REVIEW

A snapshot review on uranyl secondary phases formation in aqueous systems

N. Rodríguez-Villagra[1] · L. J. Bonales[1] · A. Milena-Pérez[1] · H. Galán[1]

Abstract

Irradiated fuel based on UO_2 is expected to be disposed of in an underground repository according to a "once-through" fuel cycle policy. In addition, those countries that have chosen reprocessing their irradiated fuel will also need this kind of repository. There is an international consensus on this option as the best to dispose properly high-level waste. In the multiple-barrier concept of repository, the fuel pellet is the first barrier to the release of fission products (FP) to the environment. Nevertheless, after storage times of several thousand years, it is foreseen that groundwater will penetrate and infiltrate in the emplacement, and will eventually interact with the spent fuel. Upon contact with groundwater both, the matrix and FP might be released. Because of water radiolysis, uranium is oxidized from its tetravalent state to the hexavalent uranyl ion, being known to be far more soluble in water than uranium (IV). Then, during this oxidative-dissolution and depending on the surface/volume ratio, secondary phases (containing uranyl ion, UO_2^{2+}) might precipitate at the whole pH range. These secondary phases play an essential role on the radionuclide release in the final disposal environment due to its capacity to seize trace radioelements, and therefore, to reduce radionuclides mobility. Some important radionuclides can precipitate into its inner solid structure. Here, we examine the state-of-the-knowledge and advances on uranyl secondary phases potentially formed under repository relevant conditions. An overview of likely uranyl compounds that can be formed under repository conditions, as well as the progress made concerning experimental data on the field is presented.

Introduction

The alteration of Spent Nuclear Fuel (SNF) under simulated geological repository conditions has been extensively studied [1–7] in long-term storage. The alteration process dominating the release of radionuclides (RN) contained in the fuel matrix is oxidative-dissolution [8]. Exposure of irradiated fuel matrix (principally made up of UO_2(cr)) to oxidizing aqueous solutions promotes the formation of alteration products (uranyl secondary phases), in different speciation forms depending on the chemical groundwater composition [9]. Locally oxidizing conditions could be attained by the presence of water radiolysis byproducts, such as H_2O_2 and/or oxygen. In particular, H_2O_2 increases the corrosion rate of the oxidative-dissolution of UO_2 by oxidizing U(IV) to the much more soluble U(VI) ion, in the form of linear dioxouranyl cation, (UO_2^{2+}) [8, 10–12], where U(VI) strongly bonds to two O atoms [10]. The U(IV) species are almost insoluble, forming mainly hydrous $UO_2 \cdot xH_2O$(s) by U(IV) hydrolysis, being amorphous UO_2(am) or microcrystalline UO_2(cr) the limits of a range of solids with different thermodynamic equilibrium constants (log K_{sp} (UO_2(am)) $= -(8.5 \pm 1.0)$ at pH > 5) and extremely insoluble as pH increases [13]. In fact, several discrepancies exist with regard to reported equilibrium constants of UO_2(am), which have been extensively discussed. In contrast, the U(VI) compounds can reach a higher solubility in groundwater, and its speciation is often complex [8, 14, 15]. U(VI) species can behave as soluble complexes (involving nanoclusters), chemical precipitates, colloids, or surface adsorbed phases [16].

In particular, the significance of thermodynamically stable uranyl phases, formed by the alteration of SNF, would not be limited only to a passivating role when it precipitates on the SNF surface, but also related to their potential capacity to retain certain RN of special concern, because of their long half-lives, radiological toxicities, and potential mobility [17–20]. Special attention is given to some radionuclides during corrosion of spent UO_2 fuels, which are [19, 21]

✉ N. Rodríguez-Villagra
  nieves.rodriguez@ciemat.es

1 Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Av. Complutense, 40, 28040 Madrid, Spain

- Actinides (mainly found in fuel matrix): ^{234}U (α), ^{237}Np (α), ^{239}Pu (α), ^{242}Pu (α), ^{241}Am (α).
- Fission products: ^{99}Tc (β^-), ^{129}I (β^-), ^{79}Se (β^-), ^{90}Sr (β^-), ^{14}C (β^-), ^{231}Pa (α), ^{134,137}Cs (β^-) and ^{154,155}Eu (β^-).

The penetrating β and γ ionizing radiation mostly comes from short-lived fission products and activation products; being the transuranium elements the main source of α-emitters [22]. A quantitative estimation of the mechanisms of UO_2 alteration (dissolution and precipitation) should be properly addressed in order to best estimate the solubility and the distribution of U in these environments.

