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CARBON-14 IN WASTE PACKAGES FOR SPENT FUEL IN A TUFF REPOSITORY

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ABSTRACT

Carbon-14 is produced naturally by cosmic ray neutrons in the upper atmosphere. It is also produced in nuclear reactors, in amounts much smaller than the global inventory. About one-third of this is released directly to the atmosphere, and the other two-thirds remains in the spent fuel. Both the Environmental Protection Agency and the Nuclear Regulatory Commission have established limits on release of the ^{14}C in spent fuel. This is of particular concern for the proposed repository in tuff, because of the unsaturated conditions and the consequent possibility of gaseous transport of ^{14}C as CO_2. Existing measurements and calculations of the ^{14}C inventory in spent fuel are reviewed. The physical distribution and chemical forms of the ^{14}C are discussed. Available data on the release of ^{14}C from spent fuel in aqueous solutions and in gaseous environments of air, nitrogen, and helium are reviewed. Projected ^{14}C behavior in a tuff repository is described. It is concluded that ^{14}C release measurements from spent fuel into moist air at temperatures both above and below the in situ boiling point of water as well as detailed transport calculations for the tuff geological environment will be needed to determine whether the 10CFR60 and 40CFR191 requirements can be met.

INTRODUCTION

The Department of Energy's Office of Civilian Radioactive Waste Management is engaged in the development of a geological repository for the storage of U.S. high-level nuclear waste. The Nevada Nuclear Waste Storage Investigations (NNWSI) project is evaluating a candidate site for the repository in tuff rock at Yucca Mountain, Nye County, Nevada. Lawrence Livermore National Laboratory has the responsibility for design, testing, and performance analysis of waste packages for the tuff site. The Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) have promulgated regulations [1,2] that set limits on the release of radionuclides from geological repositories.

NNWSI proposes to locate the repository above the water table in the unsaturated zone. In such an environment, it is possible that volatile radionuclides could move by gaseous transport. Accordingly, the NRC has amended federal regulation 10CFR60 to include consideration of "potential for the movement of radionuclides in a gaseous state through air-filled pore spaces" for candidate repositories in the unsaturated zone [3]. Of particular concern are species that have sufficiently long half-lives that they will have significant remaining activities after the 300 to 1000-year containment period specified in 10CFR60. Spent reactor fuel is expected to be the dominant form of commercial nuclear waste to be placed in the repository. The long-lived radionuclides that could enter the vapor phase at spent fuel storage temperatures are ^{14}C (as, for example, CO_2, CO, or CH_4) and ^{129}I. NRC regulation 10CFR60 limits the release rate of any radionuclide from the engineered barrier system following the containment period to one part in 100,000 per year of the inventory of that radionuclide present at 1,000 years after permanent closure of the repository. This requirement does not apply to any radionuclide that is released at a rate less than 0.1% of the calculated total release rate limit, which is one part in 100,000 per year of the total inventory of radioactive waste remaining after 1000 years.

In addition to the NRC regulation, the EPA has developed regulation 40CFR191, which limits the cumulative release of ^{14}C to the accessible environment to 0.1 curie per MTHM (metric tonne of heavy metal) for a period of 10,000 years after disposal. The NRC has proposed to incorporate this provision into 10CFR60 [4].

In order to design a waste package that will meet these limitations on ^{14}C release, it is necessary to have several pieces of information. Of particular importance are the inventory of ^{14}C in spent fuel and the fraction of this inventory that will be in the gaseous state or will readily enter it when the package and fuel cladding are eventually breached. In order to determine these quantities with reasonable assurance, it is helpful to know the reactions by which ^{14}C is originally formed in spent fuel and their relative importance, the physical distribution and chemical forms of the ^{14}C found in the various components of spent fuel, and the behavior of the ^{14}C-containing species in the presence of inert gas, air, and aqueous environments.

