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Original article

Tritium extraction in aluminum metal by heating method without melting

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ABSTRACT

Tritium was extracted from tritium-contaminated aluminum samples by heating it in a high-temperature furnace at 200, 300, or 400 °C for 15 h. The extracted tritium was analyzed by using a liquid scintillation counter (LSC); the sample thicknesses were 0.4 and 2 mm. The differences in tritium extraction over time were also investigated by cutting aluminum stick samples into several pieces (1, 5, 10, and 15) with the same thickness, and subsequently heating them. The results revealed that there are most of the hydrated material based on tritium on the surface of aluminum. When the temperature was increased from 200 or 300 °C-400 °C, there are no large differences in the heating duration required for the radioactivity concentration to be lower than the MDA value. Additionally, at the same thickness, because the surface of aluminum is only contaminated to tritiated water, cutting the aluminum samples into several pieces (5, 10, and 15) did not have a substantial effect on the tritium extraction fraction at any of the applied heating temperatures (200, 300, or 400 °C). The proportion of each tritium-release materials (aluminum hydrate based on tritium) were investigated via diverse analyses (LSC, XRD, and SEM-EDS). © 2021 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the

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1. Introduction

Aluminum metal waste is generated by facilities that use tritium. Most aluminum waste contains a maximum allowable fraction of radioactivity on the surface [1]. In a previous study, it was demonstrated that, when tritiated water vapor (HTO) and elemental tritium existed simultaneously in the atmosphere, most materials (including aluminum) absorbed significantly more radiation from tritiated water, even when the proportion of elemental tritium in the total radioactive content was higher than that of tritiated water. Because tritiated water (or vapor) cannot permeate or diffuse into metal, it can only contaminate the surface of the metal. In most cases, tritium contaminates the surface of metals, forming a surface oxide film when the metal is exposed to tritium (via HT gas or tritiated water) at ambient temperature and pressure [2]. Thus, when aluminum waste is disposed from facilities that generate radioactive waste, it is necessary to identify the surface tritium concentrations of aluminum waste for radioactive waste classification. In South Korea, aluminum was found to be included in the waste generated during the dismantling of the TRIGA MARK

* Corresponding author. E-mail address: kimhr@unist.ac.kr (H.R. Kim). II research reactor at the Korea Atomic Energy Research Institute (KAERI). Several studies have been conducted on the distribution characteristics of radioactive cobalt, cesium, and strontium during the process of melting aluminum waste. However, no research has been conducted on tritium extraction from aluminum waste via a simple heating process under the melting temperature of the aluminum [3,4]. Previous studies on tritium extraction that employed such a simple heating process focused on stainless steel, and the heating duration was approximately 4 h. Moreover, in these studies, the stainless-steel heating was carried out at temperatures higher than 600 °C [5,6]. Considering that the melting temperature of aluminum is 660 °C, the heating temperature conditions applied in previous studies would cause the melting of the aluminum [6–8]. KAERI has previously investigated the disposal of radioactive aluminum waste through the use of a melting pretreatment [9]. In this study, it was focused on the extraction of tritium from aluminum stick samples. The heating temperature and the duration were set to be lower than 600 °C and 15 h, respectively. If aluminum is melted, it may adhere to the sample boat and generate secondary contaminated waste. In the extreme cases, the sample boat may be destroyed. Methods such as wrapping the aluminum in a metal such as copper or stainless steel (i.e., a metal with a higher melting temperature than aluminum) and placing it in a sample boat to prevent contamination are also undesirable, because aluminum can







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adhere to the metal to increase the amount of metal waste produced as secondary contaminated waste. Alternatively, when aluminum is heated at a temperature lower than its melting temperature and the residual tritium concentration is lower than the minimum detectable activity (MDA) value, tritium cannot be extracted from aluminum. However, this does not imply that all aluminum hydroxides (based on tritium instead of hydrogen) will be decomposed. If there is no decomposed aluminum hydroxide at the heating temperature, the results of liquid scintillation counter (LSC) analysis alone cannot be validated. Thus, in this study, X-ray diffraction (XRD) analysis was conducted as a supplemental chemical analysis technique in order to determine whether tritium was completely extracted from aluminum. It is possible to determine the heating temperature and duration that will optimally maximize tritium extraction from aluminum; moreover, because it is not necessary to perform tritium collection and LSC analysis for each heating duration cycle sample, it is possible to minimize the amount of prepared LSC cocktail by analyzing the sample after heating it under the conditions of a specific temperature and duration. This is another technique to reduce the amount of secondary waste that is generated from the LSC cocktail waste. In this study, the tritium extractions resulting from heating four 0.4- or 2mm-thick aluminum samples at temperatures of 200, 300, and 400 °C for 15 h were analyzed. It was also investigated whether physically cutting the samples into 1, 5, 10, or 15 pieces would significantly affect tritium extraction. It was hypothesized that, if there was bulk contamination in the aluminum sample, the initial extraction fraction would differ according to the number of cut sample pieces. However, analysis of the results revealed that, only the surface of aluminum sample was contaminated, and the number of cut sample pieces is not the predominant variable.