Mitigation processes for U(VI) mobility [18, 20, 23], and then, RNs, include sorption to solid surfaces and precipitation of a varied uranyl minerals that are governed by groundwater chemistry [7, 10]. The transport of U and potential sorption of radionuclides in groundwater environments is influenced by geochemical parameters such as (1) pH, ionic strength, and redox conditions; (2) the presence and concentration of complex-forming ligands; (3) the presence of dissolved gases in the solution; and 4) the own SNF (inventory, dose rate, type, and intensity of the radiation), when the system is subjected to ionizing radiation [7]. The present paper consists of a detailed overview of uranyl compounds that are likely to be formed under repository conditions, and the progress made concerning experimental data on the field. This revision highlights the remaining questions related to the exact mechanism and the impact of complexation on mobilizing RN in water.

Antecedents of uranyl phases

The most important U(IV) mineral is uraninite, of nominal composition UO_2; conversely, most U(VI) minerals consist of uranyl cation UO_2^{2+}. The uranyl yields many different solid phases with frequent environmental ligands such as hydroxyl, phosphate, silicate, and carbonate [14]. The hydrated uranyl ion is the dominant aqueous species in most waters at a pH of nearly 5 or below [10]. Under acidic conditions in deionized water, uranyl peroxide complexes yield the precipitation of studtite [24] and increase its aqueous solubility under alkaline conditions [11]. At higher pH, the uranyl ion hydrolyzes, forming several aqueous hydroxide complexes that in the presence of dissolved carbonate combines to form uranyl carbonate complexes [10, 13, 25]. Uranyl oxyhydroxides are significantly less soluble than uranyl carbonates (except the rutherfordine, [$(UO_2)CO_3$]), and can precipitate in the absence of ligands other than OH^- ions. The uranyl carbonate and uranyl sulfate complexes are relatively stable in most groundwaters. Most other complexing ligands of UO_2^{2+} (silicates, phosphates, vanadates, arsenates, and molybdates) form relatively insoluble uranyl phases [6, 14]. Thermodynamic data of aqueous carbonate

and phosphate uranyl complexes are well reported in literature [26–28]. Other minerals containing reduced U can be also found in nature, i.e., uraninite ([UO_2] and [UO_{2+x}]), and coffinite [$USiO_4$] [10]. A critical extensive review of uranyl minerals and thermodynamic data (solubility) has been reported by Gorman-Lewis *et al.* [17, 19, 20], and also recently in [29]. We summarize below the most relevant uranyl mineral phases:

Uranyl oxide hydrates [$UO_2 \cdot nH_2O$] such as becquerelite [$Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$], metaschoepite [$(UO_2)_8O_2(OH)_{12} \cdot 10H_2O$], schoepite [$(UO_2)_8O_2(OH)_{12} \cdot 12H_2O$], and compreignacite [$K_2(UO_2)_6O_4(OH)_6 \cdot 7\text{-}8(H_2O)$] are usually the first alteration products to appear where uraninite is oxidized in U deposits [20, 30, 31]. Schoepite and metaschoepite may be important phases in the adsorption of transuranic elements into uranyl oxide hydrates such as Np, while becquerelite could possibly isolate Sr through incorporation into its mineral structure [32–35].This fact could significantly affect its future mobility under repository conditions. Although both schoepite and metaschoepite have distinct crystal structures [36, 37], they are often erroneously treated as equivalent phases in literature and improperly referred as $UO_3 \cdot nH_2O$, which is a form that ignore the existence of hydroxyl groups in the structure. Schoepite potentially undergoes dehydration to metaschoepite and paulscherrerite [$UO_2(OH)_2$] [38].

Uranyl peroxides are often found in U deposits of the SNF in the earlier stages of the paragenetic sequence due to the buildup of H_2O_2 and other oxidants resulting from water radiolysis. The most commonly forms are limited to studtite [$(UO_2)O_2(H_2O)_4$] or [$(UO_2)(O_2)(H_2O)_2](H_2O)_2$] and metastudtite [$UO_4(H_2O)_2$] [12, 39]. Studtite has a very low solubility and could thereby act passivating the SNF surface and then, inhibiting its dissolution. Studtite has been observed in the solidified lavas at Chernobyl (Ukraine) [40] due to the interaction between fuel or "lava", radiation fields, water, and air.