In a previous paper [5] we reviewed some available information on calculated and measured ^{14}C inventories in spent fuel and reported on analysis of gas from a heated air-filled canister containing a PWR spent fuel assembly before and after rupture of a fuel rod. We found that about 1.5 mCi of ^{14}C was rapidly oxidized and released as gas from the external surface of the spent fuel assembly when it was stored in air that was heated to 275°C. (The gamma radiation field from the fuel was about 10^4 rad/hour, and this may have contributed to the oxidation reaction.) We also found that an additional 0.3 mCi was released as gas after one of the 204 fuel rods breached, but we suspected that most of this also came from the external surface of the assembly. We noted that these initial gaseous releases would not exceed the 40CFR191 limit of 0.1 curie per MTHM (which actually applies to the accessible environment) but would exceed the 10CFR60 limit of 10^{-5} per year of the total ^{14}C inventory, which applies to the engineered barrier system.

This paper extends that previous work on ^{14}C behavior in waste packages for spent fuel in a tuff repository. Use has been made of data from several sources to assemble a more coherent picture and to point out where more data are needed.

NATURAL CARBON-14, REACTOR RELEASES, AND HEALTH EFFECTS

Before discussing ^{14}C in spent fuel, it is helpful to consider naturally-occurring ^{14}C, in order to provide some perspective. Carbon-14 is a beta emitter with a half-life of 5,730 years [6]. The maximum beta energy is 0.155 MeV, and the average energy is 0.0467 MeV [6]. Carbon-14 is produced naturally in the upper atmosphere, primarily by the reaction of slowed cosmic ray neutrons with nitrogen. The rate of production is estimated at 2.8×10^4 Ci/yr., and the world inventory is estimated to be 2.3×10^8 Ci, most of which exists as bicarbonate in ocean water [7]. Of this, the atmosphere is estimated to contain 3.8×10^6 Ci [7]. The atmospheric concentration was increased by nearly a factor of two in the northern hemisphere as a result of atmospheric nuclear explosive tests in the 1950's and 60's [8]. It is currently decreasing because of equilibration with the oceans, with a relaxation time of about 14 to 15 years [9], and because of dilution by CO_2 produced from the burning of fossil fuels, which are too old to contain ^{14}C. The latter is called the Suess effect, and has amounted to about a 2% decrease over 100 years [10]. The current level of ^{14}C in the atmosphere is about 20% above the natural value [9].

The specific activity of ^{14}C in biological carbon, as determined from wood samples from the 19th century, which would not have been affected by weapons tests or fossil fuel burning, is 13.6 disintegrations per minute per gram [11]. The "standard" 70 kg man contains about 0.1 microcurie of ^{14}C and receives an estimated annual effective dose equivalent of 1.2 mrem from it, compared to an estimated total of 200 mrem from all natural radiation sources, of which nearly half is due to naturally-occurring radon and its decay products [7].

Carbon-14 produced in the primary cooling water of nuclear power plants is currently released to the atmosphere, primarily as CH_4 and CO_2. It amounts to about 5 to 10 Ci/GW(e)-yr. [12]. The current world nuclear electrical generating capacity is about 300 GW(e), of which about 1/3 is in the U.S. [13].

Thomas and Brown [14] have calculated that if all the ^{14}C produced in a 400-GW(e) fuel cycle operating for 100 years were released to the environment, the global inventory would be increased by about 1×10^6 Ci (less than 1/2%). Taking account of both the regional dose to individuals close to the point of release as well as the global dose to the entire world population, they project that the increase in global cancer deaths from such a release, evaluated over a 10,000-year period, would be about 3×10^{-5}%, or an average of six deaths per year.

PRODUCTION OF CARBON-14 IN LIGHT WATER REACTORS

Carbon-14 is produced in light water reactors by neutron capture reactions involving nitrogen, oxygen, and carbon (a very small amount is also produced by ternary fission of uranium) [12]. The principal reactions are $^{14}N(n,p)^{14}C$, $^{17}O(n,\alpha)^{14}C$, and $^{13}C(n,\gamma)^{14}C$, the first of these being dominant. Nitrogen is present as an impurity in fuel, cladding and structural parts, and (in small amounts) in reactor cooling water. Oxygen-17 is a low-abundance, naturally-occurring isotope, necessarily present in both UO_2 fuel and cooling water. Carbon is present as an impurity in fuel, cladding, and structural parts. In the manufacturing of some fuel, an atmosphere of air has been left inside the fuel rods when they were pressurized with helium gas and welded shut. This contributes a significant amount of nitrogen to the fuel assemblies in addition to that present as impurities in the fuel and metal parts [15].

