Experimental Study Investigating the Effects of Concrete Conditions on the Penetration Behaviors of Cs and Sr at Low Concentration Ranges

Kazuo Yamada¹*, Go Igarashi², Norihisa Osawa³, Rohith Kiran⁴, Kazuko Haga⁵, Sayuri Tomita³ and Ippei Maruyama⁶, ⁷

Received 8 December 2020, accepted 13 June 2021 doi:10.3151/jact.19.756

Abstract

To decommission of the Fukushima-Daiichi nuclear power plant after the reactor accident, it is important to estimate the distribution of radionuclide contamination in the concrete for key elements such as Cs and Sr. A reaction transport model will be developed for these calculations. However, for a realistic model, the behaviors of Cs and Sr penetration in concrete must be experimentally investigated. A part of the results of a MEXT project called “The Analysis of Radionuclide Contamination Mechanisms of Concrete and the Estimation of Contamination Distribution at the Fukushima Daiichi Nuclear Power Station” are presented in this technical report. From our penetration analyses, the behaviors of neither Cs nor Sr were affected by each other. Additionally, the apparent diffusion coefficients of Cs and Sr were not significantly affected by the concentration or the presence of clay in the mortars. The penetration depth of Sr was smaller than that of Cs, and fly ash blended cement increased the resistance to penetration compared with ordinary Portland cement. Carbonation in the mortar samples increased the adsorption of Cs especially. Sr interacted with cement hydrates more than with clays. In oven-dried mortars, under the condition of water suction, the presence of clay retarded Cs penetration but had no effect on Sr. When the mortars were carbonated and oven-dried, the interactions between the solid phase and Cs or Sr took hours at least to complete.

1. Introduction

After the accident at the Tokyo Electricity Power Company’s Fukushima-Daiichi nuclear power plant (FDNPP), the interactions between concrete and the major radionuclides, Cs-137 and Sr-90, must be considered because this is especially important for decontamination, disposal, and design plans for disposal facilities made of concrete (Yamada et al. 2020). Because of the enormous quantity of material, a proper assessment of the concrete contamination can reduce the disposal volume by identifying appropriate decontamination approaches. Numerical models can be used to estimate the extent of contamination; however, the fundamental mechanisms driving the spread of contaminants must be understood using the existing literature and experimental studies and insufficient information have to be investigated. The FDNPP decommissioning project “Nuclear Energy Science & Technology and Human Resources Development Project -through Concentrating Wisdom” has been active under the supports by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). As a part of this project, a specialized project, “The Analysis of Radionuclide Contamination Mechanisms of Concrete and the Estimation of Contamination Distribution at the Fukushima Daiichi Nuclear Power Station”, was conducted between January 2018 and March 2020.

For those purposes mentioned above, several factors must be considered to estimate the distribution of contaminants in the concrete, such as the changes in the boundary conditions from before the accident to the final stage of decommissioning, materials and concrete conditions, the creation of an appropriate model, material constants based on experimental analysis used in the model, moisture transfer, and cracking. In this technical report, we introduce a summary of the results of experimental studies investigating the penetration of Cs and Sr in concrete, using the project report (Nagoya University 2018, 2019, 2020).

The penetration behaviors of Cs and Sr were simulated using reaction transport models that considered the thermodynamic equilibrium between ions in the pore solution and the solid phase of concrete, as well as a
Several studies have investigated the interactions between cement hydrates and Cs and Sr species. The results of these studies have been summarized by Ochs et al. (2016). Calcium silicate hydrate (C-S-H) is the most significant cement hydrate phase that interacts with Cs, and these interactions have been investigated extensively (Missan et al. 2018; Haga et al. 2019). These interactions have also been studied using atomistic models that considered molecular dynamics or quantum chemistry (Arayro et al. 2018; Jian et al. 2017; Duque-Redondo et al. 2018; Tachikawa et al. 2020). The contribution of aggregates in concrete has also been considered (Idemitsu et al. 1992; Fuller et al. 2014). These interactions have been investigated in a wide range of ion concentrations, including low levels that are representative of the concentrations at real sites.

Cs interacts with cement hydrates or clays in concrete aggregates through ion-exchange reactions, in which Cs reaches equilibrium between the pore solution and the solid phase. The incorporation of Cs into the solid phase can be referred to as adsorption, sorption, binding, or uptake. However, in this report, we use the term “adsorption” because Cs interacts with the solid phase through an ion-exchange reaction at cation-exchanging sites. Unlike Cs, Sr interacts with the major concrete phases by replacing Ca in cement hydrate to form a solid solution (Ochs et al. 2016; Evans 2008; Atkins and Glasser 1992). These Sr interactions have also been shown through an atomistic model (Dezerald et al. 2015). While many studies have investigated each phase of cement hydrates, these interactions are out of the scope of this report. For simplicity, we will consider the equilibrium between Sr in the solid phase and the pore solution to be “adsorption”.

Haga et al. (2019) described another important interaction between concrete and Cs and Sr, in which degraded cement paste significantly influences the adsorption of Cs and Sr. Depending on the location of the concrete components at the study site, some of the material experienced neutralization and Ca leaching. These degradation phenomena can increase the adsorption of Cs and Sr by several orders of magnitude and must be considered in concrete-contamination analysis after accidents. Furthermore, the moisture conditions affect solution transport. For example, carbonation is accelerated in moderate humidity, but not in water-saturated conditions. The interactions of ions and solid phase in concrete under water-saturated condition are assumed to be rapid compared with ion transport. However, under water-unsaturated condition, the movement of water can be faster than the interaction. Therefore, we must consider solution transport in partially dried concrete (Wang et al. 2019).

