

C-14 release behavior and thermal decomposition characteristics of crud particles collected from the coolant filter of commercial PWR

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Abstract

In the safety assessment of radioactive waste buried repository, it is extremely important to evaluate the migration behavior of long half-life radionuclides in the disposal environment. C-14 is a key radionuclide in waste disposal because of the long half-life (5,730years) and the considerable effect on public exposure due to the less capability of capturing C-14 by artificial barrier material. In addition, C-14 is a radioactive isotope of carbon which forms various chemical forms in the process of its formation, and the migration behavior in the buried environment greatly differs depending on its chemical form.

Some previous studies have reported the generation of insoluble C-14 in pressurized water reactor (PWR), and suggested that ion-exchange resin, which is used for purifying primary coolant, could be its origin. However, this hypothesis has not been well evidenced yet, because the information about the generation mechanism and the chemical form of insoluble C-14 is still limited.

In this study, in order to investigate the chemical form of C-14 contained in radioactive particles generated by PWR, radioactive particles collected from the coolant filter of PWR were analyzed by TG/MS, and the gas released by TG and residual C-14 in the compounds was also analyzed at the same time.

As a result, organic molecules presumed to originate from ion exchange resin were detected from the released gas components, and it was confirmed that 90% or more of C-14 was detected in residual components of heating in the inert gas.

From the results of this study, the chemical form of insoluble C-14 generated by PWR could not be clarified, but it was revealed that the majority of C-14 may exist in amorphous and thermally stable compounds.

1. Introduction

When radioactive waste is buried, safety assessment based on the retardation of migration of radionuclides contained in radioactive waste is conducted. Radioactive waste generated at PWRs contains many radionuclides. Among these radionuclides, C-14, which is a radioisotope of carbon, is a nuclide that may have various forms. The migration retardation effect for C-14 in the burial environment largely depends on its chemical form. However, only part of the chemical forms of particulate C-14 generated at PWRs has been clarified.

In Japan, concerning C-14 contained in solid radioactive waste generated at PWRs, the presence of C-14 in the forms of inorganic matter that is decomposed by an acid into CO₂, and chemical matter that is not easily decomposed unless an oxidant (e.g., potassium permanganate) is activated at high temperature, is known. It has been confirmed that in these forms (of C-14), C-14 that is present as a solid (particle), not in an inorganic form, is a “hardly soluble component” that is hardly dissolved in an organic solvent or the like.⁽²⁾

In that report, an observation result that showed the presence of crud, which is a metal oxide, in addition to particles centering on carbon is reported. Higuchi et al considered that concerning the observed particles, the particulate carbon generated at the PWR was generated from a degraded product of the ion exchange resin.

Meanwhile, Research on the crud of a primary system is advanced in some PWR plants with aim of reducing exposure. At the Callaway Plant in the United States, the result of observing flaked crud that contained carbon is reported.⁽¹⁾

The crud observed at the Callaway Plant and the crud that Higuchi et al reported have many similarities in appearance, and both contain much carbon. We considered that the origins of particles formed from flaked carbon were common to each other.

Therefore, for this paper, we first analyzed a solid specimen with C-14 collected from the commercial PWR plant that has not experienced zinc injection, and then examined the chemical form of C-14 contained in a particulate component generated at the PWR, and its generation mechanism.

2. Material and methods

2.1 Specimens

The major contamination source of solid radioactive waste generated at the PWR is considered as crud contained in the reactor coolant. Therefore, for this paper, a coolant filter that captured much crud of the primary system of the PWR was collected, and the components of the crud captured at the filter were used as a specimen for the experiment.

In the PWR, the reactor coolant, which cools nuclear fuels in the reactor, is pressurized to 15.4 MPa, and circulates in non-boiling state at approximately 325°C. Part of this reactor coolant is constantly cleaned by a coolant filter and

a mixed bed demineralizer filled with an ion exchange resin after being cooled/depressurized to 80°C or below at a chemical and volume control system (CVCS) (Fig. 1).