2. Materials and methods

2.1. Sample preparation

The aluminum used in this study was commercially available Al 6061. Al 6061 is composed of aluminum (96.85%), magnesium (0.9%), silicon (0.7%), iron (0.6%), copper (0.30%), chromium (0.25%), zinc (0.20%), titanium (0.1%), manganese (0.05%), and other metals (0.05%) [10]. Because aluminum is the major constituent, the melting point of Al 6061 can be considered to be approximately 660 °C. Aluminum plates with a thickness of either 0.4 or 2 mm were cut to form aluminum sticks with an area of 500 (5 \times 100) mm² by using an electric grinder. The aluminum powder generated during the cutting process was removed by washing with distilled water. The aluminum stick samples were dipped into diluted tritiated water with a radioactivity concentration of 6989.65 ± 9.85 kBq/L (concentration of tritium stock solution: 74.969 MBq/g) and maintained at 20 °C for 50 days. The aluminum did not react with tritiated water for 24 days. After 25 days, a sudden reaction occurred between the aluminum stick sample and tritiated water, leading to the formation of an aluminum hydrate material. The representative aluminum hydrates formed by the reaction with water were Al(OH)₃ (aluminum hydroxide) and AlOOH (aluminum oxide hydroxide). To introduce sufficient tritium contamination to the aluminum samples, each sample was maintained in tritiated water for a duration that was twice as long as the time between the initial dip and the initiation of the reaction. After confirming the absence of luster on the aluminum surface and the formation of a film due to corrosion, the aluminum sample was taken out of the tritiated water, and the sample was maintained at room temperature. Because tritium extraction by the evaporation at ambient temperature of the tritiated water droplets formed on the aluminum surface cannot be evaluated as the extraction by heating

pretreatment, a 24-h drying process at room temperature to remove the residual tritiated water droplets was applied. To increase the contact area with oxygen and improve heat conduction during heating, three of the four 0.4- and 2-mm-thick aluminum samples were cut into 5, 10, and 15 pieces. It should be noted that crushing an aluminum sample to form a powder may lead to an explosion upon heating; thus, it can be dangerous to break down a specimen to its smallest powder form to maximize the contact area with oxygen [11]. In the case of the 2-mm-thick aluminum stick samples, the process applied to ship the sample to the sample boat (quartz glass boat, Raddec International, Ltd.) is depicted in Fig. 1.

2.2. Dry purging by heating

The sample boats containing the aluminum samples were placed in a quartz glass tube in a high-temperature combustion furnace (Pyrolyser-Trio Furnace System, Raddec International, Ltd.), and air was flowed through the quartz glass tube. A bubbler base containing 20 mL of 0.1 M nitric acid solution was connected to the end of the quartz glass tube. Oxygen and air were supplied to the quartz glass tube from a gas tank, and the gases flowed from the guartz glass tube to the bubbler base with nitric acid, as shown in Fig. 2. Bubbles were generated in the bubbler base as the gases escaped through it. This allowed us to confirm that there was no gas leakage at the point of connection between the gas tank, quartz glass tube, and bubbler base. It has been reported that tritium primarily exists in the form of HTO in contaminated solid materials [12]; however, if the solid material is burned and contains carbon, tritium may exist in the form of organically bound tritium (OBT). It is for this reason that most studies on the extraction of OBT through the process of heating or burning the solid materials have been carried out at a minimum temperature of 400 °C [13–15]. Because aluminum is an inorganic material that does not burn when heated, the aluminum sample was heated for 15 h at 400 °C in this study. In a previous study, physically absorbed tritiated water (HTO) was not separated, although the aluminum sample was heated at 200 °C to extract tritium from the aluminum surface. The aluminum samples were exposed to an inert gas containing a small amount of water



Fig. 1. Aluminum sample pieces shipped to sample boat.



Fig. 2. The experimental schematic of the high temperature pretreatment for tritium capture.

vapor at a pressure of 10 Pa to separate the tritium from the HT gas via an ion-exchange reaction [12]. The ion-exchange reaction between the HT gas and water on the aluminum surface occurs as follows:

$$HT (gas phase) + H_2O (surface) \rightarrow H_2 (gas phase) + HTO (surface)$$
(1)

However, only surface tritium contamination was considered, and the physically absorbed tritiated water on the aluminum surface could not be fully extracted at 200 °C. Thus, in this study, it was necessary to set the heating temperature to be above 200 °C. The chemical reactions of aluminum with water occur as