Uranyl carbonates are particularly soluble (and stable) in aqueous solutions and may not be dominant in repository settings but are commonly found in mining environments as direct alteration of primary U-bearing rocks [20, 41, 42]. The partial pressure of CO_2 in equilibrium with groundwater is particularly relevant [18], being approximately of $10^{-3.5}$ atm when the aquifer is open to the atmosphere. Uranyl carbonates usually contain other cations in addition to uranium [43] except rutherfordine [UO_2CO_3]. In addition, uranyl carbonate mineralization has been also observed in the alteration products of the "lavas" that were formed during the accident of the Chernobyl nuclear power plant in 1986 [42, 44]. The higher solubility of these phases, in comparison with uranyl oxide hydrates and uranyl silicates or phosphates, can make them act as intermediate phases in the alteration from uraninite oxidation and solubilization

[20], and it is possible that they can affect U mobility in groundwater settings. Rutherfordine is the simplest chemical composition and the least soluble among natural and synthetic uranyl carbonates [18, 42]. It consists of uranyl hexagonal bipyramid sheets connected by hourglass dimers of edge-sharing triangles, held together through Van der Waals forces in a layered structure [42]. Discrepancies in K_{sp} values highlight how difficult is to obtain consistent results due to their high solubility and to the associated difficulty in the atmospheric composition control [20]. Grimselite [$K_3Na[(UO_2)(CO_3)_3](H_2O)$] and [$Na_4(UO_2)(CO_3)_3$] [45] could be noteworthy under repository conditions. It has been also found in the nuclear waste on Chernobyl "lava" [40].

Uranyl silicates are the most likely final uranyl mineral phases formed during oxidizing weathering of uraninite when dissolved silica is present [17, 31], because of Si^{4+} abundance in nature [29] and the lower solubility of uranyl silicates compared to that of uranyl oxide hydrates or carbonates [16]. The mobility of U as uranyl silicates is highly influenced by the availability of dissolved silica. Three groups of approximately 19 uranyl silicate minerals in natural systems are formed according to the U:Si ratio: uranophane-group (1:1), weeksite-group (2:5) and soddyite (2:1), the only mineral with U:Si > 1 [$(UO_2)_2SiO_4 \cdot 2H_2O$] [17, 46]. The best-known examples of the group (1:1) are uranophane-α or -β [$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$], kasolite [$PbUO_2SiO_4 \cdot H_2O$], boltwoodite [$K_2[(UO_2)(SiO_3OH)]_2 \cdot 3H_2O$], and natrobolt-woodite (with Na partially substituting K). The weeksite-group [$K_2[(UO_2)_2(Si_5O_{13})] \cdot 4H_2O$] includes haiweeite [$Ca[(UO_2)_2(SiO_3OH)_2(Si_3O_6)] \cdot 6H_2O$].

Uranyl phosphates are particularly important uranyl phases because of their especially low solubility under environmental conditions (only under low pH and high ionic strength it is possible to induce enough dissolution for its detection in solution), and thus, together with silicates, may limit U mobility in groundwater. Nevertheless, this certainly low U solubility shows that the database is scarce for uranyl phosphates and confirms the difficulties to reproduce experimentally these compounds. Solubility experiments are usually accomplished under low pH and high ionic strength (up to 1 M) conditions to prompt enough dissolution for measuring the dissolved species. In a recent study, experimental observations regarding the solubility of both synthetic and natural meta-torbernite under pH between 2.3 and 7.1, Cretaz *et al.* [47] found a very low solubility constant (log $K_{sp} = -52.9 \pm 0.1$) determined in both under- and supersaturated conditions. Even though they proved that working with synthetic samples is an easy approach to study the solubility properties of meta-torbernite. Authors claim that using natural samples in solubility experiments involves "a careful pretreatment in order to obtain pure and stoichiometric phase." A number of chemically basic uranyl phosphates [$MUO_2 \cdot PO_4 \cdot xH_2O$] are categorized as autunite /

torbernite group [$M(UO_2)_2(PO_4)_2 \cdot 8\text{-}12H_2O$], with a number of cation (Ca, Cu, Ba, Fe, Mg, and Mn) and anion (As or V) likely substitutions. Such group members include autunite (M = Ca), torbernite (M = Cu), and uranocircite (M = Ba). Many compounds of this group can dehydrate to a different mineral that belongs to the meta-(autunite/torbernite) group [$M(UO_2)_2(PO_4)_2 \cdot 4\text{-}8H_2O$]. The solid phase hydroxyapatite [$Ca_5OH(PO_4)_3$] has been proposed for removal of U(VI) for groundwater remediation purposes, as well as for treatment of plumes within the subsurface, by precipitating insoluble uranium minerals [48–51].

Uranyl sulfates are relatively widespread [20, 43] and formed as a consequence of the evaporation of acid sulfate-rich waters [10, 52]. In general, sulfate is the second most frequent solute after chloride in hydrothermal fluids; however, the occurrence of uranyl sulfate complexes is still poorly understood [53] because it is formed as an intergrowth of multicomponent inclusions, which makes their characterization particularly interesting [54]. The zippeite-group is one of the most common [$M_x(UO_2)_6(SO_4)_3(OH)_{10} \cdot y(H_2O)$] with M = K, Na, NH_4, Mg, Co, Ni, Fe, Mn, Zn; $(x,y) = 4,4$ for monovalent cations; and $(x,y) = 2,16$ for divalent cations [55].

