Leaching Behavior of Cesium, Strontium, Cobalt, and Europium from Immobilized Cement Matrix

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Abstract: Numerous low-level and intermediate-level radioactive wastes are generated from the decommissioning processes of nuclear power plants; these wastes are immobilized to prevent the release of radionuclides under disposal conditions. In this study, we investigated the leaching behavior of Cs, Sr, Co, and Eu, which are common in immobilized decommissioning wastes. Ordinary Portland cement (OPC) was used as an immobilization agent. During the test, leaching of the nuclides occurred in the order of Cs, Sr, Co, and Eu and decreased over time. The results showed that 41.4% of the total Cs leached over 90 days, although the other elements leached in quantities less than 1.5%. CaCO₃ was precipitated by the release of cementitious materials, indicating carbonation of the leachate. The leachability indexes in all cases exceeded the acceptable criteria (>6). The results of the present study suggest that OPC can be effectively used as a binding material to immobilize nuclides (Cs, Sr, Co, and Eu) contained in decommissioning wastes.

Keywords: decommissioning radioactive waste; Portland cement; immobilization; leaching; carbonation

1. Introduction

Many facilities that use nuclear and other radioactive materials are expected to shut down in the near future as they reach the ends of their operating lifetimes [1]. For example, in South Korea, the first nuclear power plant, Kori Unit 1, was shut down permanently in June 2017. Radioactive wastes are produced mostly from the operation or decommissioning of nuclear facilities and unexpected leakages from nuclear power plants [2,3]. These radioactive wastes are classified as High-Level Waste (HLW), Intermediate-Level Waste (ILW), Low-Level Waste (LLW), and Very-Low-Level Waste (VLLW) [4,5].

Radioactive wastes, such as ILW and LLW, produced from decommissioning processes are disposed in near-surface facilities and landfills to isolate these wastes from the natural ecosystem for sufficient periods of time [6–8]. To ensure safe disposal, fluidizable radioactive wastes such as concentrated wastes, spent resins, sludge, and dry active wastes must be solidified or immobilized homogeneously to limit the release of radionuclides and maintain the structural integrity of the disposal environment [9].

Cementation is most commonly practiced to solidify and immobilize low- and intermediate-level radioactive wastes [10–12]. Cement is used for the encapsulation of radioactive wastes due to its chemical, thermal, and radioactive stability; corrosion resistance; and beneficial compatibility with most varieties of waste [13–16]. Among the numerous types of cement, Portland cement is the most commonly used for the solidification of LLW/ILW and has high retention potential resulting from mechanisms such as sorption, ion exchange, characteristic phase formation, oxy/hydroxyl precipitation, and combinations as cement–waste interactions [7,17,18]. The physical and chemical immobilization of radioactive wastes minimizes radionuclide migration and provides sufficient structural stability [17,18].
The retention capacities of solidified matrixes for the immobilization of radioactive wastes are evaluated using leaching tests. Numerous leaching-test protocols for evaluating the performance of immobilization were used in previous studies, e.g., the American Nuclear Society ANSI/ANS-16.1 [19–24], the International Atomic Energy Agency static test [18,25], ASTM C1285 [26,27], and the Chinese GB7023-86 standard [28,29]. The leachability index derived from these leaching tests is generally used for evaluating the immobilization performance of solidified decommissioning wastes; the result should be greater than 6 as the threshold value for waste-acceptance criteria [30]. In addition, the effective diffusion coefficients for each radionuclide can be determined by leaching tests.

