Environmental Science: Processes & Impacts

Article

State of Fukushima nuclear fuel debris tracked by Cs137 in cooling water

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It is still difficult assessing the risk originating from the radioactivity inventory remaining in the damaged Fukushima nuclear reactors. Here we show that cooling water analyses provides a means to assess source terms for potential future releases. Until now already about 34% of the inventories of ^{137}Cs of three reactors were released into the water. We found that the release rate of ^{137}Cs is constant since 2 years at about 1.8% of the inventory per year indicating ongoing dissolution[†] of the fuel debris. Compared to laboratory studies on spent nuclear fuel behavior in water, ^{137}Cs release rates are on the higher end, caused by the strong radiation field and oxidant production by water radiolysis and by impacts of accessible grain boundaries. It is concluded that radionuclide analyses in cooling water allow tracking the conditions of the damaged fuel and the associated risks.

Introduction

Despite experience from the Chernobyl and the Three Miles Islands nuclear disasters, all consequences of the level 7 core melt down of the units 1 to 3 of the Fukushima Daiichi BWR (boiling water reactor) Nuclear Power plant in March 2011 are still not foreseeable. Thousands of square km of the prefecture of Fukushima in eastern Japan and large parts of the Pacific Ocean were contaminated by release of about 2% of the inventories of ^{137}Cs and ^{131}I [1] from the three accidental nuclear reactors unit 1-3. The exact release values are still being argued. Understanding of deposition and migration pattern of soil contaminants is progressing [2]. While dose assessments indicate less health risks than initially thought [3], some leakage from the plant to the environment is continuing to steer worldwide concern and the links between environmental and medical assessments still needs to be made as the uptake of radiocesium by people living in the Fukushima area is much less than that observed for the same degree of contamination in Chernobyl [4].

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† The term « dissolution » is used either for transferring a solid bound radionuclide or the entire solid to the aqueous solution acknowledging that subsequent formation of secondary precipitates may occur. The term "leaching" refers to the process of selective transfer to solution of radionuclides from a non-dissolved solid substrate. "Dissolution" or "release" of Cs may be caused either to the dissolution of the solid or by its leaching.

The largest hazard is still associated to the damaged reactor cores of units 1-3 keeping in place 98% of ^{137}Cs and ^{129}I, 99.99% of ^{90}Sr and 99.9999% of Uranium, Plutonium and the other actinides [5], many of these radionuclides being much more toxic than ^{137}Cs of ^{131}I. Cleanup of the site will probably take more than 40 years, the fuel debris removal is expected to last 25 years when starting ten years from now[6]. The potential reaction of the reactor core with water and the associated radionuclide release are a major concern.

The ill-defined partial molten and quenched debris of UO_2 fuel (and of a few MOX fuels), of the zircaloy cladding and of steel structures are often termed "corium". Knowledge of its physical and chemical state constrains decommissioning strategies and hazard assessment. Since the interior of the damaged reactor vessels is not accessible, one can only speculate on its state by analogy to the corium generated in the Three Mile Island accident or to the lava formed in Chernobyl and by simulations. These studies show that corium is a solid solution closely linked to hyperstoichiometric UO_{2+x} (x < 0.33) of tetragonal structure and it can be highly porous [7-9]. According to a recent review[10] of nuclear fuel properties related to nuclear accidents, "*at present there is no reliable way of predicting dissolution rates of damaged fuel in water under the conditions of a nuclear accident, especially one like Fukushima Daiichi in which fuel is exposed to hot or boiling seawater for periods of weeks to months. Fukushima Daiichi itself would provide a very instructive experiment if and when it becomes possible to retrieve and study the fuel.*"

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Environ. Sci.: Processes & Impacts, 2012, **00**, 1-3 | 1

