Characterization of C-14 in PWR Radioactive Wastes*

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Abstract

Characterization of C-14 in PWR Radioactive Wastes has been researched and formation mechanisms of C-14 have been discussed. It was found from the research results that the chemical form of C-14 existed in primary coolant was organic and was low molecule compounds which are soluble in water. On the other hand, most of C-14 components existed in condensed liquid waste and existed on solid waste were insoluble in water and chemically stable. The insoluble C-14 component was considered to be produced by activation reaction between neutron and substances with nitrogen. Those were thought to be decomposition substances escaped from high molecular organic materials, such as ion exchange resin, diaphragm seal, etc.

Key words: Waste Disposal, Radioactive Waste, C-14, Organic Carbon, PWR

1. Introduction

Because of the long half life:5730 years and the considerable effect on public exposure due to the less capability of capturing C-14 by artificial barrier material, C-14 contained in low level radioactive wastes has been very important aspect in waste disposal. There are different chemical forms of C-14, inorganic and organic, in LLW, so the chemical form of C-14 is thought to affect the transfer behaviors in artificial barrier material.

Organic type of C-14 would be generated in PWRs because the primary coolant is reducing condition, while it is said in BWRs that inorganic type of C-14 was generated because the primary coolant is oxidizing condition.

As the organic type of C-14 is more important to public exposure, C-14 existed in wastes generated in PWR plants has been investigated in order to find and to discuss chemical characters and formation mechanism of insoluble C-14 component in PWR wastes.

2. Investigation of Radioactive Wastes in PWR Plant

The various types of samples (liquid, solid and gaseous samples) were taken from primary system, chemical volume control system, waste stream system, and samples were analyzed by two kinds of analyzing methods in order to find organic C-14 or inorganic C-14. The C-14, which reacts with acid solution and produces carbon dioxide gas, is defined as inorganic type of C-14. The C-14, which is oxidized by oxidizing agent such as

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KMnO₄ in acid solution and produces CO₂ gas, is defined as organic type C-14. Radioactivity of C-14 recovered as CO₂ gas was measured by liquid scintillation counter (LSC). The C-14 in gas phase was separated by chromatography into each composition such as CH₄, C₂H₆, etc., and each composition was corrected and oxidized to CO₂ gas. The CO₂ gas was corrected in trap solution, which was mixed with scintillator and the activity of C-14 was measured by LSC.

The rate of organic C-14 for the samples taken from primary system in PWR is shown in Table 1. It was found that most of C-14 in primary system was organic type. The C-14 existed in liquid system was identified as the organic compounds with low molecular weight such as formic acid, acetic acid, methanol, etc. by radio-chromatography measurement. The C-14 in gaseous phase is also determined as organic gas such as CH₄, C₂H₆, etc. The analyzing results on gaseous phase are the same as the results reported by Kunz⁽¹⁾.

Table 1 Rate of organic C-14 in primary system

Sampling point	Rate (%)
Primary coolant	93
Boric acid tank	~100
Waste hold-up tank	90-99
Distilled water tank	75
Condensed solution	96-100
Refueling water tank	89
Solid waste	~100

The condensed solution produced from the liquid waste treatment system in PWR plant was separated by filtration with 0.45 μm filter. The solid and filtrate were heated and oxidized, respectively, in air atmosphere. The C-14 in each samples were corrected as CO₂ gas. Corrected gas in trap solution was mixed with scintillator and the activity of C-14 was measured by LSC. It was found that 80% to 90% of C-14 in condensed solution existed in solid part. The solid part separated from the condensed solution was treated by acid solution(1N-HNO₃), alkaline solution(1N-NaOH), hot water, or organic solvent(Cyclohexane). It was found from the dissolution tests that the most of the C-14 components in solid part was hardly dissolved in the test solution mentioned above and was chemically stable.

According to the research results of C-14 radioactivity generated in PWR, the C-14 existed in the coolant as soluble or gaseous components was estimated as the activation product by the reaction with neutron and O-17 of coolant. Because hydrogen is added into the primary coolant in PWR to suppress the decomposition of water during operation, the atmosphere in the coolant is kept in reducing condition. Therefore, it is thought that the C-14 generated in PWRs prefer organic form to inorganic form due to the reducing condition. In the radioactive wastes generated in PWR, more than 50% of C-14 in condensed solution was chemically stable and was insoluble substance. The C-14 soluble form existing on solid waste was estimated less than 5%, most of the C-14 in solid waste was estimated insoluble substance.