Several researchers have calculated the quantities of ^{14}C expected to be produced in the various components of spent fuel and in the coolant. These have been summarized by Braun et al. [16] and by Bush [12]. The most detailed calculations for U.S. spent fuel are probably those by Croff and Alexander [17]. Measurements of gaseous forms of ^{14}C released from reactor coolant have been performed, and were also summarized by Braun et al. and by Bush. Measurements of ^{14}C in UO_2, in Zircaloy cladding and in fuel rod gas from U.S. PWR spent fuel have been performed more recently, and the measurements of which we are aware are reviewed in Table I. So far, we are not aware of any ^{14}C inventory measurements reported for the stainless steel or nickel alloy parts of U.S. PWR spent fuel assemblies. Also lacking are inventory measurements for all the components of stainless steel-clad fuel as well as BWR fuel.

The main uncertainty involved in calculating the total inventory of ^{14}C in spent fuel is in obtaining reliable values for the nitrogen impurity levels in the various components. ANSI/ASTM Standard Specification C776 limits the N concentration in sintered UO_2 pellets to 75 μg/gU [22]. This limit was originally established by Westinghouse to prevent cladding rupture by nitrogen pressurization, assuming all the N would be released from the fuel [23]. Crow [24] reported that the N concentrations in UO_2 from five fabrication plants ranged from 1 to 100 ppm. Davis [15] found values ranging from <10 to >50 ppm, with average single plant values from 2.8 to

Table I. Calculated and Measured Carbon-14 in U.S. Commercial Spent Fuel

Measurements (all PWR)	Fuel Burnup (MWd/MTU)	C-14 Amount µCi/g	 Ci/MTU	 µCi/MWd	 Ci/GWe-yr.	Ref.
UO_2*						
Robinson - dissolution	32-33,000	-	0.36	11.1	11.9	[18]
Robinson - volox. & dissolution	28,000	-	0.309	11.0	11.8	[19]
Oconee-I - volox. & dissolution	11,000	-	0.081 to 0.176	7.4 to 16.0	7.9 to 17.2	[19]
Robinson - dissolution	31,660	0.33	0.37	11.7	12.6	[20]
Robinson - dissolution	30,200	0.49	0.56	18.4	19.8	[21]
Cladding (Zircaloy 4)						
Robinson	31,660	0.60	0.14	5.0	5.4	[20]
Robinson	30,200	0.53	0.12	4.2	4.4	[21]
Turkey Point	27,000	0.45 avg.	0.11	4.0	4.2	this work
Fuel Rod Gas						
Robinson	27,400 avg.	-	1.35×10^{-4} avg.	4.93×10^{-3}	5.29×10^{-3}	[20]
Calculations						
PWR						
UO_2	33,000	-	0.60	18.2	19.5	[17]
structural	33,000	-	0.95	28.8	30.9	[17]
BWR						
UO_2	27,500	-	0.54	19.6	21.0	[17]
structural	27,500	-	1.08	39.3	42.2	[17]

*volox. = voloxidation process [19]

47.8 ppm. Croff et al. [25] assumed a value of 25 µg/gU in their ORIGEN2 calculations. Other authors have assumed values that range between zero and 100 ppm, as reviewed by Braun et al. [16] and by Bush [12].

ANSI/ASTM Standard Specification B353 limits the N concentration of zirconium alloy tubes for reactor service to a maximum of 80 wt. ppm [26]. This limit was established because higher levels increase the corrosion of Zircaloy. ASME Standard SA-240 [27] currently gives a maximum of 0.10 wt.% for the N content of 304 stainless steel. Croff et al. have used 80 wt ppm for Zircaloy and 1300 wt ppm for both the stainless steels and the nickel alloys in their calculations, the latter based on an earlier version of SA-240. The results of their calculations are also shown in Table I.