Compared to the adsorption experiments, a limited number of studies have reported penetration experiments for Cs (Atkinson and Nickerson 1984; Ito et al. 2013; Garcia-Gutiérrez 2018) and for Sr (Kittnerová et al. 2020). These studies were primarily conducted in conditions with high ion concentration ranges relative to those at the FDNPP site. After the accident, concrete was exposed to water contaminated with radionuclides that leaked from cracks in the nuclear reactor. The concentrations of Cs-137 and Sr-90 were estimated to be about 1 to 10 μM at the early ages after the accident (Nagoya University 2018). Nearly no other studies have shown data for penetration experiments in this concentration range. Additionally, experiments must be conducted to clarify several other factors in the FDNPP study:

- Effects from the coexistence of Cs and Sr: the species could competitively interact on the surface of the solid phase (Li and Pang 2014).
- Concentration and its influence on diffusion and ion adsorption.
- The effects of the materials used at the FDNPP: to estimate contamination at the site, the materials used at the plant must be evaluated.
- Ca leaching and carbonation: both concrete-degradation mechanisms may affect the penetration of ions by increasing adsorption (Haga et al. 2019).
- Drying: rapid water movement will compete with the ion interactions between the solution and solids, and the phase equilibrium will not be achieved.
- Combined carbonation and drying: water movement and ion adsorption will compete as the main mechanism for concrete contamination.
- Dissolution: ions that are adsorbed to solids may be released again if ion composition of the surrounding solution changes.
- Cracks: ion penetration is much faster along cracks than in intact regions (Yamada et al. 2019); all concrete structures contain some level of cracking.

In this project, we examined all factors besides cracking behavior, which will be examined in the next MEXT project, “Quantitative Evaluation of Contamination in Reinforced Concrete Members of Fukushima Daiichi NPP Buildings Considering the Actual Environment Histories for Legitimate Treatments”, which began in October 2020 and will continue until March 2023. The dissolution of the contaminated concrete, which was also investigated in the study (Nagoya University 2019), will be reported in other papers.

To examine the penetration of Cs and Sr in dilute conditions on the order of 1 μM, we conducted radioautography using imaging plates (IPs). The immersion solution of CsCl and SrCl₂ was labeled by radioisotopes, Cs-137 and Sr-90, to detect the penetration of Cs and Sr. The penetration behaviors of each radioisotope were measured quantitatively after the immersion tests by exposing sliced mortar specimens to the IP using cement paste containing known concentrations of RI used as a standard.

In this study, we determined the penetration profiles of Cs and Sr by detecting Cs-137 and Sr-90, respectively. We measured the β-rays emitted from Cs-137 and Sr-90...
using an IP for autoradiography. Most Cs-137, which has a half-life of 30 years, decays to metastable Ba, emitting \(\beta\)-rays of 0.51 MeV of the maximum energy. The metastable Ba, with a half-life of 2.6 minutes, can then transform to stable Ba, emitting \(\gamma\)-rays of 0.66 MeV of the maximum energy. Therefore, by detecting signals using the IP, the location of Cs can be identified because during 2.6 minutes, insignificant movement of elements is expected. The radioactive decay of Sr-90, which has a half-life of 28.8 years, does not follow a simple \(\beta\)-ray emission mechanism. Instead, it decays to Y-90 once, emitting a \(\beta\)-ray of 0.55 MeV of the maximum energy. Then, Y-90 with a half-life of 64.1 hours, decays to stable Zn-90, emitting a \(\beta\)-ray of 2.28 MeV of the maximum energy. Therefore, the signal recorded on the IP comes from two different \(\beta\)-rays. Because the decay of Y-90 has a higher-energy emission, the signal from Y-90 is more significant. If Y and Sr moved at significantly different speeds through the concrete relative to the half-life of Y-90, Y-90 could emit a signal from a position that was not representative of the distribution of Sr-90, making it difficult for the IP to detect the true distribution of Sr.

Therefore, before describing the Cs and Sr penetrations in various conditions, in order to compare the transfer speeds of the species of Sr and Y, we conducted immersion experiments for stable Cs, Sr, and Y in chloride solutions.

Moreover, it is not simple to evaluate penetration behaviors when immersion experiments are conducted in different concentrations. In the case of chloride penetration, 0.5 M of NaCl solution is used in general because the corrosion by sea water is the major concern. In this case, penetration depth by some method can be a representative parameter. However, when the concentration of immersion solution is different for materials having different adsorption abilities, the situation is not so simple. Therefore, for better understanding of the evaluation of experiments in this study, the correlation between concentration of immersion solution and penetration depth is discussed first in the chapter 2.

2. Evaluation of the penetration of RI at different concentrations

In order to understand the meaning of penetration depth, thought experiment was conducted. In Fig. 1 (a), several diffusion profiles of the elements in porous solids exposed to solutions with different relative concentrations ranging from 1 to 0.001 are shown. The diffusion coefficient was assumed to be \(1 \times 10^{-13}\) m²/s, and the diffusion was analyzed for a 4 838 400 s (56 days, or 8 weeks) period. The diffusion profiles were created by analytically solving Fick’s laws of diffusion. The relative concentrations are reported on a logarithmic scale in Fig. 1 (b) to better show penetration depth at low concentrations.

When we compared the penetration depths for detectable concentrations as indicated by a thick lateral line at \(1 \times 10^{-3}\) of relative concentration, we found that the depth decreased with decreasing ion concentrations, even for more sensitive detection methods as indicated by a thick dot line at \(1 \times 10^{-6}\) of relative concentration such as IPs. However, when we evaluated the penetration depths when the decrease in relative concentration was within 3 orders of magnitude as indicated by a thin horizontal dashed line, the penetration depths remained the same.

The penetration of Cs and Sr is governed by diffusion in the concrete pore solution and by ion adsorption to the solid phase. When adsorption by concrete components is proportional to the ion concentration in the solution, the penetration profiles can be fitted to diffusion profiles. Therefore, in the study, to investigate the effects of concentration and element type, we fitted the penetration profiles to simple diffusion profiles to compare the apparent diffusion coefficients.

