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Investigation of Analytical Method for Technetium-99 in Liquid Effluent Discharged from Tokai Reprocessing Plant

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Analytical method for technetium-99 in liquid effluent was investigated and had been applied for measurement of liquid effluents discharged from the Tokai reprocessing plant in Japan. The quarterly averaged concentrations of ^{99}Tc in liquid effluents from 1990 to 2000 were ranged from N.D. ($< 5 \times 10^{-7}$ Bq·cm^{-3}) to 6.7×10^{-5} Bq· cm^{-3}. The average of the normalized annual release of ^{99}Tc was 7.4×10^{-4} GBq·(GWa)$^{-1}$and it was approximately one fifty-fifth of Iodine-129, which was one of the typical nuclides to have difficulty to remove from liquid effluent. The committed effective dose by intake of seaweed was evaluated to be less than 3×10^{-10} mSv·a^{-1}.

1. Introduction

The low level radioactive liquid effluent from the Tokai Reprocessing Plant (TRP) is discharged in batch mode at 24 m beneath the sea surface through the 3.7 km long pipeline from the shoreline.

The radioactivity concentrations in liquid effluent are certified to be less than discharge limits set. The concentrations of gross-alpha and gross-beta radioactivity, gamma–ray radionuclides and tritium are measured prior to discharge in every batch of discharge. The Pu(α) isotopes (^{238}Pu, $^{239+240}$Pu), ^{90}Sr and ^{129}I in liquid effluent are measured by radiochemical analysis in a composite sample for a month.

Technetium-99 can be measured as part of the gross-beta radioactivity with approximately ten percent counting efficiency for a sample mounted on the stainless steel plate. As salts and solid materials in liquid effluents were almost removed by duplicated distillation process, the beta-ray counting method was available for measurement of ^{99}Tc without self-absorption. Accordingly, the concentration of ^{99}Tc in discharge water had been certified to be less than the discharge limit by the beta-ray counting method with other beta-nuclides. The measured gross beta-radioactivity was assumed to be ^{99}Tc radioactivity conservatively and confirmed below the ^{99}Tc discharge limit.

As the results of these monitoring, the concentrations of ^{99}Tc in the effluents were implied to be very low compared with the ^{129}I and other detected nuclides. However, we could not determine fluctuation of ^{99}Tc concentration by these monitoring. Therefore, it was needed to develop a more sensitive method for ^{99}Tc in the liquid effluent. Consequently, the analytical method[1] of ^{99}Tc for environmental water was applied for liquid effluent[2] and concentration level of ^{99}Tc in liquid effluent from TRP was investigated.

2. Analytical Method for ^{99}Tc

A known ^{95m}Tc activity was added to a sample as chemical yield tracer at first. However, the measurement of beta-ray of ^{99}Tc was disturbed by gamma-ray of the ^{95m}Tc tracer. The chemical yields of samples in the same batch of analysis were almost similar among them. Accordingly, the yield of the sample (reference sample) to which ^{95m}Tc was added had applied for the others without adding ^{95m}Tc tracer. The 8-litter of sample was analyzed after homogenizing. The chemical separation of ^{99}Tc was adopted with the same procedure both the sample and the reference sample as follow.

After $FeSO_4$ with HCL(2+1) and $FeCL_3$ were added to the sample, the ^{99}Tc in the sample was co-precipitated with $Fe(OH)_2$ by adjusting over pH 9 by ammonia. The precipitate was dissolved by H_2SO_4(1+5) and $K_2S_2O_8$ was added to it. The ^{99}Tc in the sample was extracted by 15 mL of TBP with 2 mL of HF using a separation funnel and the organic phase was washed by using H_2SO_4(1+5) with 0.5 mL of HF in twice. After discarded aquatic phase, the 45 mL of Xylene and 15 mL of NaOH(8w/v%) were added to it and shaken. The ^{99}Tc in organic phase was re-extracted to aquatic phase. The solution was neutralized by H_2SO_4 and H_2SO_4(1+5) was more added. The process from the TBP extraction to the re-extracted procedure was repeated. Finally, the ^{99}Tc was electoroplated onto stainless steel disk for 2-hour at 0.3 A current. The beta-ray emitted from ^{99}Tc on this disk was measured by the low background gas-flow counter.

3. Results and Discussion

The chemical yield of this procedure was examined using a known ^{99}Tc activity tracer. A 9.33Bq of ^{99}Tc was added to the 500 mL test water and analyzed. The values of 80% to 90% were obtained as chemical yield by the six times tests. Furthermore, the chemical yields of 8-litter of real samples were almost constant as 70 ± 7% in the eleven quarters from 1990 to 1993. The difference of the chemical yields between the test samples and the real samples were attributed to the amount of chemical components in the samples.

Decontamination factor (DF) were also examined by using the tracers of ^{106}Ru, ^{54}Mn, ^{60}Co, ^{90}Sr, ^{137}Cs, ^{152}Eu. The DF of ^{106}Ru was measured as 10^2 and ^{90}Sr was obtained 1.6×10^3. The DF's of other nuclides were measured more than 10^3.

Detection limit of this method was approximately 5×10^{-7} Bq·cm^{-3} using 8 litter of sample, which was more sensitive than 1.8×10^{-4} Bq·cm^{-3} by the beta-ray counting method using 1 litter of sample.