As can be seen in Table I, the UO_2 is observed to contain more ^{14}C than the cladding, and a very small part of the inventory is contained in the fuel rod gas. Most of the measurements on UO_2 have shown ^{14}C concentrations smaller than the calculated value. This is probably due to an overestimate of the initial N concentration. It is not possible to make a direct comparison for the cladding, since the "structural" result includes other metal components. The low value for the fuel rod gas is consistent with the fact that CH_4, CO, and CO_2 have generally been undetectable or nearly so in mass spectrometric analyses of spent fuel rod gas [20,28-30]. It is also consistent with our observation that the amount of gaseous ^{14}C released in the rupture of one fuel rod was small compared to 1.5 mCi [5]. This fuel rod gas analysis confirms our suspicion that the additional 0.3 mCi released after rod rupture in our earlier reported measurements [5] came essentially completely from the external surfaces of the fuel assembly, since less than 1 μCi could have come from the gas in a single rod.

PHYSICAL DISTRIBUTION AND CHEMICAL FORMS OF CARBON-14 IN SPENT FUEL

The release rate of ^{14}C from spent fuel in a repository will depend on both its physical distribution and its chemical forms. Since these have not been directly measured in detail as yet, it is helpful to consider the behavior of ^{14}C in spent fuel from a theoretical point of view, to the degree possible. In this regard, we will consider three separate chemical systems, which are more or less isolated from each other in terms of transport of ^{14}C and its precursors (N, C, and O). These systems are (1) the inside of the fuel rods, including the UO_2, the fill gas, and the inner surfaces of the cladding, (2) the bulk of the cladding wall thickness and the interior of other fuel assembly structural components (spacers, etc.), and (3) the reactor primary coolant and the external surfaces of the cladding and other fuel assembly components.

Considering first the interior of the fuel rods, the UO_2 initially contains a small amount of nitrogen as an impurity in the form of uranium nitrides [23]. This originates from two sources: the ammonium diuranate process for converting UF_6 to UO_2, and the use of cracked ammonia for adjusting the stoichiometry of UO_2 during fuel manufacturing.

The Zircaloy cladding contains a small amount of nitrogen impurity also. It is probably present in solid solution, based on its high solubility at equilibrium [31]. As mentioned above, some fuel originally contains residual air in the helium fill gas inside the rods as manufactured, which is an additional source of nitrogen.

When Zircaloy-clad fuel is initially heated during reactor start-up, the inside pressure is observed to rise during the first few minutes, due to the release of nitrogen, oxygen, water vapor, hydrogen, carbon monoxide, and carbon dioxide [32]. Nitrogen is particularly dominant for fuel that has been sintered in cracked ammonia. The pressure is then observed to drop over the next few days. This is thought to be due to reaction of these gases with the fuel and cladding. Hydrogen, water vapor, and oxygen are expected to react within three days. (Getters are used in currently-manufactured fuel to limit hydriding of the cladding.) Carbon monoxide reacts more slowly, and nitrogen slowest of all. Gas analysis at low fuel burnups show nitrogen as the main residual gas present [33]. Although pure zirconium is capable of gettering pure nitrogen in the temperature range that exists on the inside wall of the cladding (300-400°C) [34], the reaction has been found to be very sensitive to traces of oxygen and hydrogen in the reacting gas [35]. In a telephone conversation, John H. Davies of the General Electric Company indicated that tests performed by the Company, the details of which are considered company proprietary, showed that most of the nitrogen reacts with the UO_2 rather than with the Zircaloy cladding. This may result from the higher temperature and larger effective surface area of the UO_2 as well as interference with gettering by the Zircaloy, caused by oxygen and/or hydrogen. As reactor operation continues, the pressure in the rod again rises, due to the release of xenon and krypton from fission [32]. It is of interest to know whether significant transport of either the nitrogen precursor or of ^{14}C itself occurs from the fuel to the cladding inside surface over longer time periods as reactor operation continues. In the case of stainless steel-clad fuels, the oxygen potential of the fuel rises, because the fission process releases the oxygen originally bound to the uranium, and the demand of the fission products for oxygen is less than that of the original uranium [36]. This excess oxygen is available to produce the irreversible release of nitrogen from the fuel as discussed by Ferrari [23,37] as well as to feed the $CO-CO_2$ transport mechanism that is thought to redistribute oxygen over the temperature gradient [38]. However, in the case of Zircaloy-clad fuels, it has been observed that the oxygen potential is held down by gettering of the O_2 on the inside surface of the cladding, maintaining the stoichiometry at very nearly UO_2 [39,40]. In this case, the transport mechanisms for nitrogen and carbon are probably less effective. This conclusion is supported by the analyses of gas from higher-burnup fuel rods in which N_2 and the other residual gases are near or below the minimum detection limits, as noted above. This is also consistent with the observation that a large part of the ^{14}C inventory is found in the UO_2 after burnup (see Table I).