Also shown in Fig. 1(b) is the effect of varying the diffusion coefficient in a solution with a relative concentration of 1. We tested the following diffusion coefficients: \(1 \times 10^{-13}\) m²/s, \(2 \times 10^{-13}\), \(4 \times 10^{-13}\), and \(1 \times 10^{-12}\).

![Fig. 1 Model diffusion profiles for different surface concentrations and diffusion coefficients (t = 4 838 00 seconds (56 days)).](image-url)

(a) Presentation of the relative concentration on a linear scale (D = \(1 \times 10^{-13}\) m²/s).

(b) Presentation on a logarithmic scale with various relative initial concentrations and diffusion coefficients.
These variations did not result in highly sensitive changes in the penetration depth. For example, increasing the diffusion coefficient by a factor of 2, 4, and 10 resulted in penetration depths that increased by 40%, 100%, and 300%, respectively.

### 3. Experiments

#### 3.1 Materials and tests

##### (1) Materials

In this study, we selected materials that resembled the concrete at the FDNPP as closely as possible (Nagoya University 2018). The cement types used were ordinary Portland cement (OPC) and siliceous fly ash (FA) blended cement (FAC). Therefore, in this study OPC with a density of 3.16 g/cm³ and a Blaine specific surface area of 3140 cm²/g, as well as FA blended cement (type II according to JISA6201:2015) with a density of 2.37 g/cm³ and a Blaine specific surface area of 4210 cm²/g of blended FA were used. The chemical compositions of these materials are shown in Table 1.

Two types of sand were used: pure crushed limestone (LS) with reduced clay levels, used as a reference, and river sand (RS). Fine particulates were washed out of the limestone. The RS, which contained small amounts of clays such as chlorite, was sourced from the same location as the sand in the FDNPP concrete.

##### (2) Mortar preparation

The mixture proportions for the concrete used in the FDNPP are shown in Table 2 (Nagoya University 2018). Because RI experiments require a small specimen size, we chose to use mortar instead of concrete. To determine the mixture proportion for the mortar, we removed the coarse aggregate from the total estimated mixture proportion and the mixture proportions of mortar examined are shown in Table 3 and the air content in mortar was set as 7% corresponding to 4.5% in concrete.

The water-to-cement ratio for the samples was 0.55, and the sand-to-cement ratio was 2.39. When creating the FAC, we replaced 15 mass% of the OPC with FA. Mortars were formed into rectangular specimens with dimensions of 20 × 50 × 50 mm. The samples were cured at 40°C for 3 months in sealed conditions or at 20°C for 1 year. There is no intention to compare the effects of curing condition in this study. Two different curing conditions were inevitable because of the nature of the project. All surfaces except for the immersion surface were coated with epoxy resin.

For specimens in the dried condition, the mortars were placed in an oven at 105°C until they reached a constant mass. The oven-drying was chosen in order to realize faster movement of moisture and to dry samples quickly. For surface carbonation conditions, the specimens were placed in a chamber at 20°C and 60% RH under a 5% CO₂ gas flow. This accelerated carbonation process resulted in a carbonation depth of 8 mm for the sample cured at 40°C for 3 months and 5 mm for the sample cured at 20°C for 1 year. Here, the carbonation depth is assumed to be equal to the neutralization depth determined by the color change after spraying the sample with phenolphthalein solution. For mortar specimens with Ca-leached surfaces, specimens were kept in ion-exchanged water with a liquid-to-solid ratio of 12. The water was replaced twice per week for 3 months. The depth of Ca leaching was 0.5 mm for samples cured at 40°C for 3 months.

##### (3) Immersion test

Table 4 shows the conditions for all immersion tests in
To prepare the solutions of 100 mM for the comparison of Cs, Sr and Y penetration, regent grade CsCl, SrCl$_2$, and YCl$_3$ were dissolved in distilled water. The elements used were stable isotope but not RI. The RI solutions used for labeling contained roughly 1 MBq of Cs-137 and Sr-90 standard solutions in 5 mL of stabilized solutions containing CsCl and SrCl$_2$, respectively (Japan Radioisotope Association). The immersion solutions, which contained CsCl, SrCl$_2$, or a mixture of both, were prepared and labeled with RI. The solution concentrations ranged from 100 nM to 100 mM, depending on the factors examined during the experiment. Prior to each immersion test, the mortar samples were placed in a 200 mL beaker with distilled water, and then put in a vacuum chamber for 24 hours for water-saturation. In this treatment, Ca-leaching is expected to be limited. Solutions were stored in aluminum-laminated bags (Al-bag). Mortar specimens were placed in the bags and exposed to different volumes of solution, depending on the design of the experiment. Because of the nature of RI experiments, it is best to reduce the amounts of RI used. Therefore, in some cases, we could not prepare large enough volumes of the solutions. The Al-bag was then closed and kept in a laboratory at an ambient temperature of about 24°C. Because strontium carbonates have low solubility and its precipitation formation by carbon dioxide from the atmosphere is expected during immersion, immersion experiments for the comparison between Sr and Y penetrations were conducted in a glovebox filled with nitrogen gas.