Different approaches and techniques are useful for identifying uranyl phases and the degree of crystallinity, such as X-ray diffraction, spectroscopic techniques (i.e., Raman spectroscopy, X-ray Photoelectron Spectrometer, Fourier transform infrared spectroscopy) and chemical analysis of the phase(s) present [20]. Recently, molecular simulation techniques and solid-state calculations have gained interest because of their applicability as a complement to spectroscopic measurements, for studying the mobility and sorption behavior of RN within various minerals [12, 37, 56–58].

Alteration compounds of fresh fuel: studtite

Extensive literature can be found with respect to dissolution experiments simulating the contact of groundwater with SNF surrogates such as $UO_2(cr)$, the so-called SIMFUEL, and α-doped $UO_2(s)$ (see review of Oversby [59]). Some of those studies have been conducted in oxidizing conditions simulating the presence of radiolytically produced H_2O_2 [60–64], or under controlled reducing conditions (in the presence of Fe^{2+} and/or H_2) [65, 66]. Studtite and metastudtite are observed on SNF under aqueous conditions subsequent to H_2O_2 generation by water radiolysis. However, there is a wide variety of U minerals synthetized and studied, including metaschoepite, uranophane, sodium boltwoodite, studtite or metastudtite, among many others. Stability of studtite has been extensively studied in a broad range of conditions (temperatures, groundwater) [24, 67–70] by both, experimental and theoretical approaches.

Most of the reviewed literature and experimental studies have been focused on the impact of α and β radiation, as the main source of radiation at medium or long-term. However, with a thorough study on the UO_2^{2+}(aq) stability under intense γ radiation fields, Rodríguez-Villagra *et al.* [71] empirically demonstrated that the H_2O_2 formed under γ radiation promotes the precipitation of studtite. This would indicate that if a young SNF (within the first 100 years of storage) is exposed to water in early stages of repository, the role of γ photons should be accounted for the total dose rate and radiolysis cascade. The penetrating γ rays could even pass through the canister in their way to the outside, making it also susceptible to radiation-induced corrosion when groundwater is present.

A recent publication from Schlegel and Jegou [8] deals with the study of radiolysis impact on the alteration of SNF. The transformations and phase precipitations occurring at a monocrystalline surface of uraninite, when exposed to oxidizing conditions (H_2O_2 solutions from 0.005 to 0.5 M), were observed by using a combination of *in situ* μ-Raman Spectroscopy (RS) and synchrotron X-ray diffraction. At low H_2O_2 concentrations, schoepite and studtite coexisted on the reacted surface. With increasing H_2O_2 content, studtite predominated. Authors highlighted that studtite transformation might occur possibly upon drying, and introduced an uncertainty when schoepite is *ex situ* observed, since it could be caused either from *in situ* formation or from sample handling.

Li *et al.* [72] performed dissolution kinetics experiments of metastudtite to study the influence of the added H_2O_2 and the impact of γ-irradiation. The observed solubility of metastudtite in the presence of H_2O_2 (in HCO_3^- containing solutions) was lower than that in the absence of H_2O_2. The authors attribute this to the fact that H_2O_2 was consumed in systems where metastudtite and studtite were dissolved as a catalytic decomposition in solutions containing UO_2^{2+} and HCO_3^-. In the same study, the authors examined metastudtite upon exposure to γ-radiation yielding rapid dissolution of metastudtite in 10 mM HCO_3^-. However, the rate was lower than that of studtite under the same conditions. This fact was attributed to a combination of the radiolytic degradation of H_2O_2 and the formation of uranyl-peroxocarbonate complexes.

In assessing the long-term storage of SNF in geological repositories and the derived thermal degradation/stability of uranyl peroxides, extensive literature has been reported. It is known that dehydration from studtite to metastudtite is irreversible. Literature discrepancies exist in the described dehydration temperature transition. An example is presented by Colmenero *et al.* [57]. The thermal behavior of studtite was conducted by *in situ* RS (at different heating rates in air), revealing lower dehydration temperatures of studtite to metastudtite (32–35 °C) at low heating rates (0.2 ºC/min)

than published (50–130 °C) [73, 74], and even when results were compared with data from thermogravimetry. Authors emphasize the influence of the heating rate on the observed dehydration temperature transition. Assuming that the temperature at early times in the near field repository is below 100 °C [53, 75, 76], it can be deduced that metastudtite would be the most likely existing phase if H_2O_2 remains being produced by water radiolysis.