The chemical form of the ^{14}C in the UO_2 is not known, but it could be carbide, oxycarbide, or elemental carbon. Work by Adamson [41] indicates that at least a good share of the carbon in UO_2, even at a concentration of <5 ppm, exists as the element, because it produces CO and CO_2 gases as though it has a chemical activity of one, independent of concentration. That is, it does not follow Henry's Law, and therefore it must not be in solution in the UO_2.

The small amount of ^{14}C in the fill gas is probably present as CO or CH_4 because of the low oxygen potential produced by Zircaloy gettering. The ^{14}C present on the inside surface of the cladding may be in the form of zirconium carbide or zirconium cyanonitride ($Zr(C,N,O)x$, where $x < 1$) [42]. Since the diffusion of both C [43] and N [44] in Zr are very slow at 300-400°C, these species are expected to remain near the surface.

Considering now the second chemical system, i.e., the bulk of the cladding wall thickness and the interior of other structural components, both the initial N present as an impurity and the ^{14}C produced from it by transmutation are expected to diffuse only slowly, and can therefore be considered stationary [43-45]. The ^{14}C will most likely be present initially as an interstitial impurity, but may diffuse to segregated carbides.

The third chemical system, consisting of the reactor primary coolant and the external surfaces of the cladding, differs considerably for the PWR's and BWR's, respectively. The BWR primary coolant is boiling high-purity water. Until recently, no additives had been used. The steadystate O_2 concentration was about 200 ppb, and there was a stoichiometric ratio quantity of dissolved H_2 [46]. Recently some BWR operators have begun adding H_2 gas to the primary coolant to suppress O_2 and stop the intergranular stress corrosion cracking of Type 304 stainless steel pipes. In PWR's, on the other hand, H_2 has always been added to the primary coolant to control the redox conditions, along with lithium hydroxide to control pH and boric acid as a neutron absorber for reactivity control [47]. In addition, the primary coolant in the PWR does not boil.

Most of the ^{14}C generated in the primary coolant is believed to come from the reaction on ^{17}O, although some nitrogen is present, particularly during start-ups after outages. Analyses of off-gas from the primary system have shown that most of the ^{14}C released from BWR's is in the form of CO_2, while most released from PWR's is in the form of CH_4 and other hydrocarbons [48]. This is consistent with the redox conditions present in the two reactor types. Roughly speaking, the amounts of ^{14}C emitted as off-gases were in agreement with the calculated production of ^{14}C in the primary coolant in the PWR's [12]. Measured amounts from BWR's were higher than the calculated amounts, perhaps because of higher, unaccounted for N_2 concentrations.