$$2AI + 6H_2O \rightarrow 2AI(OH)_3 + 3H_2 \tag{2}$$

 $2AI + 4H_2O \rightarrow 2AIOOH + 3H_2 \tag{3}$

$$2AI + 3H_2O \rightarrow AI_2O_3 + 3H_2 \tag{4}$$

All three reactions are highly exothermic, and the most stable temperatures for these three reactions are different. Within the range of room temperature to 280 °C, the reaction shown in Equation (2) is the most stable. The stable temperature ranges for Equations (3) and (4) are 280–480 °C and >480 °C, respectively. Aluminum oxide (Al₂O₃) can also react with water to form a boehmite film on the surface of the sample at elevated temperatures. Under such conditions, the film thickness can increase until boehmite reacts with aluminum on the inner side of the sample to produce hydrogen. However, in this study, aluminum was contaminated with tritiated water at room temperature [16]. Because each aluminum sample was immersed in tritiated water with a temperature lower than 20 °C for 50 d, the aluminum hydroxide resulting from the reaction between aluminum oxide and water molecules (as well as HTO molecules) was expected to exist as bayerite (Al(OH)₃) or gibbsite (Al(OH)₃) [17,18]. Although some amount of bayerite is known to exist in tritium atomic combinations instead of hydrogen atomic combinations, a previous study confirmed the complete removal of bayerite via dehydration when heating temperatures above 300 °C were applied [19]. A small amount of the aluminum hydroxide byproduct of the reaction between aluminum oxide and water molecules (as well as HTO molecules) can also exist as boehmite. The thermal decomposition of natural boehmite occurs within the temperature range of 480–520 °C [20]. Furthermore, taking into consideration the results of a previous study on the decontamination of tritium on the aluminum surface at 200 °C, the four aluminum stick samples were cut into several pieces (1, 5, 10, and 15 pieces) and heated at 200, 300, and 400 °C for 15 h; If internal contamination exists in aluminum, there may be a difference in the initial extraction fraction depending on the number of pieces. Therefore, the number of pieces was applied as a variable. During the process of heating, the 0.1 M nitric acid solution was replaced in 3-h intervals. To check for remnant tritium in the aluminum samples, all samples were heated twice at 550 °C after being heated at 200, 300, or 400 °C for 15 h. During the heating of two times at 550 °C, heating duration was 6 h, respectively. In our previous study, the solutions with tritiated water were measured and analyzed via LSC analysis [21]. Thus, in this study, the 0.1 M nitric acid solution containing the extracted tritium was mixed with a liquid scintillator solution (HiSafe 3, PerkinElmer, Inc.) to create an LSC cocktail; the LSC cotktail was analyzed via a LSC counting system (1220 Quantulus, PerkinElmer Inc.). The volume mixing ratio for the nitric acid and LSC solution was 8:12. The measurement time for each sample was 30 min. A schematic of the experimental process is presented in Fig. 3.

3. Results and discussion

3.1. Radioactivity extraction from 0.4-mm-thick samples

The tritium concentration criteria for the clearance of radioactive waste, as according to the notification of the Nuclear Safety and



Fig. 3. The schematic of experimental process.

Security Commission of South Korea, is 100 Bq/g. However, in this study, the experiment was conducted using tritium-contaminated aluminum with exempt-level tritiated water, and not actual waste. Thus, the MDA (Minimum Detectable Activity) was set to be 0.2 Bq/g, which is 1/500 of 100 Bq/g. In this study, the MDA was calculated as follows:

$$MDA (Bq/g) = \frac{2.71 + 4.65\sqrt{B}}{T \times \frac{E}{100} \times M}$$
(5)

B: Background counts of nitric acid (#)

T: Counting time (s)

E: Detection efficiency of LSC (%)

M: Mass of aluminum sample (g)

Most MDA equations are based on a 95% confidence level [22]. The background counting rate measured by the LSC was approximately 6.63 #/min (counts per minute) in this study. However, as mentioned later, the other variables differed slightly depending on the situation. For example, because tritium is a pure beta radionuclide and there is no shielding material, variables such as the spillover and attenuation factors, which were considered in other studies, were not considered [23]. In Tables 1–6, all of the tritium radioactivity concentrations, which denote the radioactivity per aluminum sample mass, are represented with respect to the heating duration. When the 0.4-mm-thick aluminum stick samples were heated at 400 °C for 15 h, the radioactivity concentrations of the tritium that was extracted from the one-piece sample were 65.517 ± 0.765 , 3.277 ± 0.139 , 0, 0, and 0 Bq/g at 3, 6, 9, 12, and 15 h, respectively, as indicated in Table 1. Note that, when the radioactivity concentration of tritium determined via LSC analysis was lower than the MDA value, it was marked as "<MDA." Additionally,

when the sample counting rate generated from the heating pretreatment of the aluminum sample was lower than the background counting rate and the net counting rate became negative, the concentration was recorded as 0. Tritium was found to be completely extracted within 9 h of heating, and the radioactivity concentration of tritium extracted thereafter was lower than the MDA value. It was guessed that the separation of physically absorbed water and the thermal decomposition of a fraction of Al(OH)₃ is the source of detected tritium. The radioactivity concentration of tritium after heating the samples at 550 °C was 2.048 \pm 0.106 Bq/g. The radioactivity concentrations of the tritium extracted from the five-piece samples were 56.771 \pm 0.572, 7.455 ± 0.195 , 0.357 ± 0.022 , 0, and 0 Bq/g at 3, 6, 9, 12, and 15 h, respectively. It should be noted that, as compared to the one-piece sample, more time was required for the radioactivity concentration of the tritium extracted from the five-piece to become lower than the MDA value. This was found to be the case for the 10- and 15piece samples as well. At the same heating temperature, at longer heating durations, the tritium radioactivity concentration was lower, and the counting rate of nitric acid decreased to a value lower than the background counting rate (denoted as 0). However, this does not imply that all tritium was extracted from the aluminum. In a previous study, complete thermal decomposition could be achieved at a temperature of 550 °C. This means that undecomposed aluminum hydrate may also remain in this study [20]. Considering the LSC analysis results, although the radioactivity concentrations of the tritium that was extracted at each heating temperature (i.e., 200, 300, and 400 °C) decreased to values lower than the corresponding MDA value within the 15-h period (or, the net counting rates became lower than zero), a small amount of tritium was also detected in the 0.1 M nitric acid during heating at 550 °C. This implies that the sole use of LSC analysis is not sufficient to accurately determine whether all tritium was extracted. Thus, XRD analysis was performed. It was also interesting to find

Table	1
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Radioactivity concentration of extracted tritium from 0.4 mm aluminum at 400 °C for 15 h.

