Technical report

General Overview of the Research Project Investigating the Radionuclide Solution Behavior in Mock Mortar Matrix Modeled after Conditions at the Fukushima-Daiichi Nuclear Power Station

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Abstract
Decommissioning of the Fukushima Daiichi Nuclear Power Station (FINPS) in a proper manner requires assessment of the contamination levels and mechanisms for contamination in the concrete structures. Between January 2018 and March 2020, Japan’s Ministry of Education Ministry of Education, Culture, Sports, Science and Technology (MEXT) conducted a project called “The Analysis of Radionuclide Contamination Mechanisms of Concrete and the Estimation of Contamination Distribution at the Fukushima Daiichi Nuclear Power Station”. In this review, we outline the results of this study. The experimental results from the first project indicate that concrete carbonation, Ca leaching, and drying conditions affected the adsorption behaviors of Cs and Sr and therefore, their penetration depths. Additionally, the studies showed that α-nuclides precipitated on the surface of the samples because concrete causes a high pH. A reaction transport model was developed to assess further the adsorption characteristics of Cs and Sr in carbonated cement paste and on concrete aggregates. The model used real concrete characteristics from the materials used at FINPS and historical boundary conditions at the site, including radionuclide concentrations and penetration profiles within the turbine pit wall. Capillary water suction resulting from dried concrete was evaluated by considering structural changes in cement hydrates using X-ray CR and 1H-NMR relaxometry.

1. Introduction
1.1 Background for the research project
Following the 2011 Fukushima Daiichi Nuclear Power Station (FINPS) accident, its decommissioning has been conducted as a national program that includes waste management and the retrieval of the spent fuels and fuel debris. The program also details the decommissioning of concrete structures (METI 2019). A plan for decommissioning the plant must include an assessment of the degree of concrete contamination because of the enormous quantity of material. By estimating the contamination depth and implementing appropriate decontamination methods, the volume of concrete that must be disposed can be reduced. However, before selecting a decontamination method, the extent and fundamental contamination mechanisms must be investigated. For example, radio-Cs and radio-Sr are major radionuclides for exposure. In the environment, Cs is known to become fixed in the soil, and the amount dissolved in groundwater is limited. By contrast, Sr tends to be dissolved in groundwater and can spread easily in the environment, but it will not concentrate in specific locations. These are necessities to understand how Cs and Sr behave in concrete.

To estimate the contamination depth at the time of decontamination or decommissioning, numerical simulations of the ingress of radionuclides in concrete can be useful. Numerical simulations can be used to consider contamination mechanisms such as material transport models (Meeussen 2003; Nguyen et al. 2006; Hosokawa et al. 2011; Guo et al. 2018; Yang et al. 2019; Idiart et al. 2020).

Based on the background presented above, between January 2018 and March 2020, Japan’s Ministry of
Education, Culture, Sports, Science and Technology (MEXT) completed a project called “The Analysis of Radionuclide Contamination Mechanisms of Concrete and the Estimation of Contamination Distribution at the Fukushima Daiichi Nuclear Power Station” as a part of the F1NPS decommissioning project. Another project, “Quantitative Evaluation of Contamination in Reinforced Concrete Members of Fukushima Daiichi NPS Buildings Considering the Actual Environment Histories for Legitimate Treatments”, began in October 2020 and will continue until March 2023. In the first project, the fundamental mechanisms of concrete contamination were studied, while the next project, which will consider the realistic concrete conditions, will conduct a quantitative contamination estimation for some portions of the concrete structure. These projects are composed of several independent studies that are more detailed in their investigations of adsorption/ingress of several radionuclides including α-nuclides, water suction in dried concrete, and numerical modeling. The results obtained from these studies will be published in separate papers. In this review, we introduce the outline of the results of the first project. We also focus on a literature survey of the materials used in F1NPS and the boundary condition variations before and after the accident.

1.2 Framework of the research project

Figure 1 shows the framework of the 2018-2020 study, the objective of which was to estimate the extent of contamination at the time of plant decommissioning. To do this, we investigated the fundamental mechanisms for concrete contamination to develop a numerical model for the F1NPS case.

Many previous studies have investigated chloride ingress into concrete and proposed various models to explain the transport behavior. Some of these models are empirical (JSCE 2010; Andrade et al. 2013), while others incorporate sophisticated theory. However, there are few studies that analyse the contamination in real structures; thus, the existing studies may not help estimate the contamination at F1NPS (Farfan et al. 2011; Golovich et al. 2014; Yamada et al. 2019). Therefore, the contamination estimations should be performed using a theoretical approach. We considered Cs-137 and Sr-90, which are the typical important radionuclides for exposure. We assumed that their ingress behaviors in concrete are driven by diffusion phenomena and ion interactions between the pore solution and the solid phase of concrete. To study material transport, previous works have developed reaction transport models. To estimate material ingress in concrete using these models, there are several requirements: the adsorption characteristics of all ions between the solution and concrete constituents, pore structure and porosity, tortuosity, degree of water saturation, environmental conditions and time variation, which will serve as the boundary conditions.