Various radioactive elements, such as cesium (Cs), strontium (Sr), cobalt (Co), and europium (Eu), are contained in decommissioning wastes from nuclear power plants [31–33]. These radioactive elements should be monitored for their impacts on ecosystems, particularly around nuclear facilities, due to their risk of harmful damage to the human body and long half-lives [34]. Cs is one of the most problematic and hazardous radioactive elements for the environment and human health due to its high radioactivity and long half-life [2,35]. Sr, which emits harmful radiation over a long period of time and generates heat for a short period of time, widely coexists with Cs in radioactive wastes [36]. The contamination of soils and groundwater with representative fission-product radionuclides such as Cs, Sr, and Co produces long-term radiation, which then spreads to humans through the food chain and represents an environmental hazard to human health [15,37]. Eu(III) is commonly used as a homolog for trivalent actinides due to its ionic radii, which are almost the same as those of all trivalent actinides and lanthanides, resulting in similar physical and chemical behaviors between Eu(III) and other trivalent actinides and lanthanides [38].

In addition to accidental nuclear releases, radionuclides can be released from low-level radioactive waste disposal facilities, which can lead to ecosystem contamination [39,40]. The immobilization of stable isotopes in aqueous solutions was used in most previous works to simulate radioactive isotopes since employing the actual radioactive wastes represents a significant radiation hazard, and the chemical properties of radioactive isotopes can be simulated with sufficient accuracy by non-radioactive isotopes [6]. This study investigates the leaching behaviors of Cs, Sr, Co, and Eu immobilized in ordinary Portland cement (OPC) during a leaching test of 90 days. Stable Cs, Sr, Co, and Eu were used as surrogates of their radioactive elements. Leaching parameters (i.e., the effective diffusion coefficients and leachability indices) were determined using leaching data and evaluated by comparison with the waste acceptance criteria for the disposal of radioactive waste. Moreover, we investigated the formation of precipitates in the leachate and its mechanisms.

2. Materials and Methods

2.1. Cement and Nuclides

OPC (grade: 42.5) produced from Ssangyong Cement Industrial Co. in Seoul, Korea was used in this study as a material for immobilizing Co, Cs, Sr, and Eu. The density and specific surface area of the OPC were 3.16 g/cm³ and 3910 cm²/g, respectively. The chemical composition of the OPC is summarized in Table 1. Stable nuclides of Co, Cs, and Sr were used as surrogates of their radionuclides, which are mainly contained in the solidified decommissioning wastes from nuclear power plants [41,42]. Stable Eu was also used as a surrogate for its radionuclide because radioactive Eu is commonly leached from solidified bioshield cement [43,44]. Analytical grade CsNO₃, Co(NO₃)₂, Sr(NO₃)₂, and Eu(NO₃)₃ (Sigma-Aldrich, St. Louis, MO, USA, >99.99% purity) were used.

| Table 1. | Chemical composition (wt.%) of OPC as determined by X-ray fluorescence analysis. |
|----------|----------------------------------------------------------------------------------|
|          | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | SO₃ | MgO | K₂O | Na₂O | P₂O₅ | MnO | LOI     |
|----------|-----|------|-------|-------|-----|-----|-----|------|------|-----|---------|
|          | 63.8 | 22.1 | 5.4   | 3.2   | 2.1 | 1.6 | 0.5 | 0.4  | 0.1  | 0.1 | 0.7     |

LOI: loss-on-ignition.
2.2. Cement Solidification

The cement paste containing each surrogate radionuclide was prepared by mixing OPC powder and each aqueous solution at a liquid-to-solid weight ratio of 0.4 for 6 min. The content of surrogate radionuclides in each liquid solution was 10 mmol. The cement paste was cast in a steel mold with a diameter of 50 mm and a height of 100 mm. After casting, the cement specimens doped with surrogate radionuclides were cured for 28 days in an environment at a relative humidity of 90 ± 5% and a temperature of 25 ± 2 °C. The properties of each cement specimen used in this study are summarized in Table 2.