Sample pieces	Radioactivity concentration of extracted tritium according to heating duration (Bq/g)							MDA (Bq/g)
	0–3 h	3–6 h	6–9 h	9–12 h	12–15 h	6 h (At 550 °C)	6 h (Reheat at 550 $^{\circ}C$)	
1	65.517 ±	3.277 ±	0 (-0.030)	0 (-0.234)	0 (-0.516)	2.048 ± 0.106	0 (-0.052)	0.257
5	56.771 ±	0.135 7.455 ± 0.195	0.357 ± 0.022	0 (-0.236)	0 (-0.218)	1.416 ±	0 (-0.038)	0.166
10	60.621 ± 0.757	4.186 ± 0.165	0.022 0.446 ± 0.029	0 (-0.149)	0 (-0.413)	2.286 ± 0.116	0 (-0.082)	0.270
15	48.511 ± 0.673	6.620 ± 0.219	0.704 ± 0.042	0 (-0.143)	0 (-0.347)	2.838 ± 0.134	0 (-0.125)	0.265

*A negative value of the radioactivity concentration in parentheses indicates that the sample counting rate is lower than the background counting rate.

Table 2 Radioactivity concentration of extracted tritium from 0.4 mm aluminum at 300 °C for 15 h.

Sample pieces	Radioactivity concentration of extracted tritium according to heating duration (Bq/g)						MDA (Bq/g)	
	0-3 h	3-6 h	6–9 h	9–12 h	12–15 h	6 h (At 550 ° <i>C</i>)	6 h (Reheat at 550 $^{\circ}C$)	
1	65.997	1.268	<mda< td=""><td>0 (-0.124)</td><td>0 (-0.083)</td><td>0.811</td><td>0 (-0.067)</td><td>0.276</td></mda<>	0 (-0.124)	0 (-0.083)	0.811	0 (-0.067)	0.276
5	± 0.825 60.507	± 0.070 2.690	<mda< td=""><td><mda< td=""><td>0 (-0.088)</td><td>± 0.053 1.270</td><td>0 (-0.125)</td><td>0.266</td></mda<></td></mda<>	<mda< td=""><td>0 (-0.088)</td><td>± 0.053 1.270</td><td>0 (-0.125)</td><td>0.266</td></mda<>	0 (-0.088)	± 0.053 1.270	0 (-0.125)	0.266
10	± 0.752 58.264	± 0.123 1.147	0.351	<mda< td=""><td>0 (-0.036)</td><td>± 0.075 1.031</td><td>0 (-0.085)</td><td>0.237</td></mda<>	0 (-0.036)	± 0.075 1.031	0 (-0.085)	0.237
15	± 0.715 45.170 ± 0.626	± 0.063 2.247 ± 0.105	± 0.023 <mda< td=""><td><mda< td=""><td>0 (-0.039)</td><td>± 0.063 0.844 ± 0.054</td><td>0 (-0.095)</td><td>0.239</td></mda<></td></mda<>	<mda< td=""><td>0 (-0.039)</td><td>± 0.063 0.844 ± 0.054</td><td>0 (-0.095)</td><td>0.239</td></mda<>	0 (-0.039)	± 0.063 0.844 ± 0.054	0 (-0.095)	0.239

Table 3

Radioactivity concentration of extracted tritium from 0.4 mm aluminum at 200 °C for 15 h.

Sample pieces	Radioactivity concentration of extracted tritium according to heating duration (Bq/g)								
	0–3 h	3–6 h	6–9 h	9–12 h	12–15 h	6 h (At 550 ° <i>C</i>)	6 h (Reheat at550 °C)		
1	29.951	11.863	1.520	0 (-0.046)	<mda< td=""><td>1.453</td><td>0 (-0.235)</td><td>0.316</td></mda<>	1.453	0 (-0.235)	0.316	
-	± 0.560	± 0.331	± 0.083	0.004		± 0.087	0 (0 075)	0.004	
5	16.340 ± 0.334	12.067 ± 0.280	2.741 ± 0.115	0.234 ± 0.015	0 (-0.166)	0.930 ± 0.056	0 (-0.075)	0.204	
10	19.060	7.474	0.937	<mda< td=""><td>0 (-0.228)</td><td>0.799</td><td>0 (-0.078)</td><td>0.221</td></mda<>	0 (-0.228)	0.799	0 (-0.078)	0.221	
	± 0.375	± 0.219	± 0.052			± 0.050			
15	19.428 ± 0.345	10.303 ± 0.240	2.704 ± 0.110	0.637 ± 0.037	0 (-0.057)	0.735 ± 0.045	0 (-0.116)	0.187	

Table 4

Radioactivity concentration of extracted tritium from 2 mm aluminum at 400 °C for 15 h.

Sample pieces	Radioactivi	adioactivity concentration of extracted tritium according to heating duration (Bq/g)							
	0–3 h	3–6 h	6–9 h	9–12 h	12–15 h	6 h (At 550 °C)	6 h (Reheat at 550 °C)		
1	16.757	1.238	0.069	0 (-0.012)	0 (-0.020)	0.105	0 (-0.098)	0.032	
5	± 0.151 15.775	± 0.035 2.695	± 0.004 0.139	0 (-0.016)	0 (-0.052)	± 0.007 0.050	0 (-0.107)	0.043	
10	± 0.155 8.308	± 0.060 0.772	± 0.008 0.053	0 (-0.042)	0 (-0.054)	± 0.004 0.090	0 (-0.142)	0.036	
15	± 0.103 10.643	± 0.027 1.918	± 0.003 0.211	0 (-0.003)	0 (-0.011)	± 0.006 <mda< td=""><td>0 (-0.085)</td><td>0.037</td></mda<>	0 (-0.085)	0.037	
	± 0.118	± 0.047	± 0.011						

that aluminum hydrates were not observed after the samples were heated at 550 $^{\circ}$ C, as can be seen in Figs. 4 and 5.