Many studies have explored the adsorption characteristics and interactions of Cs and Sr as summarized by Ochs et al. (2016). However, the studies on ingress in concrete are limited especially in realistic diluted concentration ranges (Yamada et al. 2020). The objective of this research project is to estimate the contamination at F1NPS, not in general concrete; therefore, we must consider the actual materials and environmental conditions in addition to the fundamental development of a simulation model. Moreover, even though there are many studies on chloride ingress in concrete, most of them are in water-saturated conditions, not in unsaturated and partially dried conditions. Based on these limitations in previous approaches, we have established a basic

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Fig. 1 The activity framework for the project conducted between January 2018 and March 2020 (Yamada et al. 2021b).
Table 1 Concrete mixture for the reactor Unit 3 of F1NPS (Nomura et al. 1974).

| Application               | Gmax (mm) | Fc (kgf/cm²) | Slump (cm) | Air (%) | W/C | s/a | W (kg/m³) | C (kg/m³) | S (kg/m³) | G (kg/m³) | AE agent (cc/m³) |
|---------------------------|-----------|---------------|------------|---------|-----|-----|-----------|-----------|-----------|-----------|-----------------|
| General use               | 25        | 225           | 12±2       | 4.5±1.0 | 55  | 45  | 182       | 330       | 790       | 1000      | 99              |
| Shielding                 | 25        | 225           |            |         | 54  | 41  | 178       | 330       | 723       | 1081      | 99              |
| Artificial rock           | 40        | 135           |            |         | 59.6| 40  | 158       | 265       | 742       | 1152      | 80              |

framework for the research project.

An estimation of radionuclide ingress in concrete requires boundary conditions, a developed model and experimental parameters relating to the material characteristics. Therefore, this study can be divided into three parts: boundary conditions, experiments and modeling. The boundary conditions depend on the concrete characteristics and the external environment to which the concrete has been or will be exposed. Concrete characteristics include the cement type and aggregate source, as well as factors affecting material transport within the concrete, such as moisture content, temperature (Kiran et al. 2021), carbonation, Ca leaching (Haga et al. 2019), and cracking (Win et al. 2004). Environmental conditions include changes in concentrations of important radionuclides such as Cs, Sr and α-nuclides in the contaminated water over time. As the reaction transport model, we used a numerical model of the thermodynamic phase equilibrium between the pore solution in saturated concrete and the cement hydrate and aggregate, combined with a multi-species transport model based on the Nernst-Planck equation (Hosokawa et al. 2011, 2019). Another model was used to describe moisture transport (Kiran et al. 2020). The parameters for these models were determined experimentally. The adsorption, ingress and dissolution of nuclides could depend on several factors, including the effects of coexisting Cs and Sr species, nuclide concentrations, and concrete materials. These conditions were investigated experimentally. At F1NPS, many concrete sections were dry and not saturated with water, particularly before the accident. Therefore, the analysis must also consider the influence of capillary water suction and ion adsorption on the concrete constituents. These behaviors were examined experimentally.

Each point of the study identified for the project requires an individual research focus. To determine boundary conditions, we conducted a literature survey. Experimental studies included the evaluation of adsorption characteristics for individual concrete components such as cement and aggregate and for cement paste degraded by Ca leaching and carbonation. The Ca silicate hydrate (C-S-H) phase has the largest impact on material transport in concrete. Since C-S-H is an X-ray amorphous material, we evaluated the crystalline structure using solid-state nuclear magnetic resonance (NMR) spectroscopy for 29Si and 27Al. To evaluate nuclides in realistic concentrations, we used the radioisotopes (RI) of 137Cs and 90Sr, and we studied the penetration by radiography using an imaging plate. To examine α-nuclides, Ra and Am extracted from MOX fuel was used, and the penetration was evaluated using a profile grinding method. The effects of water suction in the concrete were evaluated using X-ray computed radiography (XCR) and 1H-NMR spectroscopy, which could detect changes in the microstructure of C-S-H. Finally, for the contamination model, we used a thermodynamic phase equilibrium model in PHREEQC to simulate the chemical reactions between the C-S-H or the aggregate and Cs and Sr using dissolution equilibrium constants from literature and our experiments. The model incorporated all ion species that were significant in the case study.

2. Prior research on F1NPS (Nagoya University 2018)

2.1 Materials and mixture in F1NPS structures

Because this research project focuses on radionuclide penetration behaviors in the context of F1NPS, it is important to copy the mixture, materials, and curing/alteration conditions of the concrete in the F1NPS structures as accurately as possible. The mixture for the concrete at F1NPS is shown in Table 1 (Nomura et al. 1974). The only reactor unit for which there are public documents about the mixture is Unit 3, so the mortar mixture for this project was based on the composition of concrete in this unit. Based on the report (Nomura et al. 1974), fly ash cement type B (FAC), which contains extra SO3 (2.5 mass %, which is in the range specified by the JIS standard) compared with ordinary Portland cement, was used as a binder to reduce drying shrinkage. The drying shrinkage may be a cause of the restrained cracking under a high reinforcement ratio. FAC was chosen even though there are other alternatives for moderate heat cement, because a large amount of fly ash could be obtained from a thermal power station nearby (Joban Thermal Power Station).

The materials used in the concrete at F1NPS are shown in Table 2. There were two different types of cement used: ordinary Portland cement (OPC) and fly ash cement type B (FAC). According to previous literature, FAC was mainly used for the concrete in the buildings (Saeki 1962; Kaburagi 1969; Nomura et al. 1974). All the aggregates are obtained from the neighborhood and were mainly river gravel, mountain gravel and river sand. Based on the report (Nomura et al. 1974), the concrete density needed to be above 2.23 g/cm³, with a coarse aggregate density above 2.7 g/cm³.
and a fine aggregate density above 2.6 g/cm³ to ensure shielding capability. River gravel, mountain gravel and river sand passed these criteria, as shown in Table 2. Based on the reports (Saeki 1962; Kaburagi 1969), TEPCO opened its own quarrying plant and used the crushed aggregates to construct breakwaters or civil structures. The quarrying plant was closed after construction.