### Table 4 Levels of examination.

| Curing conditions | Materials | Degradation | Solution compositions  |
|-------------------|-----------|-------------|-----------------------|
| 40°C 3 months     | OPC-LS    | Sound       | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
|                   | OPC-RS    |             | 47 days 53 days Section 4.1 Section 4.2 53 days Section 4.4 |
|                   | FAC-LS    |             | Section 4.1 Section 4.2 53 days Section 4.4 |
|                   | FAC-RS    |             | Section 4.1 Section 4.2 53 days Section 4.4 |
| 20°C 1 year       | OPC-LS    | Sound       | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
|                   | OPC-RS    |             | 56 days Section 4.3 8 days |
| 40°C 3 months     | OPC-LS    | Carbonated  | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
|                   | OPC-RS    |             | 53 days Section 4.5 |
|                   | OPC-RS    | Ca-leached  | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
| 20°C 1 year       | OPC-LS    | Carbonated  | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
|                   | OPC-RS    |             | 56 days Section 4.6 |
| 40°C 3 months     | OPC-LS    | Dried       | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
|                   | OPC-RS    |             | 53 days Section 4.7 |
| 20°C 1 year       | OPC-LS    | Dried       | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
|                   |           | carbonated  | 100 mM* 100 nM 100 mM 1mM 10 μM 25 μM-CsCl +90 μM-SrCl$_2$ 25 μM-CsCl |
|                   |           |             | 40 min, 16 hr Section 4.8 |

*Stable isotopes. Others are labeled with radio isotopes.

---

**3.2 Measurement**

(1) **EPMA**

After immersion in 100 mM solutions of stable CsCl, SrCl$_2$, and YCl$_3$, the mortars were cut cross-sectionally. Elemental distributions were measured using an electron probe microanalyzer (EPMA). The electron acceleration voltage was 15 kV, the beam current was 200 pA, the beam diameter was 25 μm, and the dwell time was 40 ms/pixel, where each pixel represented an area of 50 × 50 μm. By mapping the data, we could use the differences between the chemical compositions of cement paste and aggregate to isolate the data from paste. The concentration profiles were obtained by averaging the data for the same penetration depth.

(2) **Radiation intensity**

We periodically measured the γ-ray and β-ray intensity using a NaI scintillation survey meter and a GM survey meter, respectively. Measurements were carried out for immersion solution from the bottom of the Al-bags and for the immersion surface of specimens. β-Rays from Cs-137 or Sr-90 were used for measurements near the surface because their range of detection is on the order of 0.1 mm in concrete. Because the range of γ-rays is more, the intensities of γ-rays from Cs-137 were measured to investigate behaviors in the bulk mortar (Sr-90 does not emit γ-rays). Therefore, the information from the GM survey meter was used to determine concentrations in the solution, while the information from the NaI survey meter was used to determine the total amounts of radioactive material. The duration of each measurement was 180 seconds.

(3) **Imaging by IP and quantitative profiles**

The procedure for measuring the elemental distribution using IP is shown in Fig. 2. After immersion, the surface of the mortar was wiped with paper and coated with an epoxy resin containing iron powder, which can prevent β-ray scattering between the immersion surface and the IP. After one night, we sliced thin sections with 1.6 mm thickness using a diamond wheel cutter. The specimens contain...
were exposed on an IP for several days with standard cement pastes containing 1 MBq/kg of Cs-137 or 0.33 MBq/kg of Sr-90. The IP used for these experiments was the BAS IP MS2025 (GE Healthcare). The signal stored in the IP was read by a Typhoon FLA9500 (GE Healthcare) in the phosphor mode, with a reading laser having wavelength of 635 nm, a photomultiplier voltage of 500 V, and a spatial resolution of 50 μm. The data, which was stored as a GEL file, were processed using ImageQuantTL (GE Healthcare). The intensity of radiation in each pixel was expressed as a photostimulated luminescence (PSL) value that are proportional to radiation amount. Using a standard paste containing specific concentrations of RI (Bq/kg), the PSL value could be converted to Cs-137 or Sr-90 concentrations with units of Bq/kg. Because the ratios of radiation Cs-137 and Sr-90, and material concentrations of stable Cs and Sr are known, the concentrations determined by the PLS values could be converted to determine the total material concentration in mol/kg.

(4) Distribution ratio
In order to compare the adsorption behaviors, distribution ratio to solid phase against solution phase was calculated. Distribution ratio (L/kg) is obtained by Eq. (1) from concentration in solid (mol/kg) and concentration in solution (mol/L) under the assumption that the ion exchange at the most surface of sample and contacting water is in an adsorption equilibrium even concentration profile is observed by diffusion.

\[
\text{Distribution ratio} = \frac{\text{Concentration in solid}}{\text{Concentration in solution}}
\]

Concentration in solid is obtained by quantitative evaluation of IP images. Concentration in solution is obtained by calculating the radiation dose rate change by GM survey meter for immersion solution and the initial material concentration.

4. Results and discussion

4.1 Comparison of Sr and Y penetration
Mortar specimens were immersed in 500 mL of 0.1 M chloride solutions containing Cs, Sr, and Y for 47 days at ambient temperature. The penetration profiles for Cs, Sr, and Y are shown in Fig. 3. The inset at the upper right corner shows the profiles near the surface. Y could only be detected at the surface of the mortar. It is estimated that the high pH of the cement hydrate prevented the movement of Y by forming a hydroxide of low solubility. The penetration depths of Cs and Sr were 15 mm and 3 mm, respectively. From these results, we concluded that the autoradiograph for the Sr-90 experiments could be used to accurately determine the distribution of Sr-90.

4.2 Coexisting effects of Cs and Sr
Mortar specimens cured at 40°C for 3 months were saturated in water and immersed in 6 mL solutions containing 100 nM of CsCl, SrCl₂, or both CsCl and SrCl₂ for 53 days. We selected this concentration because we expected the strongest interactions between solution and solid in dilute solutions according to the results presented by Haga et al. (2019); the smallest concentration that could be used for our measurement techniques was 100 nM.

The IP mapping image and the immersion profiles on a
The image shows that there were many positions at which Cs was concentrated. This may be because Cs preferentially adsorbs to materials such as clay included in aggregate. The penetration profile shows that Cs moved through the cement paste, decreasing in concentration with depth. By contrast, in the Sr mapping image, there was no obvious concentration maximum. The possible interactions between the cement paste and Sr are explained in the introduction.