Similarly, the use of XRD analysis alone is also not sufficient to confirm whether complete tritium extraction. Interestingly, although aluminum hydrate peaks were not observed for the 2-mm-thick sample that was heated at 400 °C (Fig. 5), they were present for the 0.4-mm-thick sample that was heated at 400 °C (Fig. 4). In the case of the relatively thick sample (i.e., the 2-mm-thick sample), the aluminum hydrate peak may not be visible if only the surface of the sample is contaminated, or if the peak counts of aluminum below the surface of the sample are relatively high and the peak counts of aluminum hydrate are very low. In the case of the relatively thin sample (i.e., the 0.4-mm-thick sample),

the aluminum hydrate peak was observed. This is because, although the peak counts of aluminum were higher, they were not significantly higher than those of the aluminum hydrate(s).

Thus, following analysis of the XRD and LSC results, and by taking into account the results of a previous study, we were able to infer that complete tritium extraction was achieved after subjecting the samples to heating at 550 °C. Moreover, after applying the 550 °C heat treatment and confirming that the counting rate was lower than the background counting rate, it was able to infer that all of the tritium was extracted from the aluminum samples. Then, by applying the assumption of complete tritium extraction, the tritium extraction fraction for the heating duration was calculated as

Table 5Radioactivity concentration of extracted tritium from 2 mm aluminum at 300 $^{\circ}C$ for 15 h.

Sample pieces	Radioactivity concentration of extracted tritium according to heating duration (Bq/g)								
	0–3 h	3–6 h	6–9 h	9–12 h	12–15 h	6 h (At 550 °C)	6 h (Reheat at 550 ° <i>C</i>)		
1	19.409	0.267	0.087	<mda< td=""><td><mda< td=""><td>0.325</td><td>0 (-0.025)</td><td>0.043</td></mda<></td></mda<>	<mda< td=""><td>0.325</td><td>0 (-0.025)</td><td>0.043</td></mda<>	0.325	0 (-0.025)	0.043	
5	± 0.174 19.315	± 0.014 0.467	± 0.005 0.067	<mda< td=""><td><mda< td=""><td>± 0.017 0.390</td><td>0 (-0.089)</td><td>0.048</td></mda<></td></mda<>	<mda< td=""><td>± 0.017 0.390</td><td>0 (-0.089)</td><td>0.048</td></mda<>	± 0.017 0.390	0 (-0.089)	0.048	
10	± 0.182 9.366	± 0.022 0.306	± 0.004 0.095	0.082	<mda< td=""><td>± 0.020 0.369</td><td>0 (-0.095)</td><td>0.056</td></mda<>	± 0.020 0.369	0 (-0.095)	0.056	
15	± 0.138 7.781	± 0.016 0.431	± 0.006 <mda< td=""><td>± 0.005 <mda< td=""><td>0 (-0.014)</td><td>± 0.020 0.305</td><td>0 (-0.038)</td><td>0.047</td></mda<></td></mda<>	± 0.005 <mda< td=""><td>0 (-0.014)</td><td>± 0.020 0.305</td><td>0 (-0.038)</td><td>0.047</td></mda<>	0 (-0.014)	± 0.020 0.305	0 (-0.038)	0.047	
	± 0.111	± 0.020				± 0.017			

Table 6

Radioactivity concentration of extracted tritium from 2 mm aluminum at 200 °C for 15 h.

Sample pieces	Radioactivity concentration of extracted tritium according to heating duration (Bq/g)								
	0–3 h	3–6 h	6–9 h	9–12 h	12–15 h	6 h (At 550 °C)	6 h (Reheat at 550 ° <i>C</i>)		
1	14.795	7.320	0.090	0 (-0.016)	0 (-0.029)	0.918	0 (-0.075)	0.053	
	± 0.169	± 0.116	± 0.006			± 0.037			
5	10.199	3.799	0.274	<mda< td=""><td>0 (-0.058)</td><td>0.860</td><td>0 (-0.068)</td><td>0.051</td></mda<>	0 (-0.058)	0.860	0 (-0.068)	0.051	
	0.138	0.082	0.015			0.035			
10	9.579	1.445	0.132	0.059	<mda< td=""><td>0.931</td><td>0 (-0.035)</td><td>0.050</td></mda<>	0.931	0 (-0.035)	0.050	
45	± 0.129	± 0.046	± 0.008	± 0.004		± 0.036	0 (0 100)	0.040	
15	6.850 ±	1.367 ±	0.117 ±	<mda< td=""><td><mda< td=""><td>0.886 ±</td><td>0 (-0.128)</td><td>0.048</td></mda<></td></mda<>	<mda< td=""><td>0.886 ±</td><td>0 (-0.128)</td><td>0.048</td></mda<>	0.886 ±	0 (-0.128)	0.048	
	0.107	0.044	0.007			0.035			



Fig. 4. XRD analysis of tritium contaminated aluminum according to heating temperature (0.4 mm).



Fig. 5. XRD analysis of tritium contaminated aluminum according to heating temperature (2 mm).

Extracted fraction (%) =
$$\frac{R_H}{R_T} \times 100$$
 (6)

 R_T : Total cumulative summation of the radioactivity concentration of the extracted tritium (considering tritium radioactivity concentration extracted upon heating at 550 °C).

