



Original Article

Analytical method for determination of ^{41}Ca in radioactive concreteYong-Jin Lee ^{a, b}, Jong-Myoung Lim ^a, Jin-Hong Lee ^b, Sang-Bum Hong ^c, Hyuncheol Kim ^{a, *}^a Nuclear Emergency and Environmental Protection Division, Korea Atomic Energy Research Institute, 989-111 Deadeok-daero, Yuseong-gu, Daejeon, 34057, Republic of Korea^b Environmental Engineering, Chung-Nam University, 99 Daehak-ro, Yuseong-gu, Daejeon, 34134, Republic of Korea^c Decontamination & Decommissioning Research Division, Korea Atomic Energy Research Institute, 989-111 Deadeok-daero, Yuseong-gu, Daejeon, 34057, Republic of Korea

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ABSTRACT

The analysis of ^{41}Ca in concrete generated from the nuclear facilities decommissioning is critical for ensuring the safe management of radioactive waste. An analytical method for the determination of ^{41}Ca in concrete is described. ^{41}Ca is a neutron-activated long radionuclide, and hence, for accurate analysis, it is necessary to completely extract Ca from the concrete sample where it exists as the predominant element. The decomposition methods employed were the acid leaching, microwave digestion, and alkali fusion. A comparison of the results indicated that the alkali fusion is the most suitable way for the separation of Ca from the concrete sample. Several processes of hydroxide and carbonate precipitation were employed to separate ^{41}Ca from interferences. The method relies on the differences in the solubility of the generated products. The behavior of Ca and the interfering elements such as Fe, Ni, Co, Eu, Ba, and Sr is examined at each separation step. The purified ^{41}Ca was measured by a liquid scintillation counter, and the quench curve and counting efficiency were determined by using a certified reference material of known ^{41}Ca activity. The recoveries in this study ranged from 56 to 68%, and the minimum detectable activity was 50 mBq g^{-1} with 0.5 g of concrete sample.

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1. Introduction

Nuclear power plants (NPPs) have been both sources of sustainable electricity and enormous contributions to modern society. As of May 2020, the total number of reactors in operation across the world is 441; among them, the number of reactors over the age of 20 years is 351, and these will enter the decommissioning phase in the next 20 years [1]. The decommissioning of NPPs presents enormous challenges, one of which is the management of radioactive wastes. Depending on the levels generated, nuclear wastes are treated in several ways, such as volume reduction, incineration, disposal, and reuse [2]. Before these treatment methods, however, the radioactive waste must be subjected to radiological characterization.

Of specific interest is the evaluation of the waste for the presence of the difficult to measure (DTM) nuclear inventory, which are typically the radionuclides with long half-life. The inventory of the radionuclides to be declared is numerous and varied, and scaling

factor methodologies are employed to estimate the radioactivity of the DTM radionuclides by their correlation with other key radionuclides, the levels of which are easily determined by gamma spectrometry without the need for complex radiochemical analysis. The scaling factor method is hence very useful for the declaration of the radioactive wastes generated during the decommissioning. However, the radiochemical analysis of DTM radionuclides inevitably requires the development of more reliable scaling factors to ensure the safe and cost-effective disposal of decommissioning wastes.

Concrete wastes are the dominant matrices during the decommissioning of NPPs. During the decommissioning of the Maine Yankee NPP, concrete wastes amounted to 64% of the total radioactive wastes [3]. Among concrete wastes generated during decommissioning, those generated from the reactor containment building and the reactor bio-shield are voluminous. Considering that the main element in concrete is Ca, ^{41}Ca is generated from neutron activation due to the exposure of the concrete during the plant lifetime, and the radionuclide of ^{41}Ca is detected in all radioactive concrete wastes that originate from the containment building parts and the reactor bio-shields. ^{41}Ca , a long-lived

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radionuclide with a half-life of 99.4×10^3 years [4], is a pure beta emitter that requires radiochemical analysis. In addition, concrete is composed of other elements, such as iron, cobalt, and nickel, and other impurities, owing to which radioactive concrete wastes typically contain high levels of the neutron-activated radionuclides, including ^{55}Fe , ^{59}Ni , ^{63}Ni , ^{58}Co , ^{60}Co , and ^{152}Eu [5].

While the fission products, such as ^{90}Sr , are deposited on the surface of the concrete sample, the neutron-activated radionuclides exist inside the sample. Therefore, the complete extraction of the radionuclides of interest from the sample matrices is necessary for ensuring accurate detection of their levels. Furthermore, the level of the target radionuclide depends on pretreatment methods, such as the extraction rate. For the determination of radionuclides in various types of solid samples, several pretreatment methods were studied, including acid leaching [6,7], microwave digestion [8] and alkali fusion [9,10]. For some analytes, the complete dissolution of the sample is not necessary if the radionuclides of interest can be quantitatively leached from the sample, such as in the case of ^{90}Sr in decommissioned wastes (cements and soils) [11,12]. However, the neutron-activated radionuclides and some natural radionuclides, such as thorium isotopes, require the complete dissolution of the sample for quantitative analysis. Concrete is a highly complex matrix, and the removal of interferences in concrete is highly challenging. Extraction chromatography has been widely employed for the purification of radionuclides, such as ^{90}Sr , ^{55}Fe , ^{59}Ni , and actinides. However, there is no suitable extraction chromatography-based method for the purification and analysis of ^{41}Ca . The basic principle involved in the purification of Ca is the difference of its solubility products with that of the other interfering products [6,9]. The solubility of $\text{Ca}(\text{OH})_2$ is 3 orders lower than that of $\text{Sr}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$. At higher concentrations of the hydroxide ion, Ca is precipitated, whereas Sr exists as an ion in the supernatant ([13]). Meanwhile, Fe, Ni, Co, and Eu can be separated from Ca by varying the pH of the medium. Recently, extraction chromatography has been widely used for the separation of radionuclides. However, the separation of Ca is not feasible with the extraction chromatography approach as it requires repeated precipitations for effective separation.

