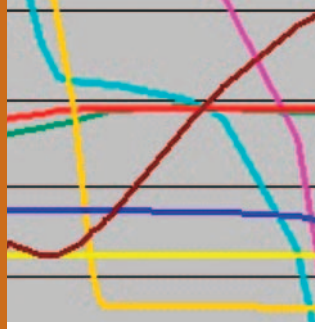
Interactions between Nuclear Fuel and Water at the Fukushima Daiichi Reactors



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Used nuclear fuel is a redox-sensitive semiconductor consisting of uranium dioxide containing a few percent of fission products and up to about one percent transuranium elements, mainly plutonium. The rapid increase in temperature in the cores of the Fukushima reactors was caused by the loss of coolant in the aftermath of the damage from the tsunami. Temperatures probably well above 2000°C caused melting of not only the UO_2 in the fuel but also the zircaloy cladding and steel, forming a quenched melt, termed *corium*. Substantial amounts of volatile fission products, such as Cs and I, were released during melting, but the less volatile fission products and the actinides (probably >99.9%) were incorporated into the corium as the melt cooled and was quenched. The corium still contains these radionuclides, which leads to a very large long-term radiotoxicity of the molten reactor core. The challenge for environmental scientists is to assess the long-term interactions between water and the mixture of corium and potentially still-existing unmelted fuel, particularly if the molten reactor core is left in place and covered with a sarcophagus for hundreds of years. Part of the answer to this question can be found in the knowledge that has been gained from research into the disposal of spent nuclear fuel in a geologic repository.

KEYWORDS: corium, spent fuel, radionuclide release, environmental impact, radiotoxicity, Fukushima Daiichi nuclear power plant

CHARACTERISTICS OF THE REACTORS AND NUCLEAR FUELS

There are six boiling water reactors (R1–R6) at the Fukushima Daiichi nuclear power plant. Four reactors (R1–R4) were destroyed by the accident: the three reactors (R1–R3) operating at the time of the earthquake and the neighboring reactor, R4, whose fuel had been removed and stored in cooling ponds. The cores of R1–R3 contained about 256 metric tons of nuclear fuel (400 fuel assemblies in R1 and 548 assemblies in each of R2 and R3; one assembly contains 60 fuel rods, each 3.70 m long, and each assembly weighs about 170 kg). Reactors R5 and R6 were shut down for routine inspection. In September 2010, 32 of the fuel assemblies in the core of reactor R3 were mixed-oxide (UO_2 + PuO_2) MOX fuel (IAEA 2011) totaling about 5.5 tons. The other assemblies were uranium oxide fuels, UO_2 (named UOX fuels). The spent fuel storage tanks located in the four destroyed reactor buildings contained an additional 461 tons of nuclear fuel, including 395 tons of discharged irradiated fuel and 66 tons of unirradiated UO_2 fuel waiting to be loaded into the reactors.

When reactors 1–3 shut down automatically after the earthquake, about 89% of the 6.1 gigawatts (GWth) of thermal nuclear fission energy being produced was immediately interrupted, i.e. the kinetic energy of fission products, neutrons, and photons. However, 11% of the energy remained in the cores of R1–R3 after shutdown, 6% (360 megawatts) in the form of beta decay heat essentially from fission products (SEE FIG. 1A) and 5% in the form of antineutrinos. Initially, this energy was rapidly released, and later, more slowly. Indeed, spent nuclear fuel is considered to be an important heat source for thousands of years in most concepts of geological disposal (FIG. 1B).

The radiotoxicity of the used fuel is in part due to the accumulation of the radioactive isotopes ("fission products") that were generated by the nuclear fission of uranium and plutonium atoms during reactor operation. It is also due to the transuranium elements (actinides beyond uranium in the periodic table) created by neutron capture on ^{238}U in the fuel. These radionuclide inventories depend on the length of time the fuel was "burned" in the nuclear reactor, i.e. on the "burnup," which is the energy released expressed in gigawatt-days per metric ton of uranium and plutonium (GWd/t). After a typical burnup during reactor operation for some years, the radioactivity of the fuel has increased by a factor of a million (10^{17} becquerels/metric ton of fuel). One year after discharge from a reactor, the dose rate measured one meter from the fuel assembly is one million millisieverts per hour (for comparison, the natural background dose is on the order of three millisieverts per year). A person exposed to this level of radioactivity at a distance of one meter would receive a lethal dose in less than a minute (Hedin 1997; Bruno and Ewing 2006). Fission-product inventories are roughly proportional to burnup, while actinide-element inventories (Pu, Am, Np, Cm) are more complicated functions of burnup because the fissile transuranium elements are partly consumed at high burnups and the production rates of higher actinides (Am, Cm) increase with burnup.

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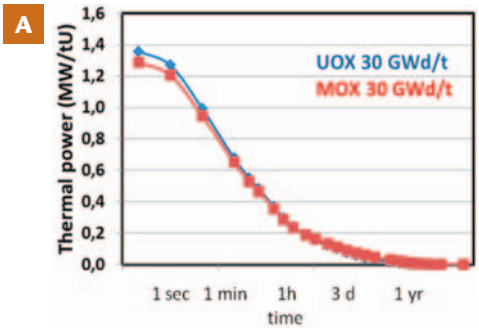