Table 2. The properties of the cement specimens used.

|                | Blank | Cs   | Sr   | Co  | Eu  |
|----------------|-------|------|------|-----|-----|
| Content (mmol) | -     | 10   | 10   | 10  | 10  |
| Geometric surface area (cm²) | 194.4 | 194.6 | 195.7 | 196.5 | 197.6 |
| Volume (cm³)   | 194.4 | 194.2 | 194.9 | 196.9 | 198.1 |
| Mass (g)       | 392.0 | 377.6 | 383.5 | 371.2 | 373.0 |

2.3. Leaching Test

Leaching tests were performed according to ANS 16.1 (Measurement of the leachability of solidified low-level radioactive wastes by a short term test procedure) [45] to investigate the leaching behaviors of each nuclide in the solidified cement specimen. Ultrapure water with electrical conductivity (EC) less than 5 μS/cm (at 25 °C) and total organic carbon (TOC) content of less than 3 ppm was used as the leachant. The test was performed by immersing the specimen for 90 days in the ultrapure water contained in a polypropylene vessel. A solidified cement specimen containing a nuclide and the leachant was placed in a polypropylene vessel with a volume of 2 L, ensuring that all sides of the specimen were in contact with the leachant. In addition, a solidified cement specimen without a nuclide was also placed in the ultrapure water as a control sample. The leachate was then sampled, and the fresh leachant was replaced at 0.08 (2 h), 0.3 (7 h), and 2, 3, 4, 5, 19, 47, and 90 days after the beginning of the test (Figure 1). From the results of the leaching tests, the leaching characteristics of nuclides from the solidified cement specimens were evaluated based on the cumulative fraction leached (CFL) and the leaching rate (LR). The effective diffusion coefficient ($D_e$) and leachability index (LI) were also derived to quantitatively evaluate whether the waste acceptance criteria were satisfied.

![Figure 1. Schematic diagram of the leaching test according to ANS 16.1.](image)

2.4. Analysis

The pH and EC of each leachate were measured at every sampling interval using a portable meter (Orion VERSA STAR Multiparameter Benchtop Meter, Thermo Fisher Scientific, Waltham, MA, USA) equipped with a pH probe (Triode gel-filled epoxy-body LM, 9107/WMMD) and a conductivity probe (Orion DuraProbe 4-Electrode Conductivity
cells 013005MD) calibrated with certified standards. The concentrations of cations and nuclides (Cs, Sr, Co, and Eu) leached from the solidified cement specimens were analyzed using an inductively coupled plasma atomic emission spectroscopy (ICP–AES, OPTIMA 4300DV, Perkin Elmer, Waltham, MA, USA) and an inductively coupled plasma mass spectrometer (ICP–MS, Thermo Elemental X-7, Agilent Technologies, Santa Clara, CA, USA), respectively, at the Korea Basic Science Institute (KBSI). The total organic carbon (TOC) in each leachate, which was used to evaluate the degree of organic leaching during the leaching tests, was analyzed with a TOC analyzer (Vario TOC Cube, Elementar, Langenselbold, Germany) at the Laboratory Center of Chungnam National University. For Fourier transform infrared spectroscopy (FTIR), an ATR–FTIR spectrometer (Cary 630, Agilent Technologies, Santa Clara, CA, USA) equipped with a single-reflection diamond ATR crystal was used to investigate the bonding structures of the precipitates. The spectra were collected at an absorbance range of 4000 to 600 cm$^{-1}$ and a resolution of 1 cm$^{-1}$. A micro X-ray fluorescence ($\mu$-XRF) analysis was conducted to investigate the precipitate in each leachate after 90 days using an M4 Tornado (Bruker, Billerica, MA, USA). A poly-capillary lens was used to obtain a spot size as small as 25 $\mu$m for Mo-K$\alpha$. The X-ray generator was operated at 50 kV and 600 $\mu$A.