Naturally occurring uranyl minerals

Given the timeframe for which the integrity of SNF is required and the resultant uncertainties associated to short-term experiments, natural analogs consist of a unique source of data for the performance assessment of the geological disposal of SNF [77–79]. Consistent experiments on uranyl secondary products, as important phases in the paragenesis associated with the alteration of SNF, represent a key issue for estimating the repository performance and U mobility. There are a number of studies [1–5] in weathering-bedrock and aquifer solids of naturally occurring U minerals that have been applied as a model for SNF corrosion, for example, using uraninite or pitchblende (hydrothermal uraninite) [7, 80–82]. During the weathering of ore mineral uraninite, a sequence of secondary compounds as precipitated U(VI) oxyhydroxides, carbonates, silicates, phosphates, and sulfates was reported [10]. As previously mentioned, the U(VI) forms several crystalline and amorphous oxyhydroxide phases in oxic subsurface environments and in the absence of dissolved phosphate or silicate [3, 83, 84]. The primary oxidized alteration phase is usually an oxyhydroxide, whichever schoepite or metaschoepite [3, 83]. However, schoepite is metastable, with a strong tendency to spontaneous and irreversible dehydration to the more stable metaschoepite; or well to transform to compreignacite or becquerelite after the incorporation of K or Ca, respectively [3, 31, 85, 86]. A number of studies have been carried out on U deposits in rocks and groundwater surrounding: (1) under reducing conditions at Oklo (Gabon) and Cigar Lake (Canada) sites; and (2) under oxidizing conditions at Koongarra (Australia) and El Berrocal (Spain) [87]. An extensive revision and discussion on this issue including geochemical calculations on U phases that may control the solubility has been reported by Bruno *et al.* [87].

Bonales *et al.* carried out the characterization by RS [86, 88] of a natural uraninite mineral (Sierra Albarrana, Córdoba, Spain). From authors analysis, the following U secondary phases were found: (1) remaining uraninite as unaltered core of the sample; (2) rutherfordine, in the inner part; (3) a mixture of uranyl silicates: soddyite, prevailing in the inner part, α-uranophane in the outer part of the sample, and kasolite, appearing intermittently. Contrary to that

expected [3], schoepite and metaschoepite were not observed suggesting its rapid transformation to rutherfordine.

Irradiated fuel

There is a lack of direct observations of uranyl secondary phases during SNF corrosion experiments. Uranyl silicates are commonly found after the SNF dissolution (burnups from 27 to 43 MW·d·kgU^{-1}) [89–92]. Secondary U minerals of Chernobyl "lava" have been examined by Burakov *et al.* [40]. These minerals were identified by X-ray diffraction as studtite, schoepite, rutherfordine, and a number of sodium carbonate phases. According to the authors, the source of Na is assumed to come from the penetrated water into the "Sarcophagus." Studtite and metastudtite have been also found on the surface of SNF stored at Hanford (Washington State, USA) nuclear site [39, 93]. Experiments performed by Hanson *et al.* [94]. on SNF in deionized water under laboratory conditions led to the formation of metaschoepite at short contact times. This phase disappeared over the 2-year contact period, then occurring studtite and metastudtite. In an attempt to simulate the influence of α-irradiation, a wide range of leaching experiments with α-doped UO$_2$ including ^{233}U, ^{238}Pu, ^{239}Pu, and ^{225}Ac-doped UO$_2$ have been conducted [95–98]. Likewise, studtite was also observed on α-doped UO$_2$ samples or UO$_2$ irradiated by an external source in water [11, 75, 99, 100].

Conclusions

There is widespread agreement that uranyl secondary phases may be potentially beneficial in terms of delay or limit RN release in geologic underground repositories for SNF. An exhaustive knowledge of these minerals is fundamental to evaluate their impact upon the release of RN from the SNF. Given the complexity of U(VI) speciation, more efforts could focus on thoroughly comprehending and standardizing the empirical approaches when considering properties of uranyl minerals. In order to predict the U mobility in groundwater, the stabilities of uranyl minerals and the concentration of U and other elements in equilibrium with these dominant uranyl phases under a range of conditions are required. For that reason, more rigorous and consistent solubility measurements from super- to undersaturated conditions with respect to the dissolved elements of interest are important for the construction of reliable databases. These issues would include a precise solid phase characterization (both before and after the solubility experiment) that is stable under the experimental conditions (pH/redox and aqueous element concentrations), and well-defined equilibrium state attained during the tests. Different approaches can be done by identifying the mineral phase and the degree of crystallinity of the phase(s) using X-ray diffraction (XRD), spectroscopy techniques (*i.e.*, Raman, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR)), and chemical analyses of the phases present. In parallel, actinide coordination chemistry is also a matter of interest, from a fundamental point of view, due to the impact on reactivity pathways under disposal conditions. The role of complexation in mobilizing RN in water at low and high temperatures must be well understood. Corrosion studies on irradiated fuel under closely related disposal conditions are desirable to reduce the risk associated with an increasing dependence on nuclear energy, but simultaneously are expensive and difficult to handle.