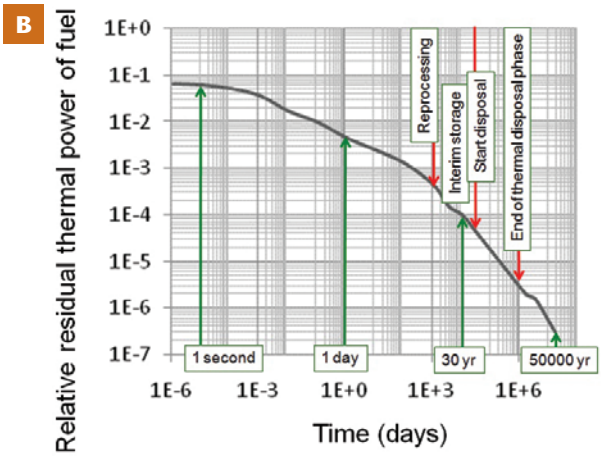

Figure 1 (**A**) The residual thermal power (in megawatts per ton of uranium) of the nuclear reactors calculated as a function of time after shutdown for the two types of spent fuel present in the Fukushima reactors, BWR UOX fuel (3.1% initial enrichment) and BWR MOX fuel (6% initial Pu content), assuming a mean burnup of 30 thermal gigawatt-days per ton uranium or plutonium (GWd/t) (calculated with the DARWIN code, using the CEA2005V4 database). (**B**) Relative residual thermal power of representative fuels over the geological timescale (data calculated with the CESAR code, Samson et al. 1998). 1E+0 = 1.0, 1E-1 = 0.1, etc.

Typical end-of-life burnups are about 40 GWd/t, which are achieved after 3 to 4 years in the reactor. Due to the replacement of only a part of the used fuel by unirradiated UO_2 fuel in normal reactor operation, a reactor core is always a mix of old and rather fresh fuel, and burnups for individual fuel assemblies range from 3 GWd/t to 41 GWd/t. The average burnup of the Fukushima Daiichi reactors is assumed to be about 20 GWd/t. The average burnup has not been reported "officially," but the "official" total ^{137}Cs inventory of reactors 1–3 can be calculated from the release fractions and total releases given in IAEA (2011) as 7.1×10^{17} Bq. This would correspond to an average burnup of about 23 GWd/tU. Endo et al. (2011a) estimated an average burnup of 17.2 ± 1.5 GWd/tU, based on the average ratio of $^{134}Cs/^{137}Cs$ (0.996 ±0.07) measured in soils within a radius of 100 km. Average core burnups were reported in the same publication as 25.8, 23.2 and 21.8 for reactors R1, R2, and R3, respectively, closely matching the value of 23 GWd/tU derived from the IAEA (2011) data. The lower burnup calculated by Endo et al. (2011a) may be due to the postulated core meltdown (i.e. differences in the degree of damage and associated Cs release for the fuel in the center of the core versus at the periphery) or to greater damage of once-burned fuel due to its higher temperature. The presence of MOX fuel in reactor 3 was considered in the world press to be a strong additional risk factor due to the higher plutonium content. For a given burnup, MOX fuel is more toxic than conventional fuel, but the short residence time in the reactor—only 5 months—means that the average fission-product inventories and associated toxicities of this type of fuel are probably lower than the average inventories of a pure UO_2 fuel. But the Pu inventory of MOX fuel is much higher. Endo et al. (2011a) report a value of 3.9 wt% Pu in the MOX fuel in reactor 3. Considering that UOX fuel with an average burnup of 23 GWd/tU contains about 0.8 wt% Pu and that only about 6% of the fuel in reactor 3 was MOX fuel, the total loaded inventory of Pu in this reactor was about 0.98 ton, roughly 30% greater than the 0.75 ton (0.8% of 95 tons of fuel) in reactor 2, which contained a similar total fuel mass but without MOX.

As an example of the evolution of toxicity over time, Figure 2 shows the toxicity inventory of one ton of spent nuclear fuel (UO_2) for a rather high burnup of 47.5 GWd per ton of the initial uranium inventory (calculations were made as part of the MICADO project; Grambow et al. 2010). Indeed, even for this UO_2 fuel, the Pu inventory dominates the long-term toxicity; therefore, the greater Pu inventory of the MOX-containing reactor would increase the long-term toxicity by about 30%. However, this does not directly represent the potential impact since the toxicity also depends on the mobility of plutonium, which can be very low depending on the chemical conditions (for instance in a reducing environment or in the presence of organics).

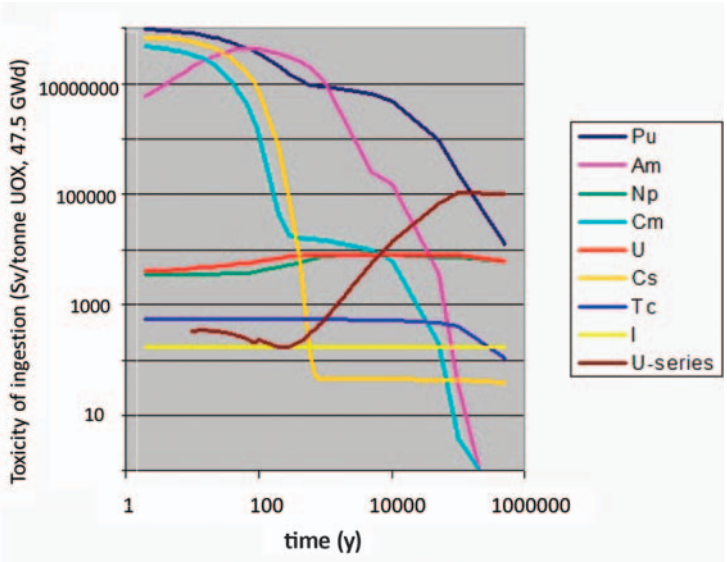

Figure 2 Evolution, in years, of the long-term toxicity (by ingestion) of one ton of spent nuclear fuel with a burnup of 47.5 GWd/tU, expressed in sieverts (Sv) per ton of UOX. The total toxicity of the 3 reactor inventories (not including fuel storage ponds) is about 100 times greater (256 tons of fuel with an average burnup of 23 GWd/t U) than the values in this figure. The data were calculated using the CESAR code (Samson et al. 1998) for fuel evolution.

Considering that the dose limit for ingestion according to regulations in Europe is 1 mSv/y (millisievert per year), the high toxicity of the radionuclides in the damaged fuel cores requires isolation well beyond hundreds of thousands of years in order to avoid exposing the fuel cores to natural waters, which might lead to the release of toxic radionuclides into the food chain. Isolation for such long times is also necessary to avoid exposing people in the vicinity of the damaged cores to lethal doses of external gamma radiation.