3. Analysis of Insoluble C-14 Component

In order to find out the chemical aspects, the coolant filter element located at the outlet of the Demineralizer (DEMI) in primary circuit was sampled. The crud, which is the radioactive corrosion product of primary component materials, was removed from the filter element by ultrasonic wash treatment. The crud was examined by Electron Probe Micro

Analyzer (EPMA), X-Ray Diffraction (XRD) and Fourier Transform - Infrared Spectroscopy (FT-IR) analysis. The research and estimation were performed about the materials that have possibilities to produce insoluble C-14 and about the C-14 radioactivity. The discussion results about the research and the estimation were described below.

3.1 EPMA

The result of EPMA analysis is shown in Fig.1. A certain amount of stable carbon was detected and metallic elements (Fe, Ni) caused from metal corrosion were also detected. The rate of elements estimated from X-ray intense is shown in Table 2. Stable carbon was detected in crud samples from two PWR plants. In PWR operation, TOC was detected in primary coolant or at the outlet of demineralizer for purification of coolant. So it is possible that a certain amount of stable carbon exists in the crud.

Fig. 1 EPMA result of crud sample from primary coolant filter

Table 2 Analysis results of elements in crud

samples	analyzing points	elements (wt%)												
		Fe	Ni	Cr	C	Si	Al	Ti	Mn	S	Zr	Cu	Ca	Sn
Crud A	point 1	9.19	6.3	9.53	61.78	2.98	8.2	0.96	0.85	0.1	0.11	ND	ND	ND
	point 2	6.9	4.97	9.01	68.19	3.73	6.62	0.92	0.61	0.05	ND	ND	ND	ND
Crud B	point 1	23.92	9.14	4.49	46	1.23	ND	0.5	ND	0.15	13.24	0.07	0.15	1.1
	point 2	32.88	12.74	5.16	32.24	0.31	ND	0.25	ND	0.07	14.91	ND	0.16	1.27

3.2 XRD

The signals of spinel compound (Nickel ferrite) and Nickel oxide were shown in diffraction data. Except metal oxide signals, several signals were detected in low angle region. The signals in low angel region were not identified. But it suggests that the component except metal oxide existed in crud. Graphite, which is typical inorganic carbon, was not detected in the crud.

3.3 FT-IR

FT-IR analysis of the crud was performed by KBr pellet method. The results are shown in Fig.2. In the spectrum in Fig.2, aliphatic C-H bond, aromatic C=C double bond and C=O bond were detected. These bonds are caused of organic compounds. As similar spectra are

detected in the crud samples taken from another plant, it suggests that the carbon in crud is organic form.

3.4 C/H Ratio

Hydrogen amount in the crud was measured by hydrogen analyzing device. The results showed a few weight % of hydrogen existed in the crud. The carbon content estimated by EPMA is not precise, but if the average value of carbon in Table 2 and the result of hydrogen measurement are used, C/H ratio in weight of crud is estimated to be about 17. This value is almost the same as that of anion exchange resin, which is mentioned in section 5. It suggests that the carbon in crud is carbon rich compound.

4. Research of Source of Insoluble C-14 Component

It is thought that C-14 is generated by activation reaction in reactor core between neutron and material containing oxygen, nitrogen, and /or carbon. From the investigation described in section 2, the soluble C-14 component in primary coolant was estimated to be generated by the activation of coolant. On the other hand, the source of insoluble C-14 component is not clear at present. Therefore, we researched for the source of insoluble C-14 component. The research results are shown in Table 3.

Materials containing C-13 are excluded from C-14 source substance because the cross section of $^{13}\text{C}(n, \gamma)^{14}\text{C}$ and the C-13 isotope ratio are small. Ion exchange resins, metallic oxides and diaphragm seal are thought as source substances, because they are possible to produce insoluble C-14 component. As the release rate to the coolant from metallic oxides by corrosion or release, is thought to be very small and as the possibility to produce organic materials from metallic oxide is low, it could not be the source substances producing insoluble C-14 component. Diaphragm seal is used in primary water tank, hold-up tank, etc. The component of diaphragm seal is the polymer with butadiene and nitrate butadiene. The seal area contacted with primary water is not ignored (about 50m²). Therefore, if the component of diaphragm seal is released into coolant and irradiated in core region, the insoluble C-14 component will be formed. There are no data on the amount of the component of diaphragm seal released into coolant. The investigation in PWR plant is required to confirm the amount of the component of diaphragm seal in near future.