2.2 Characterizing the aggregates from Abukuma River

The aggregates were collected from Abukuma River, Niida River and Takikawa River, which are thought to be the source of material for reactor No.1. Unfortunately, we could only obtain enough aggregates for preparing mortar specimens from the Abukuma River. Figure 2 shows the visual appearance of the aggregates after the sieving procedure. Rhyolite, andesite, granite and minor components such as mineral fragments were detected using this macroscopic diagnosis.

Table 2 Cement type and the origin of the aggregate (MRI 2015).

| Reactor unit | Cement type | Type of coarse aggregate | Source of coarse aggregate | Type of fine aggregate | Source of fine aggregate |
|--------------|-------------|--------------------------|---------------------------|-----------------------|-------------------------|
| 1            | OPC         | River gravel             | Niida River, Fukushima    | River sand            | Abukuma River, Miyagi   |
|              | FAC         | Crushed stone            | Takikawa River, Fukushima |                       |                         |
| 2            | FAC         | River gravel             | Niida River, Fukushima    | River sand            | Abukuma River, Miyagi   |
|              |             | Crushed stone            | Takikawa River, Fukushima |                       |                         |
| 3            | FAC         | River gravel             | Niida River, Fukushima    | River sand            | Niida River, Fukushima  |
|              |             | Crushed stone            | Takikawa River, Fukushima |                       |                         |
| 4            | FAC         | River gravel             | Niida River, Fukushima    | Mountain sand         | Kohisa/Oriki, Fukushima |
|              |             | Crushed stone            | Kohisa/Oriki, Fukushima   |                       |                         |
|              | OPC         | Mountain gravel          | Takikawa River, Fukushima | River sand            | Abukuma River, Miyagi   |
|              |             |                          | Niida River, Fukushima    |                       |                         |
| 5            | FAC         | River gravel             | Niida River, Fukushima    | River sand            | Abukuma River, Miyagi   |
|              |             |                          | Takikawa River, Fukushima |                       |                         |
| 6            | OPC         | River gravel             | Niida River, Fukushima    | River sand            | Abukuma River, Miyagi   |
|              | FAC         | Mountain gravel          | Kohisa/Oriki/Takikawa River, Fukushima | River sand | Abukuma River, Miyagi   |

Table 3 Rock types in aggregate composition.

| Rock type                | Composition (%) |
|--------------------------|-----------------|
|                          | Above 20 mm     | 5 to 20 mm | Under 5 mm |
| Rhyolitic welded tuff    | 31              | 30         | 6          |
| Andesite                 | 31              | 32         | 10         |
| Basalt                   | N/A             | 6          | 3          |
| Granite                  | 36              | 18         | 28         |
| Diorite                  | N/A             | 7          | 8          |
| Sandstone                | 2               | 2          | 1          |
| Minor components         | N/A             | 5          | 44         |

Fig. 2 Visual appearance of the aggregate from the Abukuma River.
on grain size. For example, grains greater than 5 mm contained about 30% rhyolitic welded tuff and andesite, but grains smaller than 5 mm contained only about 10% of each. Grains less than 20 mm contained basalt and diorite, but those above 20 mm did not. The sandstone component contained relatively high amounts of clay minerals.

(2) Qualitative analysis of the mineral composition

Figure 3 shows the XRD patterns for the aggregate from the Abukuma River. The measurements were conducted using an X’pert PRO MPDP from PANalytical instrument under the following conditions: Cu-Kα as X-ray source, 45 kV tube voltage, 40 mA tube current, 5 to 65° (20) scanning range, 0.033° step width and 0.42 sec/step scanning speed. Both samples contained quartz, plagioclase, K-feldspar, amphibole, muscovite and chlorite. The sample smaller than 75 μm showed stronger diffraction peaks of amphibole, muscovite, and chlorite. Even though no clay minerals were detected by XRD, these three minerals indirectly suggest that the finer particles contain more clay minerals because they tend to be clay minerals by weathering.

(3) Cs and Sr sorption test onto aggregate

Table 4 shows the summary of the sorption test when specimens were immersed into solutions having different concentrations of CsCl, SrCl2 or a combination of CsCl and SrCl2. The solutions were made in distilled water or a supernatant solution with cement paste. The grains were sieved to collect particles under 2.5 mm in diameter. The mixtures in the supernatant solution with ordinary Portland cement paste. The grains were sieved under 2.5 mm. The solution from the supernatant solution with OPC paste should contain elements from the cement composition (mainly Ca, Na and K are expected to have some influence). The data shows that Cs had higher rates of adsorption to the aggregate compared with Sr. In the mixtures containing the supernatant solution with cement paste, Cs and Sr were less likely to adsorb to the aggregate compared with the solutions in distilled water.

2.3 Boundary conditions for radionuclide concentrations and the target concrete characteristics

(1) Boundary conditions before the accident

As a result of our investigation, we could obtain in-
formation about the construction records for the first-floor building, but we could not obtain any information from public documents about the environmental conditions since the beginning of the commercial operation. Therefore, to determine the environmental conditions before the accident, we used the results from a technical concrete evaluation of the aging of Unit 1, which was submitted by TEPCO to the organization formerly known as the Nuclear and Industrial Safety Agency on 25 March 2011. We also used descriptions in the existing literature that described concrete design and construction guidelines.