HOW MUCH WAS RELEASED FROM THE REACTORS? HOW MUCH REMAINS?

Toxicity is not identical to risk. Risk depends on the accessibility of radionuclides to humans and to their mobility in the environment. In the future, important measures will have to be taken in order to reduce the short- and long-term risks of the highly toxic inventory of the reactors, for example, by strict confinement and/or geological disposal of the fuel. Today, the largest risk stems from those fractions of the toxicity inventory that have been released to the environment, i.e. 2.2% and 2.5%, respectively, of the total ^{137}Cs and ^{131}I inventories in the reactor cores 1–3 (IAEA 2011, attachment IV-2). Recent data (IRSN 2011) indicate that actual releases might have been even higher. Latest estimates by TEPCO (2012) give release fractions of 1.9% for ^{137}Cs and 8% for ^{131}I. For the most volatile elements, as indicated by ^{133}Xe data, the release is estimated to be close to 100% (Stohl 2011; IAEA 2011). However, the information is not yet sufficient to conclude that the entire cores in reactors 1–3 have melted. Indeed, considering that the diffusion of Cs or Xe is similar to that of I, which is governed by a diffusion coefficient of ~2.5×10^{-11} cm^2/s at 2200 °C, at the high temperature encountered in the accident (~2200 °C), Cs would diffuse at a velocity of 1 mm per day, which is much greater than the grain size (~8 µm) of the fuel.

The situation is quite different for the transuranium elements (Pu, Am, Np, Cm). These elements are responsible mainly for long-term toxicity (see Fig. 2) since they are long-lived alpha emitters (in case of ingestion, alpha particles, $^4He^{2+}$, cause more damage to human cells due to their larger size). But the actual risk originating from these nuclides is much lower since, even in the immediate vicinity of the damaged reactors, for example, at a distance of 500 m, Pu concentrations in the soil ($^{239/240}$Pu activities are 0.055 ± 0.029 Bq/kg) are identical to the Pu concentrations in Japanese soil that resulted from atmospheric testing of nuclear weapons (0.02–0.4 Bq/kg for $^{239/240}$Pu) (Hirose et al. 2003).

The activities of plutonium and other nuclides measured by the Tokyo Electric Power Company (TEPCO) over a period of 8 months are shown in Figure 3 (original data taken from a series of Web references from TEPCO 2011: www.tepco.co.jp). These data can be used to compare the ratios of the measured activities to the activity ratios of fission products and actinides in the nuclear fuel in the reactor. The large symbols in Figure 3, corresponding to the date of the accident, represent reference values (see explanation in the caption). As can be seen, the measured activities still have, with an uncertainty of about a factor of 2, the signature of the inventory ratios in the original fuel as far as the releases of ^{137}Cs, ^{131}I, ^{110m}Ag, and ^{129m}Te are concerned, when corrected, as in the case of ^{131}I, for radioactive decay since the date of release (March 15) from the reactors. In contrast, measured activities of the alkali earth element nuclides, such as ^{140}Ba and ^{90}Sr, are about a thousand times lower than the reference value of the activity ratios in the fuel. Finally, for the actinides ^{241}Am, ^{242}Cm, and ^{238}Pu, the measured activities are about 5 orders of magnitude lower than the reference values in the nuclear fuel. Comparing the concentrations of the actinides with each other, their measured activity ratios correspond to their inventory ratios in the fuel, indicating a similarly slow mechanism of release for all actinides.

Thus, for the Pu inventory in the reactor, about 10^5 times less is released to the environment as compared with the Cs inventory. Considering this low release of Pu, even fuels of higher Pu content, such as MOX fuel, will release very little Pu. Thus, no significant additional short-term risk will arise from Pu release from the MOX fuel. In contrast, long-term risks depend on Pu inventories, particularly if Pu release from the reactor is increased by oxidizing groundwater coming into contact with the fuel.

Recently, careful activity measurements were reported at 15 soil-sampling points between 5 and 60 km from the Fukushima plant (Endo et al. 2011b). Using these data, the activity ratios ^{129m}Te/^{137}Cs, ^{131}I/^{137}Cs, and ^{140}Ba/^{137}Cs were calculated to be 1, 20, and 0.06, respectively, which can be compared with the same ratios in the original spent fuel, i.e. 0.7, 12, and 22, respectively. This corroborates the previously discussed measurements made in close proximity to the Fukushima plant: ^{129m}Te, ^{131}I, and ^{137}Cs show similar release behaviors, whereas about 1/400th as much ^{140}Ba is released as Cs. These findings confirm that the data obtained in the vicinity of the Fukushima plant are representative of the general release patterns.

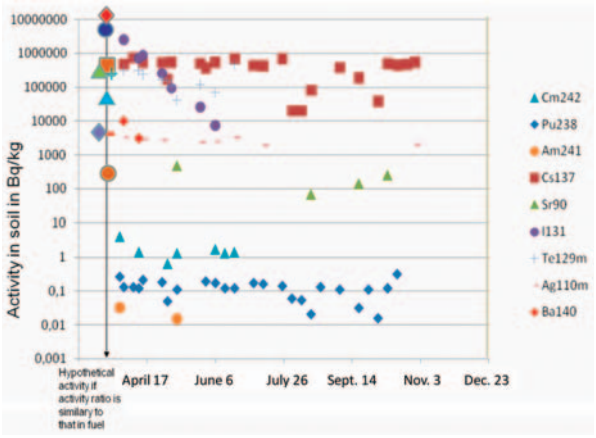

Figure 3 Graphical representation of radioactivity measurements, reported periodically by TEPCO (2011) between March and November 2011 for the Fukushima plant at soil-sampling locations (denoted "Playground") located about 500 m north-northwest of the stacks of Units 1 and 2. The large symbols at the date of the accident represent reference values, which correspond to hypothetical activities for the case in which all nuclides have been released to the same extent (i.e. the same fraction of reactor core inventory of a given nuclide) as that of Cs. Measured values lower than the reference value indicate a much lower extent of release than Cs.