Results and discussion

But significant information on potential risks from leaching fuel debris by water can be obtained already prior to retrieval. It was suggested to deduce fuel debris leaching properties directly from radionuclide contents in cooling water and to use the analogy to hyperstoichiometric UO_{2+x} and spent fuel from nuclear reactors to interpret the data [5]. Heat generated by radioactive decay principally of the remaining ^{137}Cs and ^{90}Sr inventories of the fuel debris requires cooling still today with a daily flux of about 400 m³ of water, but only molten fuel at the bottom of the reactor vessel remains permanently covered by water. Initially, sea water was used for cooling. Chemical interaction of cooling water with fuel debris leads to dissolution of radionuclides such as ^{137}Cs. The contaminated cooling water is leaking from the damaged reactor vessels and is collected in a building where it accumulates and mixes with infiltrating groundwater. Since June 9, 2011 the collected contaminated water together with the groundwater is pumped out continuously, is treated for desalination and Cs removal by zeolites and is either reused for cooling or collected in tanks for storage (see schema, Fig.1). Decontamination factors for Cs are reported to be larger than 10000 [11]. Leakage from the tanks remains an important risk for environmental contamination. Efforts for further decontamination for other radionuclides are ongoing.
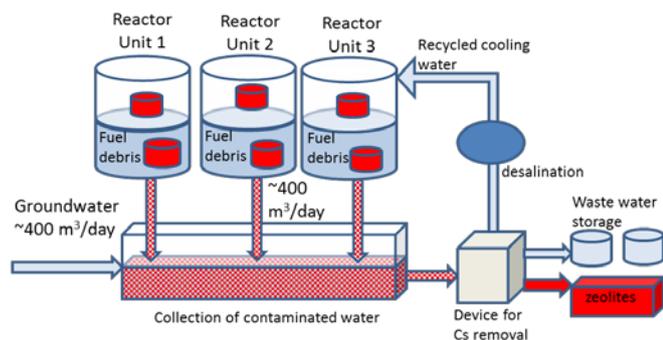

Figure 1 : Schema for cooling water recycling (sketch drawn from information given in [11]): Molten fuel debris accumulated at the bottom of the reactor vessels and covered by cooling water, residual fuel debris are above the water table and cooled by flushing water. Cs is leached from the fuel debris in the 3 reactors; dissolved Cs is accumulated in collected cooling water from which it is removed before partial recycling

Specific activities of ^{137}Cs and treated volumes of cooling water are reported in weekly press releases by the Tokyo Electric Power Company [11]. We express the reported ^{137}Cs activities (initially 1.7×10^6 Becquerel mL^{-1}) as "fraction of inventory in the aqueous phase=FIAP", a unit frequently used in spent fuel leaching studies. The total ^{137}Cs inventories of the three reactors prior to the accident of 7.1×10^{17} Becquerel [12] is used as reference. In Figure 2, we present the FIAP values in cumulative manner as a function of cooling time, starting from the day of the accident up to December 4, 2013.
In total, about 820,000 m³ were collected containing 2.40×10^{17} Becquerel. This corresponds to 34% of the ^{137}Cs inventories of the three reactors which is found dissolved in the cooling water and which is today largely retained on the zeolites. If one deduces radionuclide release pattern for the fuel debris and correcting for dilution, assuming that ^{137}Cs is only released
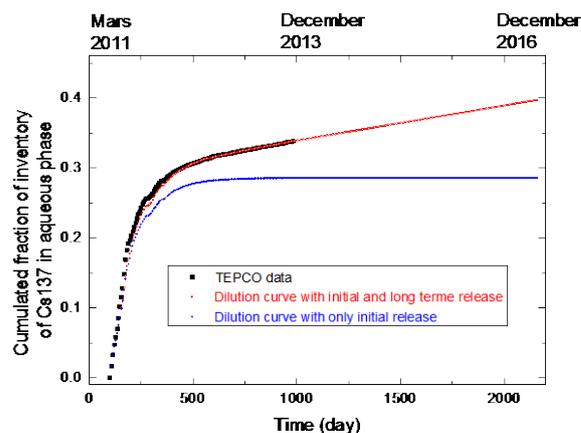