(i) Overview of the long-term performance assessment of concrete structures
The evaluation criteria for the long-term performance assessment of concrete deterioration are shown in Table 5 (TEPCO 2011). According to the technical evaluation and assessment manual at that time (summary manual, JNES-SS-0808-02, deterioration of strength and shielding capacity of concrete JNES-SS-0512-04), strength deterioration and shielding capacity can be considered as aging events for concrete, assuming long-term operation. According to JNES-SS-0512-04, strength loss and shielding capacity loss should be evaluated as concrete aging events, assuming the long-term service of the plants. In the long-term performance assessment of the F1NPS Unit 1 (TEPCO 2011), the evaluation was made as follows based on Table 5.

For each aging event factor that affects the strength deterioration and the shielding properties of concrete, evaluated the concrete structures shown in Tables 6 and 7. We selected factors that we assumed would have a significant impact on the deterioration of strength and shielding, considering the operating conditions of the concrete structure.

| Event | Factor | Evaluation guidelines |
|-------|--------|------------------------|
| Heat | Confirmation that the concrete temperature is below the temperature limit specified in standards such as JASS 5N, as assessed by temperature analysis results |
| Radiation | Confirmation that the predicted radiation dose for the assessment period was assessed to ensure that it is not at a level that would affect the strength of the concrete. |
| Carbonation | Carbonation depth measurements were carried out to assess the current level of carbonation. Checking that the carbonation depth did not reach a level at which the steel bars begin to corrode using the carbonation rate formula. |
| Chloride penetration | Using the results of the chloride ion concentration measurements and a prediction formula, check that the corrosion loss in reinforcing steel during the assessment period does not exceed the corrosion loss in reinforcing steel when cracks occur in the concrete cover. |
| Alkali silicate reaction (ASR) | Check that the test records for the aggregates show sufficient resistance to ASR. If ASR cannot be ruled out, check to ensure that measures to control ASR have been taken. In addition to confirming whether ASR has occurred by visual inspection, confirm whether it may occur in the future according to the results of accelerated expansion tests. In addition, the possibility that ASR may occur in the future can be confirmed using the results of accelerated expansion tests. |
| Machine vibration | For machine foundations, check that there are no harmful cracks on the concrete surface near the point at which the equipment is fixed to the concrete foundation. |
| Freeze-thaw cycle | For machine foundations, check that there are no harmful cracks on the concrete surface near the point at which the equipment is fixed to the concrete foundation. If there is a risk of freezing and thawing, check whether it has been assessed using the JASS document entitled “Distribution chart of freezing damage risk”. If there is a risk of freezing and thawing, check whether measures against freezing and thawing have been taken according to air volume test records. If the occurrence of freezing and thawing cannot be ruled out, the site should be checked by visual inspection, and it should be determined if the results of the freezing and thawing tests, can be used as a reference to make comprehensive judgments. |

Table 5 Evaluation criteria for the assessment of long-term performance relating to concrete deterioration.

| Event | Factor | Evaluation guidelines |
|-------|--------|------------------------|
| Heat | The temperature of the concrete at the high-temperature point can be determined using temperature distribution analysis and it can be confirmed that the temperature is below the maximum internal temperature limit for neutron shielding and γ-ray shielding, as specified in the design criteria for concrete shielding. |

Table 6 Structures affected by each environmental factor according to strength deterioration effects.

| Factor | Structures |
|--------|------------|
| Heat | Reactor building (reactor pedestal) |
| Radiation | Reactor building (primary shield wall) |
| Carbonation | Turbine building (internal wall and external wall), intake building, others |
| Chloride penetration | Reactor building perimeter wall, intake building |
| Machine vibration | Turbine building (turbine building pedestal) |
Table 7 Structures affected by deterioration factors according to shielding deterioration effects.

| Factor | Structures                          |
|--------|------------------------------------|
| Heat   | Reactor building (gamma ray shield wall) |

From the results of reactivity tests, we confirmed that reactive aggregates are not used in an alkali-aggregate reaction. Additionally, we confirmed that the environment of the site did not result in concrete deterioration from freezing and thawing or chemical erosion. Therefore, we concluded that these factors were not significant for developing countermeasures against aging. On the other hand, heat, carbonation or salt penetration would lead concrete cracking and reduction in permeability during the long-service life. In first stage of our project treats only the mortar matrix excluding any cracking to focus on the matrix character (migration, sorption and penetration of radionuclides) and its change by aging, heat or carbonation.

The results of the evaluation of the factors related to the migration, sorption, and penetration of radionuclides into the concrete (heat, carbonation, and salt penetration), which are listed in Tables 6 and 7, are described below.

i) Assessment of thermal history
The evaluation of heat effects according to strength reduction was carried out at the contact surface between the RPV support leg and the RPV pedestal concrete (a schematic figure can be found in the international report by IAEA (IAEA 2015)), which is located near the RPV and is exposed to high ambient temperature and high temperature during operation.

The concrete surface temperatures should not exceed $65^\circ$C except for localized areas, such as around penetrations, which are allowed to reach temperatures of up to $90^\circ$C according to the standard for the Structural Design of Reactor Building Structures (AIJ 1988) to ensure the design strength. As a result of the temperature distribution analysis on the contact surface between the reactor pedestal concrete and the pressure vessel support legs, we determined the maximum temperature of the concrete to be about $56^\circ$C. This value is below the temperature limit of concrete, and we concluded that the thermal history did not result in the deterioration of concrete strength.

We evaluated the deterioration of radiation shielding in the $\gamma$-ray shielding wall concrete, which is located near the reactor pressure vessel and has the highest dose of irradiation during operation.

