



Original Article

Tritium radioactivity estimation in cement mortar by heat-extraction and liquid scintillation counting

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ABSTRACT

Tritium extraction from radioactively contaminated cement mortar samples was performed using heating and liquid scintillation counting methods. Tritiated water molecules (HTO) can be present in contaminated water along with water molecules (H_2O). Water is one of the primary constituents of cement mortar dough. Therefore, if tritium is present in cement mortar, the buildings and structures using this cement mortar would be contaminated by tritium. The radioactivity level of the materials in the environment exposed to tritium contamination should be determined for their disposal in accordance with the criteria of low-level radioactive waste disposal facility. For our experiments, the cement mortar samples were heated at different temperature conditions using a high-temperature combustion furnace, and the extracted tritium was collected into a 0.1 M nitric acid solution, which was then mixed with a liquid scintillator to be analyzed in a liquid scintillation counter (LSC). The tritium extraction rate from the cement mortar sample was calculated to be 90.91% and 98.54% corresponding to 9 h of heating at temperatures of 200 °C and 400 °C, respectively. The tritium extraction rate was close to 100% at 400 °C, although the bulk of cement mortar sample was contaminated by tritium.

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1. Introduction

Tritium, the radioactive isotope of hydrogen, can exist in various forms, such as gaseous tritium, tritiated water (HTO), and organically bound tritium [1,2]. Tritium decays by emitting a weak beta particle with a maximum energy of approximately 18.6 keV [3]. Therefore, external exposure to tritium is not a serious concern [4]. However, internal exposure can cause lesions in cellular deoxyribonucleic acid [5]. Most materials in the environment near humans, as well as the human body, can be contaminated by tritium. Although tritium cannot enter the human body directly, contamination of materials such as drinking water and eatables can also endanger the safety of human beings. Concrete is the main material of partition walls in tritium handling facilities. Thus, considering that concrete is a porous adsorption material, studies about tritium in concrete are important for radiation safety [6]. The decomposition of chemical materials, including tritium, in concrete as gypsum crystal water ($CaSO_4 \cdot 2H_2O$), starts at temperatures lower than 200 °C [7]. This means that heat generation in a tritium

handling facility can be dangerous to workers. Therefore, the presence of tritium in radioactive waste generated by establishments handling tritium, including nuclear power plants, should be detected. Because cement and water are also the main constituent materials of concrete, if water is contaminated due to the leakage of HTO, several materials using contaminated water can also be contaminated. Because cement mortar is produced by mixing cement, fine aggregate, and water, contaminated water may be used for this purpose, and workers at sites where such contaminated mortar is used can be exposed to tritium hazards. Therefore, the level of tritium in cement mortar when contaminated water is used should be analyzed. In this study, tritium extraction from a contaminated cement mortar sample was performed at different temperatures and heating durations, and then analyzed using the liquid scintillation counting method.

2. Methods and materials

2.1. Cement mortar sample production

Producing a cement mortar sample with bulk contamination by tritium is one of the most critical processes. The common contamination method consists of dipping a normal cement mortar

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sample prepared with non-contaminated water in HTO. However, in this method, the core of the cement mortar sample is not contaminated. To cause bulk contamination, HTO and cement were mixed to produce the sample. The mixture was left to dry at room temperature (about 25 °C). The HTO used in this process had a radioactivity concentration of 6778 ± 14.93 kBq/L. The water/cement (w/c) ratio utilized, in mass, was 0.20 (1:5, HTO: cement). For w/c ratios lower than 0.20, the mixture was excessively dry, whereas for w/c ratios higher than 0.20, the low viscosity of the mixture hindered the molding process. Therefore, the optimum w/c ratio was determined to be 0.20.

To maintain the w/c ratio, an increase in the mass of cement mortar powder used for the sample must be followed by a proportional increase in the mass of the HTO used. An increased HTO quantity would mean an increase in the radioactivity of the tritium-contaminated cement mortar. However, whether tritium will diffuse and homogeneously contaminate the entire bulk of the cement mortar sample during the drying process is not certain. Considering this factor, five different mixtures and five different samples were produced, as listed in Table 1, while maintaining the mass ratio. Each sample was made of a form and size that could be placed in the sample boat of a high-temperature furnace with entrance dimensions of 12.5 mm × 14.5 mm and dried at room temperature for 24 h. Fig. 1 shows the samples loaded on the sample boat. The mass quantities of each specimen loaded on the sample boat were measured on an electronic scale.

2.2. Extraction of tritium by heating

Contamination in most liquid samples, including those with HTO molecules, is detected by a liquid scintillation counter (LSC) [8–14]. Because cement mortar is used in various operations such as construction and repair, it is a common waste. However, as a typical cement mortar sample is in a solid state, it cannot be directly analyzed using LSC. When mortar is in fresh state, the sample solution with impurities can be affected by heterogeneity in the quench-like sample composition and/or color [15]. Therefore, for better results, tritium in cement mortar samples should first be extracted for analysis using LSC. Dissolution of cement mortar samples in acid/base solutions can cause quench errors caused by impurities. Therefore, a heating method was adopted to extract tritium from the cement mortar samples.