The relative behavior of the different nuclides near the Fukushima plant also matches very well with experimental results. In a Knudsen cell experiment, spent nuclear fuel fragments were heated stepwise in a closed, confined space to temperatures in excess of 2000 °C, and the stepwise volatilization of the various elements were measured by mass spectrometry (Rondinella et al. 2008). Figure 4 presents a typical result obtained from MOX fuel samples. Volatilization starts at 1000 °C with the release of Te and He (produced by alpha decay), while Cs and I start to volatilize at 1100 °C. Finally, uranium begins to volatilize above 1600 °C. Interestingly, Ba shows an intermediate level of volatility. From these data, temperatures in the Fukushima reactors were probably high enough to cause the volatilization of most of the Xe inventory and a large fraction of the Cs, but certainly not the actinides (U, Pu, and minor actinides such as Am, Cm, and Np).

The confinement of most of the actinides within the reactors is, on one hand, reassuring, as these elements carry the highest long-term toxicity burden. On the other hand, a direct consequence of this confinement is that the long-term risk assessment requires the evaluation of the fate of

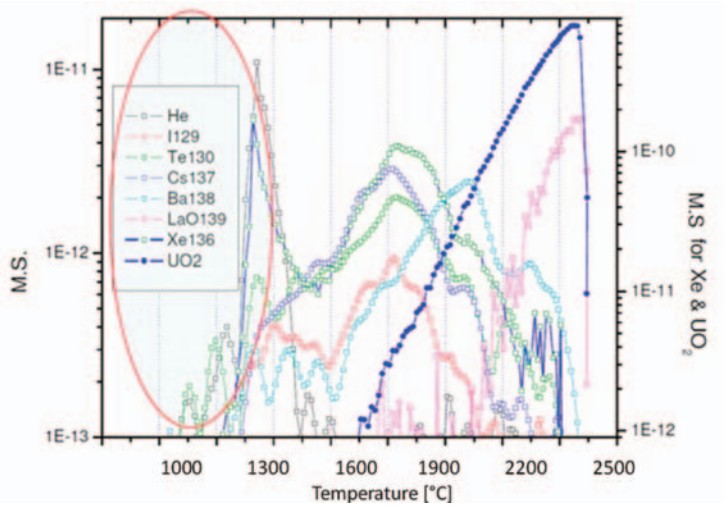

FIGURE 4 Knudsen cell analysis of the volatile release of radionuclides during heating of irradiated MOX fuel beyond normal conditions, from the European project NF-PRO. "M.S." means "mass signal"; for the present discussion, only relative values are of importance. The left scale applies to all radionuclides except Xe and UO_2, which are plotted against the scale on the right. Modified from Rondinella et al. (2008)

the remaining fuel in the reactor. How can we proceed with this assessment, considering the fact that due to high radiation fields direct access to the fuel will probably not be possible for at least a few decades? Some indirect information on the release behavior of the radionuclides in the reactor core can be derived from chemical analyses of the cooling water collected from the three damaged reactor cores. A cooling circuit was installed by TEPCO in July 2011, which runs decontaminated water through the three destroyed reactor cores and collects outflowing contaminated water for decontamination and desalination, after which the decontaminated water is reinjected. Decontamination factors for ^{137}Cs were 10^6, meaning that Cs activity in the water was a million times lower after a decontamination cycle than before. About 180,000 m^3 of highly contaminated water were collected for decontamination, with a specific activity for ^{137}Cs varying between 1.8 Bq/mL in July 2011 to 0.7 Bq/mL in November 2011 (data on the volumes collected and the associated activities are from TEPCO reports; TEPCO 2011). These data indicate a total release to the water of 1.7×10^{17} Bq, or about 27% of the total ^{137}Cs inventory in the cores of reactors 1–3. However, some fraction of the volatile elements, such as Cs, may have recondensed in the coldest parts of the primary cooling circuits during the accident. This figure is therefore a minimum amount of Cs release from the fuel. Specific activities for the nuclides $^{89+90}Sr$ were 6×10^5 Bq/mL in July 2011. No data were reported for longer contact periods. The Cs/Sr activity ratio in water collected in July is about 10 times higher than in the fuel, indicating reduced mobility of Sr as compared with Cs.

Due to the very high temperature during the meltdown, fuel pellets, as well as the zircaloy cladding and steel, melted and mixed, yielding an ill-defined material called *corium*. Earlier work, as in the French VULCANO experiments or the characterization of the core of reactor 2 at Three Mile Island, demonstrated that corium consists of several phases: an oxic phase and one or two metallic phases, depending on the accident conditions, which can cause the separation of the heavier and lighter metallic elements. How can we estimate the long-term stability of corium? In laboratory experiments performed on simulated corium, Pontillon and Durcos (2010) identified four groups of released elements:

1. Volatile fission products, including fission gases (Xe, Kr), I, Cs, Sb, Te, Cd, Rb, and Ag
2. Semivolatile fission products, including Mo, Rh, Ba, Pd, and Tc
3. Low-volatility fission products, such as Ru, Ce, Sr, Y, Eu, Nb, and La
4. Nonvolatile radionuclides, including Zr, Nd, Pr, and some of the actinides (U, Pu, Np, Am, Cu)

These laboratory results are consistent with the behavior of the measured radionuclides at the Fukushima plant: group 1 corresponds to radionuclides that have been significantly released (30 to 100%) into the cooling water (Cs) and into the environment (Xe, Cs, I, Te); groups 2 and 3, as indicated by Ba and Sr, seem to have been significantly released from the fuel (0.01%; see the discussion related to FIG. 3), but only a small part of these elements has reached the environment, probably due to their lower volatility and their propensity to recondense within the primary circuit (SEE FIG. 3); and group 4 essentially was not released from the fuel (99.9999% retained).