It is possible that a small fraction of the ^{14}C produced in the primary coolant of LWR's could be adsorbed onto the cladding surface and still not perturb the agreement between these calculated and measured amounts within the available precision. Such an adsorption process may differ between BWR's and PWR's because of the different redox conditions. However, it is interesting to note that H_2 addition does not measurably change the level of ^{15}C, a shorter-lived carbon isotope, in the main steam line of BWR's [46]. This indicates that the redox change does not affect to a large degree the fraction of ^{15}C that is retained on surfaces in the reactor core, even though its form in the water would have changed from primarily CO_2 to primarily CH_4. Nevertheless, measurements of ^{14}C in BWR cladding will be needed to check whether there are differences in adsorbed ^{14}C that are significant from a waste management viewpoint.

During the course of reactor operation, the outside surfaces of the cladding are oxidized. Some of the nitrogen originally present as an impurity in the layer of Zircaloy that is oxidized will be transmuted to ^{14}C. Its fate is not known, but it may be retained in this layer. If retained, it may be present as elemental carbon, as zirconium carbide, as zirconium cyanonitride, or as an impurity dissolved in zirconium oxide.

Measurements by one of us (H.D.S.) on a few lightly-oxidized samples of PWR cladding from one fuel rod indicate that a significant fraction (if not most) of the ^{14}C inventory in the cladding was located quite near the outside surface. This would tend to indicate that this ^{14}C originated from the reactor coolant or from the coolant present during fuel storage in water. As mentioned above, our previously reported measurements on a PWR fuel assembly heated in air to 275°C showed release of ^{14}C as CO_2 from the outside of the assembly. It has been reported that finely-divided zirconium carbide made in an arc furnace is pyrophoric [49], which would be consistent with the low temperature oxidation we observed, assuming that zirconium carbide is actually the chemical form present. However, elemental carbon would probably also be oxidized in irradiated air at this temperature.

RELEASE OF CARBON-14 FROM SPENT FUEL IN VARIOUS ENVIRONMENTS

Various experimenters have measured ^{14}C releases from spent fuel in aqueous solutions and in air, nitrogen, and helium gases. A consistent picture of ^{14}C behavior is arising from these studies.

Aqueous Solutions

In 1978, Goles and Brauer measured ^{14}C as CO_2 in the air above the spent fuel storage basin at General Electric's Morris Operation, as reported by Judson et al. [50]. They found a concentration of 3×10^{-10} μCi/ml, indicating small but measurable release. Wilson [21] has performed open system ambient temperature PWR spent fuel dissolution tests in deionized water and in water from Well J-13 near the proposed tuff repository site at Yucca Mountain, Nevada. Fuel was exposed to the solutions in various forms: with intact cladding, with cladding having holes or slit defects, and as bare fuel. It was found that a significant amount of the ^{14}C release originated from the external surface of the cladding. It was not possible to obtain quantitative total release results because of the open system and consequent exchange with atmospheric CO_2. More recently, Wilson has performed closed system tests at 85°C [51]. In this case, releases were found to be larger in the case of bare fuel than for fuel with intact or defected cladding. Nevertheless, releases were observed from all specimens. The release from the fuel with intact cladding was about an order of magnitude above one part in 10^5. Clearly, the release of ^{14}C if spent fuel were contacted with aqueous solution in a saturated or unsaturated repository is of concern even for intact fuel.

Air

Our previously-reported results [5] have shown that ^{14}C was rapidly released as CO_2 when intact PWR fuel was heated in air, and it is clear that the release occurred from ^{14}C located on the external surfaces of the fuel assembly. The mechanism appears to be thermally-induced oxidation, perhaps assisted by the gamma radiation field. This is consistent with the observation that hematite was apparently formed from the crud [52]. For the fuel assembly we used, the total release amounted to about 1.8 mCi. There could be significant differences in this amount for different fuel assemblies, depending on their histories, and particularly for BWR assemblies, since their redox environment in the reactor is quite different.