A high-temperature furnace (Raddec Pyrolyser-Trio Furnace System, RADDEC INTERNATIONAL) was used to heat the cement mortar samples for various durations and heating temperatures. The sample boats with five batches of cement mortar samples were placed into five quartz glass tubes in a high-temperature furnace. In front of each quartz glass tube, connections supplying oxygen gas and air from the gas cylinders were connected. At the end of each quartz glass tube, a container with 20 ml of 0.1 M nitric acid solution was connected to collect the extracted tritium from the cement mortar sample [16]. In a previous study, the release characteristics of HTO on concrete materials was analyzed, but temperature conditions were lower than 100 °C, and the chemical

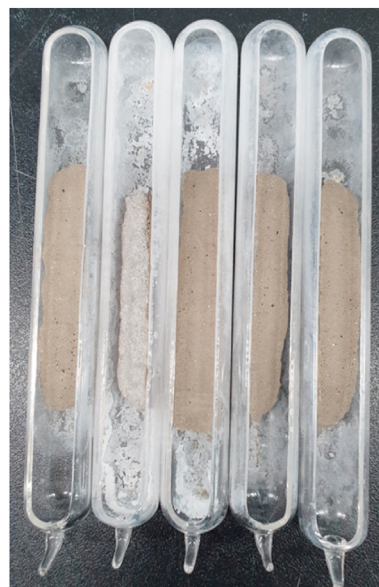


Fig. 1. Cement mortar sample loaded on the sample boat of high temperature furnace.

decomposition of hydrate material in concrete was not considered [17]. The heating temperature was set to 200 °C in the first experiment. The extraction duration was set to 9 h. To determine the extraction rate of tritium, 20 ml of 0.1 M nitric acid solution was replaced with a new one every 3 h. After the end of 9 h of heating, presuming that some residual tritium would have remained in the cement mortar samples, 20 ml of 0.1 M nitric acid solution in each container was replaced with a new one and the samples were heated at 600 °C for 5 h. Finally, the process of heating at 600 °C for 5 h was performed again for the extraction of any remaining tritium.

According to the heating temperature of the cement mortar sample, different materials with tritium were decomposed. In previous study about tritium release from the heating of the cement contaminated to tritiated water vapor, water of crystallization (gypsum crystal water) is known to decompose in the temperature range of 200–450 °C. From 450 to 550 °C, $\text{Ca}(\text{OH})_2$ is decomposed [18]. In this study, instead of tritiated water vapor, because tritiated water is used as contamination source of cement mortar sample, the properties of hydrate decomposition according to heating temperature were referenced in previous studies. Thus, to exclude the effects of the decomposition of $\text{Ca}(\text{OH})_2$, the heating temperature range was set from 200 to 400 °C. In other study using real nuclear reactor bio-shield concrete, there was strongly bound tritium originates from neutron capture on trace lithium [19]. Because there was no neutron capture on trace lithium in this study, almost no strongly bound tritium was expected. This means that there would be almost no tritium from the decomposition of $\text{Ca}(\text{OH})_2$ and calcium silica hydrate (C–S–H). Therefore, the heating

Table 1

Mixing mass ratio and real masses used in mixing between tritiated water and cement mortar powder.

Sample group	Mixing Mass Ratio (Tritiated water vs. Cement mortar powder)	The mass of tritiated water used in mixing (g)	The mass of cement mortar powder used in mixing (g)
1	1 : 5	20	100
2	1 : 5	25	125
3	1 : 5	30	150
4	1 : 5	35	175
5	1 : 5	40	200

Table 2
Radioactivity concentration of extracted tritium for each 3 h interval at 200 °C.

Sample group	Radioactivity concentration of extracted tritium before heating for 14 h (Bq/g)					Residual tritium radioactivity concentration after heating for 14 h (Bq/g)
	(Average ± SD)					
	0–3 h (at 200 °C)	3–6 h (at 200 °C)	6–9 h (at 200 °C)	9–14 h (at 600 °C)	Total	Residual tritium (<MDA)
1	3.939 ± 0.01666	0.6729 ± 0.001721	0.4644 ± 0.001289	0.5997 ± 0.001482	5.677 ± 0.01687	(<MDA)
2	4.087 ± 0.01961	0.9526 ± 0.003187	0.5847 ± 0.001694	0.5952 ± 0.001325	6.220 ± 0.01998	(<MDA)
3	4.708 ± 0.02065	1.046 ± 0.003410	0.4919 ± 0.001783	0.4592 ± 0.0015	6.706 ± 0.02106	(<MDA)
4	4.217 ± 0.01768	1.165 ± 0.002951	0.7289 ± 0.001655	0.4854 ± 0.002193	6.5964 ± 0.01813	(<MDA)
5	4.447 ± 0.01566	0.8801 ± 0.002189	0.5597 ± 0.002265	0.7026 ± 0.001201	6.5897 ± 0.01602	(<MDA)

temperature conditions for the extraction of tritium from the decomposition of crystal water were considered. However, for an accurate verification, by increasing the heating temperature to 900 °C, tritium extraction from cement mortar samples at various temperature conditions was conducted. The heating temperatures were 400, 450, 600, and 900 °C. In fact, after heating at 600 °C, almost no extraction of tritium was observed at 900 °C (<MDA value). This means that all tritium was extracted at 600 °C. Therefore, 600 °C was set as the heating temperature required to check the remaining tritium in the cement mortar sample.

Experiments were repeated at temperatures of up to 400 °C (starting at 200 °C) by raising the temperature in increments of 50 °C, that is, 250 °C, 300 °C, 350 °C, and 400 °C, followed by two periods of heating at 600 °C. The heating duration and the time interval of 0.1 M nitric acid solution replacement were kept unchanged.

2.3. Liquid scintillation counter analysis

Each time the 0.1 M nitric acid solution was replaced with a new one, 8 ml of the withdrawn 20 ml solution was removed and mixed with 12 ml of the liquid scintillator (GOLDSTAR, MERDIAN Biotechnologies Ltd) in a plastic vial. This solution captured the tritium extracted from the cement mortar sample. To mix the liquid scintillator and the 0.1 M nitric acid solution, the closed plastic vial was shaken more than ten times. This solution is called a liquid scintillator cocktail. Each vial with a liquid scintillator cocktail was examined in a liquid scintillator counter (1220 QUANTULUS, PerkinElmer Life and Analytical Sciences). Using the measured results, the extraction rates (D_t) of tritium corresponding to the interval preceding the withdrawal of the nitric acid solution were calculated as Eq. (1).

$$D_t = \frac{\sum_{x=1}^n R_x}{R_T} \quad (1)$$

where R_T is the summation of the radioactivity (Bq) from every nitric acid solution sample withdrawn during the total heating duration (14 h), and R_x is the Bq from the nitric acid solution samples withdrawn until the point at which the extraction rate is desired. Because not all tritium in HTO reacts with materials in cement, an accurate determination of the radioactivity concentration of tritium in cement is not possible. However, the results of LSC

analysis and X-ray diffraction (XRD) analysis can provide information on the extraction of tritium. With increasing heating temperature, although the decomposition of the candidate material expected to include tritium was observed from XRD analysis, tritium extraction was considered complete when tritium was not detected in the LSC analysis.