LONG-TERM CORIUM ALTERATION IN WATER

Characteristics of the Two Main Alteration Mechanisms

Oxic corium is a solid solution with a tetragonal structure. Although it has not been demonstrated that corium is a single phase, it may be possible to consider the oxic corium as hyperstoichiometric UO_{2+x}: stoichiometric deviations of the fuel were about $x = 0.14$ for samples obtained from the molten core of the Three Mile Island Unit 2 reactor (Bottomley and Coquerelle 1989). This value is lower than the threshold value of $x = 0.25$, which corresponds to U_4O_9. Corium compositions obtained from fuel treated in the PHEBUS severe-accident facility (Barrachin et al. 2008) were close to $U_{0.99}Zr_{0.01}O_{2.23}$ and $U_{0.86}Zr_{0.12}Fe_{0.005}Cr_{0.001}Nd_{0.006}Pu_{0.004}Ce_{0.004}O_{2.42}$ for irradiated fuel and to $U_{0.95}Zr_{0.04}Fe_{0.001}O_{2.32}$ for nonirradiated fuel. In the latter cases, these compositions correspond to an average deviation of $x = 0.33$ from the normal stoichiometry.

Considering corium as hyperstoichiometric UO_{2+x} allows the use of certain analogue materials for assessing the long-term behavior of corium in contact with natural waters. Indeed, many studies have been performed worldwide over at least 30 years on different types of uranium oxides in order to assess the long-term behavior of spent nuclear fuel under geological repository conditions. For instance, solid–water reactions have been studied for different solid solutions, such as UO_{2+x}; partly oxidized or fresh spent nuclear fuel; pure UO_2; oxidized UO_2; alpha-doped UO_2 simulating long-term irradiation fields; and natural uraninite (Forsyth 1995; Grambow et al. 1996, 2000; Stroes-Gascoyne et al. 1997; Röllin et al. 2001; Ollila et al. 2003; Werme et al. 2004; Poinssot et al. 2005; Ollila 2008). The European-funded MICADO project (Grambow et al. 2010) recently assessed the uncertainties in the different models describing the dissolution processes of spent nuclear fuel disposed of in a deep repository for geological periods. Based on this knowledge, some key issues can be considered.

First, as for UO_2-derived solids, two radionuclide fractions can be distinguished: (1) fast-dissolving radionuclide inventories (the so-called "instant release fraction," or IRF), which correspond to radionuclides that are not bound into

the matrices (either corium or spent fuel); (2) a slow-release fraction of radionuclides, which are located in the matrices (corium or spent fuel) and released as the corium matrix dissolves.

Instant Release Fraction (IRF)

The so-called IRF release is not governed by any mechanism but corresponds to radionuclides that are dissolved fast upon fuel–water contact. Therefore the only issue to address is the quantity of fast release upon water contact. No experimental data are available for corium. For spent fuel, IRF values are in the range of 5–10% of the total inventory, depending on the radionuclides (Ferry et al. 2007). Considering the typical corium-formation scenario (a transient event at very high temperature, >2300 °C, followed by a decade-long phase during which the corium is cooled under water), it is likely that a large part of the unbound radionuclides has already been released in the reactor core and to the cooling water and that these radionuclides are no longer retained in the fuel matrix. The remaining long-term IRF fraction in the corium is therefore anticipated to be very limited.

Slow-Release Fraction

The dissolution process of the corium matrix in water is likely to be electrochemically controlled, as for spent fuel (see Figure 5 for spent fuel). Due to the large difference in uranium solubility under oxidizing and reducing conditions (roughly $10^{-6.5}$ and $10^{-9.5}$ mol L^{-1}, respectively), the corium matrix will probably undergo two competing dissolution mechanisms: (1) under oxidizing conditions, a relatively fast surface-interaction-controlled dissolution and (2) under reducing conditions, a slow solubility-controlled dissolution.

Under **oxidizing conditions**, spent fuel or UO_2 leaching requires, first, a surface oxidation of UO_2 to a mixed U(IV)/(VI) oxidation state of hyperstoichiometric UO_{2+x}, with $x > 0.33$ (U_3O_7), and then complete oxidizing dissolution as dissolved U(VI) species. As measured on synthetic samples, the corium matrix is likely to be already oxidized so that its stochiometric deviation is given by $x = 0.33$, and no additional surface-oxidation step prior to oxidative leaching is probably necessary. One can anticipate a faster oxidation rate than for spent nuclear fuel. Oxidant influx is however necessary for transforming the remaining U(IV) into U(VI): oxygen may come from an external source under aerated conditions or from the radiolytic decomposition of water (oxidizing radiolysis products are H_2O_2 and O_2). The fractional release rates for fractured spent fuel rods under oxidizing conditions are between 10^{-5} and 10^{-7}/day. The fractional release rates for corium may be underestimated due to the preoxidized state. Finally, the alteration rate strongly depends on surface areas, which are unknown and likely different from that of the original spent nuclear fuel.

Under **reducing conditions**, corium stability is anticipated to be higher and governed, as for spent fuel, by the relative solubilities of the dissolving phases (UO_2 in the case of spent fuel, $UO_{2+x,\ x \approx 0.33}$ for corium). This implies that equilibrium U concentrations would be lower than in the previous case, in the range of 10^{-9} to 10^{-10} M for spent fuel (Grambow et al. 2010). However, corium solubility will depend on the actual chemical state of the corium, and its solubility might be much higher than that of UO_2. Due to the lack of information on the state of the corium, and for the sake of simplicity, all the radionuclides that have not been released into the cooling water and the environment are assumed to be integrated into the corium matrix as solid solution components. This implies that equilibrium conditions will govern the maximum concentrations in the aqueous solution of uranium and other radionuclides (like actinides, fission products, and activation products).