In a mixed bed demineralizer inlet filter (hereafter called “inlet filter”) installed in the CVCS, particulate components (crud) that are generated due to corrosion or the like of the material constituting the primary cooling system are captured, and the particles captured in the filter can be considered to represent radioactive particles generated at the PWR.

For the commercial plant specimen, the inlet filter collected from Ikata Unit 3 of Shikoku Electric Power Co., Inc. was used. The plant, from which this specimen was collected, does not adopt zinc injection.

In this study, we prepared mock crud by autoclaving the ion exchange resin used at the PWR under conditions close to the water quality of the primary system of the PWR, and obtained data through an experiment described later, with the aim of comparing the mock crud with the commercial crud specimen.

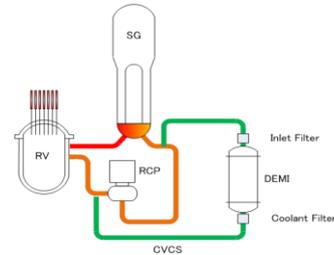


Fig. 1: Schematic diagram of the primary cooling system and the chemical and volume control system of the PWR

2.2 Preparation of an experimental specimen

The inlet filter collected from the plant was partially cut (Fig. 2) and cleaned by ultrasonic washing to disperse the particles captured in the filter into ultrapure water, and crud captured on a milli-pore membrane filter (hereafter called “MF”) of 0.45 μm was collected (Fig. 3).

2.3 Analysis of the particulate components using SEM/EDS

To check similarity between the specimen used for an experiment in this study and flaked crud containing carbon, which has been reported in Japan and the United States in the past, we conducted a scanning electron microscopic observation of the experimental specimen.

Using scanning electron microscopes (SEM: S-3400N by Hitachi High-Technologies, Tokyo, Japan; EDX: 350xt/Wave500, Oxford inst Energy, Oxford, UK), we observed the shapes of the particles captured on the 0.45 μm MF, and conducted element composition analysis using an energy dispersive X-ray micro analyzer for the respective visual field.

2.4 Molecular structure analysis using FT-IR

To check part of the chemical structure of the carbon component in the crud specimen used in this study, we conducted an FT-IR analysis.

The FT-IR spectra (transmission spectra in a wavenumber range of 4,000 to 400 cm^{-1}) of the particulate components collected on the 0.45 μm MF were measured using the KBr method. For the FT-IR analyzer, FTIR-8400 of Shimadzu Corporation (Kyoto, Japan) was used.

2.5 Analysis of the thermal decomposition behavior of C-14 with TG/MS

The thermal decomposition behavior of the crud was checked using a thermo-balance. In addition, an off-gas released by heating with the thermo-balance was divided, and part of the off-gas was induced to a mass spectrometer, and the rest to a tubular furnace filled with an oxidative catalyst. The mass spectra of the off-gas released were analyzed with the mass spectrometer, and the C-14 radioactivity of the components oxidized in the tubular furnace was analyzed.

(1) Experiment method

For the thermo-balance, STA449F3 (manufactured by NETZSCH) was used. For the mass spectrometer, JMS-Q1500GC (manufactured by Japan Electron Optics Laboratory) was used. The gas released from the thermo-balance was mixed with a supporting gas (pure air) via a stainless steel piping kept heated at 200°C, induced to a tubular furnace (furnace tubing: quartz; oxidative catalyst: Co_3O_4 [2 mm mesh] 50 g) heated to 900°C, and the released gas was oxidized to CO_2 . The components containing C-14 oxidized to CO_2 was collected using a bubbler filled with a 1 mol sodium hydride solution (Fig. 6). C-14 collected in the sodium hydride solution was re-condensed to a carbon dioxide absorbent (Carb-Sorb E by Perkin Elmer) for liquid scintillation counter measurement, then mixed with a liquid scintillator (Permafluor E+ by Perkin Elmer), a beta ray emitted from C-14 was quantified with the external standard source channel ratio method (ESCR) using a liquid scintillation counter (LSC-5000 by Aloka, Japan).