When cladding rupture occurred on one rod, the additional ^{14}C release was negligible, because of the low concentration of ^{14}C in the fuel rod gas (see Table I). Additional releases from inside the ruptured rod as well as all external surfaces over a time period of several months, even when the canister gas was evacuated and replaced on a monthly basis to promote "breathing" of the ruptured rod, and then re-evacuated and analyzed, were found to be small compared to the initial release on heating. The ^{14}C concentrations were found to be at least 4 orders of magnitude lower in the canister gas samples taken by evacuation. The ratio of concentrations of ^{14}C to ^{85}Kr were more than a factor of ten lower in the evacuated gas than in the samples taken earlier without evacuation. ^{14}C was not detectable in several of the samples taken by evacuation, while additional ^{85}Kr release continued to be observed. The accumulated ^{14}C released during the 22 months after the initial gas was evacuated and replaced by fresh air each month is estimated to be at least 3 orders of magnitude less than that released during the initial 2 months following the heating in air.

Nitrogen and Helium

These inert gases are being studied for use in dry fuel storage. Our measurements on gas samples taken from a BWR spent fuel storage cask containing 52 fuel assemblies at the General Electric Morris Operation showed barely detectable ^{14}C release from fuel stored alternately in nitrogen and helium gases, even though ^{85}Kr releases indicated a leaking fuel rod [53]. Analysis of gas samples from a similar test involving a PWR spent fuel storage cask at Idaho National Engineering Laboratory also showed only small ^{14}C releases. These results are considered less reliable because of deficiencies in the sampling equipment, which allowed the entry of air into the samples [54]. In any case, the results so far are consistent with the proposed release mechanism, i.e, the necessity for O_2 to oxidize the ^{14}C to CO_2 to enable significant gaseous release to occur.

PROJECTED RELEASE BEHAVIOR OF CARBON-14 FROM SPENT FUEL WASTE PACKAGES IN A TUFF REPOSITORY

As noted in the Introduction, the proposed horizon for the tuff repository is above the water table. It is planned to design the repository in such a way that the temperature at the surfaces of most of the waste packages will remain above the boiling point of water for the duration of the mandated containment period, a duration of 300 to 1000 years, and that containment will be substantially complete during this period. We do not expect substantial changes in the chemical and physical forms of the ^{14}C

during the period in which the containers are intact, since water and oxygen will be excluded. Any change would probably be in the direction of additional gettering of gaseous ^{14}C by the solid phases. After the temperature falls below the boiling point, liquid water in small amounts is expected to enter the repository region. The environment at this time is expected to consist of moist air and films of liquid water on the solid surfaces.

No ^{14}C release is expected as long as the waste containers remain intact. When the waste package containment barriers eventually fail, moist air and variable amounts of liquid water will be able to contact the spent fuel. Prior to this time, the fuel assemblies would have been surrounded by an inert gas, and ^{14}C release to this gas should have been small.

When oxygen enters the waste packages, oxidation of ^{14}C to CO_2 can take place. However, at this time the temperature should be below the boiling point of water for the majority of failed containers, and the external gamma radiation field should be no more than a few rad/hr. Under these conditions, the rate of oxidation should be slow. This rate will need to be evaluated as a function of temperature by experiments.

It is expected that the cladding on most of the fuel rods will still be intact (or substantially so) at the time of waste package containment failure. Under these circumstances, only the ^{14}C on or near the external surfaces of the fuel assemblies would be available for release. At present, the only estimate of this inventory available is from a single PWR fuel assembly, and amounts to 1.8 mCi, compared to a total assembly inventory calculated to be 690 mCi, i.e. 2.6×10^{-3} of the calculated inventory. If only 4% of the surface inventory were released in a single year, it would exceed 1 part in 10^5 of the calculated total inventory. Clearly, if 10CFR60 is to be satisfied, account must be taken of the fact that not all waste packages will fail in the same year, and that the oxidation rate probably will be slower at low temperatures.

When the fuel rod cladding fails, the pressurized gas in the rods will be released. Based on the measurements available, and assuming no change in the ^{14}C content of the gas during the containment period, this may represent about 10^{-4} of the calculated total ^{14}C inventory (if there is a change, one would expect it to be a decrease, since there is excess Zircaloy available for gettering). Again, account must be taken of the time distribution of cladding lifetimes to satisfy the 10CFR60 limit of 10^{-5} per year.