Fig. 2 : Cumulative fraction of inventory of ^{137}Cs released from the three accidental nuclear reactors collected in cooling water. Comparison of measured data given by TEPCO (18) with two model curves: one assuming only dilution of initial release, the other considers as well continued short and long term release. Model data beyond 1000 days (December 2013) are predictions up to end of 2016.

initially during the accident, we would underestimate the observed data (Figure 2). Very good agreement to the observed data is obtained (Fig. 2) when assuming an initial leaching of 28.6% of ^{137}Cs into the water volume present in reactor vessels and reactor building prior to the begin of water treatment at June 9, 2011, thereafter dilution of this activity by fresh or recycled cooling water and by infiltrating groundwater and a continued release with rate of 2×10^{-4} day^{-1} from the fuel debris for up to 200 days after the accident and thereafter a constant long-term release rate from corium of 5×10^{-5} day^{-1}. To calculate dilution effects, the assumption is made that the known volumes of treated cooling water equal the sum of cooling water added to the 3 reactors plus the groundwater volume infiltrating into the reactor building at each given time interval. This assumption corresponds to the hypothesis that the total water volume in reactor vessel and building remain about constant. The initial 28.6% does not account for the 2% of Cs released to the atmosphere, neither to the soils nor to the ocean. There may as well be adsorption of Cs on the concrete structures of the reactor building. Typical distribution coefficients (K_d values) of Cs between cementitious materials and water (pH 8-13) are reported [13] to be well below 1 m³ kg^{-1}. The total surface of the reactor building accessible to the contaminated water may be estimated from the size of the reservoir for collected water volume of about 74000 m³ and conservatively assuming water penetration into the concrete by about 1 cm, one can conclude that less than 1% of the Cs activity in the water is sorbed on the concrete. This quantity is not expected to increase with time (sorption reactions are fast). Hence, the data in Fig. 2 provide a lower limit for the release rate of ^{137}Cs. From the already two years constant long term release rate of 5×10^{-5} day^{-1} (1.8%/year), on predicts total Cs release of 39.5% in December, 2016. If the current rate would remain constant until completion of decommissioning in 40 years, about 80% of ^{137}Cs would have become dissolved, indicating significant changes of the physical and chemical state of the fuel, if the release mechanism of Cs is the dissolution in the state of the fuel debris (and potential precipitation of solid alteration products).

One may speculate on the Cs release mechanism by analogy to spent fuel studies. Indeed, the observed pattern of ^{137}Cs release are similar to spent fuel data, collected for various nuclear waste disposal programs worldwide; see reviews in [14, 15]. Also the reaction of spent fuel with water is characterized by a fast initial release of ^{137}Cs, slower release for intermediate times and a slow long term release. The fast initial (order of days) release is caused by dissolution of ^{137}Cs deposits on fuel fracture surfaces formed during reactor operation, the slower release for intermediate periods by release from accessible grain boundaries and the slow long term rate by dissolution of the UO_2 grains [14]. The magnitude of the fast initial release is dependent on the temperature during reactor operation [16]. Typical values are a few percent in BWR fuels. The much higher initial release in the present case may correspond to the much higher temperatures during the accident. The observed long term rate of 5×10^{-5} day^{-1} is also very high when compared to spent fuel data: for the latter, constant long term ^{137}Cs release rates are observed over as much as 19 years [17] with rate values depending on redox conditions, for example a Cs release rates after 1 year are about 1×10^{-6} day^{-1} in oxidizing conditions [14] and about three orders of magnitude lower in hydrogen saturated water [18]. Associated release rates of ^{137}Cs, ^{90}Sr and [238]U are similar if precipitation of secondary phases can be avoided by fast water flow [18], indicating oxidative radiation enhanced dissolution of the ^{137}Cs and ^{90}Sr containing UO_2 grains as release mechanism. Long term release rates of ^{137}Cs similar to that derived in Fig. 2 are observed for high burnup fuel at 60 thermic gigawatt-day per ton uranium (5×10^{-5} day^{-1} [19]), for some CANDU fuel [17] exposed to high temperature ("high power") in the reactor or for salt brines for a burnup of 50 thermic gigawatt-days per ton uranium [20] (3×10^{-5} day^{-1}).

