

Radiochemical Separation and Quantification of Tritium in Metallic Radwastes Generated from CANDU Type NPP – 13279

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ABSTRACT

As a destructive quantification method of ^3H in low & intermediate level radwastes, bomb oxidation, sample oxidation, and wet oxidation methods have been introduced. These methods have some merits and demerits in the radiochemical separation of ^3H radionuclides. That is, since the bomb oxidation and sample oxidation methods are techniques using heating at high temperature, the separation methods of the radionuclides are relatively simple. However, since ^3H radionuclide has a property of being diffused deeply into the inside of metals, ^3H which is distributed on the surface of the metals can only be extracted if the methods are applied. As another separation method, the wet oxidation method makes ^3H oxidized with an acidic solution, and extracted completely to an oxidized HTO compound. However, incomplete oxidized ^3H compounds, which are produced by reactions of acidic solutions and metallic radwastes, can be released into the air. Thus, in this study, a wet oxidation method to extract and quantify the ^3H radionuclide from metallic radwastes was established. In particular, a complete extraction method and complete oxidation method of incomplete chemical compounds of ^3H using a Pt catalyst were studied.

The radioactivity of ^3H in metallic radwastes is extracted and measured using a wet oxidation method and liquid scintillation counter. Considering the surface dose rate of the sample, the appropriate size of the sample was determined and weighed, and a mixture of oxidants was added to a 200 ml round flask with 3 tubes. The flask was quickly connected to the distilling apparatus. 20 mL of 16 wt% H_2SO_4 was given into the 200-ml round flask through a dropping funnel while under stirring and refluxing. After dropping, the temperature of the mixture was raised to 96 °C and the sample was leached and oxidized by refluxing for 3 hours. At that time, the incomplete oxidized ^3H compounds were completely oxidized using the Pt catalysts and produced a stable HTO compound. After that, about a 20 ml solution was distilled in the separation apparatus, and the distillate was mixed with an ultimagold LLT as a cocktail solution. The solution in the vial was left standing for at least 24 hours. The radioactivity of ^3H was counted directly using a liquid scintillation analyzer (Packard, 2500 TR/AB, Alpha and Beta Liquid Scintillation Analyzer).

INTRODUCTION

Tritium is generated in the fuel of all reactors and also in their coolant and moderator, due to neutron capture in deuterium and hydrogen. In particular, because CANDU NPP uses the heavy water as a coolant, unlike PWR, the tritium that is produced in a CANDU reactor is 30 to 100 times higher than that in PWR. Most pathways of tritium generation in LWR and CANDU NPP are very similar. That is, tritium is generally produced in nuclear reactors by neutron activation of boron-10 and lithium-6. However, because the coolant in CANDU is deuterium, Tritium is also produced in heavy water-moderated reactors whenever a deuterium nucleus captures a neutron. This reaction has a quite small absorption cross section, making heavy water a good neutron moderator, and relatively the tritium production rate is small. However, because of huge quantities of heavy water, the quantity of tritium produced from this source is considerably large.

In the case of the Korean CANDU, it can be observed that the coolant water of PWRs have tritium concentrations of approximately $3.0\text{E-}3$ MBq/m³ until 2003, which have increased gradually since 2004 to reach a level of $1.0\text{E-}2$ MBq/m³ by 2006. Compared to PWR NPPs, the coolants of CANDU NPPs have tritium concentrations that are approximately 50 times higher.

To obtain tritium concentration radiochemically, some fuel bundles used in this study were obtained from Korean CANDU NPP. The samples were also approximately 50 cm in length and 10 cm in diameter and generated approximately 1 GWh of electricity during its time in the reactor. To allow the neutrons to flow freely between the bundles, the tubes and bundles are made of neutron-transparent zircaloy (zirconium + 2.5% wt niobium). The samples were cut with proper size to assay in KAERI hot cell and transferred to a radiochemical laboratory to separate and quantify tritium with a wet oxidation method.

METHODS AND RESULTS

Sample preparation

In KAERI hot cell, the cross section of a ring type pressure tube sample was cut to 5 mm thickness using a tube cutting machine, which was controlled by remote handling. At that time, the both ends of the tubes were removed due to the homogeneity of radionuclide distributions. The cutting process was carried out by a diamond wheel cutter, and the cutting speed was 0.02 mm /sec at the condition of 600 ~ 700 rpm. Eventually, the sample was cut to 5 mm of cubic size.