Finally, as the moist air and liquid water gain access to the insides of the fuel rods, release of the main part of the calculated ^{14}C inventory could begin. At the expected low temperatures (< 95°C) and low water infiltration rates, this process should be relatively slow. Release of the ^{14}C present in the bulk of the cladding and structural parts should likewise proceed slowly, because of their corrosion resistance.

When ^{14}C enters the air-water environment of the tuff repository, it will be diluted by and will undergo isotopic exchange with the carbon already present as CO_2 in the gas phase and HCO_3^- in the liquid phase. CO_2 has been observed to be present at levels as high as about 20% in gas samples taken from a drill hole near Yucca Mountain [55]. The groundwater from wells in the vicinity of the site contains HCO_3^- at concentrations between 100 and 569 ppm. Well J-13, which supplies the water taken to be of reference composition for the tuff repository, has an HCO_3^- concentration of about 124 ppm [56]. It is interesting to note that the groundwater from wells in the vicinity of Yucca Mountain has apparent ages between 3,800 and 30,300 years, based on its natural ^{14}C content. For J-13, the value is 9,900 years [56]. In other words, the ^{14}C released from the waste packages will be diluted with carbon that is depleted in ^{14}C relative to carbon in the earth's atmosphere. Efforts are now underway by the U.S. Geological Survey to perform ^{14}C analyses on water samples from the unsaturated zone. The ^{14}C abundance of air or water that could reach the accessible environment from the tuff repository will have to be calculated by a detailed transport model that takes account of this mixing process.

SUMMARY AND CONCLUSIONS

1. Published measurements of the carbon-14 inventory in U.S. spent fuel are few and pertain mostly to Westinghouse Zircaloy-clad fuel.
2. In this fuel, the UO_2 contains more ^{14}C than the clad, and only a small amount of ^{14}C is present in the fuel rod gas. The chemical form of the ^{14}C in the UO_2 is not known, but some apparently exists as the element. In the Zircaloy cladding, the ^{14}C probably exists as interstitial carbon or zirconium carbide. In the fuel rod gas, it is probably present as CO or CH_4.
3. In an atmosphere of nitrogen or helium gas, only a negligible amount of ^{14}C is released from heated, intact spent fuel.
4. When an intact PWR fuel assembly was heated in air, ^{14}C on the external surfaces was oxidized to CO_2 and released. This ^{14}C may have originated from N impurity in the Zircaloy or may have been adsorbed from the reactor cooling water. The amount present on different fuel assemblies may vary depending on the redox conditions in the reactor coolant (PWR or BWR) and the prior treatment of the spent fuel.
5. In aqueous solution, more than 10^{-5} of the ^{14}C inventory can be released from intact spent fuel in a time of less than one year.
6. When the cladding on a fuel rod ruptures, ^{14}C released by escape of the pressurized gas may represent about 10^{-4} of the calculated total inventory of the rod, but the cladding lifetimes will be distributed in time.
7. In order to determine whether the 10CFR60 limit can be satisfied for ^{14}C release from waste packages in an unsaturated tuff repository, it will be necessary to measure the oxidation and release of ^{14}C from the external surfaces and the rod interiors of spent fuel in moist air at temperatures both above and below the in situ boiling point of water.
8. In order to determine whether the 40CFR191 release limit to the accessible environment can be met for ^{14}C release from an unsaturated tuff repository, it will be necessary to do detailed transport modeling, taking account of dilution by the naturally-occurring carbon, which is depleted in ^{14}C abundance relative to the earth's atmosphere.
9. It would be desirable to measure the ^{14}C content in the non-Zircaloy structural components of Westinghouse Zircaloy-clad PWR spent fuel, in all the components of fuel from other manufacturers, especially BWR spent fuel, and in stainless steel clad fuel. Our present estimates of the ^{14}C inventory are based largely on calculations, which need to be tested against measurements.

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