Radioactivity concentration (Bq/g) of the sample and its associated uncertainty were calculated as Eqs. (2) and (3), where the number of significant figure's digit was set to 4 [20].

$$A = \frac{N}{t \epsilon m} \quad (2)$$

A: Radioactivity concentration of the sample (Bq/g).
N: Net (sample) counts (#)
T: Counting time (s).
 ϵ : Detection efficiency of counter
M: Sample mass (g)

$$\sigma_A = A \sqrt{\left(\frac{\sigma_N}{N}\right)^2 + \left(\frac{\sigma_\epsilon}{\epsilon}\right)^2 + \left(\frac{\sigma_m}{m}\right)^2} \quad (3)$$

σ_A : Standard deviation of radioactivity concentration, A (Bq/g).
 σ_N : Standard deviation of sample counts ($\sigma_N = N_{S+B} + N_B$).
 N_{S+B} : Gross counts (or sample counts), N_B : BKG.
 σ_ϵ : Standard deviation of efficiency.
 σ_m : Standard deviation of sample weight (g).

2.4. X-ray diffraction analysis

To determine whether the decomposition of $\text{Ca}(\text{OH})_2$ and C–S–H material is not related to tritium release, XRD analysis was conducted after heating at temperatures of 400, 450, 600, and 900 °C, with 2 theta from 5° to 60° [7,21–23]. The target materials were $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{OH})_2$ (calcium hydroxide), CaCO_3 (calcium carbonate), and C–S–H.

3. Results and discussion

3.1. Minimum detectable activity

The radioactivity concentration measured by the liquid scintillator cocktail was found to be lower than the minimum detectable activity (MDA) when the cement mortar samples were heated at

Table 3
Radioactivity concentration of extracted tritium for each 3 h interval at 250 °C.

Sample group	Radioactivity concentration of extracted tritium before heating for 14 h (Bq/g)					Residual tritium radioactivity concentration after heating for 14 h (Bq/g)
	(Average ± SD)					
	0–3 h (at 250 °C)	3–6 h (at 250 °C)	6–9 h (at 250 °C)	9–14 h (at 600 °C)	Total	
1	4.316	0.5194	0.3891	0.8920	6.117	(<MDA)
	± 0.01226	± 0.001001	± 0.001591	± 0.002809	± 0.01272	
2	4.357	0.6358	0.4475	0.8757	6.316	(<MDA)
	± 0.01430	± 0.001425	± 0.001393	± 0.002738	± 0.01469	
3	4.974	0.7298	0.4267	0.5917	6.722	(<MDA)
	± 0.01449	± 0.02470	± 0.001480	± 0.001065	± 0.01482	
4	4.089	0.6721	0.4887	0.9088	6.159	(<MDA)
	± 0.01432	± 0.001671	± 0.001607	± 0.002394	± 0.01471	
5	7.5656	0.7076	0.5521	1.658	10.48	(<MDA)
	± 0.01755	± 0.002037	± 0.002096	± 0.004763	± 0.01842	

Table 4
Radioactivity concentration of extracted tritium for each 3 h interval at 300 °C.

Sample group	Radioactivity concentration of extracted tritium before heating for 14 h (Bq/g)					Residual tritium radioactivity concentration after heating for 14 h (Bq/g)
	(Average ± SD)					
	0–3 h (at 300 °C)	3–6 h (at 300 °C)	6–9 h (at 300 °C)	9–14 h (at 600 °C)	Total	
1	4.037	0.5800	0.3165	0.1813	5.115	(<MDA)
	± 0.01048	± 0.001865	± 0.0005449	± 0.0005993	± 0.01068	
2	4.712	0.6635	0.2718	0.2493	5.897	(<MDA)
	± 0.01608	± 0.002394	± 0.0007469	± 0.001012	± 0.01631	
3	5.073	0.5739	0.2417	0.1269	6.0151	(<MDA)
	± 0.01743	± 0.001931	± 0.0007111	± 0.0003986	± 0.01756	
4	4.474	0.6836	0.3170	0.1920	5.666	(<MDA)
	± 0.01454	± 0.002957	± 0.0009855	± 0.0005151	± 0.01488	
5	4.651	0.6914	0.3467	0.2003	5.889	(<MDA)
	± 0.01556	± 0.002547	± 0.001077	± 0.0005175	± 0.01582	

600 °C for 5 h for the second time, and a newly replaced 0.1 M nitric acid solution captured the extracted tritium from the samples. In Tables 2–6, the right-end columns show the radioactivity concentrations of residual tritium remaining after 14 h of heating. These values are lower than the MDA values in all five cement mortar sample groups and at all temperatures. The residual tritium radioactivity concentrations that remained beyond the 14 h heating period were not exceed the MDA value in any of the 25 cases. Hence, it was considered that all the tritium in the cement mortar samples was extracted by heating for 14 h, that is, 9 h at each temperature condition and the next 5 h at 600 °C.