The concentration of Cs on the surface was approximately $1 \times 10^{-8}$ mol/kg, and the penetration depth was 15 mm. For Sr, the concentration was $1 \times 10^{-7}$ mol/kg, and the depth was 5 mm. The interactions between Sr and solid were much stronger than Cs, resulting in less penetration. For a solution containing both Cs and Sr, the resulting profile was equal to the sum of the individual Cs and Sr profiles. This suggests that there were no additional effects from the coexistence of Cs and Sr, and for these material combinations, Cs and Sr behaved independently. Cs does not interact with cement hydrates and limestone (Ochs et al. 2016; Haga et al. 2019). By contrast, Sr can interact with cement hydrates through an ion exchange with Ca, as explained in the introduction. Therefore, we concluded that the coexistence of species had no additional effects at least in this combination of materials.

4.3 Effects of concentration

Water-saturated mortar specimens were fabricated from OPC and LS or OPC and RS cured at 20°C for 1 year. The specimens were immersed in CsCl solutions having different concentrations and volumes: 10 mL of 100 mM, 10 mL of 1 mM, and 100 mL of 10 μM. The dose rate measurements for each solution and sample are depicted in Fig. 5. Using β-ray measurements from the GM survey meter, the Cs concentrations of the solution were kept constant during immersion. Cs concentrations on the surface of the specimens increased with time, but the surface quickly became saturated. In the LS samples, the dose rates were high, with $10 \mu$M > 1 mM > 100 mM. The dose rates for RS samples were greater than those for LS samples. According to γ-ray measurements from the NaI survey meter, the solution concentration did not have significant effects on the amount of Cs penetrating the mortar in LS specimens. The dose rate was linearly correlated with the square root of time, suggesting that diffusion governed the behavior of Cs. In RS specimens, the correlation was also linear, but the slope was higher than that for LS, suggesting greater rates of Cs adsorption.

The penetration profiles of Cs on a logarithmic scale and the fitted diffusion profiles are illustrated in Fig. 6. Before reaching the detection limits, the penetration profiles fit the diffusion profiles well. We concluded that this occurred because of the limited interactions between Cs and the cement hydrates. The adsorption of Cs was almost one order of magnitude higher in RS compared with LS.

The distribution ratios of Cs between the specimen surface and the solution for different solution concentrations are shown in Fig. 7. Although the interactions between Cs and the solid surfaces were weak, the distribution ratio tended to increase at lower concentrations. In RS, this ratio was relatively high, at 1.8 L/kg but still limited. In pore solution of mortar, the concentration of K is relatively high, at 0.1 M order. This is thought to lower...
Fig. 5 Dose rates in the solution (upper) and in ordinary Portland cement (OPC) mortar specimens (lower) immersed in different concentrations of CsCl. Legend indicates that cement type-sand type-solution concentration. RS is river sand and LS is limestone sand. The dose rate of the solution is shown for $\beta$-rays measured with a GM survey meter. As an example, the $\beta$-ray dose rate measured using a GM survey meter is shown in the lower right panel, and $\gamma$-ray dose rate measured using a NaI scintillation survey meter is shown in the lower left panel.

Fig. 6 Penetration profiles for solutions containing different concentration of CsCl during 56 days and the fitted diffusion profiles. Legend indicates sample condition (no-carbonated)-sand type-solution concentration. LS is limestone sand and RS is river sand. For fitting, the surface concentrations were fixed as measured values. The flat regions beyond 20 mm are lower than the detection limit. The fitting ranges span from the surface to the position of the detection limits.

Fig. 7 Ratio of Cs distribution at the specimen surface of limestone mortar (LS) and river sand mortar (RS) to that in solution at various solution concentrations.
the distribution ratio of Cs in low ranges. The estimated diffusion coefficients calculated from the Cs and Sr penetration profiles at different concentrations are given in Fig. 8 (these penetration profiles are shown in Figs. 1, 4, and 6). In Fig. 8, two more data points obtained from the same kind of specimens but immersed in different solution conditions are added based on the project report (Nagoya University, 2018). The mortars used in these experiments were not degraded by Ca leaching or by carbonation. We found that concentration distributions in the range of $1 \times 10^{-12}$ to $5 \times 10^{-12} \text{ m}^2/\text{s}$ resulted in no significant effects on the apparent diffusion coefficients. The diffusion coefficients for Sr were approximately $1 \times 10^{-13} \text{ m}^2/\text{s}$, one order of magnitude lower than for Cs.

### 4.4 Effects of materials

Water-saturated mortar specimens were made of OPC or FAC and LS or RS cured at 40°C for 3 months. The samples were immersed in a 6 mL solution containing 25 μM CsCl and 90 μM SrCl$_2$ for 53 days. These concentrations were selected because they were the initial concentrations reported for the contaminated water after the FDNPP accident (Nagoya University 2018). The changes in the dose rate are depicted in Fig. 9. The γ-ray data from the NaI survey meter revealed a faster decrease in Cs concentration in RS samples compared with LS samples. The β-ray data followed a similar trend. In Fig. 10, the penetration profiles are shown. Because the experiments contained a solution with both Cs and Sr species, we could not separate Cs and Sr profiles quantitatively. However, from qualitative observations of the intensity on the linear scale, we found that RS absorbed more of the species than LS did. On the logarithmic scale, we found that penetration depths in FAC were smaller than in OPC; the depths were approximately 1/3 of those of OPC when the specimens were compared at a PSL of 0.1. The sand type did not show any significant effects on the penetration depth.