References

1. D.E. Grandstaff, Econ. Geol. **71**(8), 1493–1506 (1976)
2. Finch, R. and R. Ewing, *Uraninite alteration in an oxidizing environment and its relevance to the disposal of spent nuclear fuel*. 1990, Swedish Nuclear Fuel And Waste Management Co (SKB).
3. R.J. Finch, R.C. Ewing, J. Nucl. Mater. **190**, 133–156 (1992)
4. J. Janeczek et al., J. Nucl. Mater. **238**(1), 121–130 (1996)
5. L.P. del Villar et al., Chem. Geol. **190**(1), 395–415 (2002)
6. A. Espriu-Gascon et al., J. Hazard. Mater. **353**, 431–435 (2018)
7. D.M. Stanley, R.T. Wilkin, J. Hazard Mater. **377**, 315–320 (2019)
8. M.L. Schlegel, C. Jegou, J. Nucl. Mater. **572**, 154056 (2022)
9. C.A. Velasco et al., Environ. Sci. Technol. **55**(23), 16246–16256 (2021)
10. R. Finch, T. Murakami, Rev. Mineral. Geochem. **38**(1), 91–179 (1999)
11. C.R. Armstrong et al., Proc. Natl. Acad. Sci. USA **109**(6), 1874–1877 (2012)
12. F. Colmenero et al., J. Phys. Chem. C **122**(10), 5254–5267 (2018)
13. R. Guillaumont et al., Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium, in *Chemical Thermodynamics*. ed. by F. Mompean et al. (Elsevier, Amsterdam, 2003)
14. Z. Wang et al., Geochim. Cosmochim. Acta **69**(6), 1391–1403 (2005)
15. K.E. Knope, L. Soderholm, Chem. Rev. **113**(2), 944–994 (2013)

16. G. Lu, A.J. Haes, T.Z. Forbes, Coord. Chem. Rev. **374**, 314–344 (2018)

17. F.V. Stohl, D.K. Smith, Am. Miner. **66**(5–6), 610–624 (1981)

18. Finch, R., *Secondary Uranium-Phase Paragenesis and Incorporation of Radionuclides into Secondary Phase*. Vol. ANL-EBS-MD-000019 REV 00. 2001, United States: US Department of Energy.

19. Burns, P.C., R.J. Finch, and D.J. Wronkiewicz, *Direct Investigations of the Immobilization of Radionuclides in the Alteration Phases of Spent Nuclear Fuel*. 2003: United States. p. 5.

20. D. Gorman-Lewis, P.C. Burns, J.B. Fein, J. Chem. Thermod. **40**, 335–352 (2008)

21. Caruso, S., et al., *Horizon 2020. NFRP-2018–6. COFUND-EJP. Proposal number: 847593. European Joint Programme on Radioactive Waste Management (EURAD)*. 2018.

22. P.C. Burns, R.C. Ewing, A. Navrotsky, Science **335**(6073), 1184–1188 (2012)

23. R.J. Baker, Coord. Chem. Rev. **266–267**, 123–136 (2014)

24. P.C. Burns, K.-A. Hughes, Am. Miner. **88**, 1165–1168 (2003)

25. I. Grenthe et al., Chemical thermodynamics of uranium, in *Chemical Thermodynamics Series*, vol. 1, ed. by H. Wanner, I. Forest (North-Holland, Amsterdam, 1992), p.734

26. A. Sanding, J. Bruno, Geochim. Cosmochim. Acta **56**(12), 4135–4145 (1992)

27. R.J. Finch, Thermodynamic stabilities of U(VI) minerals: Estimated and observed relationships, in *Scientific Basis for Nuclear Waste Management*. ed. by W.J. Gray, I.R. Triay (The Materials Research Society, New York, 1997), pp.1185–1192