3. Results

3.1. Leaching of the Solidified Cement Specimen

3.1.1. Temporal Variations in pH, EC, and TOC

The pH values of the leachates leached from the solidified cement specimens for up to 90 days are shown in Figure 2. The pH value of the ultrapure water used in the test was about 5.6 because the ultrapure water was exposed to carbon dioxide in the atmosphere. The pH of the leachate ranged between about 10.5 and 12.0 during the leaching test. These high-alkaline conditions in the leachate were caused by dissociation of the cement material. The main component of OPC, lime (CaO), reacts with water to form portlandite [Ca(OH)$_2$], producing an alkaline solution with a pH of about 12.4 because of the relatively high dissociation constant of Ca(OH)$_2$ (Reactions (1) and (2)) [17,46,47]. In addition, the porewater chemistry in cement paste is influenced by the cement’s alkali content, the alkali availability of the solution, the water/cement ratio, and the presence of soluble waste components [48].

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$$  

(1)

$$\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{(OH)}^-$$  

(2)

All leachates, except for the leachate from the cement specimen doped with Cs, showed similar temporal pH trends. The pH slightly increased to 12.0 until 19 days and decreased to approximately 11.0 by the end of testing (Figure 2). The decrease in pH after 19 days...
might have resulted from the consumption of hydroxides during the dissociation process of cementitious material.

The correlation between pH and EC of the leachate is shown in Figure 3. The pH of the leachates was positively correlated with EC. The EC was proportional to pH due to the dissociation and diffusion of the cement material. Two distinct linear correlations between pH and EC in two pH ranges (11.0–11.7 and 11.4–12.0) were observed because these values were determined using non-time-sequential data from the tests. The EC linearly increased from approximately 300 to 900 μS/cm as the pH increased from 11.0 to 11.7 in the early period of testing, whereas the EC increased linearly from approximately 900 to 2100 μS/cm as the pH increased from 11.4 to 12.0 in the later period of testing. Due to the increase in reaction time during the later period, the release of cementitious material increased, and, therefore, EC in the earlier period was lower than that in the later period.

![Figure 3. Correlation of pH and electrical conductivity (EC) for each leachate.](image)

The TOC in the leachates was measured periodically during the leaching tests (Figure 4). Organic materials in immobilized wastes are physicochemically decomposed by microorganisms, which can accelerate the migration of radionuclides and impair the physical stability of the disposal facility [46,47]. Therefore, the temporal trends in TOC were similar, regardless of specimen type. The TOC in the leachate was approximately 1 mg/L for up to 5 days and then increased slightly to approximately 2.5 mg/L at 90 days. This increase in TOC may have been caused by the dissociation and diffusion of organic materials in the cement specimens. These TOC results are comparable to the results of the increase in EC in the later period (Figure 3).

![Figure 4. TOC in the leachates as a function of elapsed time.](image)
3.1.2. Leaching Rate (LR)

The LR is defined as the amount of a constituent of a solidified waste form that is leached during a given time interval [45]. The LRs of the nuclides from the cement specimen were calculated by the following equation:

$$LR = \left(\sum \frac{a_n}{A_0}\right) \left(\frac{V}{S}\right) \left(\frac{1}{t}\right)$$

where $a_n$ is the quantity of a nuclide released from the specimen during leaching interval $n$, $A_0$ is the total quantity of a given nuclide in the specimen, $V$ is the volume of the specimen (cm$^3$), $S$ is the geometric surface area of the specimen (cm$^2$), and $t$ is the leaching time from the beginning of the leaching test (day) [45].

The LRs of the nuclides (Cs, Sr, Co, and Eu) as a function of elapsed time are shown in Figure 5. The LRs of the nuclides occurred in the order of Cs, Sr, Co, and Eu during the test. In all cases, the LR significantly decreased during the early stages of leaching (<5 days) but then gradually decreased over time. Among the four nuclides, Cs had the highest LR because of its low field strength, making it substantially soluble under highly alkaline conditions [18,49–51]. Soler [52] reported that the easy release of Cs from its cementitious waste form can be attributed to its high solubility in high pH (12.5–13.6) hydrated cement and the low sorption potential of Cs in cement. Thus, numerous studies to reduce the leaching of Cs from the cement matrix have been conducted. Using zeolite as a blending material in cement was found to cause a reduction in Cs leaching [13,53–55]. Slag is also used for immobilizing Cs within matrices [6,56]. Meanwhile, studies considering the binding capacity and bond strength of Cs were also conducted. Hong and Glasser [57] and Glasser [58] reported that the binding capacity and bonding strength of Cs ions in cementitious pastes are enhanced as the Ca/Si ratio in the paste decreases.