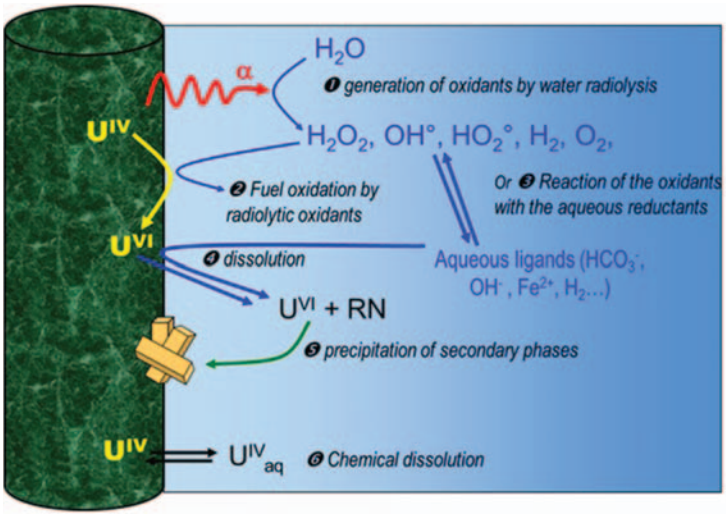

Figure 5 The various alteration mechanisms affecting spent nuclear fuel in contact with water as a function of the environmental redox conditions (oxidation potential, Eh). "RN" stands for "radionuclide." The numbers refer to the consecutive steps in the alteration process. Modified from Poinssot and Gras (2008)

Whether oxidizing or reducing conditions prevail in the damaged reactor cores may be assessed by analyzing the concentrations of U and Pu in the cooling water and by studying solubility controls: high concentrations ($>10^{-5}$ mol/L) are, for example, typical of oxidizing conditions. The experimental database on the interaction of UO_2-derived solids with water shows that temperature, the solubility limits of radionuclides, fuel-damage conditions, burnup, and the presence of remaining cladding play major roles in the effective radionuclide release from the corium matrix. Furthermore, the dissolution rates are not expected to be directly proportional to the specific surface areas. As far as water chemistry is concerned, redox potential and carbonate concentrations are key parameters (Bruno and Ewing 2006), whereas salinity (seawater versus freshwater) will play only a minor role in radionuclide release (Loida et al. 1994). Colloidal particles and dissolved organic matter are important for the transport of sparingly soluble radioelements such as Pu and Am (Kim and Grambow 1999).

Potential Influence of Radiation Fields

The temporal evolution of the redox conditions at the corium–water interface has an important effect on the radionuclide release behavior. The evolution of this behavior will be quite different under oxic surface conditions than under the reducing conditions in a deep geological repository. Air ingress is indeed omnipresent under oxic surface conditions, but in a geological repository, it only occurs during the operations phase, and thereafter all remaining air is consumed by redox reactions, in particular, with the metal of the disposal containers.

Spent nuclear fuel and the corium short-term radiation field mainly give off oxidizing gamma radiation, while over the very long term (>>100 years) the radiation field is characterized mainly by alpha-decay radiation. During the first few hundred years, gamma radiation may strongly increase

the oxidation potential, even under oxic surface conditions. Over the long term, many thousands of years, as for geological disposal, alpha radiation will locally produce at the solid–water interface oxidizing species that could significantly increase the material dissolution rate, as has already been demonstrated on α-doped UO_2 samples (Cachoir et al. 2005). However, the net effect is directly related to the overall balance at the local scale between the oxidants produced by the radiolytic decomposition of water [of which the primary oxidizing or reducing products are the radicals $OH^{\cdot}$, $OH_2^{\cdot}$, $e^-(aq)$, and $H^{\cdot}$, or molecular species like H_2O_2, and H_2], the transport constraints involving the radiolytic producs, and the reactive reducing species that are present in the environment.

OPTIONS FOR CORIUM MANAGEMENT

From the available data on the total inventory of radionuclides that were released into the environment during the Fukushima accident, we have derived some important information regarding the potential state of the spent nuclear fuel in the three melted cores of the reactors. In particular, the relative behavior of the different radionuclides is consistent with the knowledge gained about fuel behavior at high temperature: volatile elements are released at much lower temperatures (<1300 °C) than actinides. This is consistent with the absence of a significant release of actinides around the Fukushima site. The ratios of the activities of ^{137}Cs, ^{131}I, ^{110m}Ag, and ^{129m}Te reported for soil samples correspond to inventory ratios in the reactors, and the ^{131}I content in soil samples is much larger than the value that would be expected if a large contribution came from the fuel storage ponds. The large quantity of radionuclides released from the three reactors probably masks any contribution from the fuel storage ponds, which confirms a much lower fuel alteration in the ponds.

Furthermore, from the large data set that has been acquired in the last few decades about the long-term evolution of spent nuclear fuel in water, some insights may be gained about the behavior of the oxic corium, whether in a geological repository or in long-term storage (such as within a protective sarcophagus). By comparison with spent nuclear fuels, after the passage of cooling water, oxic corium is anticipated to have a much lower IRF, potentially zero, and its radionuclide release behavior should be dominated by matrix alteration, which should be faster than for spent nuclear fuel. Three main options are therefore possible for corium management:

- Recovery of the corium in order to condition it inside suitable containers without further treatment, as was done with reactor 2 at Three Mile Island, while waiting for subsequent disposal in a deep geological repository. However, the amount of fuel lost in the melted core at Three Mile Island in 1979 was about 30 tons, less than one-twentieth the inventory at Fukushima (reactors and pools). In this case, the long-term release behavior of the corium is anticipated to be less desirable than that of spent nuclear fuel, since the long-term alteration rate of the corium will be higher. However, little or no IRF is anticipated, which would be favorable since the IRF dominates the long-term impact of spent fuel in a repository.
- Treatment, in order to decrease long-term toxicity and to optimize the stabilization of corium in dedicated waste matrices. Indeed, the most toxic elements, such as the actinides, could be recovered by separation processes, such as hydrochemistry or pyrochemistry. Pyrochemical processes may be of great interest due to the presence of numerous metallic components and the anticipated refractory behavior of part of the corium. Such treatment may allow confining the most mobile radionuclides in a stable matrix instead of having them dispersed in the ill-defined corium matrix. In this option, the long-term release performance of the waste will depend on the specific matrix to be used. If vitrification of corium is chosen, good performance for up to 10^6 years can be anticipated.
- Finally, the site can be stabilized by creating some kind of protective sarcophagus. During a period lasting hundreds of years, natural waters will probably find access to the corium inside the sarcophagus, and the corium will likely corrode and release radionuclides; these would have to be recovered and managed. This is not a long- term option (thousands of years), but it may be a solution for a time period during which institutional control can be assured, which is intrinsically difficult to assess (what about the stability of current societies over hundreds of years?).