### 4.5 Effects of degradation: Ca leaching and carbonation

Water-saturated degraded mortar samples were fabricated from OPC and LS or RS cured at 40°C for 3 months. The samples were then degraded through carbonation or Ca leaching and immersed in a 6 mL solution containing 25 μM of CsCl and 90 μM of SrCl$_2$ for 53 days. The dose rate changes are presented in Fig. 11. According to the γ-ray data measured by the NaI survey meter, nearly all of the Cs was adsorbed to the carbonated samples within a few days. RS had no significant effects on the behavior. In the samples degraded by Ca leaching, the dose rate decreased, but to a limited extent than in...
carbonated samples. This difference can be attributed to differences in the degradation depth: Ca leaching had a depth of 0.5 mm, while carbonation reached a depth of 5 mm. For specimens with Ca leaching, RS adsorbed more Cs than LS. The β-ray data showed that Sr behaved differently than Cs. In carbonated specimens, decrements in β-ray signals were less significant that for γ-rays, suggesting that less Sr (no γ-ray emitter) adsorbed on the carbonated cement. By contrast, in the Ca-leached specimens, especially those containing LS, β-ray signals decreased more than did γ-ray signals. Additionally, the effects of RS were reduced. These results suggest that Sr adsorbed more on Ca-leached specimens. We concluded that Cs interacted preferentially with carbonated materials and with the clay particles in RS, while Sr interacted preferentially with cement hydrates during Ca exchange.

In cement paste, the products of the carbonation reaction include calcite and amorphous aluminosilicate or silica and alumina gel. Amorphous aluminosilicate formed could be a geopolymer, which can adsorb alkali metals through an ion-exchange reaction corresponding the amount of Al(IV) contained. The formation of a geopolymer-like material in concrete could be the reason for the strong adsorption of Cs on the carbonated cement even in high K concentration because of the high Cs ion selectivity (Ichikawa et al. 2020). Additionally, Ca leaching could contribute to increased adsorption because of the decreased Ca/Si ratio in C-S-H. A previous study showed that C-S-H with lower Ca/Si ratios could adsorb larger amounts of Cs (Ochs et al. 2016).

![Fig. 10](image1.png) The effects of materials on the penetration profiles. Legend indicates cement type-sand type. OPC is ordinary Portland cement, FAC is fly ash blended cement, LS is limestone sand, and RS is river sand. The specimens were immersed in a solution containing 25 μM Cs and 90 μM Sr for 53 days. Because specimens were immersed in a mixed solution of Cs and Sr, it is difficult to convert the PSL to molar concentration. On the left, PSL is shown on a linear scale, and on the right, PSL is shown on a logarithmic scale.

![Fig. 11](image2.png) Dose rate changes in the solution during an immersion test using various combinations of sand and degradation conditions. Legend indicates sand type-degradation conditions. LS is limestone sand, RS is river sand, Carb. is carbonation, and Leach. is Ca leaching. The specimens were immersed in a mixed solution of 25 μM Cs and 90 μM Sr. The left represents the γ-ray dose rate, and the right represents the β-ray dose rate.
The penetration profiles for this experiment are illustrated in Fig. 12. Because the experiments were conducted in mixed solutions, we could not quantitatively separate Cs and Sr profiles. However, from the intensities on the linear scale, we could qualitatively observe that the carbonated samples adsorbed Cs and Sr more than the Ca-leached samples and the undegraded specimens (Fig. 10). This was consistent with the dose rate measurements. On the logarithmic scale, we observed that the penetration depths were smaller in carbonated specimens than in Ca-leached specimens. However, because Cs was completely adsorbed in carbonated samples, it is unclear whether the effects of carbonation on penetration were influenced by the limited quantity of Cs. We can conclude that carbonation affected Cs penetration more than Sr, but to further investigate penetration in carbonated samples, we intend to perform further experiments with greater volumes of solution.

4.6 Effects of carbonation on Cs

As discussed in the previous section, Cs rapidly and completely adsorbed to carbonated specimens, making it difficult to discuss the effect of carbonation on penetration depth. Therefore, we repeated the experiments using larger quantities of Cs in solution. The mortar specimens were cured at 20°C for 1 year, carbonated, and saturated with water in a vacuum. The volume for the 100 mM and 1 mM solutions was 10 mL, while the volume for the 10 μM solution was 100 mL. The immersion time was 56 days. The dose rate changes in these solutions are shown in Fig. 13. For every case, we observed a decrease in concentration; however, the decrease was less significant than in the cases shown in Fig. 11. At higher concentrations, the decreases were less significant. The decrease in RS was slightly greater than in LS, suggesting that RS-based mortars adsorbed more Cs. However, carbonation had a greater effect on adsorption than RS. For the solution with the lowest concentration of Cs at 10 μM, a decrease in concentration was less than the solution with 1 mM because the volume of solution was greater.

The penetration profiles of Cs in carbonated and non-carbonated specimens are depicted in Fig. 14. In general, the surface concentration of Cs increased significantly in carbonated samples, and the concentration decreased more rapidly than non-carbonated specimens. The total amounts of penetration, which are governed by the higher concentrations near surfaces, increased but the penetration depths seemed limited. For example, when LS was exposed to 100 mM of Cs (red curves), the surface concentration increased by one order of magnitude in the carbonated sample, and the concentration (thick red curve) decreased by more than two orders of magnitude in 5 mm from the surface. By contrast, in the non-carbonated LS sample in 100 mM (thin red curve), the position at which the Cs concentration decreased as much as two orders of magnitude was 15 mm. For LS at 10 μM (blue curves), the increase in the surface concen-
tration was more than two orders of magnitude greater in the carbonated sample, and the concentration of carbonated sample (thick blue curve) decreased by two orders of magnitude in 2 mm from the surface. In the non-carbonated sample under the same conditions (thin blue curve), the position at which the concentration decreased by two orders of magnitude was 10 mm from the surface.

However, this experiment could not determine whether the precise location of penetration depth increased or decreased in carbonated samples. In an experiment using cement paste and large volumes of 500 mM solution and high concentration of 1 M (Haga et al. 2019), the Cs rapidly moved through and beyond the carbonated portion, showing a similar diffusion profile to Cs in non-carbonated paste. Therefore, it is possible to conclude that carbonated paste can behave as an adsorbing material, but its effect on diffusion is limited, and the penetration depth continued to increase throughout the carbonated region.