28. K. Müller, V. Brendler, H. Foerstendorf, Inorg. Chem. **47**(21), 10127–10134 (2008)

29. J. Plášil, Minerals **8**(12), 551 (2018)

30. D.J. Wronkiewicz et al., J. Nucl. Mater. **190**, 101–106 (1992)

31. D.J. Wronkiewicz et al., J. Nucl. Mater. **238**, 78–95 (1996)

32. P.C. Burns, Y. Li, Am. Miner. **87**(4), 550–557 (2002)

33. P.C. Burns, K.M. Deely, S. Skanthakumar, Radiochim. Acta **92**(3–2004), 151–160 (2004)

34. M. Douglas et al., Radiochim. Acta **93**(5–2005), 265–272 (2005)

35. P.C. Burns, A.L. Klingensmith, Elements **2**(6), 351–356 (2006)

36. R.J. Finch, F.C. Hawthorne, R.C. Ewing, Can. Mineral. **36**(3), 831–845 (1998)

37. M.C. Kirkegaard et al., Inorg. Chem. **58**(11), 7310–7323 (2019)

38. P.F. Weck, C.F. Jové-Colón, E. Kim, Chem. Phys. Lett. **757**, 137878 (2020)

39. K.-A.H. Kubatko et al., Science **302**(5648), 1191–1193 (2003)

40. B.E. Burakov, E.E. Strykanova, E.B. Anderson, MRS Online Proc. Libr. **465**(1), 1309–1311 (1996)

41. D.L. Clark, D.E. Hobart, M.P. Neu, Chem. Rev. **95**(1), 25–48 (1995)

42. V.V. Gurzhiy et al., Crystals **11**(6), 704 (2021)

43. Frondel, C., *Systematic Mineralogy Of Uranium And Thorium*. 1958: U. S. Geological Survey Bulletin. p. 1064.

44. Y.A. Teterin, A.S. Baev, S.A. Bogatov, J. Electron. Spectrosc. Relat. Phenom. **68**, 685–694 (1994)

45. Y. Li, S.V. Krivovichev, P.C. Burns, Mineral. Mag. **65**(2), 297–304 (2018)

46. Lõfvendahl, R., *Secondary uranium minerals in Sweden*. Vol. 779. 1980, Uppsala Sveriges geologiska undersokning, Ser. C.

47. F. Cretaz et al., J. Nucl. Mater. **442**(1), 195–207 (2013)

48. A. Krestou, A. Xenidis, D. Panias, Miner. Eng. **17**(3), 373–381 (2004)

49. H.L. Lobeck et al., Am. Miner. **105**(2), 182–193 (2020)

50. S. Szenknect et al., J. Hazard. Mater. **392**, 122501 (2020)

51. N. Seigneur et al., Minerals **11**(11), 1201 (2021)

52. J. Brugger, P.C. Burns, N. Meisser, Am. Miner. **88**(4), 676–685 (2003)

53. A. Kalintsev et al., Geochim. Cosmochim. Acta **267**, 75–91 (2019)

54. M. Louvel et al., Nat. Commun. **13**(1), 1456 (2022)

55. C. Frondel et al., Can. Mineral. **14**(4), 429–436 (1976)

56. L.J. Bonales et al., Phys. Chem. Chem. Phys. **18**(24), 16575–16584 (2016)

57. F. Colmenero et al., Spectrochim. Acta Part A **174**, 245–253 (2017)

58. F. Colmenero et al., RSC Adv. **9**(27), 15323–15334 (2019)

59. Oversby, V.M. and V.M.O. Konsult, *Uranium dioxide, SIMFUEL, and spent fuel dissolution rates—a review of published data*, in *SKB Technical Reports*. 1999, SKB: Stockholm.

60. J. Abbot, D.G. Brown, Inter. J. Chem. Kinet. **22**, 963–974 (1990)

61. E. Ekeroth, M. Jonsson, J. Nucl. Mater. **322**(2–3), 242–248 (2003)

62. S. Sunder, N.H. Miller, D.W. Shoesmith, Corros. Sci. **46**(5), 1095–1111 (2004)

63. I. Casas et al., Radiochim. Acta **97**(9), 485–490 (2009)

64. Bosbach, D., et al., *DISCO Deliverable D4.3 "Model materials experiments: Final dissolution results" (EC H2020 Grant Agreement: 755443)*. 2021.

65. *Fast/Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel FIRST-Nuclides. Final scientific report. FP7-295722.* 2014.

66. A. Espriu-Gascon et al., J. Radioanal. Nucl. Chem. **318**(2), 1201–1207 (2018)

67. F. Clarens et al., Environ. Sci. Technol. **38**(24), 6656–6661 (2004)

68. A. Rey et al., Am. Miner. **94**(2–3), 229–235 (2009)

69. P.F. Weck et al., Dalton Trans. **41**(32), 9748–9752 (2012)

70. Labs, S., *Secondary Uranium Phases of Spent Nuclear Fuel - Coffinite, $USiO_4$, and Studtite, $UO_4 \cdot 4H_2O$ - Synthesis, Characterization, and Investigations Regarding Phase Stability*. Energy & Environment Band. Vol. 267. 2014, Forschungszentrum Jülich GmbH.