(2) Experiment conditions

A mock specimen irradiated with a gamma ray after heat treatment, and the components captured in the inlet filter collected from the commercial equipment, were placed on a thermo-balance, and the heating of them was started under the following conditions. The C-14 release behavior was checked only for the commercial equipment specimen. The heating of an inert gas using the TG was performed after “in an inert gas (He)” and pure air were selected. In the heating in the inert gas, a supporting gas was added to the gas components released from the TG to combust the gas, and C-14 was collected as CO_2 in an alkaline solution (Fig. 7).

◎TG treatment temperature	r.t. to 900°C
◎Heating rate	20°C/min
◎Carrier gas	He or air
◎Range of mass spectrometer scanning	m/z = up to 1000

In addition, the specimen, for which the released components and mass change were checked by applying each carrier gas, was cooled to the room temperature, and then heated again to 900°C in an air stream. Subsequently, the released gas was heated to 950°C and oxidized into CO_2 using an oxidative catalyst to produce C-14, which was then collected, and the portion of C-14 remaining in the particles was obtained.



Fig. 2: The mixed bed demineralizer inlet filter after being cut



Fig. 3: Particulate components captured on the 0.45 μm MF

3. Results

Fig. 4 shows the result of a property observation using an SEM. In the SEM observation, flaked crud was observed. On this flaked crud, small-grain particles were further observed.

Table 1 shows the result of an element composition analysis in the observation visual field. It was found that 58.6% of the element composition in this visual field was carbon (Table 1). Fig. 5 shows the FT-IR spectra of crud whose main component is this carbon. In the FT-IR spectra, transmission peaks that characterize a carboxyl group and a hydroxyl group were observed (Fig. 5).

Fig. 8 shows the result of TG/MS analysis in the He stream. In the thermal decomposition behavior of the commercial equipment specimen with TG using He as the carrier gas, the mass change was minimal in a range from the start of heating to 200°C. However, a mass reduction

was observed around 400°C. Beyond 400°C, no characteristic mass change was observed from 500°C to 900°C. In addition, around 430°C where a major mass reduction was observed, peaks were observed at $m/z = 44$, 77 and 105 on the mass spectrometer. The signals detected for the respective mass-electrolysis ratios are considered as the following analytical fragments (Fig. 8)

$m/z = 44$: CO_2

$m/z = 77$: C_6H_5

$m/z = 105$: $\text{C}_6\text{H}_5\text{CHCH}_2$

Fig. 9 shows the result of TG-DSC analysis in which He and He+O₂ are used as the carrier gases.

In the TG analysis in the carrier gas containing oxygen, since the organic components in the specimen were oxidized, the minimum value is observed in the DSC voltage at temperature where a mass reduction became obvious (around 430°C), and the mass reduction ratio was larger than the TG test in a helium stream (Fig. 9). Based on this result, the particulate carbon contained in the commercial equipment specimen is considered as a flammable organic component that ignites around 430°C.

In the TG analysis in the He + O₂ carrier gas, most of the gas components released from the thermo-balance is released as H₂O ($m/z = 18$) and CO₂ ($m/z = 44$).

Table 2 shows the result of analyzing radioactivity of C-14 released in an off-gas during the thermal decomposition test of the hardly soluble particles.

It was confirmed that C-14 contained in the hardly soluble particles collected from the commercial equipment was little contained in CO₂ released to the gas phase through thermal decomposition in a helium stream, or in the organic components of various aromatic ring structures as observed in Fig. 4, but released to the gas phase only under conditions where oxygen was contained in the carrier gas.

In the TG-DSC analysis, the mass reduction ratio in helium was approximately 40%, while the mass reduction ratio the He + O₂ carrier gas was approximately 70%. Based on this result, the component remaining in the helium stream is considered to be a stable carbon component.