In general, long-lived radionuclides can be measured by mass spectrometry because the specific activity for them is inversely proportional to the half-life. Therefore, mass spectrometry is a more sensitive measurement tool rather than radiometric analysis [14,15]. Inductively coupled plasma mass spectrometry (ICP-MS) is the most widely used mass spectrometry for the determination of elements in trace concentration and long-lived radionuclides [16–18]. However, the main issue in regard to determination of radionuclides using ICP-MS is the existence of isobaric interferences [18]. ICP-MS is not suitable for the analysis of ^{41}Ca due to the presence of tailing interferences from ^{40}Ca , ^{40}Ar , and other nuclides, as well as the interference from the isobaric effect of ^{41}K [15]. However, the determination of ^{41}Ca is available through accelerator mass spectrometry (AMS) and resonance ionization mass spectrometry RIMS [7,19–21]. AMS is the most sensitive mass spectrometric technique capable of isotope ratio 10^{-12} to 10^{-15} for $^{41}\text{Ca}/^{40}\text{Ca}$ [7,19,21]. RIMS is less sensitive, capable of measuring $^{41}\text{Ca}/^{40}\text{Ca}$ in the range of 10^{-10} to 10^{-11} [19,20]. However, this approach is not suitable for the routine measurement of ^{41}Ca in regard to NPP-decommissioning waste due to difficulties in accessing the instrumentation, and high operational costs of the analysis. Furthermore, considering the vast number of samples generated during the decommissioning of nuclear facilities, this mass spectrometric technique is not practical despite its sensitivity in determination of the presence of ^{41}Ca .

Calcium-41 emitting X-rays and Auger electrons (0.3–0.6 keV) through decay to the ^{41}K ground state by electron capture is

measurable by X-ray spectrometry and liquid scintillation counter (LSC). X-ray spectrometry is a simple method, but is not sensitive enough due to low counting efficiency (<0.08%) and low abundance of X-rays (11.4% for 3.31 keV) [15,18]. In comparison with X-ray spectrometry, the LSC technique shows higher counting efficiency. Due to the poor energy resolution of LSC and the low energy of Auger electron spectrum of ^{41}Ca , Calcium-41 should be completely separated from the sample matrix and any interfering radionuclides [18]. Therefore the complete chemical separation of calcium from the sample matrix and other interfering radionuclides, which is labor-intensive and time-consuming work, is inevitable [6,7,9,21]. In spite of the drawbacks of the LSC approach for the determination of ^{41}Ca , it is the most suitable and practical technique for measuring purified ^{41}Ca from concrete wastes due to the counting efficiency and accessibility of the LSC technique, which has been reported to be comparable to that of AMS and RIMS [7].

In this work, we developed an analytical method for the determination of ^{41}Ca in concrete. Three pretreatment methods, including acid leaching, microwave digestion, and alkali fusion were compared using NIST SRM (soil), to find the most suitable pretreatment method for extraction of the neutron-activated radionuclides from concrete samples. Using several hydroxide and carbonate-based precipitations, Ca from the concrete sample was separated from the sample matrix and interferences. We traced the interferences and Ca at each step to gain insights into the Ca chemistry and those of other interferences. The levels of ^{41}Ca were measured using LSC, and the quench curve of ^{41}Ca was determined using an IRMM ^{41}Ca reference material (Institute for Reference Materials and Measurements) of known ^{41}Ca concentration. The performance of the developed method was evaluated with a concrete sample spiked with a known level of ^{41}Ca .

2. Experimental

2.1. Reagents and apparatus

All chemicals were of analytical grade. Na_2CO_3 (Sigma-Aldrich), NaOH (Yakuri), NH_4OH , HNO_3 , and HCl (Merck) were purchased from commercial sources. Ni, Co, Eu, Sr, and Ba solutions (AccuStandard, KRIAT) were used as hold-back carriers. The reagents were diluted to the desired concentrations using deionized water (DIW, MilliQ-Plus, 18 $\text{M}\Omega\cdot\text{cm}$, Merck Millipore, Burlington, Massachusetts, USA). Concrete samples were milled (8530 Enclosed Shatterbox, SPEX) before the analysis. NIST (National Institute of Standard and Technology) SRM (Standard Reference Material) 2709a (San Joaquin Soil) was used for comparison of the pretreatment methods for the extraction of Ca from the sample matrix. Microwave digestion (ETHOS EASY, Milestone) and alkali fusion (K2 PRIME, Katanax) were used as pretreatment techniques. The ^{41}Ca standard solution (IRMM-ERM-AE701) was purchased from the Institute for Reference Materials and Measurements (Geel, Belgium). The purified ^{41}Ca solution was mixed with Ultima Gold AB in a polyethylene vial and was analyzed with a liquid scintillation counter (LSC, Quantulus 1220, PerkinElmer). The concentration of the stable ion was measured using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy, Spectro).