 R_{H} : Cumulative summation of the extracted tritium radioactivity concentration for heating duration.

The calculated tritium extraction fractions were 97.11%, 98.25%, 96.62%, and 95.16% for the one-piece, five-piece, 10-piece, and 15piece samples, respectively. Of course, a larger number of fragmented samples means finer cuts. Nevertheless, the relationship between the number of samples and tritium extraction fraction cannot be determined. If the hydration reaction is only generated on the surface of aluminum, the tritium extraction fraction is not affected by the number of samples. Thus, determination of the chemical composition via XRD analysis is required. The significance of XRD analysis was evidenced by the results. For example, within the initial 3 h, the extraction fractions were 92.48%, 86.37%, 89.76%, and 82.68%. However, within the initial 6 h, the cumulative extraction fractions were 97.11%, 97.71%, 95.95%, and 93.96% for the one-, five-, 10-, and 15-piece samples, respectively. Although the one-piece sample had the highest extraction fraction after the initial 3 h, the five-piece sample had the highest extraction fraction after 6 h. After being heated for 6 h, the radioactivity concentration of the one-piece sample was zero, and tritium was still extracted from the other samples. The tritium subsequently extracted from

the other three samples (i.e., the 5-, 10-, and 15-piece samples) between 6 and 9 h, respectively accounted for only 0.54%, 0.66%, and 1.20% of the total extracted tritium. Although tritium was extracted most rapidly during the initial 3 h from the one-piece sample, considering the amount of tritium that was extracted from the other three samples between 6 and 9 h of heating, there was no significant difference in the speed of extraction. Regarding the extraction fractions after 9 h of heating, the fractions for the multi-piece samples were 98.26%, 96.62%, and 95.16%, respectively. Although the fraction for the five-piece sample (i.e., 98.26%) was higher than that for the one-piece sample, it was difficult to infer whether the extraction efficiency was highest when the sample was cut into five pieces. It was also interesting to find that the final extraction fractions converged to >95%, implying that the proportions of aluminum hydrates decomposed at 400 °C were similar for all samples.

When the one-piece 0.4-mm-thick aluminum stick sample was heated at 300 °C for 15 h, the radioactive tritium concentrations were 65.997 ± 0.825 , 1.268 ± 0.070 , <MDA, 0, and 0 Bq/g, at 3, 6, 9, 12, and 15 h, as indicated in Table 2. After 6 h, the concentration was lower than the MDA value. The concentration of radioactive tritium in the sample was measured to be 0.811 ± 0.053 Bq/g after it was heated at 550 °C. These results are similar to those obtained for the 400 °C heating experiment. A comparison of the 400 and 300 °C results (Tables 1 and 2, respectively) revealed that the concentrations of residual radioactive tritium extracted from the 300 °C heattreated aluminum samples were lower than the 400 °C samples after they were each heated at 550 °C. However, the extraction fractions were higher than those for the 400 °C samples. The extraction fractions for the one-, five-, 10-, and 15-piece 300 °C

samples were 98.81%, 98.04%, 98.31%, and 98.26%, respectively. Although tritium ceased to be extracted from any of the samples after 6 h, with the exception of the 10-piece sample, there was minimal difference between the cumulative extraction fractions of the one-, five-, 10-, and 15-pieces samples; particularly, the values were 98.81%, 98.03%, 97.73%, and 98.25% at 6 h. The fraction of tritium extracted from the 10-piece sample between 6 and 9 h was only 0.58% of the total amount of extracted tritium. After 9 h, the total fraction of tritium extracted from the 10-piece sample was 98.31%. This was the second highest value among the four samples.

After 3 h of heating at 200 °C, the fractions of tritium extracted from the 0.4-mm-thick one-, five-, 10-, and 15-piece aluminum samples were 66.87%, 50.57%, 67.06%, and 57.47%, respectively (Table 3). Although the 3-h tritium extraction fractions for the 200 °C samples were significantly lower than those for the 300 and 400 °C samples, the final extraction fractions were 96.76%, 97.12%, 97.19%, and 97.83% for the one-, five-, 10-, and 15-piece samples, respectively. In the case of each temperature condition (200, 300, and 400 °C), the time required for complete tritium extraction significantly differed among the samples (i.e., the one-, five-, 10-, and 15-piece samples); however, under the condition of 200 °C heating, the differences in the extraction fractions were very small, as was observed in the cases of 300 and 400 °C heating. Additionally, the proportions of tritium extracted from the five- and 15piece samples between the 6- and 9-h period were only 0.72% and 1.88%. respectively.

Although the fraction of extraction was higher at 300 °C, it cannot be concluded that the extraction efficiency at 300 °C was higher than that at 400 °C. At both temperatures, as the heating duration increased, the counting rate decreased, eventually becoming lower than that of the background. Thus, the higher extraction efficiency at 300 °C (as compared to that at 400 °C) can be attributed to the difference in the amount of material that was not decomposed. Although there were clear heating temperaturerelated differences for the 0.4-mm-thick samples, the differences in the extraction fractions were only significantly large for the initial 3 h. Furthermore, there were no significant differences in the extraction fractions after 15 h of heating. Hydroxide material such as AlOOH is known to begin to decompose at a temperature of 480 °C. Thus, assuming that the chemical composition of all of the contaminated 0.4-mm-thick aluminum samples were nearly identical at all heating temperatures, because the temperatures applied in this study were lower than 480 °C, the heating temperature cannot be the most significant variable affecting the tritium extraction fraction. Beyond 12 h, the tritium extraction fractions were found to converge to 95-98%, regardless of the heating temperature.