3.2. Non-uniform contamination in samples

Although the same HTO and w/c ratio was used for all samples, the radioactivity of the extracted tritium per unit mass of cement mortar was not the same for all the samples. Unlike a uniform mix obtained when HTO and general distilled water are mixed, tritium is non-homogeneously distributed inside the cement mortar

sample. Tables 2–6 show the tritium radioactivity concentration observed by LSC analysis of the liquid scintillator cocktails obtained every 3 h at each temperature condition. It can be observed that the total radioactivity concentration of the extracted tritium is different between sample groups 1 to 5 for a certain temperature condition, and also different from Table 2 through Table 6 for a given sample group. This further indicates that when the water molecules and HTO molecules evaporate during the drying process of the cement mortar, the evaporation rate between water molecules and HTO molecules was not constant for all the cement mortar samples.

3.3. Effect of heating duration

As shown in Table 2, the radioactivity concentrations of extracted tritium from sample groups 1 to 5 during the first 3 h (0–3 h) heating were 3.939 ± 0.01666 , 4.087 ± 0.01961 , 4.708 ± 0.02065 , 4.2170 ± 0.01768 , and 4.447 ± 0.01566 Bq/g, respectively, at a heating temperature of 200 °C. These values were higher than those during the second 3-h interval (3–6 h) for a given sample group at the same

Table 5
Radioactivity concentration of extracted tritium for each 3 h interval at 350 °C.

Sample group	Radioactivity concentration of extracted tritium before heating for 14 h (Bq/g)					Residual tritium radioactivity concentration after heating for 14 h (Bq/g)
	(Average ± SD)					
	0–3 h (at 350 °C)	3–6 h (at 350 °C)	6–9 h (at 350 °C)	9–14 h (at 600 °C)	Total	
1	4.492 ± 0.007964	0.6552 ± 0.001979	0.3752 ± 0.001224	0.2498 ± 0.001020	5.772 ± 0.008361	(<MDA)
2	5.047 ± 0.01056	0.6063 ± 0.002443	0.2981 ± 0.0008129	0.1693 ± 0.0006126	6.121 ± 0.001088	(<MDA)
3	5.262 ± 0.02195	0.6215 ± 0.001739	0.2834 ± 0.0006859	0.1314 ± 0.0005224	6.298 ± 0.02203	(<MDA)
4	4.683 ± 0.01019	0.7587 ± 0.001767	0.4717 ± 0.001078	0.2922 ± 0.0006599	6.205 ± 0.01042	(<MDA)
5	2.401 ± 0.01047	0.8165 ± 0.003162	0.5846 ± 0.002197	0.3040 ± 0.0007663	4.106 ± 0.01181	(<MDA)

Table 6
Radioactivity concentration of extracted tritium for each 3 h interval at 400 °C.

Sample group	Radioactivity concentration of extracted tritium before heating for 14 h (Bq/g)					Residual tritium radioactivity concentration after heating for 14 h (Bq/g)
	(Average ± SD)					
	0–3 h (at 400 °C)	3–6 h (at 400 °C)	6–9 h (at 400 °C)	9–14 h (at 600 °C)	Total	
1	4.115 ± 0.01454	0.4800 ± 0.001462	0.3913 ± 0.0007630	0.1721 ± 0.0004325	5.158 ± 0.01463	(<MDA)
2	4.834 ± 0.008223	0.5449 ± 0.001135	0.2549 ± 0.0007725	0.1034 ± 0.0004365	5.737 ± 0.008349	(<MDA)
3	5.059 ± 0.01565	0.5012 ± 0.001513	0.2736 ± 0.0004808	0.0888 ± 0.0003058	5.922 ± 0.01574	(<MDA)
4	4.496 ± 0.02178	0.5922 ± 0.001750	0.3879 ± 0.001729	0.1094 ± 0.0002821	5.585 ± 0.02192	(<MDA)
5	4.202 ± 0.01156	0.6881 ± 0.002912	0.4404 ± 0.001020	0.1534 ± 0.0004269	5.484 ± 0.01197	(<MDA)

heating temperature; the values for the second interval were 0.6729 ± 0.001721 , 0.9526 ± 0.003187 , 1.046 ± 0.003410 , 1.165 ± 0.002951 , and 0.8801 ± 0.02189 Bq/g, respectively. Furthermore, for the third 3-h interval (6–9 h), the concentrations (0.4644 ± 0.001289 , 0.5847 ± 0.001694 , 0.4919 ± 0.001783 , 0.7289 ± 0.001655 , and 0.5597 ± 0.002265 Bq/g, respectively) were the lowest. The tendency was similar for other temperature conditions, as can be observed from Tables 3–6. Thus, it can be concluded that most of the tritium was extracted during the first 3 h interval, and the amount of extracted tritium decreased over time.

Tritium extraction rates until 9 h of heating at 200 °C were lower

than 95% for all sample groups (see Table 7). For sample groups 1 and 5, after heating for 9 h, the subsequent heating for 5 h at 600 °C showed tritium extraction values of 0.5997 ± 0.001482 and 0.7026 ± 0.001201 Bq/g, respectively. These values were higher than those for the third 3-h interval, which were 0.4644 ± 0.001289 and 0.5597 ± 0.002265 Bq/g, respectively. This shows that although the heating duration was increased beyond 3 h at 200 °C, tritium could not be fully extracted. At 250 °C (Table 3), the tendencies were similar to those shown in Table 2. However, the tritium extraction rate did not reach 95%. The standard deviation of tritium extraction rates between cement mortar samples was higher at 200 °C than at

Table 7
Maximum and average tritium extraction rate (%) for 9 h interval at each temperature in all sample groups (from group 1 to 5).