Whether option 1 or 2 is chosen, only a preliminary estimate of the long-term performance is possible based on the present knowledge of spent nuclear fuel behavior. Studies of real corium samples from Fukushima will have to be performed, either to develop a treatment process or to characterize the radionuclide release properties of untreated corium. In the absence of relevant and robust experimental data, conservative assumptions in performance assessment will probably lead to prohibitively expensive solutions.

Upper limits for radionuclide release predictions from the corium matrix can be obtained by developing a site-specific performance model for the Fukushima corium. Such a model could be created based on actual observations of the corium in the reactors in the presence of water. In the present study, we used the reported activities of ^{137}Cs and ^{90}Sr in the outflowing cooling water to conclude that about 30% of the Cs inventory and about 3% of the Sr inventory were mobilized from the three reactors. In a similar way, one could analyze the evolution of the activities of other radionuclides (^{239}Pu, etc.) in the cooling water of the reactor to assess the mobility of these nuclides in the core and to quantify source terms for water contact for the various conditioning and disposal scenarios. The continued flushing of the molten cores with water will in the long term also reduce the inventories of radionuclides that can be mobilized rapidly during disposal.

CONCLUSION

Comparison of radionuclide release from the reactors with the radionuclide inventories remaining in the reactor and estimation of corium–water interaction from known spent fuel–water interaction provide important insight for developing assessment and management strategies for the molten fuel in the reactor cores. If corium is to be disposed of without treatment, models for corium stability and for radionuclide release from corium upon contact with water will have to be developed based on (1) analyses of radionuclide activities in actual cooling waters, (2) chemical modeling of the analytical results in the context of the kinetics and thermodynamics of actinide and fission product release (solubility constraints, redox states, etc.), and (3) comparison with spent fuel behavior and experimental corium databases. If corium treatment is being considered in view of either confining it in a more stable matrix or even recovering the most radiotoxic radionuclides, specific processes will have to be developed based on the corium properties and the wide knowledge available about fuel treatment.

REFERENCES

Barrachin M, Chevalier PY, Cheynet B, Fischer E (2008) New modelling of the U–O–Zr phase diagram in the hyper-stoichiometric region and consequences for the fuel rod liquefaction in oxidising conditions. Journal of Nuclear Materials 375: 397-409

Bottomley PD, Coquerelle M (1989) Metallurgical examination of bore samples from the Three Mile Island unit 2 reactor core. Nuclear Technology 87: 120-136

Bruno J, Ewing RC (2006) Spent nuclear fuel. Elements 2: 343-349

Cachoir C and 13 coauthors (2005) Effect of alpha irradiation field on long-term corrosion rates of spent fuel. In: Grambow B (ed) European Commission Report JRC-ITU-SCA-2005/1

Endo T, Sato S, Yamamoto A (2011a) Estimation of average burnup of damaged fuels loaded in Fukushima Dai-Ichi reactors by using the $^{134}Cs/^{137}Cs$ ratio method. Symposium on Nuclear Data, Techno Plaza Ricotti, Tokai-mura, Ibaraki-ken, Japan, November 17, 2011

Endo S, Kimura S, Takatsuji T, Nanasawa K, Imanaka T, Shizuma K (2011b) Measurement of soil contamination by radionuclides due to the Fukushima Daiichi Nuclear Power Plant accident and associated estimated cumulative external dose estimation. Journal of Environmental Radioactivity, doi:10.1016/ j.jenvrad.2011.11.006

Ferry C, Piron JP, Poulesquen A, Poinssot C (2007) Radionuclides release from the spent fuel under disposal conditions : re-evaluation of the instant release fraction. In: Lee WE. Roberts JW, Hyatt NC (eds) Scientific Basis for Nuclear Waste Management XXXI, Materials Research Society Proceedings, Sheffield

Forsyth R (1995), Spent nuclear fuel. A review of properties of possible relevance to corrosion processes. Swedish Nuclear Fuel and Waste Management Co., Stockholm, SKB technical report TR 95-23, 46 pp

Grambow B, Loida A, Geckeis H, Dressler P, Casas I, Torrero ME, Giménes J, de Pablo J, Gago J (1996) Chemical Reaction of Fabricated and High Burnup Spent UO_2 Fuel with Saline Brines. Final Report of EU Project, Wissenschaftliche Berichte, FZKA 5702, Forschungszentrum Karlsruhe. Commission of the European Union EU 17111 EN, 222 pp

Grambow B, Loida A, Martinez-Esparza A, Diaz-Arocas P, de Pablo J, Paul JL, Marx G, Lemmens JPK, Ollila K, Christensen H (2000) Source Term for Performance Assessment of Spent Fuel as a Waste Form. Final Report for the EU contract FI4W-CT95-0004, Forschungszentrum Karlsruhe Final Report FZKA 6420, European Commission EUR 19140 EN, 222 pp

Grambow B and 35 coauthors (2010) MICADO Model Uncertainty for the Mechanism of Dissolution of Spent Fuel in Nuclear Waste Repository. Final Report. European Commission, EUR 24597 EN, 52 pp

Hedin A (1997) Spent Fuel – How Dangerous is It? Swedish Nuclear Fuel and Waste Management Co., Stockholm, SKB Technical Report TR 97-13, 60 pp