2.2. Extraction of Ca from sample matrix

NIST SRM 2709a with the known concentration of Ca was used for comparing the extraction rate of Ca from the solid sample using acid leaching, microwave digestion, and alkali fusion techniques. Acid leaching is a method of extracting target nuclides from a sample using strong acid, which makes it difficult to extract radionuclides existing inside of the sample. Microwave digestion is

usually accomplished by exposing a sample to a strong acid in a closed vessel and raising the pressure and temperature through microwave irradiation, which is slightly more powerful digestion method rather than the typical acid leaching approach. Alkali fusion is a method of converting poorly soluble salts that are not completely decomposed to soluble salts by reacting with an acidic or alkali flux at high temperature. One gram of SRM 2709a was applied in each technique in triplicate. For the acid leaching test, 1 g of SRM 2709a was mixed with 10 mL of aqua regia (mixture of HCl and HNO₃, volume ratio of 3:1) in a Teflon beaker, and the mixture was refluxed at 180 °C for 4 h, followed by centrifugation. An aliquot of the supernatant was diluted with DIW for the ICP-OES measurement. In the microwave digestion method, 0.25 g of SRM 2709a was placed in the vessel provided by the manufacturer, and was mixed with 10 mL of aqua regia. It was then conducted at 200 °C for 35 min with 1800 W of power. In regard to the application of 1 g of the sample, four vessels containing 0.25 g each were prepared and then mixed together. The resulting mixture was filtered through a 0.45 µm syringe filter and then diluted for the Ca analysis with ICP-OES. For the alkali fusion test, 1.5 g of LiBO₂ and 0.3 g of LiBr were mixed with 1 g of SRM 2709a in a platinum crucible. The mixture was heated at 1000 °C for 30 min. Upon fusion, the melt was mixed with 60 mL of 0.7 M HNO₃ [22], and the obtained solution was filtered and subjected to ICP-OES measurement.

2.3. Chemical separation

2.3.1. Removal of metals from Ca by hydroxide and carbonate precipitations

We prepared five samples of concrete, consisting of 0.5 g per sample. Each concrete sample was digested using the above-mentioned alkali fusion method. An aliquot was taken from the mixture of the melt, and 0.7 M HNO₃ was added, followed by a dilution with 0.4 M HNO₃ at various concentrations from 30 to 1000 times for the determination of the initial concentration of Fe, Co, Ni, Eu, and Ca. Two mg of Co, Ni, Eu, Ba, and Sr were added as carriers, because its concentration is too low to precipitate. Depending on the pH value and the number of the precipitated hydroxide, the recovery of Ca and the removal rate of the interferences, such as Fe, Co, Ni, and Eu, were evaluated. The pH of the five samples in the first set was adjusted to 5, 6, 7, 8, and 9, respectively, using 10 M NaOH. The supernatant was separated from the precipitate by centrifugation. An aliquot from the supernatant was measured using ICP-OES to estimate the recovery of Ca and the removal rate of other cations of interest. The obtained precipitates from this single-precipitation step were dissolved with 5 mL of 3 M HNO₃ again, and the pH values of the solutions were adjusted to the above-mentioned values from 5 to 9 using NaOH. The supernatants were separated by centrifugation. The supernatants were separated from the solution and mixed with the previously prepared supernatant from the single precipitation step. The concentration of Ca and the other cations were analyzed with ICP-OES. The recovery of Ca and removal rate of interfering elements were estimated at different pH levels and the number of precipitation (single-precipitation and double-precipitation).

After hydroxide precipitation, the supernatant was reduced by evaporation to approximately 10 mL and transferred to a 50-mL conical tube. The pH of the solution was adjusted to 10 using a 25% NH₄OH solution, and 500 mg of Na₂CO₃ was added and mixed using a Vortex mixer. The solution was placed in a bath at 90 °C for 30 min, and the mixture was centrifuged. After separation of the supernatant, the precipitate was dried at 80 °C. The obtained precipitate was dissolved in 5 mL of 3 M HNO₃. The measurement of Ca and other metal ions was performed using ICP-OES after dilution of

the samples. An aliquot of the supernatant was used for the measurement of Ca and other metal ions after dilution.

2.3.2. Separation of Ca from Sr and Ba

Six samples containing 100 mg of Ca and 10 mg each of Sr and Ba were prepared in 20 mL of DIW. The concentration of NaOH in each sample was adjusted to between 0.3 and 2.0 M (0.3, 0.5, 0.7, 1.0, 1.5, 2.0 M) by the addition of NaOH powder. The samples were mixed thoroughly using a Vortex mixer and placed in the 90 °C bath for 30 min. The supernatant was removed by centrifugation, and the precipitate was dissolved in 5 mL of 3 M HNO₃. The levels of Ca, Sr, and Ba were measured using ICP-OES after the dilution. NaOH powder was used for adjusting the concentration of NaOH in the solution to between 0.3 and 2.0 M. The above-mentioned process was repeated thrice. The concentrations of Ca, Sr, and Ba present in each of the solutions produced by the dissolution of the precipitate at each step were measured by ICP-OES.