3.2. Radioactivity extraction from 2-mm-thick samples

Tables 4–6 present the 400, 300, and 200 °C results for the 2mm-thick aluminum stick samples. As shown in Table 4, when the aluminum stick sample was heated at 400 °C, the concentrations of radioactive tritium extracted from the samples were 16.757 ± 0.151 , 1.238 ± 0.035 , 0.069 ± 0.004 , 0, and 0 Bq/g for the one-, five-, 10-, and 15-piece samples, respectively. Note that the concentration of radioactive extracted tritium was lower at longer heating durations. This tendency was observed for all samples (i.e., the one-, five-, 10-, and 15-piece samples). The extraction fractions were found to be 92.22%, 84.54%, 90.07%, and 88.31% for the one-, five-, 10-, and 15-piece samples at 3 h, indicating relatively large differences. However, the 6-h total extraction fraction results revealed differences of less than 1% (i.e., 99.04%, 98.99%, 98.45%, and 98.25% for the one-, five-, 10-, and 15-piece samples, respectively). The final extraction fractions were 99.42%, 99.73%, 99.02%, and 99.99% for the one-, five-, 10-, and 15-piece samples, respectively. When the 15-piece sample was heated at 550 °C, the concentration of radioactive tritium extracted from the sample was lower than the MDA value. The tritium was determined to be completely extracted from the 15-piece sample after 9 h of heating at 400 °C. In the case of the other three samples (i.e., the one-, five-, and 10-piece samples), the final extraction fractions were higher than 99%.

Analysis of the 300 and 400 °C sample results (Tables 5 and 4, respectively) revealed similar tendencies with respect to the heating duration. The fractions of tritium extracted from the 300 °C one-, five-, 10-, and 15-piece samples during the first 3 h were 96.62%, 95.43%, 91.66%, and 91%, respectively. The largest difference between the sample extraction fractions was 5.26%. However, the cumulative extraction fractions at 6 h were 97.95%, 97.74%, 94.66%, and 96%, respectively, corresponding to a maximum difference of 3%. The final extraction fractions were 98.38%, 98.07%, 96.39%, and 96.42% for the one-, five-, 10-, and 15-piece samples, respectively, as shown in Table 5. The 15-piece sample was the fastest as it reached the maximum extraction fraction in 6 h, and the sample with 10 pieces required 12 h, but the amount of tritium extracted during the 9-12-h period accounted for only 0.8% of the total amount. Additionally, the one-piece sample had the highest final extraction fraction. Although more time was required for the 300 °C samples to reach a radioactivity concentration that was lower than the MDA than in the case of the 400 °C samples, there were no large differences in the extraction fraction at 15 h.

The final extraction fractions for the 200 °C one-, five-, 10-, and 15-piece samples were 96.03%, 94.32%, 92.33%, and 90.39%, respectively. It is noteworthy that these fractions were lower than those for the 300 °C and 400 °C samples. The largest difference in the extraction fractions among the samples was 5.64%. This value is significantly larger than 1.06%, which was the largest difference for all 0.4-mm-thick samples (Table 3). In addition, the fractions of tritium extracted from the 200 °C samples during the initial 3 h were very low compared to the corresponding extraction fractions for the 300 °C and 400 °C samples (i.e., 63.98%, 67.40%, 78.87%, and 74.30% for the one-, five-, 10-, and 15-piece samples. This phenomenon was also observed in the case of the 0.4-mm-thick samples (Table 3). Although the rate of extraction differed, after 15 h, the radioactivity concentration was lower than the corresponding MDA value, or the sample counting rates were lower than the background counting rates for all temperature conditions. It was also found that, subsequently heating the samples at 550 °C extracted the residual tritium. Furthermore, we confirmed that, under the conditions of applying a temperature at which a specific hydrated material will not decompose, the extraction fraction will converge to a specific section, regardless of the heating duration; additionally, the amount of undecomposed hydrated material can be roughly determined by the amount of residual tritium. According to the results shown in Tables 1–6, even though the time to reach the maximum extraction fraction differed, the differences in final extraction fraction after 15 h were insignificant, confirming that the sample that first reaches the maximum extraction fraction will not necessarily yield the highest extraction fraction.