Tritium extraction rate (%)	Heating temperature (°C)				
	200	250	300	350	400
Average ± SD	90.99 ± 1.602	86.43 ± 2.457	96.67 ± 0.6855	95.74 ± 1.852	97.72 ± 0.6816
Maximum	93.18	90.91	97.90	97.67	98.54

250 °C, as shown in Table 7. Subsequently, the tritium extracted by heating for 5 h at 600 °C increased to 0.8920 ± 0.002809 , 0.8757 ± 0.002738 , 0.5917 ± 0.001065 , 0.9088 ± 0.002394 , and 1.658 ± 0.004763 for all the sample groups, similar to the observations made for the 200 °C sample. This indicates that when the temperature was maintained and the heating duration was increased, although there was an increase in tritium extraction, the tritium extraction rate gradually decreased. As the amount of tritium in each cement mortar sample was different, it cannot be concluded that the tritium extraction efficiency attained by heating at 250 °C was worse than that at 200 °C. However, based on the above observations, it can be stated that tritium was not extracted at these temperatures even after 9 h of heating, and remained within the cement mortar sample. This also indicates that the amount of tritium extracted from the cement mortar sample at a constant heating temperature was not proportional to the heating duration for temperatures lower than 250 °C.

3.4. Effect of temperature

Table 4 lists the radioactivity concentration of the extracted tritium at 300 °C. For the first 3 h of heating, the values were 4.037 ± 0.01048 , 4.712 ± 0.01608 , 5.073 ± 0.01743 , 4.474 ± 0.01454 , and 4.651 ± 0.01556 Bq/g for sample groups 1 to 5, respectively. The values decreased for the second and third intervals, as the tendency on Tables 2 and 3, respectively. Unlike the observations made from Tables 2 and 3, in Table 4, the radioactivity concentration of the extracted tritium when heated at 600 °C for 5 h was lower than that for the third 3-h interval. This tendency extends to higher temperatures, as can be observed from Tables 5 and 6. The radioactivity concentrations of the extracted tritium at 350 °C (see Table 5) for the first 3-h interval were 4.492 ± 0.007964 , 5.047 ± 0.01056 , 5.262 ± 0.02195 , 4.683 ± 0.01019 , and 2.401 ± 0.01047 Bq/g for sample groups 1 to 5, respectively. The values decreased for the second and third interval, but were higher than those for the final 5-h interval (0.2498 ± 0.001020 , 0.1693 ± 0.0006126 , 0.1314 ± 0.0005224 , 0.2922 ± 0.0006599 , and 0.3040 ± 0.0007663 Bq/g, respectively). Similarly, at 400 °C (see Table 6), the radioactivity concentration values of the extracted tritium for the first 3 h were 4.115 ± 0.01454 , 4.834 ± 0.008223 , 5.059 ± 0.01565 , 4.496 ± 0.02178 , and 4.202 ± 0.01156 Bq/g for sample groups 1 to 5, respectively, which gradually decreased, as seen in Tables 2–5. Although the tritium extraction rate for the 3-h intervals gradually decreased, a notable increase in the temperature sensitivity of the tritium extraction rate was observed for temperatures from 300 °C.

Using equation (1) and the data from Table 2, the calculated average tritium extraction rate during the first 3 h (0–3 h) heating was 67.35% at a temperature of 200 °C. Further, this rate was 70.42%, 80.22%, 75.55%, and 81.31% at 250 °C, 300 °C, 350 °C, and 400 °C, respectively. A previous study using thermogravimetric analysis (TGA) showed that the hydration of natural gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) occurred in the temperature range of 131–245 °C [7]. At temperatures higher than 245 °C, a large mass loss due to dehydration was not observed. This indicates that gypsum, including HTO, can also be dehydrated in these temperature ranges. However, the tritium extraction rate did not reach 100% even at 350 °C in this study. The higher the heating temperature, the higher the tritium extraction rate, except at 350 °C. The extraction rate at a specific period simply denotes the ratio of the amount of tritium extracted during a specific heating time period to that extracted during the total 14 h of heating. As shown in Tables 4 and 5 for the first 3-h interval, unlike other sample groups, for sample group 5, the radioactivity concentration of the extracted tritium was 4.651 ± 0.01556 Bq/g at 300 °C, which was higher than the

2.401 ± 0.01047 Bq/g at 350 °C. The corresponding extraction rates were 78.98% at 300 °C and 58.46% at 350 °C, resulting in a lower average rate for the 350 °C case, as stated above. The difference in these rates was higher than 20%. However, the extraction rate over 9 h was 96.60% at 300 °C and 92.60% at 350 °C. Although the rate at 300 °C was still higher, the difference was approximately 4%. The increase observed in the tritium extraction rate for the 350 °C case from the first 3 h to the third 3 h interval was 34.14%, which was significantly higher than the 17.62% increase observed for the 300 °C case. As mentioned in previous study, although there were same hydrated materials, the decomposition temperature is not just one point. Decomposition temperature has some specific range. If cement sample was homogeneous, the decomposition reaction of hydrated material may occur in one temperature. However, non-homogeneous distribution of hydrated material in cement mortar sample may cause this difference. The tritium radioactivity (Bq) for the first 3 h of Table 5 was higher than those of Table 4. This means that although the radioactivity of extracted tritium is high, if the total tritium in the cement mortar sample is large, the tritium extraction rate can be evaluated as low, and the standard deviation of tritium extraction rates in cement mortar samples can be large. By comparing Tables 2 and 3, although most of the tritium radioactivity (Bq) for the first 3 h of Table 3 were higher than those of Table 2, in some cases, tritium extraction was higher at a temperature of 200 °C. Indeed, although the samples exhibited the same gypsum crystals including tritium, all tritium was not extracted at one temperature but over a wide temperature range [21,22]. The maximum temperature range does not indicate the fastest tritium extraction rate, but simply means that until the temperature reaches the maximum point, tritium is still released. This means that before the heating temperature reaches the maximum point temperature range, an increase in the tritium extraction rate with an increase in the heating temperature cannot be determined. Although the tritium extraction rate for the first 3 h was relatively low, presumably because of the difference between the core and the surface distribution of tissue free water tritium by physical bonding, the tritium extraction rate may significantly increase with heating duration at this temperature.