2.4. Determination of ⁴¹Ca by LSC

The purified ⁴¹Ca obtained from the developed method in this study was dissolved in 8 mL of 0.5 M HNO₃. It was then mixed with 12 mL of Ultima Gold AB in a 20-mL polyethylene vial. The measurement was conducted at C-14 mode and low biased of LSC (Quantulus 1220). The quench curve for ⁴¹Ca by LSC was determined using the standard solution (ERM-AE701/1) containing 6.39 ± 0.04 Bq g⁻¹ of ⁴¹Ca. The activity concentration of ⁴¹Ca in ERM-AE701/1 was calculated based on the half-life of ⁴¹Ca, [Ca] = 50 mmol g⁻¹, and the isotopic ratio of ⁴¹Ca/⁴⁰Ca (1.0114×10^{-6}) provided by IRMM. The Quenching is a phenomenon in which the intensity of light, that is, the number of photons, decrease in the path where light generated in a beta event goes to PMT. This occurs due to various mechanisms that interfere with the excitation of flour. An external standard method, SQP(E), was used to correct these phenomena [23]. We prepared the quenching standard sample, comprising of 3 Bq of the ⁴¹Ca standard by mixing 0.5 M HNO₃ with the Ultima Gold AB cocktail (PerkinElmer). Multiple quenching samples with the volume ratio of between 4:16 and 14:6 were prepared to obtain different quench levels. The external standard method SQP(E) by LSC was used to measure the quench level.

3. Results and discussion

The most notable difference of this study compared with existing articles is the explanation of chemistry at each separation step, including the behavior of Ca and other interferences. The commercialized instrument for alkali-fusion used for this separation scheme required modification in comparison to those used in previous studies.

3.1. Comparison of three pretreatment method

The neutron-activated radionuclides such as ⁴¹Ca require complete extraction from the sample matrix for their reliable analysis. NIST SRM soil, with the known concentration of stable Ca, was digested by acid-leaching, microwave digestion, and alkali fusion, respectively. Fig. 1 shows the results of the leaching efficiency of Ca from the sample depending on the pretreatment method employed. The acid-leaching and microwave digestion methods showed measured Ca values of 1.48 ± 0.03 wt% (Average, Avr ± Standard deviation, SD) and 1.55 ± 0.1 wt% (Avr ± SD), respectively. These results indicate that acid-leaching and microwave digestion are not suitable for ⁴¹Ca analysis in the solid sample, due to the insufficient extraction of Ca from the sample matrix.

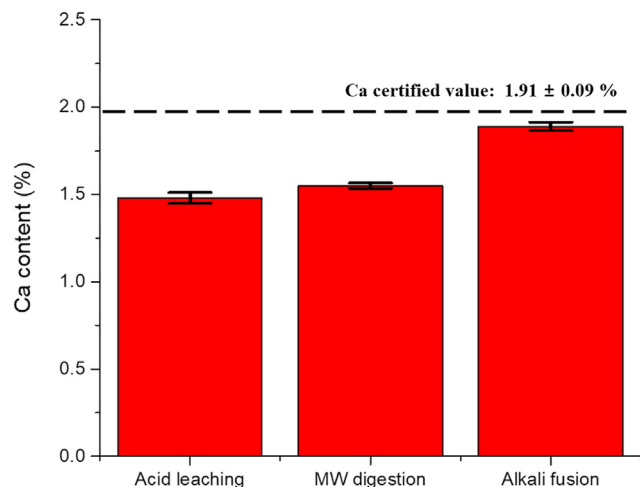


Fig. 1. Results of Ca extracted from NIST SRM 2709a depending on the pretreatment method (n = 3).

However, the alkali fusion method showed more comparable results with a measured Ca value of 1.89 ± 0.02 wt% (Avr \pm SD) in a comparison of the assigned Ca values (1.91 ± 0.09 wt%, Avr \pm uncertainty, $k = 2$). The relative deviation was calculated from a comparison of the measured and assigned Ca values. The acid leaching, microwave digestion and alkali fusion methods showed the relative deviations of -22.3 , -18.6 , and -0.8% , respectively. Among them, the alkali fusion method shows the smallest relative deviation, indicating that it is considered as a complete extraction.

Therefore, the alkali fusion method, due to its ability to completely decompose the matrix, is more suitable for the determination of neutron-activated radionuclides such as ^{41}Ca .

3.2. Separation of Ca from the transition metals

Fig. 2 shows the behavior of Ca and the other transition metals from the 0.5-g concrete sample at different pH levels. At pH 5, the recovery of Ca was 80% at the single-precipitation step, as a certain amount of Ca was lost with the other hydroxide precipitates. The recovery of Ca was studied as a function of the number of precipitations performed, and the decontamination factor of transition metals was determined through comparison with the initial concentration after two cycles of precipitations. The higher the pH, the

greater the loss of Ca, although the decontamination factor (DF) of the transition metals increased from 10 at pH 5 to 100 at pH 9 for Ni and Co, respectively. Furthermore, the recovery of Ca increased with the additional precipitation step. After the first precipitation step, the supernatant was separated from the precipitates containing some levels of Ca. These precipitates were dissolved in a weak acidic solution, and the pH of the solution was adjusted to the desired level. The supernatant of this solution was separated and mixed with the previously prepared supernatant. Upon carrying out double-precipitation steps, the recovery of Ca increased from 68 to 86% at pH 8. The optimum pH for the removal of the transition metals was determined as pH 8 due to the relatively high recovery of Ca and the successful removal of transition metals. At pH 8, the DF for Fe and Eu were over 500, but those for Ni and Co were approximately 35, significantly less than those of Fe and Eu (see Table 1).