Quench correlation curve for radiation counting

To obtain the counting efficiency from quench levels in tritium counting, 73,059 Bq of a tritium standard (spec-check, Packard) was put into each of 10 scintillation vials. And 14 mL of Ultima Gold LLT cocktail was added to each vial. Finally, nitromethane used as a quenching agent was also added in the range of 0 ~ 100 μl to each vial. A quench indicator, in which we use the gamma activity of ^{133}Ba as the external quench standard monitoring prior to application, was adjusted to tSIE/AEC (transformed spectral index of external standard) mode, and a quenching correction curve was prepared.

Table I. Results of quenching correlation of tritium using nitromethane

| | | | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|
| t-SIE | 791.9 | 627.5 | 528.7 | 444.1 | 357.3 | 265.9 | 195.6 | 125.9 | 91.7 | 50.18 |
| QID | 50.33 | 43.37 | 38.6 | 33.48 | 27.46 | 19.9 | 13.31 | 6.68 | 3.75 | 1.07 |

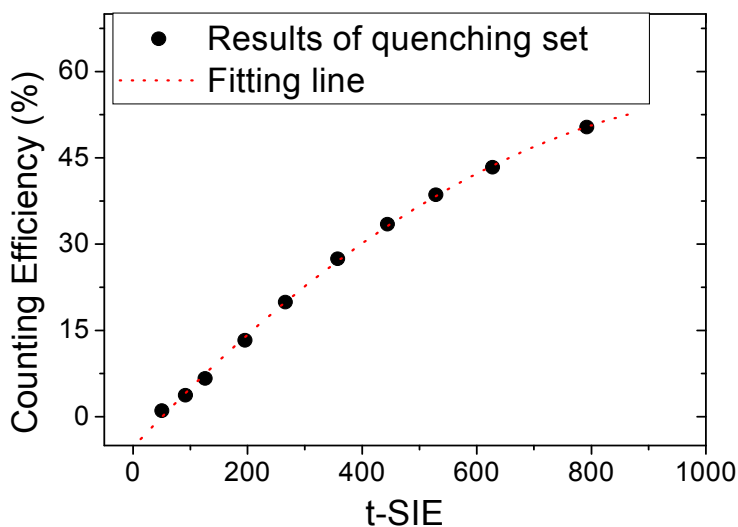


Figure 1. Quenching correlation curve for tritium counting using LSC

The quench correction data and curve indicated in Table IV-2-3 and Figure IV-2-13 were obtained from the quench set of the standard solution. Since the quench level generally increases

when amount of added nitromethane as a quenching agent increases, the counting efficiency decreases which corresponds to the results of Figure IV-2-13. Moreover, according to increase of the tSIE, an increase in the counting efficiency was observed. The counting efficiency of the quench set without any addition of nitromethane was 50.33 %. The quenching correlation curve should be freshly prepared by periods, and also should be freshly prepared even whenever change of some counting features occurs.

Tritium separation and quantification

The cut metallic samples with the size of 5×5×5 mm were analyzed by using the wet oxidation method for tritium quantification. The samples were treated with oxidative agents, such as potassium persulfate and sulfuric acid. Reactive hydroxide radicals were produced from the oxidation agents, which oxidized gaseous or organic tritium to produce HTO. After 3 hours, tritiated water was distilled from the leached solution. The distilled species solution including tritiated water was mixed with a cocktail and counted by LSC. Then, unreacted gaseous tritium with the oxidation agents in the reactor was oxidized by using Pt catalyst and collected. The oxidized tritium was counted by LSC. The distilled extracts were mixed with Ultrama-Gold LLT cocktail, which is mixed with volume ratio of 1:3 for the extracts to the cocktail.

Result of tritium measurements

Through the wet oxidation method, tritium concentration in the sample was analyzed to be 4.9E+2 Bq/g when the separation method was applied for 3 hrs. Also, to confirm the complete leaching of tritium from the sample, the method was repeated for the leached sample. As a result of 2nd acid leaching, tritium concentration was measured as 4.2 Bq/g, which tritium detection amount reaches about 0.8% level comparing to the result of 1st acid leaching. It was confirmed that 99% of tritium in the sample was detected through 1st acid leaching.

CONCLUSIONS

To obtain tritium concentrations radiochemically in the metallic samples generated from Korean CANDU NPP, a wet oxidation method was developed and applied. The wet oxidation method is to leach samples with some acids to extract tritium species from the samples. In conclusions, tritium concentrations in the metallic sample was determined to be $4.9E+2$ Bq/g, which was the result that almost all tritium species were leached out of samples.

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