets. In single-pin shearing, the grid spacer is removed so spent fuel rods are individually cut. As a result, the cuts are smoother than with whole bundle shearing and there is less pellet fracture [12].

#### **Dissolution of SNF**

Nitric acid at high temperatures is used in all reprocessing plants to dissolve SNF after shearing [12]. In the UK, the Magnox RP uses a continuous dissolver to obtain a fuel liquor that feeds the reprocessing plant. THORP uses three batch dissolvers that work in sequence. While one dissolver receives the SNF, the second is leaching and the third is transferring the fuel liquor to the reprocessing plant. In THORP, the sheared SNF directly falls in a basket within the dissolver vessel. Then, the vessel is heated up to the leaching temperature and the dissolution takes place. La Hague reprocessing plants use a rotating wheel dissolver (Taylor, 2015). Both Magnox and THORP RP dissolvers use air to increase the conversion of NOx, generated the dissolution of fuel in HNO<sub>3</sub> to the more soluble NO<sub>2</sub> gas. The dissolution process generates a dissolution product liquor (DPL) that contains dissolved fission products in nitric acid and IFPs [6].

### Dissolution of UO,

As already mentioned, most SNF typically is composed of  $UO_2$  prior to irradiation/burn-up. Nevertheless, the  $UO_2$  dissolution mechanism in  $HNO_3$  is not yet completely understood. The following stoichiometric equations have been proposed to explain its dissolution reaction [13-15]. The dissolution process produces nitrogen oxides (NOx) in various propositions, if an acid recombination process is operated a 'fumeless dissolution' can be operated that produces minimal amounts of NOx.

$$UO_2 + \frac{8}{2}HNO_3 \rightarrow UO_2(NO_3)_2 + \frac{2}{2}NO + \frac{4}{2}H_2O$$
 (1)

$$UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$$
 (2)

$$UO_2 + \frac{5}{2}HNO_3 \rightarrow UO_2(NO_3)_2 + \frac{1}{4}N_2O + \frac{5}{4}H_2O$$
 (3)

$$UO_2 + \frac{1}{2}O_2 + 2HNO_3 \rightarrow UO_2(NO_3)_2 + H_2O$$
 (4)

The dissolution rate of UO<sub>2</sub> increases with HNO<sub>3</sub> concentration [14, 16-19] and temperature [14, 16, 17]. The physical characteristics of UO<sub>2</sub>, particularly surface area, affect its chemical dissolution. For this reason, for laboratory-scale experimentation, the manufacturing process of solid materials plays an important role in dissolution [20]. An increase in UO2 density results in a reduction in porosity and a decrease in dissolution rates [17, 19]. Density is also affected by the addition of dopants as phase modifiers or burnable neutron poisons. Dissolution experiments of impure UO<sub>2</sub> (Al<sub>2</sub>O<sub>3</sub>, Pd, Rh, Ru or ZrO<sub>2</sub>) showed the presence of impurities increased the dissolution rate [21]. Contrary to the previously mentioned research, the presence of 25% of lanthanides (Ce, Gd, Nd, Th) in UO<sub>2</sub> generated a lower dissolution rate than the ones produced by pure UO, [22]. The crystallographic structure also affects UO, dissolution behaviour because it affects the characteristics of the solid surface layer. UO, grains with (111 ) planes showed lower dissolution rates than UO<sub>2</sub> with (100) planes [23, 24]. The effect is produced due to the higher surface energy, thus less stability, of the (100) plane.

Other experimental conditions, such as mixing, also affect the dissolution kinetics of  $UO_2$ . Results show that the dissolution rate of  $UO_2$  decreases with increasing stirring speed [14, 16, 17, 19]. The effect suggests the presence of a catalytic species, which promotes dissolution. Nevertheless, neither the catalytic species nor the catalytic mechanism has been determined [15].

#### Dissolution of MOx and Pu-rich oxide residues

Plutonium is found at relatively high concentration in all SNF and forms 5-40% of the MOx SNF of a typical thermal and Fast Reactor fuel (FRs). The dissolution of SNF becomes progressively slower with increasing Pu concentration [19, 25-30] and becomes practically insoluble when dissolved in HNO<sub>2</sub> at low concentrations [31]. For this reason, methods of accelerating the dissolution of PuO, and Pu-rich oxides have been developed. This includes the use of complexing agents, such as HF or redox-based methods to reduce or oxidise PuO2. In an industrial context, dissolution by an oxidation process has been adopted, as these provide good kinetics and minimise the corrosivity of the DPL after the dissolver. Fluoride, i.e. HF or fluoride salts, added to nitric acid are commonly used for analytical applications. Oxidation additives include Ce(IV) ([19, 26, 32], Ag(II) or Co(III) [33-35], Am(VI) [36] generated electrochemically or by O<sub>2</sub> [19] have been used to improve the dissolution rate of PuO<sub>2</sub> in HNO<sub>2</sub>.