For radiation protection, "Design criteria for concrete shielding" (Jaeger et al. 1975), which is applied to the design of concrete shielding, states that the maximum ambient and internal temperature limits of concrete shielding are $88^\circ$C or less for neutron shielding and $177^\circ$C or less for $\gamma$-ray shielding. The temperature distribution analysis shows that for the core region of the concrete in the $\gamma$-ray shielding wall, the maximum temperature is about $67^\circ$C. This value is below the concrete temperature limit. Therefore, we concluded that the heat does not affect the shielding capability of the concrete.

Although there is no information about the thermal history of the buildings and building components other than the reactor pedestal and the $\gamma$-ray shielding wall, we assumed that the work area was at an ordinary temperature.

ii) Assessment of carbonation
Based on the results of the environmental measurements (carbon dioxide concentration, temperature, and relative humidity), and the presence or absence of coating, we selected several locations in which carbonation was likely to develop. Using the carbonation depth measurements, we assessed the areas with the greatest carbonation depth. The carbonation depths were measured at two indoor locations [see site map by Tokyo Electric Power Company (TEPCO 2012)]: the inside wall of the machine tool room in the turbine building and the inside wall of the air compressor room in the activated carbon rare gas hold-up system building, the inner wall of the seawater piping tunnel, and the southeast foundation of the exhaust stack.

The depth of carbonation at which steel bars begin to corrode is specified in "AIJ Recommendations for Durability Design and Construction Practice of Reinforced Concrete (Draft)" (AIJ 2004). The carbonation depth is defined as the time at which the depth of carbonation reaches the thickness of the cover of steel bars in outdoor areas exposed to rain and the time at which the depth of carbonation reaches 2 cm from the thickness of the cover of steel bars in indoor areas. For indoor areas, the carbonation depth is defined as a depth 2 cm deeper than the steel bar. For each building assessed in the study, the design cover thickness is 4 cm; therefore, the carbonation depth at which the reinforcement begins to corrode is 6 cm indoors and 4 cm outside the exterior walls. The minimum cover thickness for the outdoor structures is 10 cm for the intake structure, 6 cm for the condensate storage tank foundation and buried duct, 10 cm for the seawater piping tunnel, and 6 cm for the exhaust stack foundation.

The estimated carbonation depths for each building and outdoor structure after 60 years of operation are shown in Table 8. The depths were calculated using the Kishitani, Yoda and Morinaga equations, and the $\sqrt{t}$ equation based on the measured carbonation depths. The estimated depths ranged from 3.3 to 5.2 cm indoors and from 1.4 to 3.1 cm outdoors. From these results, we concluded that the maximum estimated carbonation depth after 60 years of operation is less than the carbonation depth at which the steel bars were expected to begin corroding for all buildings and outdoor structures.

We also concluded that the strength of the concrete was not affected by carbonation.

Using the estimated carbonation depth at 60 years of operation, we back-calculated the carbonation depth at the time of the accident according to the $\sqrt{t}$ equation.
\[ X(t) = A_{60} \sqrt{t} \]  

where \( X(t) \) is carbonation depth, and \( A_{60} \) is fixed from the estimated carbonation depth after 60 years.

Thus, the depth was calculated to be between 2.7 and 4.2 cm indoors and between 1.1 and 2.5 cm outdoors.

### iii) Assessment of chloride penetration

We assessed the chloride penetration for buildings with seaside walls, in addition to the intake structures, which are subject to the most severe chloride penetration environments due to the influence of seawater and airborne chloride on the concrete structures.

According to the long-term performance assessment of the concrete structures in Unit 1, cores were removed from the reactor building in 2007 and from the intake structure in 2008 to measure the chloride ion concentration at the location of the reinforcing steel. Using these values and the prediction formula proposed by Morinaga, we calculated the corrosion loss of the reinforcing steel at 60 years of operation.

The results of this analysis are shown in **Table 9**. The corrosion loss of the reinforcing bar after 60 years of operation was \( 2.0 \times 10^{-4} \) g/cm² in the air zone, \( 8.0 \times 10^{-4} \) g/cm² in the tidal zone, \( 0 \) g/cm² in the undersea zone, and \( 15.9 \times 10^{-4} \) g/cm² in the outer wall. All zones were exposed to corrosion loss, which caused crack initiation \( (81.3 \times 10^{-4} \) g/cm² in the air zone, \( 79.9 \times 10^{-4} \) g/cm² in the tidal zone, \( 77.0 \times 10^{-4} \) g/cm² in the undersea zone, and \( 51.0 \times 10^{-4} \) g/cm² in the outer wall). According to these results, we concluded that chloride penetration did not result in the deterioration of concrete strength.

The real chloride ion penetration in the cores from the reactor building and the intake structure was unclear because the chloride ion concentration profiles and diffusion coefficients were not available.

Of the various structures subjected to constant vibration during plant operation, the turbine generator frame, which was exposed to the highest levels of vibration, was evaluated for machine vibration. In 2007, specimens from the turbine generator frame concrete were sampled for destructive testing. According to the results, the average compressive strength of the concrete was 51.7 N/mm², which is higher than the design strength of 22.1 N/mm². Referring to the deterioration of the material by the mechanical vibration, the Technical Assessment on F1NPS Unit 1 (TEPCO 2011) states “Concerning the deterioration of concrete strength, visual observation of the concrete surfaces of each building and structure are carried out regularly to check for cracks and deterioration of the coating. Based on monitoring of the width of cracks or so on by the visual observation, the repair is planned and carried out within a few years after the inspection”.