This analogy between the ^{137}Cs release from the fuel debris at the Fukushima Daiichi nuclear power plant and typical spent fuel leaching data invites to derive important conclusions: 1) the fuel debris continues to react with the cooling water with a constant rate even 960 days after the accident, 2) if this long term reaction is similarly to spent fuel caused by the dissolution rates of UO_2 grains one could deduce from ^{137}Cs release rate the release rates of other nuclides and inversely, from the determination of the release rate of other nuclides one could deduce the mechanism of interaction of the fuel debris with water as well as the state of the fuel during retrieval.

Taking the analogy between spent fuel and the fuel debris a step further, the situation of the rate data at the high end of literature values indicates that essentially all fuel debris surfaces are accessible to the cooling water. The high rates cannot be explained by high fuel burnup, since the average burnup is only about 20 thermic gigawatt-day per ton uranium[5]. Other explanations are either that corrosion conditions are very favorable by oxidizing reactions, and by rather high surface area (see porous structure in experimental studies with simulated corium[8]) or that there is fast leaching of Cs accumulated at grain boundaries at high temperatures during the accident.

Strongly oxidizing conditions may be caused by the extremely high radiation field in the reactor. Typical gamma dose rates from a single spent fuel assembly after 50 to 1250 days of cooling time for a burnup of 20 thermic gigawatt-day per ton uranium are in the range of 1 kGray·h^{-1} [21]. Considering the gamma irradiation by the other fuel assemblies (400 in reactor unit 1, 548 in units 2 and 3), total gamma dose rates in the reactor vessel in contact with the fuel assemblies will be well

above 100 kGray·h^{-1}. Average alpha dose rates at the fuel surface (average depth of penetration of 5MeV alpha particles in water =30µm) can be estimated from the alpha activity of the fuel of 20 thermic gigawatt-day per ton uranium as $1.32 \cdot 10^8$ Becquerel·g^{-1} (calculated by Origin-ARP[22]) as 400 Gray·h^{-1}. Hence, gamma dose is expected to be dominant in the reactor core. Also in mixed alpha/gamma radiation fields, gamma radiolysis controls the reaction rate of UO_2 in water. Decomposition of water by gamma radiation (Gamma radiolysis) of cooling water produces very reactive oxidative radicals like OH$^{\bullet}$ and molecular species like H_2O_2 or various oxy-chloride species in presence of seawater used for initial cooling and has been observed to strongly increase spent fuel dissolution rates particularly in presence of air [23]. Recently it was reported that over OH$^{\bullet}$ and H_2O_2 radiolytic water decomposition products, the oxidation reactivity of the radical cation $H_2O^{\bullet+}$ formed under irradiation of liquid water should be taken into account. This radical considered to react with water molecules by proton transfer forming OH$^{\bullet}$ radical, can also react with molecules at contact by very fast oxidation[24]. The yield of $H_2O^{\bullet+}$ at a few tens of femtoseconds after energy deposition is estimated to be around 5.3×10^{-7} mol·J^{-1}. Any molecule or metallic system at contact of $H_2O^{\bullet+}$ can be oxidized by this radical cation. A simple estimation of the reduction potential of this short-lived radical cation shows that it is the most powerful oxidizing species, even stronger than radical OH$^{\bullet}$. When the core of nuclear power plant is into contact with water, the amount of radiation deposited at the interface of the exposed fuel/water is important and metal corrosion as well as nuclear fuel oxidation by $H_2O^{\bullet+}$ is involved and accelerates the dissolution (see schema, Fig. 3). Moreover, high linear energy transfer (LET) radiation at the interface of corium and water can also be an important parameter for oxidation because an important amount of this radical cation can be formed at interface and oxidizes the materials. In addition, porous materials present high interface area with water present more favorable oxidizing condition.
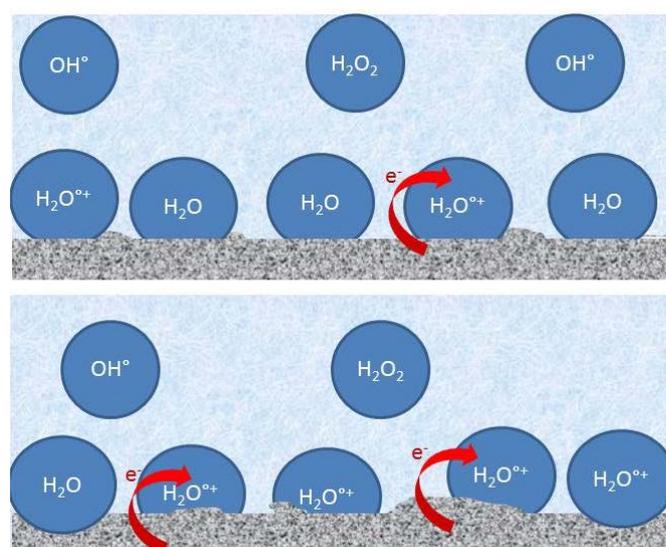