The supernatant in which the Ni and Co remained was adjusted to pH 10 using NH_4OH and carbonate precipitation. Ni did not precipitate as $\text{Ni}(\text{OH})_2$, but as $\text{Ni}(\text{NH}_3)_2^{2+}$ by complexation with NH_3 . Because approximately 1% of Ni and Co remained in this carbonate precipitate in comparison to the initial amount, an additional process was required for obtaining a higher decontamination factor. Next, 4 mg of Co and Ni were injected as a hold-back carrier into a solution in which carbonate precipitates were dissolved in 3 M HNO_3 . The Ni and Co were separated from Ca by adjusting the pH of the solution to 9 using NaOH and hydroxide precipitation. The concentration of Co and Ni in the supernatant was thus reduced to less than 0.1% in comparison with the initial concentration (see Table 1). When Ni and Co were precipitated as hydroxides at pH 9 after the carbonate precipitation, 95% of the Ca existed as Ca^{2+} in the solution, compared to before the precipitation of Ni and Co hydroxide. Unlike the previous hydroxide precipitation, Ca did not co-precipitate with Fe, because Fe had already been removed from the sample.

Table 1
Concentration of elements selected at each separation step (unit: mg).

	Fe	Eu	Co	Ni
Initial concentration ^a	12.2	2.2	2.1	2.1
Double-precipitation at pH 8 ^b	0.007	0.005	0.05	0.06
Upon addition of hold-back carrier of Co, Ni ^c			4.1	3.9
Single-precipitation at pH 9 ^b			0.004	0.004

^a Addition of carrier after alkali fusion.

^b Concentration in the supernatant.

^c After carbonate precipitation.

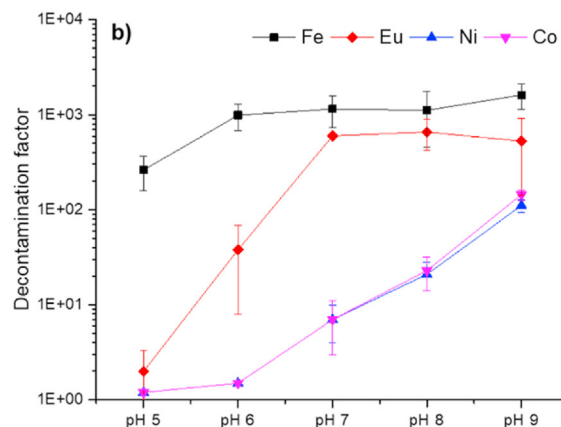
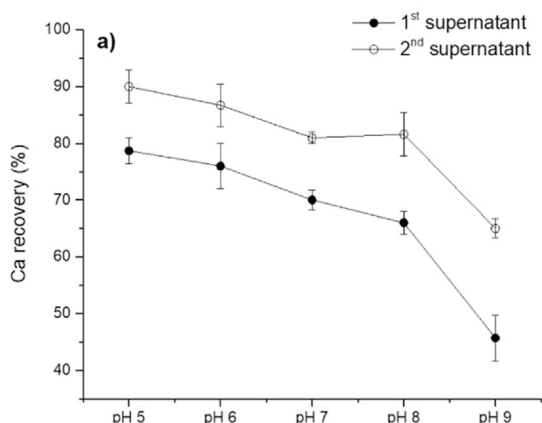


Fig. 2. Recovery of Ca (single and double precipitation) and removal of transition metal (double precipitation) from the concrete with varying pH (n = 3).

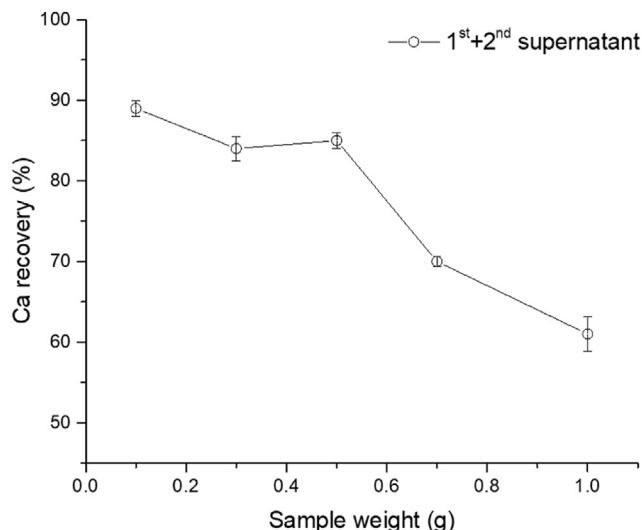


Fig. 3. Recovery of Ca from the concrete sample with varying weight at pH 8 (n = 3).

The complete decomposition of the sample is inevitable for carrying out the quantitative analysis of the neutron-activated radionuclides. However, the complete decomposition poses some challenges in the chemical separation process. Insoluble sulfates and silicates, which are the dominant species in concrete, were

converted to acidic soluble sulfates and silicates by alkali fusion [6]. Silicate and sulfate hinder the recovery of Ca at a high pH level. The optimum weight of the concrete sample for this separation method was determined by the alkali fusion with 0.1–1.0 g of concrete. Fig. 3 shows the recovery of Ca from the concrete sample with two-steps of hydroxide precipitation at pH 8. The results indicate that the higher the amount of the concrete, the lower the Ca recovery. The recovery of Ca was approximately 89 ± 1% (Avr ± SD) for 0.1 g of the concrete sample and reduced by 61 ± 2% (Avr ± SD) for 1.0 g of the sample. 1 g of the concrete was completely decomposed by alkali fusion, but the concentration of the interferences during the recovery of Ca increased concurrently. By considering the lower MDA (Minimum Detectable Activity) and higher recovery of Ca, the optimal concrete sample weight for the developed separation method was determined to be 0.5 g.