There are several risks that may induce cracking in concrete. However, cracking from mechanical vibration or drying shrinkage is most likely since the aggregates used were not involved in an alkali-aggregate reaction, and since the results of the long-term performance assessment show that cracking due to the corrosion of the reinforcing bars caused by neutralization or chloride penetration is unlikely. Drying and wetting cycles from rainfall on the outside of the building should be considered.

### Table 8 Estimated carbonation depths.

| Target structure | Design cover thickness | Estimated carbonation depth after 60 years | Estimated carbonation depth at the time of accident |
|------------------|------------------------|------------------------------------------|-----------------------------------------------|
| Indoor           |                        |                                          |                                               |
| Inner walls of the machine shop in the turbine building | 4 cm | 3.3 to 5.2 cm | 2.7 to 4.2 cm |
| Inner walls of the air compressor room in the activated carbon noble gas hold-up unit building | 4 cm | 3.3 to 5.2 cm | 2.7 to 4.2 cm |
| East walls of turbine building (1st floor) | 4 cm | 1.4 to 3.1 cm | 1.1 to 2.5 cm |
| Outdoor          |                        |                                          |                                               |
| East exterior walls in the activated carbon noble gas hold-up system building (1st floor) | 4 cm |
| In-air zones of intake structure | 10 cm |
| Inner walls of the shielding wall at the base of the condensate storage tank | 6 cm |
| Inner walls of the buried duct for the condensate storage tank | 6 cm |
| Inner walls of the seawater piping tunnel | 10 cm |
| Southeast foundation of the exhaust stack | 6 cm |

### Table 9 Result of the chloride penetration analysis.

| Assessment portion | Corrosion loss after 60 years | Corrosion loss at crack initiation |
|-------------------|-------------------------------|-----------------------------------|
| Intake building   |                               |                                   |
| (Air zone)        | \( 2.0 \times 10^{-4} \) g/cm² | \( 81.3 \times 10^{-4} \) g/cm²   |
| (Tidal zone)      | \( 8.0 \times 10^{-4} \) g/cm² | \( 79.9 \times 10^{-4} \) g/cm²   |
| (Undersea zone)   | \( 0 \) g/cm²                 | \( 77.0 \times 10^{-4} \) g/cm²   |
| Perimeter walls of the reactor building | \( 15.9 \times 10^{-4} \) g/cm² | \( 51.0 \times 10^{-4} \) g/cm² |
Some parts of the concrete surface may not have a coating because the carbonation assessment was reported in the presence and absence of coating, but the specific point does not report.

(ii) Summary of the boundary conditions before the accident
From the information described in the previous section, we estimated the following boundary conditions in the building concrete of F1NPS Unit 1 at before the accident:

i) Thermal history
According to the results of the analysis, the maximum temperature in the reactor pedestal concrete was about 56°C, and the maximum temperature in the γ-ray shielding wall concrete was about 67°C. We did not obtain information on the thermal history of other buildings and building components, but we expect that all structures were in the ordinary temperature range.

ii) Carbonation
The depth of carbonation at the time of the accident was calculated to be 2.7 to 4.2 cm indoors and 1.1 to 2.5 cm outdoors based on the back-calculation from the estimated carbonation depth at 60 years. The depth of carbonation indoors was larger than the depth outdoors.

iii) Chloride penetration
At the time of cracking, the corrosion loss was smaller than the value calculated for 60 years of operation. However, the real chloride penetration is unknown because the concentration profile and diffusion coefficient of chloride ions were not measured.

iv) Other factors
From the statement after checking the width of the cracks by visual observation, we assumed that the cracks were caused by machine vibration or drying shrinkage and that the rainfall on the outside of the building created a drying/wetting cycle. No information on the painted areas or the location of the cracks was available.

(2) Boundary conditions after the accident
(i) Predicted status during the accident
Figure 4 shows the predicted status of the concrete at the time of the accident. According to the boundary conditions before the accident that were described in the previous section, we assumed that a portion of the surface layer was carbonated, and that drying shrinkage had resulted in micro-cracks.

The earthquake on 11 March 2011 caused an emergency shutdown of Units 1 to 3, which were in operation at the time. The subsequent tsunami submerged the facilities at Units 1 to 4 entirely in seawater, resulting in the loss of power and the loss of cooling in the reactors, which led to a hydrogen explosion in Units 1, 3, and 4. Seawater injection was then used as an emergency measure in response to the loss of cooling. Therefore, we assumed that the inside of the buildings at the beginning of the accident, including the reactor cores and containment vessels, were immersed in contaminated water including seawater, and that the contaminated water, which contained Cs and Sr released during the accident, was in contact with the building concrete as liquid water or as steam.

TEPCO reported 400 m$^3$ water is being injected to cool the reactor core and 400 m$^3$ groundwater and rainwater flow into the building, and those 800 m$^3$ contaminated water is being circulated and treated per day (TEPCO 2013c). They are thought to have washed away the contaminants on the concrete in contact with the initial contaminated water immediately post-accident.

(ii) Literature review of the site contamination
Several site investigations and analyses have been reported to consider ways to reduce exposure and improve the working environment in the contaminated buildings (Goto et al. 2013; IRID and JAEA 2017a; Koma et al. 2017).