Sr has higher leaching rates than Co and Eu. In the case of Co and Eu, the leaching rate is very low, suggesting that leaching of Co and Eu from the cement matrix rarely occurs. In a previous study, Co was potentially found to be immobilized by irreversible reactions with calcium silicates in the waste-form matrix [59].

Eu has the lowest levels of leachability, which can be attributed to the low solubility of lanthanides in the high pH environment of hydrated cement [18]. Most lanthanides were found to be strongly retained on the calcium–silicate–hydrate (C–S–H) of cement. Also, it was reported that Eu adsorbed on the surface of the cement matrix was not precipitated in the solution despite its low solubility limit [60].

![Figure 5. Leaching rates of nuclides (Cs, Sr, Co, and Eu) from the cement matrix.](image-url)
3.1.3. Cumulative Fraction Leached (CFL)

The CFL is defined as the sum of the fractions leached during all previous leaching intervals, including the fraction leached during the last leaching interval using the initial amount of the nuclide contained in the specimen [45]. The CFL of each nuclide was calculated by the following equation:

$$\text{CFL} = \sum \frac{a_n}{A_0}.$$  (4)

The CFLs of Cs, Sr, Co, and Eu mobilized from the cement specimen over 90 days are shown in Figure 6. Nuclides were rapidly released from the cement specimen within the first 5 days. After that, the leaching of nuclides was significantly reduced. Elemental leaching from the cementitious materials occurs in three steps: surface wash-off, diffusion, and dissolution [13,61,62]. The initial rapid release of mobile elements attached to the solid waste surface occurred due to surface wash-off. Following the first step, mass transfer occurred due to diffusion from the pore space of the solidified waste to the solution. In the last step, the leaching of cementitious materials was caused by dissolution, which can accelerate diffusion but occurs only after long periods of leaching (ANS 2017). In the leaching test performed in the present study, the leaching of nuclides may have been dominantly controlled by surface wash-off in the early period and diffusion in the later period for 90 days.

The CFLs of nuclides occurred in the order of Cs > Sr > Co > Eu throughout the leaching experiments. We observed the rapid leaching of Cs from the solidified cement specimen doped with Cs, and the CFL reached about 0.4 by the end of the test. The additional leaching of Cs may have occurred continuously even after the experiment was completed because 90 days might not have been a sufficient reaction time for Cs to fully leach from the cement specimen. The solidified cement specimen doped with Sr, which had a CFL of about 0.01 at the end of the test, had a lower CFL than that in the specimen doped with Cs due to the lower leaching rate of Sr compared to that of Cs. Co and Eu had low CFLs, indicating minor leaching from each cement specimen, although the CFL of Co was higher than that of Eu. These CFL results are comparable to the results of the LR (Figure 5).

3.1.4. Effective Diffusion Coefficient ($D_e$) and Leachability Index (LI)

The intrinsic mass transfer properties ($D_e$ and LI), calculated using the CFL and LR, are commonly used as mathematical parameters to simulate the long-term leaching behavior of nuclides [18]. As mentioned in Section 3.1.3, after the initial rapid leaching of the mobile nuclides attached to the surface (wash-off), the LRs are mostly controlled by diffusion [45].
Leaching of less than 20% of the leachable species in a uniformly and regularly shaped solid means that diffusion is the rate-determining mechanism, with leaching behavior similar to that in a semi-infinite medium [45]. Under these conditions, $D_e$ can be calculated using the mass transport equation (i.e., Fick’s second law) as follows:

$$D_e = \pi \left[ \frac{(a_n/A_0)}{((\Delta t)_n)} \right]^2 \left[ \frac{V}{S} \right]^2 T$$