3.3. Purification of Ca from alkali earth metal by hydroxide precipitation

The chemical behavior of Sr and Ba is similar to that of Ca. ⁹⁰Sr and ¹⁴⁰Ba are beta emitters and hence interfere with the measurement of ⁴¹Ca by LSC. The solubility product constants of Ca(OH)₂ is 100–1000 times lower than that of Ba(OH)₂ and Sr(OH)₂. In regard to the 0.5 M NaOH solution, 97% of Ca precipitated as Ca(OH)₂, but approximately 1% of Ba and 2% of Sr remained with the Ca(OH)₂ precipitate (Fig. 4). To further remove Ba and Sr, the Ca(OH)₂ precipitate was dissolved in 3 M HNO₃, and the

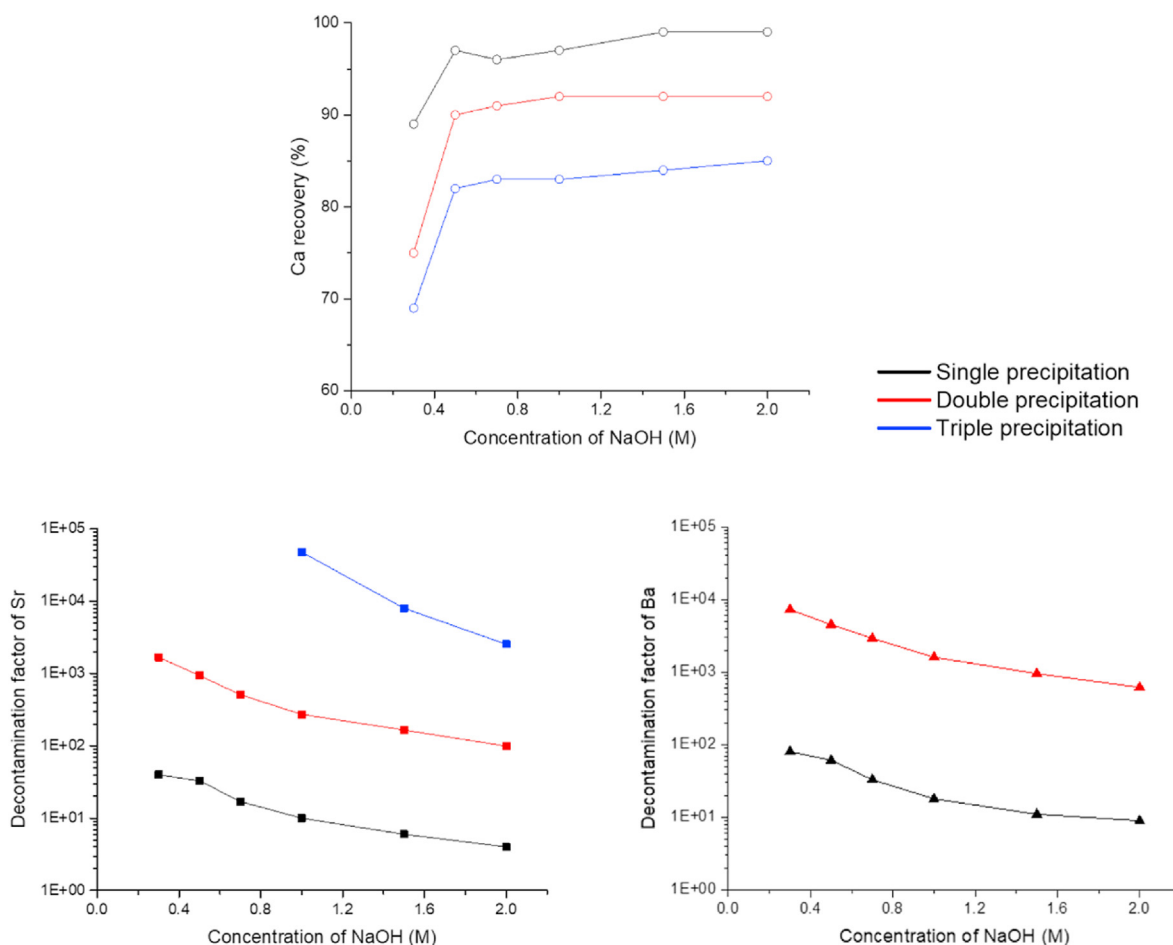


Fig. 4. Behavior of Ca, Ba, and Sr with varying concentrations of NaOH (single, double and triple precipitation; No detection of Ba over 0.3 M NaOH).

concentration of the NaOH in this solution was adjusted to 0.5 M by the addition of NaOH powder. While the recovery of Ca was reduced to 90% at double-precipitation, the DF for Ba and Sr increased to 4500 and 940, respectively. After repeating this process (triple-precipitation), the recovery of Ca was reduced to 82% in 0.5 M NaOH solution, but more importantly, Ba and Sr were no longer detectable by the ICP-OES measurement. We repeated these tests with various concentrations of NaOH. The recovery of Ca depended on the concentration of NaOH. Throughout the solution over 0.5 M NaOH, the recovery of Ca was over 80% and constant, and the DF for Ba and Sr were over 1.0×10^5 (Fig. 4). As Ba was not detected at triple-precipitation throughout samples over 0.3 M NaOH, it was not shown in the plot of Fig. 4.