Fig. 3. Scheme of the distribution of oxidizing spices produced at the interface of water/corium system. Upper part shows the gamma radiation contribution for which in addition to the oxidation by H_2O_2 and OH$^{\bullet}$ the oxidation by $H_2O^{\bullet+}$ is also possible. Down: α particles contribution: In that case the LET is very high and the probability of oxidation of corium by $H_2O^{\bullet+}$ is higher because the proton transfer reaction is less favored by lower probability of presence of water molecule in contact of $H_2O^{\bullet+}$.

Therefore, the radiation may indeed explain fast dissolution rates of the surface of the fuel debris.

One cannot rule out the possibility that ^{137}Cs release rates are controlled by a large specific surface area or by release from grain boundaries of the fuel debris and not by dissolution of the fuel surface. In case of release control by dissolution of the surface of the damaged fuel, all soluble radionuclides will become dissolved with the same rate than ^{137}Cs, while in case of grain boundary leaching release rates of other nuclides (like ^{90}Sr) may be much lower. Indeed, release of as much as 62 radionuclides has been observed in treated cooling water prior to further water purification by a multi-nuclide removal equipment (ALPS)[25]. Future analyses of solution concentrations of these nuclides and in particular of uranium in the cooling water prior to treatment and comparison to inventories in the fuel debris, may allow distinction between different release mechanisms. In addition, analyses of uranium in the water would help to assess the solubility of the fuel debris that is related to the degree of oxidation of the fuel, since oxidized uranium fuel (UO_3, U_3O_7…) is much more soluble in water than UO_2.

Extending the argument of radiation enhanced fuel debris dissolution; radiation may also be an important factor for assessing risks of continued reactor vessel corrosion. Analyses of dissolved Fe and pH may allow providing insight into a potentially ongoing corrosion process.

Conclusions

Confirming the analogy between spent fuel leach data and ^{137}Cs release pattern from the reactor cores, our approach shows that one can track the physical and chemical state of the damaged nuclear fuel in the three reactor cores by the analyses of the time dependent evolution of the radionuclide concentrations in the cooling water. The results can be used to assess source terms for radionuclide release and to develop methods to reduce the risk of fast fuel debris dissolution for example by allowing to adjusting cooling water chemistry. This allows for better targeted fuel core risk management and decommissioning strategies, using water chemistry as a probe for the state of the inaccessible fuel core. The present approach can be improved by separate analyses of ^{137}Cs in the cooling water of each of the three damaged reactors, allowing comparing the risk potentials of the reactor cores. Finally, this approach allows as well assessing the risk of direct disposal of corium in waste management strategies for the time after decommissioning.

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