71. N. Rodríguez-Villagra, L.J. Bonales, J. Cobos, MRS Adv. **24**, 1–9 (2020)

72. J. Li, Z. Szabó, M. Jonsson, Dalton Trans. **50**(19), 6568–6577 (2021)

73. X. Guo et al., Proc. Natl. Acad. Sci. **111**(50), 17737–17742 (2014)

74. N.B.A. Thompson et al., J. Radioanal. Nucl. Chem. **327**(3), 1335–1347 (2021)

75. G. Sattonnay et al., J. Nucl. Mater. **288**(1), 11–19 (2001)

76. P. Jansson et al., Ann. Nucl. Energy **172**, 109082 (2022)

77. J. Bruno, R.C. Ewing, Elements **2**(6), 343–349 (2006)

78. W.R. Alexander, H.M. Reijonen, I.G. McKinley, Swiss J. Geosci. **108**(1), 75–100 (2015)

79. Badley, M. and D. Shoesmith, *The Corrosion/Dissolution of Used Nuclear Fuel in a Deep Geological Repository*. 2022, Nuclear Waste Management Organization: Toronto

80. R. Finch, T. Murakami, 3 Systematics and Paragenesis of uranium minerals, in *Uranium*. ed. by C.B. Peter, J.F. Robert (De Gruyter, Berlin, 2018), pp.91–180

81. J. Janeczek, R.C. Ewing, *Oxidation of Uraninite* (Stockholm, SKB, 1993)

82. J. Janeczek, R.C. Ewing, L.E. Thomas, J. Nucl. Mater. **207**, 177–191 (1993)

83. E. Reinoso-Maset et al., Geochim. Cosmochim. Acta **207**, 298–321 (2017)

84. D.B. Hunter, P.M. Bertsch, J. Radioanal. Nucl. Chem. **234**(1), 237–242 (1998)

85. M.C.A. Sandino, B. Grambow, Radiochim. Acta **66**(67), 37–43 (1994)

86. L.J. Bonales, C. Menor-Salván, J. Cobos, J. Nucl. Mater. **462**, 296–303 (2015)
87. J. Bruno, L. Duro, M. Grive, Chem. Geol. **190**(1–4), 371–393 (2002)
88. L.J. Bonales et al., MRS Adv. **1**(62), 4157–4162 (2017)
89. C.N. Wilson, Summary of results from the series 2 and series 3 NNSWI bare fuel dissolution test, in *Scientific Basic for Nuclear Waste Management XI*. ed. by M.J. Apted, R.E. Westerman (Material Research Society, Boston, 1987), pp.473–483
90. C.N. Wilson, *Results from NNWSI Series 3 Spent Fuel Dissolution Tests* (Pacific Northwest Laboratory, Richland, 1990)
91. R.J. Finch, M.L. Miller, R.C. Ewing, Radiochim. Acta **58–59**(2), 433–444 (1992)
92. P.A. Finn et al., Corrosion mechanism of spent fuel under oxidizing conditions, in *Scientific Basis for Nuclear Waste Management*. ed. by I.G. McKinley, C. McCombie (The Materials Research Society, New York, 1998), pp.123–131
93. Abrefah, J., S.C. Marschman, and E.D. Jenson, *Examination of the surface coatings removed from K-East Basin fuel elements*. 1998: United States. p. 34.
94. B. Hanson et al., Radiochim. Acta **93**, 159–168 (2005)
95. J. Cobos et al., Radiochim. Acta **90**, 597–602 (2002)
96. K. Ollila et al., *Dissolution rates of unirradiated UO2, UO2 doped with 233U, and spent fuel under normal atmospheric conditions and under reducing conditions using an isotope dilution method* (Swedish, SKB, 2003)
97. Spahiu, K., et al., *The effect of dissolved hydrogen on the corrosion rates of ^{233}U doped $UO_2(s)$, high burnup spent fuel and MOX fuel*, In: *Technical Report*, K. Spahiu, Editor. 2004, SKB. p. 63.
98. Poinssot, C., et al., *Spent fuel stability under repository conditions-final report of the European Project*, CEA, Editor. 2004, European Commission 5th Euratom Framework Programme 1998–2002.
99. C. Jégou et al., J. Nucl. Mater. **341**(1), 62–82 (2005)
100. R. Mohun et al., J. Nucl. Mater. **509**, 305–312 (2018)