3.4. Chemical separation procedure of Ca from concrete sample

As stated before, Ca is the dominant element in concrete samples, and hence a Ca carrier is not necessary for the determination of ^{41}Ca by LSC. The quantitative analysis of the neutron-activated radionuclides, specifically ^{41}Ca , requires the complete decomposition of the sample. Based on the comparison of results between the several pretreatment methods, alkali fusion was the most suitable because acid-leaching and microwave digestion methods exhibited lower extraction rates of Ca by 20% while using NIST SRM 2709. The neutron-activated radionuclides such as ^{55}Fe , ^{63}Ni , ^{60}Co , and ^{152}Eu , were found to be significant interfering contaminants of ^{41}Ca due to their similar production mechanisms and the overestimation of

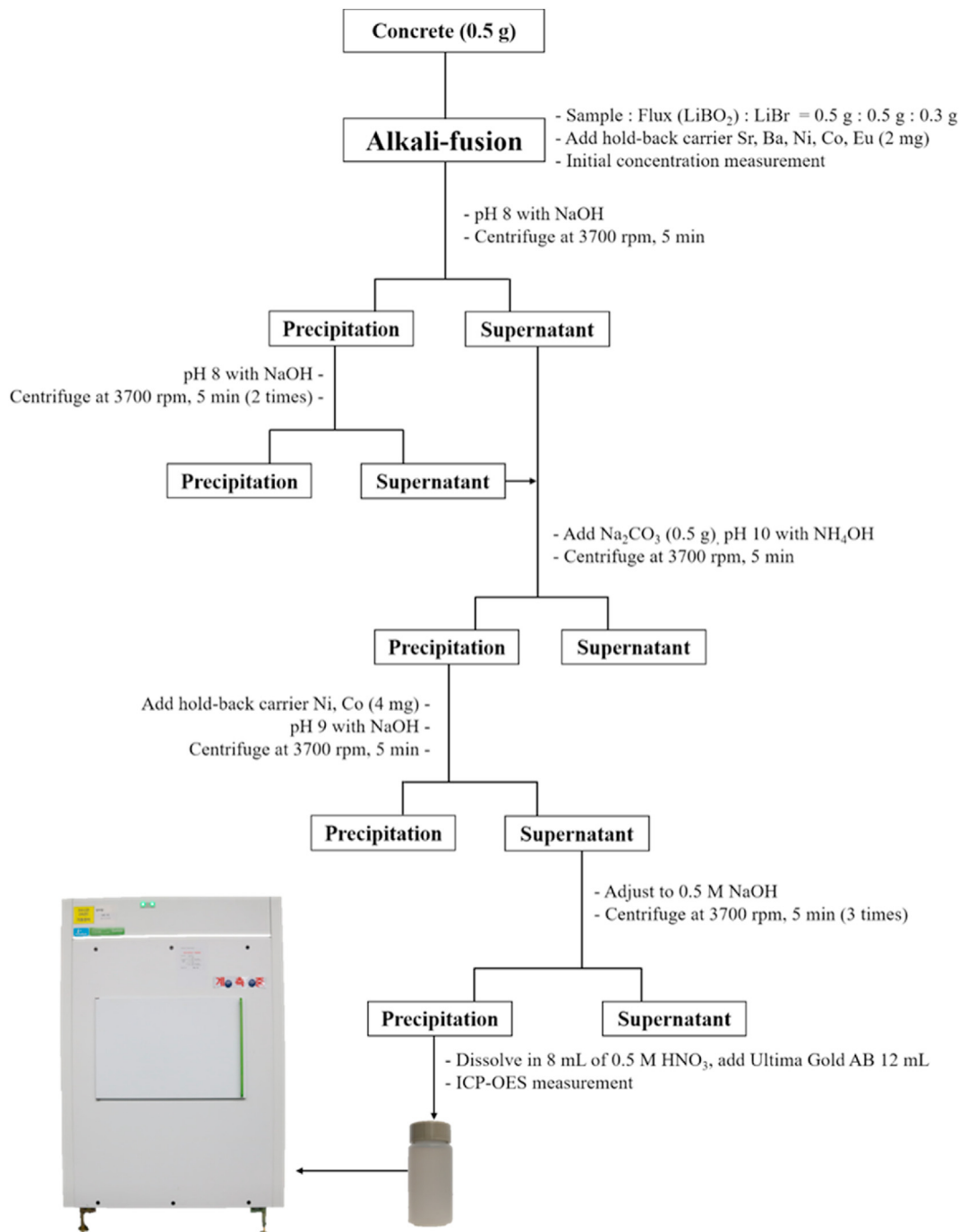


Fig. 5. Schematic of method for chemical separation of ^{41}Ca in concrete samples.

Table 2
Decontamination factor of interferences in the purified ^{41}Ca solution.

	Decontamination Factor
Fe	>2800
Eu	>1200
Co	>1900
Ni	>1500
Sr	>157000
Ba	>561000

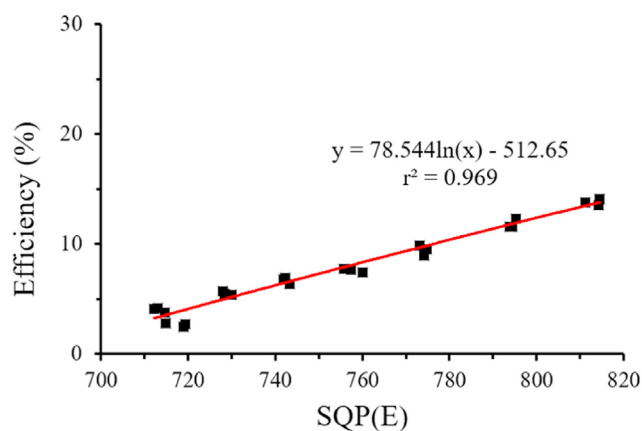


Fig. 6. Counting efficiency of ^{41}Ca with quenching level (SQP(E)).