It is known that ion exchange resins are damaged by heat and oxidizing reagent such as H₂O₂ that is generated in oxidizing condition during reactor shutdown. From the research on thermal decomposition of ion exchange resins, it is found that amine radical is released from anion exchange resin and polystyrene sulfonic acid (PSA) is released from cation exchange resin ⁽²⁾⁽³⁾. It is also reported that PSA is released from cation exchange resin in oxidizing condition ⁽⁴⁾. In case of ion exchange resins being sources of insoluble C-14 component, two cases are possible. In first case, anion exchange resin having nitrogen are

damaged and destroyed into small size pieces and is released into coolant and enters to the reactor core. In second case, PSA released from cation exchange resin combines with amine radicals in coolant and enters to the reactor core. In the reactor core, the damaged resin or PSA with amine radicals is heated up to more than 300°C. Then the insoluble polymer will be generated from these substances. As the substances mentioned above have nitrogen, they are activated in reactor core and are capable to produce insoluble C-14 component. The result of element analysis in Table 2 showed that sulfur which is one of the constitution elements of PSA is detected. The FT-IR spectrum in Fig.2 showed that the organic compound existed in crud. These results indicate that ion exchange resins are possible source to produce insoluble C-14 component.

Table 3 Research results on sources of insoluble C-14 component

C-14 generation reaction	Candidates substances	Possibility to produce insoluble C-14 component
$^{17}\text{O}(\text{n}, \alpha)^{14}\text{C}$	Primary coolant	Mostly soluble C-14. The possibility to produce insoluble C-14 is low.
	Metallic oxide	Insoluble C-14 enclosed in crud. The possibility to make organic form is low.
$^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$	Dissolved nitrogen in coolant	Mostly soluble C-14. The possibility to produce insoluble C-14 is low.
	Organic materials (Ion exchange resin, diaphragm seal, etc.)	Originally high molecular organics. It suggests the possibility to produce insoluble C-14.
	Impurity nitrogen in materials*	Hardly dissoluble. The possibility to make organic form is low.
$^{13}\text{C}(\text{n}, \gamma)^{14}\text{C}$	Organic materials (Ion exchange resin, diaphragm seal, etc.)	Originally high molecular organics. It suggests the possibility to produce insoluble C-14.
	Impurity nitrogen in materials*	Hardly dissoluble. The possibility to make organic form is low.

*: primary coolant pipe, conductive pipe of steam generator, fuel cladding, etc.

5. Verification of Radioactive Source of Insoluble C-14

The verification test was performed to verify whether the ion exchange resins would be the source of insoluble C-14. To simulate the thermal and chemical conditions in reactor core, the anion exchange resins was heated to 350°C to give thermal damage in the mixture gas atmosphere of steam and inert gas (Ar) for about one month. The heat treatment condition simulates the surface temperature on fuel cladding and the average staying period of crud in core. Nitrogen in the heat treated resin was analyzed by CHN analyzer and a few weight % of nitrogen was detected. From the above results, it indicated that nitrogen could remain in the resin after thermal damage in primary system.

The heat treated resin was irradiated in JRR-3 test reactor of JAEA under the thermal neutron flux of $10^{14}\text{n/cm}^2/\text{s}$ for 50 hours. After the irradiation, C-14 was detected in the irradiated sample. The measured radioactivity of C-14 was consistent with the calculated radioactivity by the activation of nitrogen in the resin. The dissolution rates of C-14 from the irradiated sample were measured in acid, alkaline solutions and organic solvent and less than 1% of dissolution rates were obtained. The results indicated that the C-14 produced was stable and kept in the heat treated resin.

In the case of carbon content being 50% in crud and of nitrogen content being 1% in carbon, the C-14 radioactivity per 1g of crud was calculated about 10^6 Bq/g for one year. The calculation value was almost the same as the C-14 activity (10^6 - 10^7 Bq/g) in crud existing on fuel cladding. The estimation suggested that ion exchange is possible substance to produce the insoluble C-14 component.

6. Summary

From the research and estimation on insoluble C-14 component observed in PWR, followings were obtained:

- Most of C-14 produced in PWR were organic form,
- Two chemical type, soluble and insoluble, of C-14 exist in primary system. Soluble type of C-14 was produced by activation of primary coolant and was low molecular organic component, while insoluble C-14 was very stable organic component,
- A certain amount of insoluble C-14 activity would exist in waste condensate solution(>50% of C-14) and solid waste(>95% of C-14),
- Ion exchange resin, metallic oxide and diaphragm seal were thought to be the candidate substances of the source of insoluble C-14.

From the point of organic materials produced, ion exchange resin or diaphragm seal was guessed a source of insoluble C-14 component.

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