Subsequently, we have investigated for the concentration

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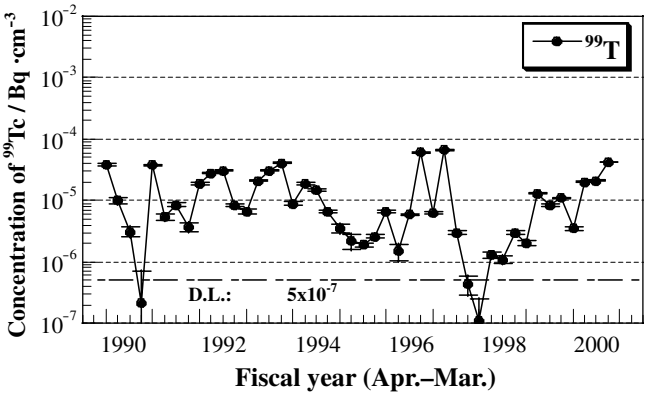

Figure 1. Quarterly Averaged Concentrations of ^{99}Tc in Liquid effluent from TRP.

level of ^{99}Tc in liquid effluent from TRP using this method since 1990. The quarterly averaged concentrations of ^{99}Tc in liquid effluents from 1990 to 2000 were ranged from N.D. (< 5 $\times 10^{-7}$ Bq·cm^{-3}) to 6.7 $\times 10^{-5}$ Bq·cm^{-3}. The maximum concentration was approximately one ten thousandth of the discharge concentration limit of ^{99}Tc for liquid effluent as 1 Bq·cm^{-3} (Figure 1), which is authorized by Japanese law for nuclear facilities.

On the other hand, annual releases of ^{99}Tc were ranged from 1.3×10^{-5} GBq·a^{-1} to 1.5×10^{-3} GBq·a^{-1} and the normalized releases of ^{99}Tc, which were normalized by annual energy generated (GWa) derived from the treated spent fuels, were ranged from 1.3×10^{-6} GBq·(GWa)$^{-1}$ to 2.1×10^{-3} GBq·(GWa)$^{-1}$. They were smaller than that of other detected radionuclides (Table 1).

TABLE 1: Normalized Annual Releases of Nuclides/GBq (GWa)$^{-1}$

	Range	Average
Tc-99	1.3×10^{-6} ~ 2.1×10^{-3}	(7.4×10^{-4})
H-3	7.2×10^{4} ~ 3.3×10^{5}	(2.1×10^{5})
I-129	2.0×10^{-2} ~ 8.3×10^{-2}	(4.1×10^{-2})
Pu(α)	2.7×10^{-3} ~ 1.1×10^{-2}	(5.1×10^{-3})
		1990–2000

The release rates of ^{99}Tc to the inventory of ^{99}Tc in the treated spent fuel were estimated below 10^{-7} from 1990 to 2000. However, the release rate of ^{99}Tc was not so consistent with the inventory of it. The release rate was depended on both the storage and the operation of the treatment process of liquid waste.

Based on these data, the concentrations of ^{99}Tc in the sea water and seaweed were evaluated by the diffusion equation using the safety assessment of TRP. The diffusion equation was introduced by the field experiments offshore JNC Tokai Works. The diffusion equation can be described as:

$$C = \frac{q}{uHY}\, erf\left(\frac{Yu}{4\sqrt{\alpha\chi}}\right)$$

Where C is the concentration of radionuclide in sea water (Bq·m^{-3}), q is the discharge rate (Bq·s^{-1}), u is the current speed as 0.1 (m·s^{-1}), H is the vertical mixing layer as 6.9 (m), Y is the horizontal width of vertical mixing layer as 2 (m), α is the experimentally obtained constant as 0.1415, χ is the distance from the discharge point, and erf is the error function as:

$$erf(y) = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-t^2)dt.$$

The radioactivity concentrations of ^{99}Tc in the sea water near the discharge point and the shore where seaweed lives, 5km apart from discharge point, were calculated. The maximum value of annual concentration of ^{99}Tc in the sea water near the discharge point and the shore could be estimated approximately 9×10^{-11} and 1×10^{-11} Bq·cm^{-3}, respectively. The concentration of ^{99}Tc in seaweed (as Eisenia bicyclis) was evaluated as 3×10^{-5} Bq·kg^{-1}-fresh by using bioaccumulation factor[3] as 2600 in Bq·g^{-1} per Bq·cm^{-3} based on the experiment by ^{95m}Tc tracer. The committed effective dose of intake of the seaweed was evaluated to 3×10^{-10} mSv·a^{-1} using a consumption rate[4] of seaweed as 40 g·d^{-1} for adult and the dose factor (6.4×10^{-7} mSv·Bq^{-1} as f_1 = 0.5) based on the ICRP publication 72.

On the other hand, the evaluation of committed effective dose through food chain due to intake of all nuclides discharged to the sea from TRP were ranged from 2×10^{-6} to 8×10^{-5} mSv·a^{-1} during the ten year, which were lower than the dose limit for the public as 1 mSv·a^{-1}.

Consequently, the committed effective dose by intake of seaweed for the public due to release of ^{99}Tc was negligibly smaller than the dose due to all nuclides.

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