Using equation (1), the tritium extraction rates averaged for all the sample groups (1–5) after 9 h of heating at each temperature were calculated and are listed in Table 7. The maximum extraction rates were 97.90%, 97.67%, and 98.54% at 300 °C, 350 °C, and 400 °C, respectively. At temperatures of 200 °C and 250 °C, owing to the relatively large amount of residual tritium in the cement mortar samples, the maximum extraction rates were 93.18% and 90.91%, respectively. However, as stated earlier, at temperatures higher than 300 °C, the amount of residual tritium was lower than that at temperatures of 200 °C and 250 °C, thus, the extraction rates were higher than 95%. The highest rate was observed at 400 °C. Although the temperature increased from 200 °C to 250 °C, the extraction rate decreased. This phenomenon was also observed when the temperature was increased from 300 °C to 350 °C. However, as all the other extraction rates were higher than 95% for temperatures above 300 °C, this phenomenon was not significant.

3.5. Mixture homogeneity test

The total radioactivity concentrations of tritium extracted from the same cement mortar sample prepared by the same manufacturing process were observed to be different owing to the non-homogeneous distribution and unequal evaporation of tritium from the cement mortar sample. In a specific cement mortar sample, if tritium is distributed more centrally than at the surface, it may not be extracted well at temperatures ranging from 200 °C to 250 °C. In Tables 2 and 3, the tritium concentrations extracted from

Table 8
Maximum and average tritium extraction rate (%) for 9 h interval at each temperature in 25 samples made from one large cement mortar dough.

Tritium extraction rate (%)	Heating temperature (°C)				
	200	250	300	350	400
Average ± SD	79.26±4.239	84.94±3.738	89.46±1.773	95.76±1.521	98.43±0.4109
Maximum	84.62	88.43	91.86	97.09	98.92

most of the sample groups for the first 3 h of heating were higher at 250 °C. However, if a higher amount of tritium was present in the cement mortar sample used in the 250 °C experiment and was more concentrated within the core of the sample, the tritium extraction rate could be lower even with an increase in the temperature. Such a non-homogeneous distribution, leaving a higher amount of residual tritium within the cement mortar sample, caused an observation at a temperature of 350 °C, where the extraction rate for the first 3-h interval was significantly different. However, when the heating duration was increased to 9 h, the difference became insignificant.

When cement mortar sample was heated at temperature of 200 °C for 3 h, minimum tritium extraction rate was 63.93%. It was expected that if heating duration is increased, tritium extraction rate will be increased. However, although a 9-h heating duration was adopted, at lower temperatures of 200 °C to 250 °C, the tritium extraction rate was not largely increased. In other words, simply increasing the heating duration did not significantly affect the tritium extraction rate. As observed for the 200 °C and 250 °C cases, the radioactivity concentration of the extracted tritium for consecutive 3 h intervals (0–3, 3–6, 6–9 h) decreased, but subsequently increased when the temperature was raised to 600 °C. Therefore, the heating duration longer than 9 h was meaningless.

Although the w/c ratio was the same for all the sample groups, as the mass of the materials (HTO and cement) to be mixed for each sample group increased, the amount of mixture varied. Therefore, differences may have occurred during the evaporation process, causing the radioactivity concentration of the extracted tritium per unit mass to be significantly different for each cement mortar sample. Therefore, this difference may not be indicated as the cause of tritium extraction rate decrease even if the temperature is increased.

To confirm this proposition, a mixture was prepared using 100 g of HTO and 500 g of cement mortar powder. The mixture was cut to a size for loading on a sample boat in a high-temperature furnace. A total of 25 cement mortar samples were prepared and heated at temperatures of 200 °C, 250 °C, 300 °C, 350 °C, and 400 °C for 9 h (5 samples for each temperature). The tritium extraction rates calculated after additional heating at 600 °C for 5 h are listed in Table 8. The rates corresponding to 9 h of heating were 79.26% ± 4.239, 84.94% ± 3.738, 89.46% ± 1.773, 95.76% ± 1.521, and 98.43% ± 0.4109, respectively. With an increase in the heating temperature, the average extraction rate increased, but the standard deviation decreased. Comparing the standard deviation of the tritium extraction rate, the maximum tritium extraction rate at a lower temperature was in some cases higher than the minimum tritium extraction rate at a higher temperature. This demonstrates that with samples made from one large cement mortar mixture, the effect of the non-homogeneous distribution of tritium inside the samples on the tritium extraction rate decreases.

3.6. XRD analysis

The existence of tritium in cement mortar cannot be determined by radioactive analysis using LSC. It should be confirmed whether diverse hydrated materials are not decomposed. Although the

hydrated material is decomposed, if there is no tritium-based hydrated material in the cement sample mortar, tritium would not be detected. In addition, the amount of tritium-based hydrated material in the cement sample mortar is very small compared to that in the hydrogen-based hydrated material, and extraction may not be possible in this case. Therefore, comparing the results from XRD analysis with the results from LSC analysis, the decomposition of hydrated material in the cement mortar sample and the radioactivity concentration of the remaining tritium in the cement mortar sample according to the heating temperature should be considered together. Figs. 2–5 show the XRD analysis results for the main hydrated materials in the cement mortar sample at temperatures of 400, 450, 600, and 900 °C, respectively. CaCO₃, C–S–H, Ca(OH)₂, and CaSO₄·2H₂O were used as target materials. In a previous study, considering the decomposition temperature range of CaSO₄·2H₂O, Ca(OH)₂, and C–S–H, the heating temperatures in this study were set to 400, 450, 600, and 900 °C [17–19]. The peak points of CaCO₃ and CaSO₄·2H₂O at approximately 29.5° in the 2θ range almost coincide. Thus, although there was the decomposition of CaSO₄·2H₂O at temperatures of 400, 450, and 600 °C, using only XRD analysis results cannot provide accurate information about the material related to a peak [7,21,22]. As mentioned earlier, the decomposition temperature range of gypsum crystal water was 200–450 °C. Therefore, from Figs. 2–4, most of material of peak in 29.5° in the 2θ range should be CaCO₃. It was not observed an efficient decrease in the peak count of 29.5° in the 2θ range from Figs. 2 to 3. It should be considered that the decomposition start temperature of CaCO₃ by TGA analysis is higher than 650 °C [21].