We calculated the distribution ratios between Cs concentrations at the carbonated surface and the surrounding solution, shown in Fig. 15. Even for carbonated samples, the distribution ratio was relatively small at high concentrations such as 100 mM. Upon lowering the concentration, the distribution ratios increased to 1000 L/kg. The results from this study are consistent with a study that measured in an immersed ground powder of carbonated cement paste (Haga et al. 2019).

4.7 Effects of drying

Oven-dried mortar specimens were made of OPC and LS or RS cured at 40°C for 3 months. The samples were immersed for 6 hours in two different 6 mL solutions: a 25 μM CsCl solution and a solution containing 25 μM CsCl and 90 μM SrCl2. In this experiment, the Cs concentrations were kept constant for all sample ages and cases. The penetration profiles for these conditions are presented in Fig. 16. In 6 hours, the Cs penetrated 6 mm and 3 mm into the LS and RS mortars, respectively. The Cs concentration on the surface of RS samples increased significantly compared to the case of LS. Even during water suction, the interactions between Cs and RS retarded the Cs penetration.

4.8 Penetration behaviors in oven-dried carbonated mortar

Finally, oven-dried carbonated mortar specimens cured at 20°C for 1 year were immersed in 500 mL of 10 μM CsCl or 600 mL of 10 μM SrCl2. The carbonation depth was approximately 5 mm. The carbonation resulted in a hydrophobic mortar surface; water did not adsorb to the surface of the carbonated material when it was immersed. Therefore, water was forced to penetrate the sample by placing the solution and specimen in a vacuum chamber for 40 minutes. Then, the specimens were sliced into two pieces. One piece was used for penetration measurement and the cut surface of another piece was coated with rapid hardening resin and immersed in the same solution until 16 hours under vacuum. The concentration of the solution was kept constant during this process. The mapping of Cs and Sr penetration in oven-dried mortar during a 40-minute period, measured using IP, is illustrated in Fig. 17. Cs had a penetration depth of 20 mm, while Sr had a depth of 10 mm. As described earlier in this report, when water moved rapidly through the mortar, some of the Cs and Sr adsorbed to the carbonated cement paste and cement hydrates, respectively. In both speci-
ments, there were highly concentrated locations, but the mechanism for the formation of these spots is unclear.

The penetration profiles for these experiments are shown in Fig. 18. When we evaluated the profiles on a linear scale, we found that more Cs adsorbed to carbonated parts than Sr. Furthermore, the amount of Cs adsorbed increased significantly from $4 \times 10^{-5}$ mol/kg to $2 \times 10^{-4}$ mol/kg between 40 minutes and 16 hours, and $3 \times 10^{-3}$ mol/kg after 56 days as shown in Fig. 14, suggesting that it can take hours or days for interactions between the solid phase and Cs to achieve an equilibrium. Sr showed also increase in surface concentration between 40 minutes and 16 hours and takes more than hours for the interaction with solid phases.

When we examined the data on a logarithmic scale, we found that the penetration nearly spanned the entire length of the mortar specimen after 16 hours. Although the concentration decreased by three or more orders of magnitude within the first 10 to 20 mm, these depths were significantly larger than in water-saturated specimens. Additionally, the profile was uneven, implying that there may be a preferential route for water movement, such as cracks. Further experiments are needed to understand these phenomena in detail.

5. Conclusions

In this technical report, we examined the penetration behaviors of Cs and Sr in mortar by considering the factors that affect adsorption and diffusion. Our experiments were conducted in a wide concentration range, from 100 nM to 100 mM. For measurements in dilute conditions, we quantitatively evaluated the penetration behaviors with autoradiography using radioisotopes and an imaging plate. From our results, we made the following conclusions:

- The coexistence of Cs and Sr did not result in changes in behavior for either element.
- Changes in concentration and the presence of clay had no effects on the apparent diffusion coefficients for Cs and Sr, even though Cs is adsorbed by clays.
- The penetration depth of Sr was much smaller than that of Cs. FAC is significantly more resistant to penetration than OPC.
- Carbonation increased the amount of adsorption, especially for Cs. The adsorption of Cs increased more in carbonated cement than in mortars containing clay. Sr was not affected by the clays used in this study.
- Ca leaching increased the adsorption both Cs and Sr.
- In the oven-dried condition, clays retarded the penetration of Cs but not for Sr.
- In oven-dried carbonated concrete, the penetration depths under vacuum suction condition were 20 mm
for Cs and 10 mm for Sr during a 40-minute period. This was significantly more than the depths of 15 mm for Cs and 5 mm for Sr over 53 days in the water-saturated condition.

- The interactions between Cs or Sr and the solid phase took hours or days to reach equilibriums.

Acknowledgements
This study expands on the 2018 fiscal year report for the “Nuclear Energy Science & Technology and Human Resources Development Project through Concentrating Wisdom” supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan Grant Number JPMX 17D17948568, and the JAEA Nuclear Energy S&T and Human Resource Development Project through the Concentrating Wisdom Grant Number JPJA20P2033545.

References
Arayro, J., Dufresne, A., Zhou, T., Ioannidou, K., Ulm, J.-F., Pellenq, R. and Béland, L. K., (2018). “Thermodynamics, kinetics, and mechanics of cesium sorption in cement paste: A multiscale assessment.” Physical Review Materials, 2, 053608.

Atkins, M. and Glasser, F. P., (1992). “Application of Portland cement-based materials to radioactive waste immobilization.” Waste Management, 12 105-131.

Atkinson, A. and Nickerson, A. K., (1984). “The diffusion of ions through water-saturated cement.” J. Mater. Sci., 19, 3068-3078.