Goto et al. (2013) reported an analysis of the floor, wall and instrument surfaces in the reactor buildings of Units 1 to 3 to estimate the level of contamination in the reactor buildings and to obtain fundamental data to select a decontamination technology suitable for the situation. Some of these strategies may be feasibly implemented remotely. In particular, the walls and floor of Unit 1 and the floors of Units 2 and 3 were analyzed by classifying the forms of contamination into three categories: loose contamination such as dust that was dispersed during the hydrogen explosion, immobilized contamination in areas exposed to steam and on epoxy coatings, and permeable contamination in the concrete core. An image of the contamination conditions in the 1F building is shown in Fig. 5. Goto et al. (2013) found that there was local contamination in the damaged areas, but no penetration into the concrete occurred through the epoxy-coated surfaces. The form of contamination depended on the

![Fig. 4 Predicted status diagram for the accident.](image-url)
unit, with Unit 1 and Unit 3 having slightly more loose contamination, and Unit 2 having relatively more immobilized contamination.

The properties of solid wastes generated after the accident are different from those of conventional nuclear wastes, and it is essential to understand the properties of these wastes to obtain a safety plan for the treatment and disposal of the wastes. To clarify the characteristics of the radionuclide contamination, analyses of the rubble and contaminated water have been continually conducted (IRID and IAEA 2017a; Koma et al. 2017).

According to the analyses, several nuclides (including Cs, Sr and α-nuclides) can be detected in the 1F building, and their concentrations vary depending on the building and area. Between the first and fifth floors of the reactor buildings in Units 1 to 3, radioactive Sr had a concentration of 1/100 to 1/1000 compared with that of the Cs; however, the forms of contamination and adsorption have not been confirmed. According to one estimation in a previous report (Nagoya University 2018), the nuclide concentrations of radioactive Cs and radioactive Sr in the reactor were of the same order, and we assumed that in the basement of the reactor building and the turbine building, where the radionuclides were discharged directly from the reactor by seawater, they came into contact with stagnant contaminated water with a concentration ratio close to that in the reactor. We assumed that the fuel debris is almost completely absent to the reactor; thus, in the early stages of the accident, the stagnant water, including the core and containment vessel (PCV), were exposed to high concentrations of seawater components.

(3) Contaminated water in contact with the concrete
Contaminated water stagnates in the basement of the nuclear reactor building and is therefore in contact with the concrete of the building floor. The contaminated water contains Cs and Sr as well as a small number of α-nuclides such as Pu, and these nuclides may adsorb on or penetrate the concrete, accumulating in the building. Therefore, it is important to evaluate the adhesion and permeation behaviors of α-nuclides, Cs and Sr in concrete to appropriately decontaminate the building and treat and dispose of wastes.

Therefore, we summarized the properties of the contaminated water in contact with concrete below.

(i) Stagnant water
i) Transition of retained water
F1NPS was hit by an earthquake on 11 March 2011, which caused the emergency shutdown of Units 1 to 3, which were in operation at the time. The subsequent tsunami, which caused the loss of the cooling system and a hydrogen explosion in Units 1, 3 and 4, resulted in a severe accident (TEPCO 2013b).

a) Inflow of seawater
The tsunami flooded the entire facility of Units 1 to 4. As a result, the power supply and the cooling system were lost. For emergency cooling, seawater was injected into the reactor; thus, in the early stages of the accident, the stagnant water, including the core and containment vessel (PCV), were exposed to high concentrations of seawater components.

b) Damage to the core fuel in Units 1 to 3
In Units 1 to 3, the core fuel could no longer be cooled, and the water level in the pressure vessel (RPV) dropped, exposing the fuel, and causing further damage. According to the estimated current in-core conditions, we considered that the fuel debris is almost completely absent from the RPV in Units 1 and 2, and has decreased in the PCV, however, it is possible that some debris remains in the RPV of Unit 3 (IRID 2018). At the time of the accident, Unit 4 was undergoing routine inspection, and the fuel in the reactor had been moved to a spent fuel pool; thus, there was no fuel in Unit 4.

ii) Decontamination and dilution of retained water
Radionuclides that migrated from the fuel debris to the stagnant water, flowing from the PCV to the reactor building (R/B), turbine building (T/B), and centralized radiation waste treatment facility (CRW/TF), where the water is treated by a water treatment plant. The circulation of stagnant water from the reactor building is shown in Fig. 6.

To remove radionuclides from the contaminated water, a cesium adsorption apparatus (KURION), a secondary cesium adsorption apparatus (SARRY), a mobile Sr removal system, and an advanced liquid processing system (ALPS) were installed successively. The reverse osmosis (RO) membrane treatment was used to produce fresh water.

Water is continuously injected to cool the reactor core, and stagnant water is continuously circulated and treated as the groundwater and rainwater flow into the building. The concentrations of radionuclides in the stagnant water have gradually decreased by radionuclide decontamination processes and dilution by water inflow. The ana-

![Fig. 5 Schematic of the contamination on a concrete member.](image-url)
lytical values for the concentrated radioactive wastewater containing Cl and $^{134}$Cs are plotted in Figs. 7 and 8, respectively (Asami et al. 2017).

iii) Status (2020-12-24)
The current status of the stagnant water discharge in each unit is shown in Fig. 9 (TEPCO 2020). The water level varies across the units. Water injection continues to be injected in the reactor buildings in the Units 1 to 3. All the T/B and RW/B drainage has been completed, and the stagnant water has been removed, leaving the floor exposed since December 24, 2020.

