

EVALUATION OF THE RELATIONSHIP BETWEEN ^{14}C AND ^{60}Co IN A PWR PLANT

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ABSTRACT

Low level radioactive waste (LLW) generated at nuclear power stations in Japan will be disposed of at the burial site located at Rokkasho Village, Aomori Prefecture, near the Shimokita Peninsula from December 1992.

Every LLW waste drum to be disposed of must be inspected and certified for compliance with government regulation for shallow land burial. The main items to be confirmed are the packaging method, specific activity, radioactive contamination of the package surface, mechanical strength of the waste package, etc.

One item to be confirmed is that the concentration and amount of radionuclides in the drum must be less than the values in the license application documents for the site. So we evaluate the radionuclide concentration in the following way. The concentration of dominant gamma emitting nuclides can be directly measured from the outside of the drum and the concentration of nuclides which do not emit gammas are estimated indirectly by relating the difficult to measure radionuclides to other readily measurable radionuclides by the application of "scaling factors".

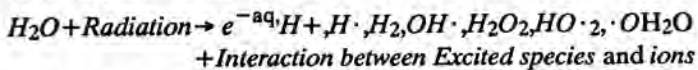
When we adopt scaling factors for the estimation of the concentration of nuclides which do not emit gammas, we must select an appropriate nuclide which should be one of the dominant gamma emitting nuclides and which behaves in the nuclear power plant in a similar way to the nuclide which does not emit gammas. Therefore we relate ^{14}C to ^{60}Co because their production mechanisms are similar. Before applying the scaling factor for $^{14}\text{C}/^{60}\text{Co}$ to the estimation of ^{14}C for shallow land burial purposes, we should confirm this relationship theoretically. We already have a good understanding of the behavior of ^{60}Co in a Pressurized Water Reactor (PWR) plant, but have less information about ^{14}C behavior. Therefore we investigated the behavior of ^{14}C and ^{60}Co in PWR plants and evaluated the validity of the scaling factor for $^{14}\text{C}/^{60}\text{Co}$.

INTRODUCTION

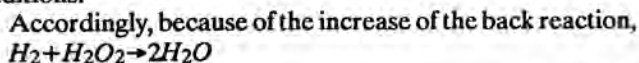
Mechanism of ^{14}C production

In Light Water Reactors (LWR), ^{14}C is produced by neutron capture from ^{17}O and ^{14}N in the primary reactor coolant. ^{17}O is a major component of the primary coolant, whereas ^{14}N is only present as dissolved gas and so the amount of ^{17}O is much more than that of ^{14}N . Therefore the main source of ^{14}C is production from ^{17}O in the primary coolant.

When coolant water at high temperature is exposed to ionizing radiation such as γ -rays and x-rays. The following chemical species are produced. They react with ^{14}C to produce organic ^{14}C compounds.



In a PWR, hydrogen is injected into the primary coolant during the normal power operation to maintain reducing conditions.



the production of oxidizing compounds is suppressed. Under these conditions, the products are predominantly $^{14}\text{CH}_4$, $^{14}\text{CH}_2$ and $^{14}\text{CH}_3$ and it is supposed that the main products of organic ^{14}C are low molecular weight hydrocarbons, such as methane, ethane, etc. Also other compounds may exist in the reactor coolant, such as methanol, ethanol, formaldehyde, acetaldehyde, formic acid, acetic acid, etc.

Assumed behavior of ^{14}C in a plant

^{14}C produced in the reactor coolant forms many kind of compounds, which are both volatile and non-volatile, gases and solids, and may be ionized. Therefore the behavior of ^{14}C in a plant depends on the physical and chemical characteristic of its compounds. Based on these characteristics and the performance of plant components, we made some assumptions about the behavior of ^{14}C in the plant. The results are as follows:

- Demineralizer: Mainly ionized ^{14}C is removed.
- Volume Control Tank (VCT): Gaseous compounds transfer from the liquid to the vapor phase and go to the waste gas system with other gases.
- Evaporators: Many of gaseous compounds transfer to the waste gas system.
- Filters: Solid compounds are removed with crud and sludge.
- Behavior during plant shut down: Gaseous and volatile components transfer to the containment vessel atmosphere when the reactor vessel is opened and the cavity is filled.

METHODS

Analysis of ^{14}C

In our investigation, we measured the concentration of total ^{14}C and ratio of organic ^{14}C / inorganic ^{14}C compounds

The "Total ^{14}C combustion method" was adopted for the measurement of total ^{14}C and the "Wet oxidation method" was used for the organic ratio of ^{14}C /inorganic ^{14}C compounds.

Wet oxidation method:

- The sample is oxidized to carbon dioxide by potassium permanganate-sulfuric acid or peroxodisulfuric acid-nitric acid. Then that carbon dioxide is absorbed by monoethanolamine and the β -rays are measured by a liquid scintillation counter to obtain the amount of ^{14}C .

Total combustion method:

- The sample is heated to 950°C in an air atmosphere and oxidized to carbon dioxide in the presence of a catalyst existence. After that the measuring method is the same as for the "Wet oxidizing method".

Procedure

For this investigation, the process streams which appear to have an effect on the ^{14}C and ^{60}Co behavior in a nuclear power plant were sampled. The most important sampling point was the liquid waste concentrates line upstream of the solidification system. Also as we assumed that the behavior of these nuclides would be different for various plant conditions, we took the samples in both normal operation and during a shut down. From the radiochemical analysis, we obtained data for the ^{14}C concentration and information about the chemical form of the ^{14}C compounds, i.e. the ratio of solid components and soluble components and the ratio of organic and inorganic compounds. We investigated the ^{14}C behavior at 2 PWR plants. Based on these data, we evaluated the behavior of ^{14}C and ^{60}Co in the plants and estimated the relationship between ^{14}C and ^{60}Co .