During the dissolution of MOx it is common that a small proposition of the Pu does not dissolve in nitric acid dissolutions, due to the presence of Pu-rich oxide grains. These Pu-rich grains are present as most MOx is manufactured by the co-milling of  $UO_2$ and  $PuO_2$ . During irradiation in thermal reactors, the Pu-rich regions reduce in plutonium content and solubility improves. However, small quantities of Pu-rich grains remain and do not dissolve in nitric acid only dissolvers. For this reason, the secondary oxidative dissolution process could be used to improve Pu recovery.

#### **Mechanical separation of IFP**

Big and dense particles are directly separated from the liquor by sedimentation in the dissolver vessel. The separation of mediumsized IFPs after dissolution in the head-end is achieved mechanically using centrifugation. The bowl centrifuge consists of a rotating bowl within a static vessel. The DPL is fed to the inner bowl which spins between 1000-2000 rpm to separate the IFPs. With time, the IFPs accumulate in the inner bowl and the DPL overflows from the top of the inner bowl to the outer bowl and the separation takes place [37]. Small particles (<2  $\mu$ m) pass with the DPL downstream. The separation efficiency of SiO2 particles with a centrifuge like the one used in La Hague (France) was found to be 93-97 % for particles with diameters between 1.6-2.0  $\mu$ m and 82-91 % for particles between 1.3-1.6  $\mu$ m in size [38]. The separation efficiency of centrifugation of liquors from a dissolved FBR fuel was 75-77 % for the Al<sub>2</sub>O<sub>3</sub> (p= 4 g/ cm<sup>3</sup>) and 93-94 % for the Fe<sub>2</sub>O<sub>3</sub> particles (7 g/cm<sup>3</sup>) [39].

#### Chemical and physical characteristics of Insoluble Fission Products

There are two different phases in the residues formed when nuclear fuel is treated with HNO<sub>3</sub>. Primary phases originated from the incomplete dissolution of fuel and cladding, and the secondary phases formed by dissolution species reprecipitation due to radiolytic or chemical influences. Analysis of the composition of Insoluble Fission Products (IFP) from MOx post-irradiated spent fuel described in 1983 [6]. The IFPs were leached three times with HNO<sub>3</sub> and KF. First, the SF was leached in 7 M HNO3 at 95°C for 4 h. Then, the centrifugated residue was refluxed in 8 M HNO<sub>3</sub> and 0.05 M KF for 2 h. The elemental composition of IFP was found to be formed mainly by U, Pu, Ru, Pd, Rh, Fe after HNO<sub>3</sub> treatment; with

Ru commonly found at the highest concentration. Other elements such as W, Ag, Pd, Rh, Ru, Mo and Tc were found when the sample was treated with  $HNO_3$  and KF, with Ru and Rh found at the highest concentrations. The density of the insoluble phase after two  $HNO_3$  treatments was found to be 7.74 g/cm<sup>3</sup>, and it increased to 8.32 g/ cm<sup>3</sup>, after further treatment with  $HNO_3$  and KF. Additionally, the results show the samples formed aggregates up to 10  $\mu$ m and that aggregation was promoted as  $HNO_3$  concentration increased.

A few years later, in 1990, a similar study analysed the composition of LWR fuel residues after their dissolution in 7 M HNO<sub>3</sub> [40]. The elemental analysis showed that Ru and Mo were found to be present in the highest concentrations while Pu, Sr, Cr and Ni (structural material residue) were found to be present in the lowest concentrations. XRD experiments showed that approximately 10 % of the residue was Mo-Tc-Ru-Rh-Pd alloy probably in the form of Mo-Ru-Rh<sub>0.5</sub>-Pd<sub>0.5</sub>. The remaining fraction was formed by oxides and hydrated oxides. However, they could not confirm the presence of the hydrated oxides due to the complexity of their XRD patterns.