(5)

where $D_e$ is the effective diffusion coefficient (cm$^2$/s), $(\Delta t)_n$ is the duration of the nth leaching interval (s), and $T$ is the leaching time representing the mean time (s) of the nth leaching interval for a semi-infinite medium [45]:

$$T = \left[ \frac{1}{2} \left( \sqrt{T_n} + \sqrt{T_{n-1}} \right) \right]^2$$

(6)

However, if more than 20% of a leachable species is removed over time, $D_e$ should be calculated using the following equation [45]:

$$D_e = \frac{Gd^2}{t}$$

(7)

where $G$ is a dimensionless time factor for the specimen, $d$ is the diameter of the specimen (cm), and $t$ is the elapsed leaching time since the beginning of the first leaching interval (s). The value of $G$ identified by the length-over-diameter ($l/d$) ratio of the specimen can be determined by the convenient tabular method in ANS 16.1 [45].

The $D_e$ values of nuclides (Cs, Sr, Co, and Eu) are summarized in Table 3. In this study, the CFL exceeded 20% in the specimen doped with Cs after 19 days, but the other specimens presented less than 20% CFL. The mean $D_e$ values of the nuclides were in the order of $\text{Cs} > \text{Sr} > \text{Co} > \text{Eu}$ throughout the test. The $D_e$ values of Cs and Sr ranged from $2.19 \times 10^{-8}$ to $4.57 \times 10^{-8}$ cm$^2$/s and $1.35 \times 10^{-12}$ to $1.76 \times 10^{-10}$ cm$^2$/s, respectively. In addition, the $D_e$ values of Co and Eu ranged from $3.40 \times 10^{-19}$ to $1.76 \times 10^{-17}$ and $1.28 \times 10^{-24}$ to $4.55 \times 10^{-19}$ cm$^2$/s, respectively. In most cases, the $D_e$ values were higher in the earlier period and gradually decreased in the later period. These results agree with those of the LR (Figure 5) and CFL (Figure 6) described in Sections 3.1.2 and 3.1.3, respectively.

### Table 3. The effective diffusion coefficients of the nuclides (Cs, Sr, Co, and Eu).

| Time   | Cs         | Sr         | Co         | Eu         |
|--------|------------|------------|------------|------------|
| 2 h    | $4.57 \times 10^{-8}$ | $1.35 \times 10^{-12}$ | $6.51 \times 10^{-18}$ | $1.06 \times 10^{-22}$ |
| 7 h    | $2.21 \times 10^{-8}$ | $6.84 \times 10^{-11}$ | $1.17 \times 10^{-17}$ | $4.55 \times 10^{-19}$ |
| 1 d    | $2.58 \times 10^{-8}$ | $9.96 \times 10^{-11}$ | $1.31 \times 10^{-17}$ | $3.10 \times 10^{-19}$ |
| 2 d    | $2.48 \times 10^{-8}$ | $1.15 \times 10^{-10}$ | $1.56 \times 10^{-17}$ | $5.16 \times 10^{-23}$ |
| 3 d    | $2.83 \times 10^{-8}$ | $1.28 \times 10^{-10}$ | $1.16 \times 10^{-17}$ | $8.77 \times 10^{-23}$ |
| 4 d    | $2.66 \times 10^{-8}$ | $1.45 \times 10^{-10}$ | $1.36 \times 10^{-17}$ | $1.23 \times 10^{-22}$ |
| 5 d    | $2.19 \times 10^{-8}$ | $1.76 \times 10^{-10}$ | $1.76 \times 10^{-17}$ | $1.59 \times 10^{-22}$ |
| 19 d   | $2.92 \times 10^{-8*}$ | $1.61 \times 10^{-11}$ | $2.38 \times 10^{-18}$ | $9.09 \times 10^{-21}$ |
| 47 d   | $2.80 \times 10^{-8*}$ | $8.73 \times 10^{-12}$ | $8.50 \times 10^{-19}$ | $1.42 \times 10^{-24}$ |
| 90 d   | $2.25 \times 10^{-8*}$ | $3.43 \times 10^{-12}$ | $3.40 \times 10^{-19}$ | $1.28 \times 10^{-24}$ |
| Mean   | $2.75 \times 10^{-8}$ | $7.62 \times 10^{-11}$ | $9.33 \times 10^{-18}$ | $7.75 \times 10^{-20}$ |