RESULTS

The identification of the chemical species of ^{14}C

From the separation of liquid compounds, we can get the following information:

- In the primary coolant and the evaporator concentrates organic compounds were detected, but it is difficult to specify the organic species.
- Those species which occur with high probability and were detected in almost all cases are oxalic acid, acetic acid, ethylene glycol, methanol and ethanol.

From the separation of gaseous compounds, we can get the following information:

- $^{14}\text{CH}_4$, $^{14}\text{C}_2\text{H}_6$ and $^{14}\text{C}_3\text{H}_8$ accounted for 87% of the ^{14}C compounds in the reactor coolant, about 85% in the VCT and about 90% in the gas decay tank. These three chemical species of ^{14}C were the main gaseous compounds in a PWR and this result corresponds with C. Kunz's (1) results.

Evaporator concentrates:

- The probability of solid ^{14}C compounds occurring was very high. They were found in 61 - 98% of the cases.
- The concentration of total ^{60}Co varied but was of the order of 1.0×10^4 Bq/ml.
- For both nuclides, the distribution of the diameter of solid particles containing ^{14}C and ^{60}Co was measured

and the probability of the nuclides occurring tended to increase with particle size. For particles with a diameter of over $0.45 \mu\text{m}$, the probability was about 94% for ^{14}C and about 82% for ^{60}Co .

The following ^{14}C components were found in evaporator concentrates.

- ~50% →Hydrophilic organic compounds soluble in water
- 2~3% →Hydrophilic organic compounds soluble in acid
- 3~6% →Oleophilic organic compounds soluble in organic solvent
- 25~45% →Compounds which were thermally and chemically stable

Behavior of ^{14}C

Behavior in the plant:

- Gas/Liquid interface of the VCT
The gas/Liquid partition coefficient for gaseous ^{14}C compounds in the VCT was in accordance with the theoretical values calculated by the Henry constant of methane, ethane, etc. and ^{14}C occurred mainly as low molecular weight hydrocarbons, such as methane, ethane, etc.
- Demineralizer
During two plant operation modes (normal operation, oxidizing operation), the decontamination factor (DF) for ^{14}C in the reactor coolant mixed bed demineralizer was as shown in Table I.

TABLE I

DF of ^{14}C

	Normal Op.	Oxidizing Op.
Total ^{14}C	0.93	0.67
Solid ^{14}C	8.6	1.6
Ion ^{14}C	1.03	0.67

- For each ^{14}C components, the DF decreased during the oxidizing operation.
- Ionic components of ^{14}C were saturated in the demineralizer during normal operation.

- Evaporator

- The concentration of total ^{14}C increased as the evaporation proceeded and corresponded to the concentration of boric acid. At the end of the evaporation, the total ^{14}C concentration was in the range of $3.7 \times 10^2 - 7.4 \times 10^2$ Bq/ml.
- The probability of solid ^{14}C compounds occurring didn't depend on boric acid concentration and was about 70 - 96%.

- Effect of plant operation

The concentration of ^{14}C in the primary coolant was measured for different modes of operation. The concentration tended to vary as follows:

- Total ^{14}C

- The concentration of total ^{14}C at hot shut down (HSD) was 1/7 less than during normal operation.
- The concentration increased when the plant went from HSD to the oxidizing operation. This may be caused by ^{14}C shedding from the demineralizer (resin).
- Solid ^{14}C compounds
 - The probability of solids ^{14}C compounds occurring increased one decade when the modes of operation changed. As follows:

Normal operation	→	HSD	→	CSD
(0.5%)		(7%)		(44%)
 - When the plant was being shut down, the behavior of particle containing ^{14}C was similar to those containing ^{60}Co and ^{58}Co .

Results

As a result of our investigation, we got the following information.

- The amount of ^{14}C in the liquid waste concentrates was less than 5% of the total ^{14}C production.
- The concentration of ^{14}C in the form of solids in the primary coolant during plant shut down was about two decades higher than in normal operation. We considered that the cause of the increase of ^{14}C

concentration in the solid form was the change of coolant conditions such as pH, temperature, pressure, etc., which affect crud components in a similar way, i.e. corrosion deposit behavior.

- ^{14}C concentration in the evaporator concentrates was about the same as in the upstream liquid at the start of evaporator operation and the concentration increased as the operation proceeded. In other words, there was little carryover of ^{14}C to the condensate and ^{14}C compounds behaved like crud.
- Over 60% of the ^{14}C in the concentrates was in the form of solid compounds. These solid compounds were insoluble under PWR water conditions.

Evaluation

^{14}C was principally present in the form of organic compounds and solid compounds. These tended to be concentrated in the evaporator. Also ^{60}Co is a constituent of crud and it is known that crud is concentrated in the evaporator. That is to say both solid ^{14}C and ^{60}Co are concentrated in an evaporator and their production mechanisms are similar. Accordingly, the concentration of ^{14}C and ^{60}Co has a good relationship and we may use a scaling factor for $^{14}\text{C}/^{60}\text{Co}$ to estimate the ^{14}C concentration from a measurement of ^{60}Co .

REFERENCES

1. C.KUNZ, "Carbon-14 Discharge at Three Light-Water Reactors", Health Physics, Vol. 49, No. 1, pp. 25-35 (1985)