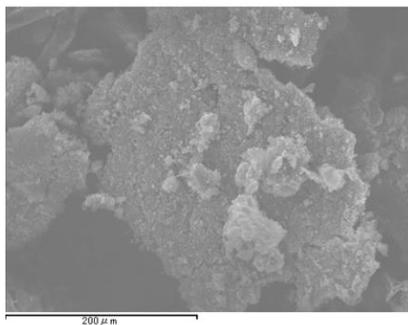


Fig. 4: A SEM image of the particulate components of the commercial equipment

Table 1: Result of analyzing the element composition of the particulate components of the commercial equipment

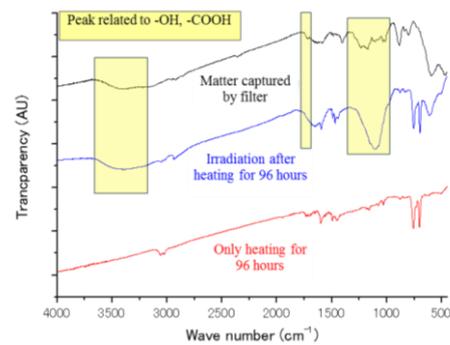
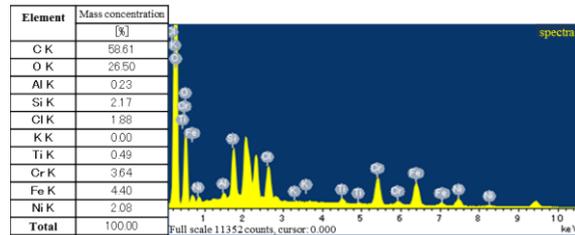


Fig. 5: FT-IR spectra of the mock specimen and the commercial equipment specimen

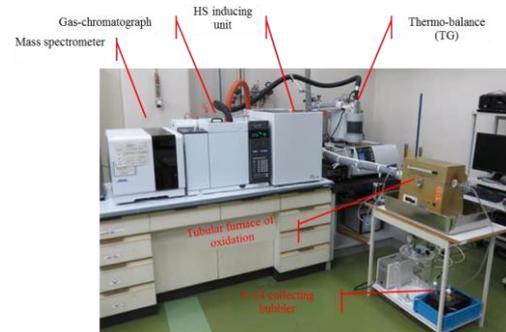


Fig. 6: Experiment apparatus for checking the thermal decomposition behavior of hardly soluble particulate C-14

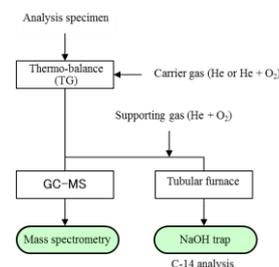


Fig. 7: Experiment flow for checking the thermal decomposition behavior of hardly soluble particulate C-14

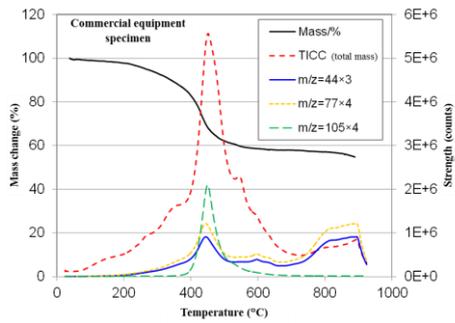


Fig. 8: Result of TG/MS measurement when the commercial equipment specimen is heated in a He stream

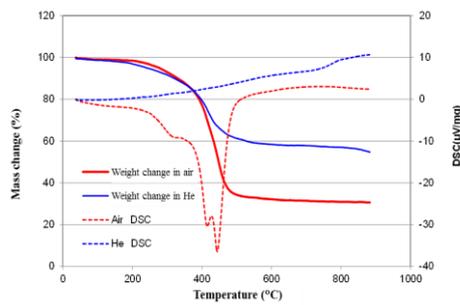


Fig. 9: Result of TG-DSC measurement when the commercial equipment specimen is heated in a He stream and an air stream