* Values calculated by Equation (7). Unit: cm$^2$/s.

The LI is related to the leaching characteristics of solidified waste materials. The LI of each nuclide was calculated by the following equation [45]:

$$\text{LI} = \frac{1}{10} \sum_{1}^{10} \left[ \log \left( \frac{\beta}{D_e} \right) \right]_n$$

(8)
where $\beta$ is a defined constant ($1.0 \text{ cm}^2/\text{s}$).

The LI is used to evaluate the efficiency of nuclide immobilization and characterize the leaching resistance of species of interest. A LI greater than 6 is recommended as a threshold value for the waste-acceptance criterion of radioactive waste [30]. The LIs derived for all nuclides contained in the solidified cement specimens are presented in Table 4. The LIs of the nuclides were in the order of Eu $>$ Co $>$ Sr $>$ Cs, where Cs had the lowest LI (7.6) among the nuclides. These results agree with the CFL and $D_v$ values for each nuclide during the test. All solidified cement specimens doped with nuclides had higher LIs than the threshold value of 6, indicating their acceptability for the disposal of radioactive waste [30]. Accordingly, the OPC can be used as a binding material to immobilize nuclides contained in solidified waste, such as Cs, Sr, Co, and Eu.

Table 4. Leachability indices (LIs) for nuclides (Cs, Sr, Co, and Eu) from the solidified cement specimens.

|     | Cs | Sr  | Co  | Eu  |
|-----|----|-----|-----|-----|
| LI  | 7.6| 10.5| 17.3| 21.5|

3.2. Precipitation in Leachate

3.2.1. ATR–FTIR Analysis

The FTIR spectra of precipitates formed in the leachate from the solidified cement specimens doped with Cs and Sr are shown in Figure 7 along with the blank cement specimen after 90 days. An increase was observed in the bands of the CO$_3^{2-}$ bond peak located at 1390 cm$^{-1}$, which likely resulted from the formation of a hydrated carbonate phase or calcite in the leachate [6,63]. Carbonate is classified as a complex anion and complex inorganic compound due to its functional group (CO$_3^{2-}$). Since the anionic carbonate is tightly held by covalent bonds, the bending vibrations of carbonate create sharp bands in the regions of 711, 871, and 1793 cm$^{-1}$ [61,64,65]. In addition, a broad peak is located at 1390 cm$^{-1}$, which can be assigned to the asymmetric stretching vibrations of the carbonate phases [62,66–68]. The intensity of the CO$_3^{2-}$ peak present at 1390 cm$^{-1}$ indicates that more carbonate-containing precipitate was produced in the leachate from the solidified cement specimen doped with Cs than in the specimen doped with Sr or the blank specimen.

Figure 7. FTIR spectra of the precipitate in each leachate after 90 days.

3.2.2. Micro-XRF Analysis

The micro-XRF analyses of the precipitates formed in each leachate after 90 days revealed a distribution of elements (Ca, Cs, and Sr) (Figure 8). Co and Eu were not observed in the precipitate because their contents were below the detection limit. For the
solidified cement specimen doped with Cs, Ca was present in most of the precipitate, while Cs did not appear (Figure 8a). Conversely, for the solidified cement specimen doped with Sr, Ca and Sr revealed similar spatial distributions to each other (Figure 8b), indicating that these elements might be co-precipitated as Ca(Sr)CO\(_3\) because of their similarities in charge and ionic radius \[69,70\].