Hirose K, Igarashi Y, Aoyama M, Kim CK, Kim CS, Chang BW (2003) Recent trends of plutonium fallout observed in Japan: plutonium as proxy for desertification. Journal of Environmental Monitoring 5: 302-307

IAEA (2011) Report of Japanese Government to the IAEA Ministerial Conference on Nuclear Safety – The Accident at TEPCO's Fukushima Nuclear Power Stations. Nuclear Emergency Response Headquarters Government of Japan June 2011, www.iaea.org/news-center/focus/fukushima/japan-report

IRSN (2011) Synthèse actualisée des connaissances relatives à l'impact sur le milieu marin des rejets radioactifs du site nucléaire accidenté de Fukushima Dai-ichi, 26 octobre 2011

Kim JI, Grambow B (1999) Geochemical assessment of actinide isolation in a German salt repository environment. Engineering Geology 52: 221-230

Loida A, Grambow B, Dressler P, Friese K, Geckeis H (1994) Chemical durability of high burnup LWR-spent fuel in concentrated salt solutions. Materials Research Society Symposium Proceedings 333: 417-424

Ollila K (2008). Dissolution of Unirradiated UO_2 and UO_2 Doped with ^{233}U in Low- and High-Ionic-Strength NaCl under Anoxic and Reducing Conditions. Working report 2008-50, Posiva Oy Olkiluoto, Finland, 34 pp

Ollila K, Albinsson Y, Oversby V, Cowper M (2003) Dissolution Rates of Unirradiated UO_2, UO_2 Doped with ^{233}U, and Spent Fuel under Normal Atmospheric Conditions and under Reducing Conditions Using an Isotope Dilution Method. Swedish Nuclear Fuel and Waste Management Co., Stockholm, SKB Technical Report TR-03-13, 88 pp

Poinssot C, Gras JM (2008) Key scientific issues related to the sustainable management of spent nuclear fuels in the back-end of the fuel cycle. Materials Research Society Symposium Proceedings 1124: 85-97

Poinssot C and 22 coauthors (2005) Spent Fuel Stability under Repository Conditions – Final Report of the European Project. European Commission 5th Euratom Framework Program, contract nº FIKW-CT-2001-00192, 104 pp

Pontillon Y, Ducros G (2010 Behaviour of fission products under severe PWR accident conditions. The VERCORS experimental programme—Part 3: Release of low-volatile fission products and actinides. Nuclear Engineering and Design 240: 1867-1881

Röllin S, Spahiu K, Eklund UB (2001) Determination of dissolution rates of spent fuel in carbonate solutions under different redox conditions with a flow-through experiment. Journal of Nuclear Materials 297: 231-243

Rondinella VV, Serrano-Purroy D, Hiernaut JP, Wegen D, Papaioannou D, Barker M (2008) Grain boundary inventory and instant release fractions for SBR MOX. Proceedings of the 12th International High-Level Radioactive Waste Management Conference, pp 418-424

Samson M, Grouiller JP, Pavageau J, Marimbeau P, Pinel J, Vidal JM (1998) CESAR: A simplified evolution code for reprocessing applications; RECOD 98. 5th International Nuclear Conference on Recycling, Conditioning and Disposal, Nice, France

Stohl A, Seibert P, Wotawa G, Arnold D, Burkhart JF, Eckhardt S, Tapia C, Vargas A, Yasunari TJ (2011) Xenon-133 and caesium-137 releases into the atmosphere from the Fukushima Dai-ichi nuclear power plant: determination of the source term, atmospheric dispersion, and deposition. Atmospheric Chemistry and Physics Discussions 11: 28319-28394

Stroes-Gascoyne S, Johnson LH, Tait JC, McConnell JL, Porth RJ (1997) Leaching of used CANDU fuel: Results from a 19-year leach test under oxidizing conditions. Materials Research Society Symposium Proceedings 465: 551-558

TEPCO (2011) Data source: measurements at Fukushima Daiichi nuclear power station at periodic soil sampling spot of activities "Playground" at about 500 m from stacks of Unit 1 and 2 in direction west/north-west. Updated periodically on the Web

TEPCO (2012) The estimated amount of radioactive materials released into the air and the ocean caused by Fukushima Daiichi nuclear power station accident due to the Tohoku-Chihou-Taiheiyou-Oki earthquake (as of May 2012). Tokyo Electric Power Company press release, May 24, 2012

Werme LO, Johnson LH, Oversby VM, King F, Spahiu K, Grambow B, Shoesmith DW (2004) Spent Fuel Performance under Repository Conditions: A Model for Use in SR-Can. SKB Technical Report TR 04-19, Stockholm, 34 pp

Call for Session Proposals for IMA 2014

Preparations are well under way for the 21st meeting of the International Mineralogical Association (IMA) in South Africa. The overall theme of the IMA 2014 meeting is "Delving Deeper – Minerals as Mines of Information." The logo is symbolic of South Africa's rich mineral resources, from which has sprung its dynamic mining heritage, also the backbone of the country's economy. The meeting will take place on 1–5 September 2014 at the Sandton Convention Centre, in the heart of Johannesburg, the City of Gold.

The IMA 2014 meeting will be held under the auspices of the Geological Society of South Africa and the Mineralogical Association of South Africa, and is already generating sponsorship from the mineral industry, which will enable a professional, vibrant atmosphere for a memorable conference. South Africa's sizeable community of mineralogists will contribute to the hosting of this first IMA meeting on African soil, and all aspects of mineralogy will be covered. The Organizing Committee is headed by Dr Sabine Verryn as conference chair, along with Dr Desh Chetty as scientific committee chair and Dr Craig Smith as finance chair.

Proposals for sessions and topics to be covered are invited (e-mail: info@ima2014.co.za), and further information is available on the conference website (www.ima2014.co.za). Please register to receive updated information if you are not already on the communications list. The Organizing Committee looks forward to welcoming everyone to South Africa in September 2014.