Dezerald, L., Kohanoff, J. I., Correa, A. A., Caro, A., Pellenq, R. J.-M., Ulm, F. J. and Saül, A., (2015). “Cement as a waste form for nuclear fission products: The case of $^{90}$Sr and its daughters.” Environmental Science & Technology, 49, 13676-13683.

Duque-Redondo, E., Yamada, K., Lopez-Arbeloa, I. and Manzano, H., (2018). “Cs-137 immobilization in C-S-H gel nanopores.” Phys. Chem. Chem. Phys., 20, 9289-9297.

Duque-Redondo, E., Yamada, K. and Manzano, H., (2021). “Cs retention and diffusion in C-S-H at different Ca/Si ratio.” Cement and Concrete Research, 140, 106294.

Evans, N. D. M., (2008). “Binding mechanisms of radionuclides to cement.” Cement and Concrete Research, 38, 543-553.

García-Gutiérrez, M., Missana, T., Mingarro, M., Morejón, J. and Czormenzana, J. L., (2018). “Cesium diffusion in mortars from different cements used in radioactive waste repositories.” Applied Geochemistry, 98, 10-16.

Fuller, A. J., Shaw, S., Peacock, C. L., Trivedi, D., Small, J. S., Abrahamsen, L. G. and Burke, I. T., (2014). “Ionic strength and pH dependent multi-site sorption of Cs onto a micaceous aquifer sediment.” Applied Geochemistry, 40, 32-42.

Haga, K., Watanabe, S. and Yamada, K., (2019). “Quantification of interaction between alkali metal ions and C-(A)-S-H/cement paste for a wide range of ion concentrations.” 15th International Congress on the Chemistry of Cement, 339.

Hosokawa, Y., Yamada, K., Johannesson, B. and Nilsson, L-O., (2011). “Development of a multi-species mass transport model for concrete with account to thermodynamic phase equilibriums.” Materials and Structures, 44(9), 1577-1592.

Hosokawa, Y., Yamada, K., Haga, K. and Ogawa, S., (2019). “Numerical modelling of the alkali penetration into cementitious materials using the coupled thermodynamic phase equilibrium mass transfer system.” Proc. 15th Int. Congr. on the Chemistry of Cement, 339.

Ichikawa, T., Watanabe, S., Arai, H., Haga, K. and Yamada, K., (2020). “Metakaolin-based geopolymer for immobilizing concentrated Cs generated by volume reduction of $^{137}$Cs-contaminated waste.” J. of the Society for Remediation of Radioactive Contamination in the Environment, 8(1), 3-16.
Idemitsu, K., Furuya, H., Hara, T. and Inagaki, Y., (1992). “Migration of Cesium, Strontium and Cobalt in water-saturated Inada Granite.” J. of Nuclear Science and Technology, 29, 454-460.
Ito, M., Nakarai, K., Hayashi, A. and Kawai, K., (2013). “Effects of moisture content and immersion condition on the cesium penetration and dissolution in mortar.” Cement Science and Concrete Technology, 67, 210-215. (in Japanese)
Jiang, J., Wang, P. and Hou, D., (2017). “The mechanism of cesium ions immobilization in the nanometer channel of calcium silicate hydrate: a molecular dynamics study.” Physical Chemistry Chemical Physics, 19, 27974-27986.
Kittnerová, J., Drtinová, B., Štamberg, K., Vopalák, D., Evans, N., Deissmann, G and Lange, S., (2020). “Comparative study of radium and strontium behaviour in contact with cementitious materials.” Applied Geochemistry, 122, 104713.
Li, K. and Pang, X., (2014). “Sorption of radionuclides by cement-based barrier materials.” Cement and Concrete Research, 65, 52-57.
Missana, T., García-Gutiérrez, M., Mingarro, M. and Alonso, U., (2018). “Comparison between cesium and sodium retention on calcium silicate hydrate (C-S-H) phases.” Applied Geochemistry, 98, 36-44.
Nagoya University (2018, 2019, 2020). “Estimation of contamination distribution in concrete members of Fukushima Daiichi NPS buildings based on mechanism-understanding of radioactive nuclides contamination of cement-based materials.” (Report for MEXT project mentioned in the acknowledgement). (in Japanese)
Ochs, M., Mallants, D. and Wang, L., (2016). “Uptake values for caesium, strontium, radium, and silver.” Radionuclide and Metal Uptake on Cement and Concrete, Springer Int. Publisher, 45-79.
Tachikawa, H., Haga, K., Watanabe, S. and Yamada, K., (2020). “Local structures and electronic states of C-S-H–Sodium–H2O interface: NMR and DFT studies.” J. Physical Chemistry C, 124, 5672-5680.
Tokyo Electric Power Co., Inc., (2019). “Mid-long-term roadmap for decommissioning of Fukushima Daiichi nuclear power station, Tokyo Electric Power Co., Inc.” The cabinet members conference on Countermeasures for Decommissioning and Contaminated Water, Tokyo, Japan, Dec. 27, 2019. Retrieved from: <https://www.meti.go.jp/earthquake/nuclear/pdf/20191227.pdf> [Accessed 16 June 2020]. (in Japanese)
Wang, P., Zhang, Q., Wang, M., Yin, B., Hou, D. and Zhang Y., (2019). “Atomic insights into cesium chloride solution transport through the ultra-confined calcium–silicate–hydrate channel.” Physical Chemistry Chemical Physics, 21, 11892-11902.
Yamada, K., Takeuchi, Y., Igarashi, G. and Osako, M., (2019). “Field survey of radioactive cesium contamination in concrete after the Fukushima-Daiichi nuclear power station accident.” Journal of Advanced Concrete Technology, 17(12), 659-672.
Yamada, K., Osako, M. and Yasutaka, T., (2020). “Study on the strategy for final disposal and reuse of decontamination wastes after the Fukushima Daiichi NPP Accident.” Proc. WM Symposia, 20426.