3.2.3. Water-Soluble Ions

During the leaching tests, the major elements (i.e., Ca, Na, K, and Si) contained in the solidified cement specimens doped with nuclides were ionized and diffused from the porewater in the specimens to the leachant. The cumulative concentrations of major elements (Ca, Na, K, and Si) and nuclides (Cs and Sr) leached from the solidified cement specimens over 90 days are shown in Figure 9. Fe and Mg were not observed in the leachate because their concentrations were below the detection limit during the test period.

The cumulative concentrations of Cs and Sr with the square root of time are shown in Figure 9a,b, respectively. The cumulative concentration was proportional to the reaction time, suggesting that the leaching process was controlled by diffusion \[6\]. However, there was a difference in the temporal trends between the cumulative Cs and Sr concentrations. The cumulative concentration of Cs steadily increased with time (Figure 9a). However, the cumulative concentration of Sr significantly increased in the early period (<5 days) but only gradually increased in the later period (>5 days) (Figure 9b). These results suggest that surface wash-off and diffusion might be the dominant processes behind Sr leaching during the early and later periods, respectively. These results suggest that the precipitation of Ca(Sr)CO\(_3\) previously discussed in Sections 3.2.1 and 3.2.2 affected the cumulative concentrations of Sr and Ca in the later period. However, Cs, which was not observed in the precipitates, was continuously released even after the early period.
3.2.3. Water-Soluble Ions

During the leaching tests, the major elements (i.e., Ca, Na, K, and Si) contained in the solidified cement specimens doped with nuclides were ionized and diffused from the porewater in the specimens to the leachant. The cumulative concentrations of major elements (Ca, Na, K, and Si) and nuclides (Cs and Sr) leached from the solidified cement specimens over 90 days are shown in Figure 9. Fe and Mg were not observed in the leachate because their concentrations were below the detection limit during the test period.

![Figure 9](image)

**Figure 9.** Cumulative concentrations of nuclides: (a) Cs and (b) Sr and major elements: (c) Na, (d) K, (e) Ca, and (f) Si leached from the solidified cement specimens up to 90 days of testing.

The temporal trends in cumulative concentrations of Na and K were similar to those for the cumulative concentration of Cs (Figure 9a,c,d). The cumulative concentrations of these elements constantly increased with time. The differences in the leaching rates of alkali-metal cations (Na, K, and Cs) were attributed to their periodic properties, such as their different ionic radii and bonding strength within the cement matrix. Komljenović et al. reported that Na has a stronger ability to transport into the surface cavities and thus reside in the silicate channel for a longer period than K due to its smaller hydration shell and stronger Na\(^{+}\)-O\(_{s}\) connections [6].

In addition, the temporal trends in the cumulative concentrations of Sr and Ca were identical (Figure 9b,e). The cumulative concentrations of Sr and Ca significantly increased in the early period but gradually increased in the later period. These results were attributed
to the similarities in their charges and ionic radii \[69,70\]. Evans \[71\] also reported that the behavior of Sr in cement may reflect the behavior of Ca.

### 4. Conclusions

In this study, leaching tests were conducted for 90 days on solidified cement specimens doped with Cs, Sr, Co, and Eu to simulate the solidified radioactive waste generated from decommissioning processes. The $D_e$ and LI values of nuclides were determined using the diffusion-release models of ANS 16.1 \[45\]. The CFL and $D_e$ values of the nuclides were in the order of Cs > Sr > Co > Eu due to the differences in their physicochemical properties such as the binding capacity and solubility. CaCO$_3$ was precipitated in the leachate resulting from dissociation of the cement material and carbonation. The LIs of all specimens tested in the present study exceeded the acceptance criteria (>6) for the disposal of radioactive wastes. The results of this study, therefore, suggest that OPC can be effectively used for a binding material to immobilize nuclides (Cs, Sr, Co, and Eu) contained in decommissioning wastes.

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