Element	wt% from [6]	wt% from [43]	wt% from [42]	wt% from [41]	wt% from [40]
U	0.1	1.5-12	2.6-4.0	0.8-2.6	0.7
Pu	0.1	1.8-5.9	1.8-4.3	0.37-2.80	0.1
Wa	4.5	-	-	-	-
Ag	1.4	-	-	-	-
Pd	8.3	6.4-8.0	6.4-9.4	-	6.5
Rh	8.8	4.6-8.0	5.5-8.0	-	4.4
Ru	37.3	15-22	19-27	18-20	34.2
Мо	22.8	12-23	16-23	19-31	15
Тс	6.9	4.1-7.2	4.6	-	4.1
Zr	-	<1.5	<1.6	-	4.1
Sr	-	-	-	-	0.4
Ва	-	-	-	-	3.3
Sn	-	-	-	-	1.0
Те	-	-	-	-	8.9
Ti	-	-	-	-	0.8
Fe	0.1	-	-	-	2.1
Cr	-	-	-	-	0.3
Ni	-	-	-	-	0.2

#### Table 3: Elemental composition of IFPs from different sources

In 2012 and 2013 a series of experiments studied the composition of irradiated mixed oxide fuel (MOX) for fast reactor reprocessing and irradiated fuel from a LWR [41, 42]. The results show that the dissolution rate of SNF in HNO<sub>3</sub> is 10<sup>3</sup> times higher than the same non-irradiated material. Additionally, it was found that the amount of insoluble residue increased as the amount of Pu content in the sample increased. The behaviour was attributed to the formation of refractory alloys (Mo-Tc-Ru-Rh-Pd) [3]. Additionally, the dissolution of irradiated fuel from LWR (in HNO<sub>3</sub> at different concentrations and at 95°C) concluded that the dissolved fraction contained U, Pu, Zr, Mo, Tc, Ru, Rh, Pd, Sb<sup>125</sup>, Cs<sup>137</sup>, and Ce<sup>144</sup> with Ru and Mo found at the highest concentrations in the sludge. Moreover, it was found that smaller samples dissolved faster than bigger samples.

In 2016, Aihara et.al. characterised the insoluble sludge from the dissolution of irradiated fast breeder reactor fuel [43]. Analysis of the sludge revealed the amount of IFPs was less than 1 % in weight of the total weight of fuel and that Mo, Tc, Ru Rd and Pd were their main components. Also, the XRD of the sample revealed the formation of  $Mo_APu_ARhPd$  alloy.

#### 1. CONCLUSIONS

Reprocessing is being proven to improve the sustainability of the nuclear cycle process. The design of a reprocessing plant depends on the type of fuel that needs to be reprocessed. This review article provides information about the head-end process as a whole. The review gives information about: the physical and chemical characteristics of SNF, the sharing process, the dissolution process and the IFPs the dissolution process produces, the dissolution of (UO and MOx fuels) and the mechanical separation of IFPs.

The first step of PUREX, head-end, is composed of three different steps: shearing, dissolution and fuel clarification. Once the SNF is taken from the cooling ponds, the SNF is sheared either using

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single or whole bounding shearing. Then, the SNF is dissolved in  $\rm HNO_3$  at high temperature. Nevertheless, IFPs remain solid after the dissolution step. The physical and chemical characteristics (e.g. composition) of the IFPs depend on the type of fuel. Then, IFPs are removed with the help of centrifuges and the clarified liquor is conditioned to pass to the next step of the process, extraction.

Out of the 43 documents consulted in this review, 30 % were industrial review papers. Additionally, out of the 43 documents, 66 % had more than 10 years old. The age of the papers is, even more pronounced, in the case of  $UO_2$  or  $PuO_2$  dissolution related research papers, where 90% of the documents consulted were written before 2000. The literature research shows there was a lot of nuclear-related research for nuclear plants design and manufacture but, since then, the number of articles that could help understand the dissolution mechanics of SNF, thus improving the sustainability of the cycle, have drastically decreased. This information is useful for the assessment of further clarification technologies against the requirements of candidate future solvent extraction equipment, such as centrifugal contactors.

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Bruce Hanson was the Leadership Chair in Nuclear Process Engineering at the University of Leeds. He is a named investigator on 10 grants, lead EPSRC's ATLANTIC programme and served as Co-Director of the GREEN CDT. Before his appointment at Leeds, he spent 25+ years in the nuclear and chemical industries in a range of roles, specialising in actinide separations and treatment of irradiated nuclear fuel. He was the Technical Authority for Spent Fuel and Nuclear Materials at the National Nuclear Laboratory, where he was a Visiting Senior Fellow.