Table 2: Released proportion of C-14 during the thermal decomposition test of the hardly soluble particles

Unit: Bq

Carrier gas	Helium	Air
Specimen's mass	3.9mg	4.1mg
Off-gas collection C-14	< 0.317 (<2.045E-4%)	7.87E+4 (99.99%)
Remaining portion	1.55E+5	6.96
Inventory	1.55E+5	7.87E+4

4. Discussion

Based on the result of the SEM/EDX analysis, it was found that a metal oxide produced through corrosion of the plant's components, and flaked crud whose main component is carbon, were captured in the coolant filter of the PWR plant. Such flaked crud has also been reported in past studies conducted at the Callaway Plant in the United States and PWR plants in Japan.⁽²⁾ Therefore, this flaked crud whose main component is carbon is considered to have originated in a common source that could be produced also at PWR plants that have not experienced zinc injection.

In the analysis with FT-IR, absorption peaks that characterize a carboxyl group and a hydroxyl group were observed. For the specimen analyzed as a reference in the analysis, hardly soluble particles that

were adjusted from the ion exchange resin while simulating the RCS environment of the PWR to the extent possible (the actual in-core temperature and radiation environment were not reproduced) were used. The FT-IR spectra of both specimens have common characteristics and this result indicates that part of a deteriorated product of the ion exchange resin is captured in the coolant filter of the PWR plant.

In the analysis with TG/MS, an organic component having an aromatic ring structure was observed in the component released through heating in inert gases, and this result supports that the particles captured in the coolant filter of the PWR plant originate in the ion exchange resin.

In the meantime, only little C-14 radioactivity was detected in the gas components with aromatic ring organic matter released with TG/MS, and therefore, it is considered that C-14 was not induced in molecules that constitute the framework of the ion exchange resin. It is considered that much C-14 is contained in thermally stable molecular structures, which are not contained in thermally decomposed components that are not associated with oxidation reaction through heating in inert gases.

It has been confirmed in a TG analysis using a carrier gas containing oxygen that this C-14 is oxidized to CO₂ at temperature of 400 to 500°C, and it has been confirmed that C-14 is contained in flammable particles.

With these results, it is considered likely that crud containing a carbon component that is contained in hardly soluble particles produced at the PWR is formed when the iron exchange resin leaking from a demineralizer installed in the CVCS is altered in a high-radiation environment with high temperature, high pressure and reducibility in the reactor. C-14 produced in the reactor is taken in these hardly soluble particles, and considered as being contained in particles composed of more thermally stable components. In the meantime, if C-14 originating in impurity nitrogen is released into the reactor coolant in the form of crud in addition to corrosion of metal material, crud containing C-14 is also considered as a thermally stable molecule.

5. Conclusion

The result of a simulation using an ion exchange resin indicates that the more exposed to the primary environment of a PWR, the more amorphous form of carbon the resin is altered to. Since the hardly soluble particles collected from the commercial equipment include particles having aromatic ring structures that constitute the framework of the ion exchange resin, analysis data that support the result of the simulation were obtained. In the meantime, a result indicating that C-14 contained in hardly soluble particles produced at the commercial PWR is not contained in molecules that have aromatic ring structures forming the framework of the iron exchange resin and are thermally decomposed

relatively easily, but much C-14 is contained in amorphous carbon components exposed to the reactor environment for a long period, was obtained. An experiment result indicating that these molecules are thermally stable in a reducing atmosphere, and C-14 is not easily released from their structures, was obtained. To assess the migration behavior of C-14 in the burial environment, our future study tasks will be to analyze the surface characteristics of hardly soluble particles containing C-14, and its stability, etc. in the actual burial environment.

6. Acknowledgement

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7. References

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