The peak of the C–S–H material, estimated to be jennite, and the peak of CaSO₄·2H₂O almost coincided at approximately 32° in the 2θ range [7,23]. Considering that the decomposition temperature range of C–S–H (jennite) is approximately 500–700 °C, it was also observed that there was a decrease in the peak at 32°, as shown in Fig. 4 [24]. Therefore, from Figs. 2–4, most of material of peak in 32° in the 2θ range should be C–S–H.

In the case of Ca(OH)₂, when the heating temperature increased from 400 to 450 °C, there was a slight decrease corresponding to (Ca(OH)₂ → CaO + H₂O). When the heating temperature was increased to 600 °C, there were few calcium hydroxides. At 900 °C in Fig. 5, CaCO₃ and C–S–H decomposed and decreased. Based on previous studies and XRD analysis results, CaSO₄·2H₂O and Ca(OH)₂ were evaluated as decomposed. As shown in Table 9, the radioactivity concentration from CaSO₄·2H₂O was the highest at 4.320 ± 0.03052 Bq/g. This was 97.36% of the total probable radioactivity concentration in the cement mortar sample. From these results, it can be explained that the peak points at approximately 29.5° and 32° in the 2θ range at 400 °C were caused by Ca(OH)₂ and C–S–H. Although the peak counts of Ca(OH)₂ slightly decreased when the temperature was increased from 450 to 600 °C, there was a considerable decrease in the peak of C–S–H. Therefore, from Table 9, the radioactivity concentration at a temperature of 600 °C is expected to be caused by C–S–H. Even at 900 °C there was a decrease in the peak of C–S–H, but the extracted radioactivity concentration was lower than the MDA value. Tritium-based C–S–H was in a small concentration and almost decomposed at 600 °C.

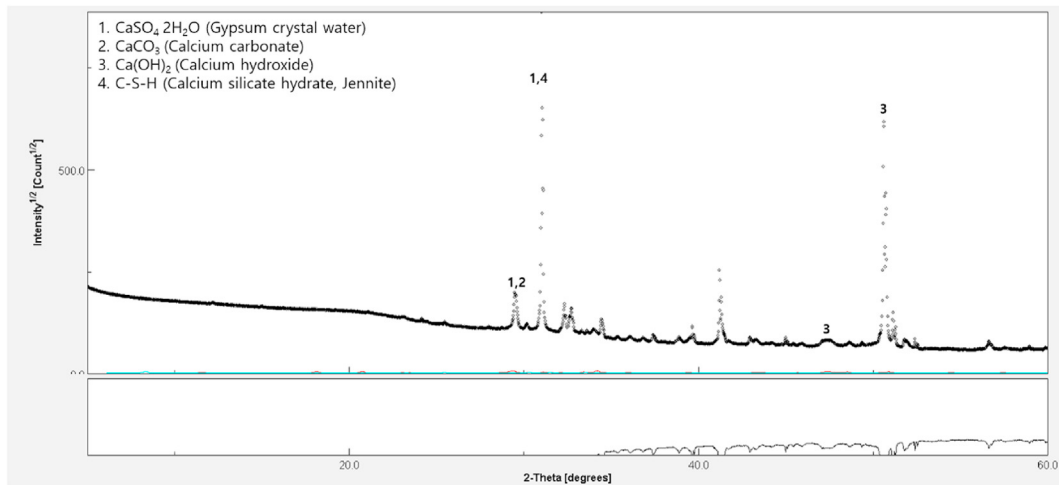


Fig. 2. XRD analysis results of cement mortar sample at the temperature of 400.°C

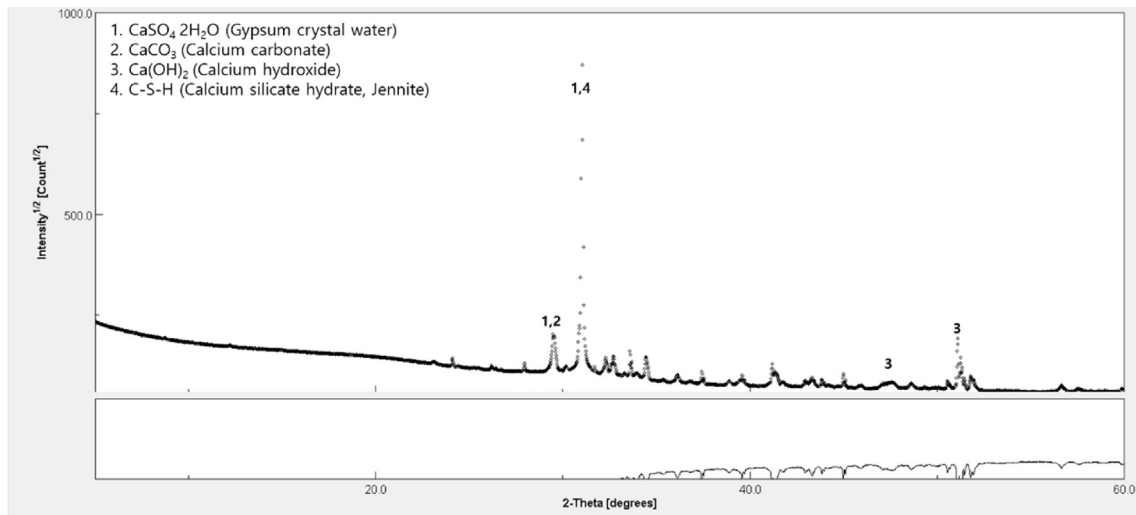


Fig. 3. XRD analysis results of cement mortar sample at the temperature of 450.°C