3.3. XRD analysis of 0.4-mm-thick samples

Fig. 4 shows the XRD results for the 0.4-mm-thick tritiumcontaminated aluminum samples according to heating temperature. Although the results of XRD analysis do not yield the exact value, they can confirm the presence of each material. In some cases, materials with similar peaks cannot be clearly distinguished. As can be seen in the no-heat graph (Fig. 4), prior to being subjected to the heat treatment, aluminum (Al), aluminum hydroxide (Al(OH)₃), and aluminum oxide hydroxide (AlOOH) were present in the 0.4-mm-thick tritium-contaminated samples. Taking the results for the unheated sample as the reference, the peak counts for Al(OH)3 were reduced by the 200 °C heat treatment. This treatment also reduced the peak counts for Al(OH)₃ and AlOOH. Considering that Al(OH)₃ and AlOOH are known to begin thermal decomposition at approximately 200 and 480 °C, respectively, the relatively lower peak counts for Al(OH)₃ and AlOOH can be attributed to the decomposition of Al(OH)₃. Regarding the 300 °C heat-treatment results, XRD analysis confirmed most of the Al(OH)₃ to be removed. It is also noteworthy that no hydration materials were observed in the peaks around 20°, 33°, 41°, and 53° after heating at 300 °C. The removal of the peak representing both Al(OH)₃ and AlOOH verified the decomposition of Al(OH)₃. The XRD results also revealed that heating the samples at 400 °C resulted in peak counts for the hydration materials that were lower than those for aluminum. In the peak with both Al(OH)₃ and AlOOH, the remaining hydroxide material was inferred as AlOOH. In the case of the 400 °C heat treatment, owing to the presence of a hydroxide material such as AlOOH, although the concentration of the extracted radioactive tritium became lower than the background within the 9–12-h interval, more tritium was extracted when the sample was subsequently heated at 550 °C. The XRD results confirmed the existence of a hydration material after the secondary 550 °C heat treatment. As can be ascertained from Fig. 4, the 550 °C heat treatment removed most of the confirmed hydration materials. This implies that most of the hydration materials on the surface of the tritium-contaminated aluminum sample existed as Al(OH)₃.

3.4. XRD analysis of the 2-mm-thick samples

Fig. 5 shows the XRD results for the 2-mm-thick tritiumcontaminated aluminum samples. The heating conditions were the same as those for the 0.4-mm-thick samples. As can be seen in Fig. 5, although the sample was not heated, the peak counts for aluminum were higher than those for the other hydroxide materials. This implies that the hydration reaction between aluminum and tritiated water primarily occurred on the surface. In the case of the 0.4-mm-thick aluminum samples (Fig. 4), because the thickness was relatively low (i.e., the distance from the surface to the internal center was relatively small), it was presumed that the peak counts for the hydroxide material were higher than those for aluminum.

However, because the surface-to-center distance of the 2-mmthick samples was larger than thickness of the surface hydroxide film, the peak counts of the aluminum did not become hydrated were higher than those for the hydroxide materials. Table 7 shows the results of scanning electron microscopy—energy-dispersive Xray spectrometry (SEM-EDS) analysis, which was applied to determine the mass fractions of aluminum oxide materials and aluminum on the surface of the unheated tritium-contaminated samples. Regarding the 0.4-mm-thick sample results, the mass fractions of aluminum oxide materials and aluminum were 52.36% and 47.64%, respectively. Because SEM-EDS cannot distinguish between oxide and hydroxide materials, all aluminum compounds, including oxygen, were marked as oxide materials. Regarding the 2mm-thick sample results, the mass fractions of aluminum oxide materials and aluminum were 51.63% and 48.37%, respectively. Because SEM is only applicable to the surface of materials, these results confirm a larger proportion of oxides on the sample surface as compared to that of aluminum. Although oxides were predominant on the surface, it can be inferred that only the surface was contaminated, because aluminum was more abundant throughout the samples.

Because the most of contamination was the surface contamination, the number of sample pieces cannot be the most significant factor affecting the tritium extraction fraction. As can be seen in Fig. 5, another difference from the 0.4-mm-thick sample results is that an AlOOH peak cannot be observed near 38°. Because aluminum occupies the largest volume and most of the surface hydroxide material film comprised Al(OH)₃, the AlOOH count can be considered to have been too low to be detectable. However, this does not imply that there was no AlOOH in the 2-mm-thick tritiumcontaminated aluminum samples. Additionally, although AlOOH was not observed in the XRD pattern results for the 300 °C and 400 °C 2-mm-thick samples (Fig. 5), tritium was detected in the sample that was heated at 550 °C (Tables 4 and 5). Thus, although the results of XRD and radioactivity concentration analysis indicated similar tendencies of hydroxide material formation on the aluminum sample surface, the results of these two techniques should be compared according to sample thickness.

4. Conclusion

Tritium extraction was experimentally characterized in aluminum metal by applying a below-melting-temperature heat treatment. Although some tritium was not detectable under certain heating temperature conditions, XRD and SEM-EDS were applied for further analysis because undecomposed (tritium-based) aluminum hydrate was assumed to exist in the aluminum sample. XRD and SEM-EDS analysis allowed us to confirm that, when aluminum is contaminated with tritiated water, only the contamination on the surface of the aluminum and aluminum hydrate was also made on the surface. As a result of confirming that only the sample surface was contaminated, it can be determined that neither the number of sample fragments nor the sample thickness were factors that significantly affected the extraction fraction. Moreover, given that the applied decomposed material demonstrated the same tendencies at two different heating temperatures (300 and 400 °C), if two different heating temperatures are in the decomposition temperature range the same aluminum hydrate, the temperature was determined to be a non-dominant factor affecting the extraction efficiency. This means that the aluminum hydrate decomposition temperature was the most significant factor affecting the tritium extraction fraction. Because the decomposition temperature differed according to the aluminum hydrate, the most dominant tritium-based aluminum hydrate was determined. Based on this information, the differences between the final tritium extraction fractions for each heating condition were deemed to be non-significant. Additionally, it was found that, even under the condition of a relatively long heating time and the application of a heating temperature below the hydrated material decomposition

Table 7

Weight percent on sample surface according to SEM-EDS analysis of no heated tritium contaminated sample (0.4 mm and 2 mm).

Sample thickness (mm)	Weight percent (%)		
	Al	Aluminum oxide material (including hydroxide material)	
0.4	47.64 48.37	52.36 51.63	
2	10.07	51.05	

temperature, the tritium did not separate from the tritium-based hydrated material.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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