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#### REFERENCES

- Nash, K.L. and M. Nilsson, 1 Introduction to the reprocessing and recycling of spent nuclear fuels, in Reprocessing and Recycling of Spent Nuclear Fuel, R. Taylor, Editor. 2015, Woodhead Publishing: Oxford. p. 3-25.
- [2] Energy, U.S.D.o., Characteristics of spent fuel, high-level waste, and other radioactive wastes which may require long-term isolation.
  1987, USDOE Office of Civilian Radioactive Waste Management, Washington, DC (US).

#### **REFERENCES (CONT.)**

- [3] Schwenk-Ferrero, A., German Spent Nuclear Fuel Legacy: Characteristics and High-Level Waste Management Issues. Science and Technology of Nuclear Installations, 2013. 2013: p. 293792.
- [4] Kleykamp, H., The chemical state of the fission products in oxide fuels. Journal of Nuclear Materials, 1985. 131(2): p. 221-246.
- [5] Kato, M., et al., Uranium Oxide and MOX Production☆, in Reference Module in Materials Science and Materials Engineering. 2019, Elsevier.
- [6] Goode, J.H.a.A., P.C., Characterization of insoluble residues from the dissolution of irradiated (I,Pu)O2. 1983, Oak Ridge National Laboratory.
- [7] Feiveson, H.M., Z.; Ramana M.V. and von-Hippel, F. . Spent Fuel from Nuclear Power Reactors. An Overview of a New Study by the International Panel on Fissile Materials 2011.
- [8] Gauld, I.C., et al., Integral nuclear data validation using experimental spent nuclear fuel compositions. Nuclear Engineering and Technology, 2017. 49(6): p. 1226-1233.
- [9] Michel-Sendis, F., et al., SFCOMPO-2.0: An OECD NEA database of spent nuclear fuel isotopic assays, reactor design specifications, and operating data. Annals of Nuclear Energy, 2017. 110: p. 779-788.
- [10] F. Michel-Sendis, I.G., M. Bossant, N. Soppera, A New OECD/ NEA Database of nuclide compositions of spent nuclear fuel, in Proceedings of the PHYSOR 2014 International Conference. 2014 Kyoto, Japan.
- [11] Weil, B.S. and C.D. Watson, Method for shearing spent nuclear fuel assemblies. 1977: United States.
- [12] Agency, N.E., State of the Art Report on the Progress of Nuclear Fuel Cycle Chemistry 2018, Nuclear Energy Agency, Organisation for Economic Co-Operation and Development
- [13] Philippe, M., et al., Dissolution of uranium dioxide in nitric acid media: what do we know? EPJ Nuclear Sciences & Technologies, 2017. 3.
- [14] Herrmann, B., Dissolution of unirradiated UO 2-pellets in nitric acid. 1984, Kernforschungszentrum Karlsruhe GmbH (Germany.
- [15] Marc, P.M., A; Vaudano, A; Delahaye. T; Schaer, E, Dissolution of uranium dioxide in nitric acid media: what do we know? EPJ Nuclear Sci. Technol., 2017. 3.
- [16] Taylor, R., Processing in Limited Geometry. Part 3. The Dissolution of Uranium Dioxide Sintered Pellets in Nitric Acid. 1962: Atomic Energy Research Establishment.
- [17] Taylor, R.F.a.S., E. W. and De Chazal, L. E. M. and Logsdail, D. H., Dissolution rates of uranium dioxide sintered pellets in nitric acid systems. Journal of Applied Chemistry, 1963. 13.
- [18] Shabbir, M. and R. Robins, Kinetics of the dissolution of uranium dioxide in nitric acid. I. Journal of Applied Chemistry, 1968. 18(5): p. 129-134.
- [19] Uriarte, A.L.a.R., R.H., Uriate AL, Rainey RH. Dissolution of high-density UO2, PuO2, and UO2-PuO2 pellets in inorganic acids, 1965. 1965, OAK RIDGE NATIONAL LABORATORY. p. 92.
- [20] Greiling, H.-D. and K. Lieser, Properties of ThO2, UO2 and PuO2 as Function of Pretreatment and their Dissolution in HNO3. Radiochimica Acta, 1984. 35(2): p. 79-90.
- [21] Ikeda, Y., et al., Acceleration Effect of Noble Metals on Dissolution Rate of UO2 Powders in Nitric Acid. Journal of Nuclear Science and Technology, 1993. 30(5): p. 485-487.
- [22] Tocino, F., et al., Dissolution of uranium mixed oxides: The role of oxygen vacancies vs the redox reactions. Progress in Nuclear Energy, 2014. 72: p. 101-106.
- [23] Briggs, A., Dislocation etching and chemical polishing studies on UO2 single crystals. 1961: United Kingdom Atomic Energy Authority.