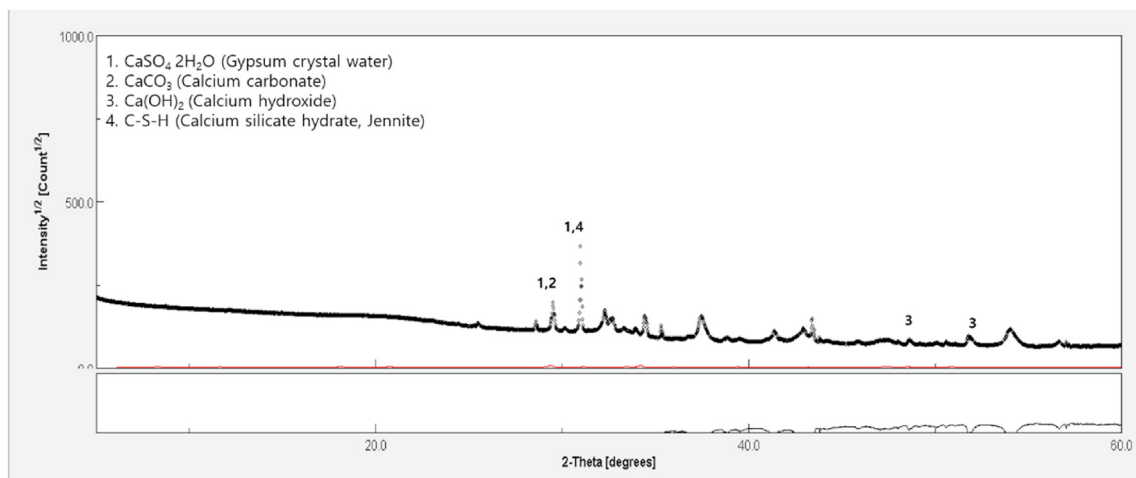


Fig. 4. XRD analysis results of cement mortar sample at the temperature of 600.°C

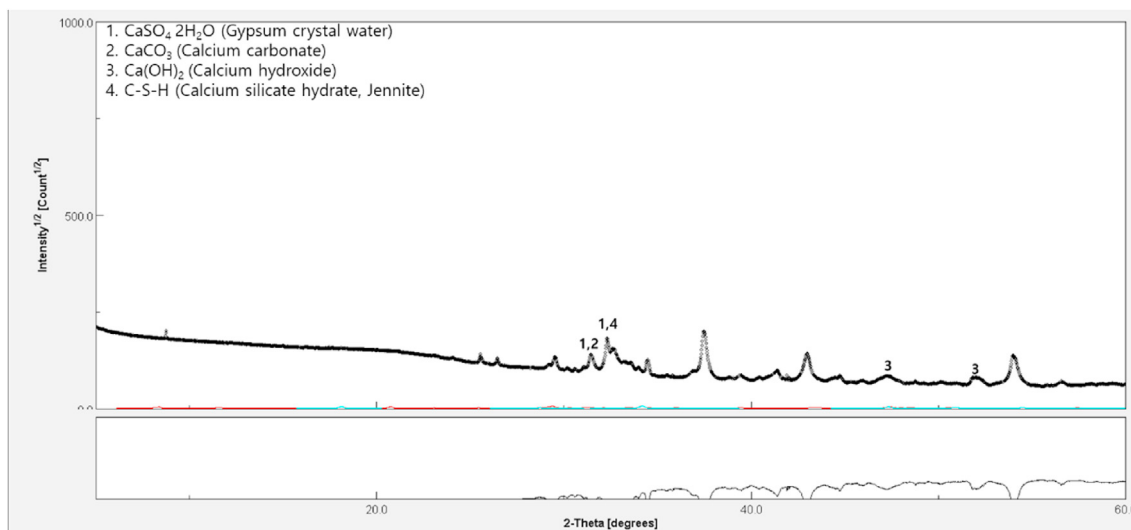


Fig. 5. XRD analysis results of cement mortar sample at the temperature of 900 °C

Table 9

Radioactivity concentration of extracted tritium for continuous temperature rise.

	Heating temperature (°C)			
	400	450	600	900
Radioactivity concentration (Bq/g)	4.320	0.1087	0.005758	(<MDA)
Average ± SD	± 0.03052	± 0.0004019	± 0.00002519	
Probable decomposed material	CaSO ₄ · 2H ₂ O	CaSO ₄ · 2H ₂ O Ca(OH) ₂	C–S–H	C–S–H

4. Conclusions

When HTO is mixed with cement, the hydrated materials are CaSO₄ · 2H₂O, Ca(OH)₂, and C–S–H. By XRD and LSC analyses, it was confirmed that most of the tritium-based hydrate material in the cement mortar sample was CaSO₄ · 2H₂O. Although the decomposition temperature range of CaSO₄ · 2H₂O is 200–400 °C, if the heating temperature is lower than 400 °C, tritium cannot be completely extracted. Tritium inside the cement mortar sample could not be completely extracted at a relatively low temperature of 200 °C, because most of the tritium was extracted in the first 3 h, and the tritium extraction rate for the next 3 h gradually decreased. The increase in heating duration was not the dominant variable for the tritium extraction rate when the heating temperature was relatively low in the decomposition temperature range of CaSO₄ · 2H₂O. When the amount of tritium in the cement mortar sample is very small, the decrease in hydrated material in the XRD or TGA analysis results does not exactly mean tritium extraction. If the decomposition of various hydration materials occurs simultaneously, several analyses should be used to track the source of tritium extraction. Radioactive analysis by comparison with the MDA value can have advantages for low radioactivity concentration in samples.

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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