^{41}Ca in the LSC spectra due to the poor energy resolution of LSC. These transition metals were removed at pH 8 with double precipitations. Some of the Ni and Co remained with the Ca, and hence, the carbonate precipitation using NH_4OH solution at pH 10 was carried out. Then, Ba and Sr, which chemically mimic Ca, were removed from the Ca in the 0.5 M NaOH solution after three precipitations. Fig. 5 shows the schematic diagram of the method for the chemical separation of ^{41}Ca from the concrete sample. Table 2 shows the decontamination factors of the interferences in the purified ^{41}Ca solution for the LSC measurement. Overall, the interferences were removed significantly and were present in less than 0.1%. Fig. 6 shows the quench curve for ^{41}Ca by LSC. The quench level of the purified ^{41}Ca solution in the concrete samples ranged from 713 to 814, as obtained from the SQP(E) method value of LSC. This quench curve was used to determine the counting efficiency of the purified ^{41}Ca solution, which ranged from 3 to 14%.

We did not carry out the study with neutron-activated concrete; as such, we spiked a known amount of ^{41}Ca from 0.4 g (~2.6 Bq) of IRMM sample to the 0.5 g concrete sample. The chemical separation was followed by the process described in Fig. 5. The concrete sample was completely decomposed by the alkali fusion method, and the transition metals were removed from the matrix by double-precipitation. The carbonate precipitation using carbonate ion and NH_4OH solution was applied for the removal of the

remaining transition metal. Sr and Ba, behaving chemically like Ca, were removed by three times of hydroxide-precipitation at 0.5 M NaOH solution. The recovery of Ca is shown in Table 3, $64 \pm 5\%$ ($n = 5$), which was slightly lower due to the implementation of multiple precipitation processes, compared to that of those in the previous study ($85.0 \pm 1.0\%$, $\text{Avr} \pm \text{SD}$, $n = 3$) shown in Fig. 3. In this study, we focused on the complete removal of the interferences of the activated nuclides, such as ^{55}Fe , ^{63}Ni , ^{60}Co , ^{152}Eu , ^{90}Sr , and ^{133}Ba , that interfere with the quantitative measurement of ^{41}Ca by LSC. Therefore, even if we had lost a portion of ^{41}Ca , we chose to completely remove the interferences of the previously mentioned neutron-activated nuclides to avoid the overestimation of the ^{41}Ca . The purified ^{41}Ca solution was measured 10 times by LSC with a counting time of 100 min for each run. The relative deviation of the ^{41}Ca measurement ranged from -10 to 2% , which is acceptable for the routine characterization of wastes during decommissioning. The MDA for ^{41}Ca in the concrete sample by LSC calculated with the equation from Currie [24] is 50 mBq g^{-1} with 0.5g of sample, 0.4 cpm of blank sample, 10% of counting efficiency, 1000 min of counting time, and 64% of recovery.

4. Conclusion

This study presented an analytical method for the determination of ^{41}Ca in concrete samples. With the growing number of nuclear facilities that will reach decommission in the near future, the characterization of wastes generated during the decommissioning process is critical for the safe management of radioactive wastes. The dominant matrix of the radioactive wastes generated during the decommissioning process is the concrete used for the bio-shield and the plant structure, and Ca is the dominant element in concrete. Because ^{41}Ca is a neutron-activated radionuclide, which has a long half-life, it is important to quantitatively analyze ^{41}Ca found in concrete for safe and reasonable management of radioactive disposal sites and appropriate classification of radioactive wastes.

In order to determine ^{41}Ca in concrete, other neutron-activated radionuclides such as ^{55}Fe , ^{63}Ni , ^{60}Co , and ^{152}Eu should be removed from the sample. These radionuclides interfere with the measurement of ^{41}Ca by LSC. The radionuclides of ^{90}Sr and ^{133}Ba need to be separated from ^{41}Ca because they chemically mimic Ca. The central concept of the method developed in this study involves the classical separation of Ca from the other interfering metal nuclides, based on the differences in the solubility of the products generated by its reaction and those of the interfering contaminants. Unlike the resins available for the extraction of Sr, Ni, and DIBK, extraction chromatography approaches are not available for ^{41}Ca . Therefore, several precipitation processes were undertaken and were sufficient for the analysis of ^{41}Ca in concrete. Compared with the previous study for the analysis of ^{41}Ca , the chemical recovery of Ca in this study was slightly lower. However, as shown in the reproducibility study for the ^{41}Ca recovery, the developed technique showed the best performance. Although the minor loss of ^{41}Ca is unavoidable in our study, the developed method is suitable for the

Table 3
Analytical results of ^{41}Ca in a concrete sample.

	Measured value ^a (Bq)	Calculated value ^a (Bq)	Relative deviation (%)	Recovery (%)
Concrete #1	2.70 ± 0.09	2.63 ± 0.09	2.8	64.2
Concrete #2	2.89 ± 0.11	2.62 ± 0.11	10.4	56.0
Concrete #3	2.56 ± 0.10	2.61 ± 0.10	-1.9	64.1
Concrete #4	2.72 ± 0.09	2.60 ± 0.09	4.8	67.6
Concrete #5	2.69 ± 0.10	2.61 ± 0.10	2.9	68.4

^a $\text{Avr} \pm$ uncertainty ($k = 1$).

quantitative analysis of ^{41}Ca in the concrete wastes generated during the decommissioning of NPPs.

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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