- [24] Shabbir, M. and R. Robins, EFFECT OF CRYSTALLOGRAPHIC ORIENTATION ON THE DISSOLUTION OF URANIUM DIOXIDE IN NITRIC ACID. 1968, Univ. of New South Wales, Kensington, Australia.
- [25] Schulz, W.W., Aqueous decladding and dissolution of plutonium recycle test reactor fuels. Part 2. PuO2–UO2 fuels. 1966, Pacific Northwest Laboratory Richland, Washington.
- [26] Horner, D.E., D.J. Crouse, and J.C. Mailen, Cerium-promoted dissolution of PuO2 and PuO2-UO2 in nitric acid. 1977: United States.
- [27] Goode, J.H., HOT-CELL DISSOLUTION OF HIGHLY IRRADIATED 20% Pu02–80% U02 FAST-REACTOR. 1965, Oak Ridge National Lab., Tenn.
- [28] Carrott, M.J., et al., The Chemistry of (U,Pu)O2 Dissolution in Nitric Acid. Procedia Chemistry, 2012. 7: p. 92-97.
- [29] Vollath, D., Wednemeyer, H., H. Elbel, and E. Gunther, On the dissolution of (I,Pu)O2 solid-solutions with different plutonium contents in boiling nitric acid. Nuclear Technology, 1985. 71: p. 240-245.
- [30] Ziouane, Y., A.-C. B., and G. Letureg, Impact of the plutonium content on dissolution kinetics of (U1-xPux)O2+/-g powders. Hydrometallurgy, 2020. 108: p. 105504.
- [31] Ryan JL, B.L., Dissolution of plutonium dioxide–a critical review. 1980, Pacific Northwest Laboratory, Battelle Memorial Institut.
- [32] Harmon, H.D., Dissolution of PuO2 with Cerium (IV) and Fluoride Promoters. 1975, Savannah River Laboratory.
- [33] Ryan, J.L. and L.A. Bray, Dissolution of Plutonium Dioxide—A Critical Review, in Actinide Separations. 1980, AMERICAN CHEMICAL SOCIETY. p. 499-514.
- [34] Madic, C., P. Berger, and X.M. Machuron-Mandard, Mechanisms of the rapid dissolution of plutonium dioxide in acidic media under oxidizing or reducing conditions. 1992, United States: American Chemical Society.
- [35] Zawodzinski, C., Smith, W H, and Martinez, K R., Kinetic studies of electrochemical generation of Ag(II) ion and catalytic oxidation of selected organics. 1993, Los Alamos National Lab., NM (United States).
- [36] Gelis, V., et al., Use of ozone for dissolving high-level plutonium dioxide in nitric acid in the presence of Am(V,VI) ions. Radiochemistry, 2011. 53.
- [37] Arm, S. and C. Phillips, 3 Chemical engineering for advanced aqueous radioactive materials separations, in Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment, K.L. Nash and G.J. Lumetta, Editors. 2011, Woodhead Publishing. p. 58-94.
- [38] Duncan, J.B., Engineering evaluation of solids/liquids separation processes applicable to sludge treatment project. 1998: United States. p. 52.
- [39] Takeuchi.M, K.T., Noguchi.Y, Washiya.T Development of High Performance Clarification System for FBR Dissolver Liquor. International Journal of Chemical and Molecular Engineering, 2011. 5: p. 836-842.
- [40] Kleykamp, H., Post-irradiation examinations and composition of the residues from nitric acid dissolution experiments of high-burnup lwr fuel. Journal of Nuclear Materials, 1990. 171(2): p. 181-188.
- [41] Ikeuchi, H., et al., Dissolution Behavior of Irradiated Mixed-oxide Fuels with Different Plutonium Contents. Procedia Chemistry, 2012. 7: p. 77-83.
- [42] Ikeuchi, H., et al., Dissolution behavior of irradiated mixed oxide fuel with short stroke shearing for fast reactor reprocessing. Journal of Nuclear Science and Technology, 2013. 50(2): p. 169-180.
- [43] Aihara, H., et al., Characterization of the Insoluble Sludge from the Dissolution of Irradiated Fast Breeder Reactor Fuel. Procedia Chemistry, 2016. 21: p. 279-284.