(ii) Status of stagnant water (22 February 2018)
i) Water depth and amount
The water level in each building varies according to water injection and drainage conditions. A semi-annual plot of the T/B and R/B water levels is shown in Fig. 10. The water levels in the buildings of each unit are reported periodically. Originally, the water levels were described in terms of O.P. (Onahama Peil, Onahama Bay mean sea level); however, since 2015, the levels have been reported in terms of T.P. (Tokyo Peil, Tokyo Bay mean sea level). In our figure, all data was converted to T.P. and the floor T.P. was subtracted to determine the water depth. The drainage of Unit 1 T/B was completed in March 2017; other buildings are still immersed in several meters of water, but the levels have decreased since the accident (22 February 2018). The total volume of stored water in the buildings is approximately 36460 m$^3$ for Units 1 to 4, and approximately 19430 m$^3$ for the process main building and the high temperature incinerator building.
ii) Water temperatures
At the time of the accident, the S/C (suppression chamber) pool water temperature data from 2 April to 15 May 2011 were recorded as being related to liquid temperature (TEPCO 2013a). Unit 1: about 55°C; Unit 2: 99°C, gradually decreasing to 65°C; Unit 3: 60°C, gradually decreasing to 40°C. Spent fuel pool (SFP) water temperatures were monitored for current plant parameters. In addition, the liquid temperature of the stagnant water in the PCV was measured during a previous internal PCV survey. The spent fuel pool water temperatures at 5:00 on 31 January 2018 (TEPCO 2018b) were the following: Unit 1: 26.3°C; Unit 2: 29.4°C; Unit 3: 27.2°C; Unit 4: 11.6°C. The water temperature measured at the time of the internal PCV survey on 20 October 2015 (TEPCO 2015) was approximately 33 to 35°C in the Unit 3 PCV.

As the stagnant water leaked from the S/C to the torus chamber and T/B, the stagnant water in the torus chamber (R/B) may have been partially warm at first, but upon reaching the T/B, the stagnant water was at room temperature.

iii) Chemical composition and pH
a) Estimated initial composition
Radionuclides migrate to stagnant water after contact between fuel debris and water is established. As shown in Fig. 8, the changes in radionuclide concentrations are different in the early stage and later stage, and this dissolution behavior can be divided into two stages: early dissolution and continuous dissolution. Based on the concentrations of radioactive material in the stagnant water, we considered that radionuclides are continuously transferred to the stagnant water (Koma et al. 2017). The initial concentrations of radionuclides in the retained water were estimated from the analytical values of the retained water in the building using a mass transfer model that assumes continuous inflow in addition to the radionuclides transferred to the water in the early stages of the accident (Shibata et al. 2016). Table 10 shows the concentrations of radioactive material in the retained water, which were estimated from the mass transfer model and the elemental equivalent concentrations. If it could be ascertained that the flow rate of the seawater injection into the reactor core, then there would be a higher level of confidence in the calculated baseline. Since the ratio of radionuclides to stable nuclides changed with time, the conversions were calculated using the fuel composition at the time of the accident shown in Table 11 (Nishihara et al. 2012). Table 11 also shows the percentage of radionuclides after 10 years (data from March 2021).

Table 10 Estimated initial composition of stagnant water in the building.

| Nuclide concentration (Shibata et al. 2016) | According to the elemental concentration* |
|------------------------------------------|------------------------------------------|
| **Element** | **(g/m³)** | **(g/m³)** |
| _H* | 4.4E+09 | H | 1.4E-05 |
| _54Mn | 6.2E+07 | Mn | 3.9E-06 |
| _63Ni | 2.7E+06 | Ni | 1.7E-03 |
| _90Sr | 8.9E+11 | Sr | 3.0E-01 |
| _106Ru | 7.0E+07 | Ru | 1.6E-05 |
| _125Sb | 4.4E+08 | Sb | 4.1E-04 |
| _137Cs | 2.1E+12 | Cs | 1.6E+00 |
| _238Pu | 5.7E+03 | Pu | 5.9E-07 |

*Calculated using the left column in Table 10 and the left column in Table 11.

Table 11 Mass ratios of the main radioisotopes to the elements in the fuel damaged during the accident (Nishihara et al. 2012).

| Nuclide/ Element | Elapsed time (years) |
|------------------|----------------------|
|                 | 0 y | 10 y |
| _H/H* | 0.910 | 0.852 |
| _54Mn/Mn | 0.055 | 9.34E-06 |
| _63Ni/Ni | 0.001 | 0.001 |
| _90Sr/Sr | 0.582 | 0.539 |
| _106Ru/Ru | 0.036 | 4.31E-05 |
| _125Sb/Sb | 0.028 | 3.47E-03 |
| _137Cs/Cs | 0.789 | 0.813 |
| _238Pu/Pu | 0.026 | 0.001 |
| _137Cs/Cs | 0.409 | 0.363 |
| _238Pu/Pu | 0.015 | 0.016 |

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(on 22 February 2018).

Fig. 10 Water depth (relative to T. P.) in each building (2018-2-22).
b) Analytical values for stagnant water

Tables 12 and 13 show the analytical values for the water in the PCV (IRID and JAEA 2017b) and building (TEPCO 2018a), respectively. In this section, we present the factors that have been analyzed and the quantitative values that have already been obtained.

The results of the elemental analysis by ICP-AES show that the concentrations of B, Na, Mg, Si, Ca, Mn, Fe, Zn, Sr, Ba, and Pb are all below the lower limit of quantification (less than 5 ppm), reflecting the nature of the RO-treated cooling water being injected.

The stagnant water in the building was sampled and analyzed regularly. The concentration of $\alpha$-nuclides is low, while elements such as Cl, Mg and Ca can be detected in significant concentrations, although there is a large variation between locations. The water concentrations are also affected by the seawater that was injected in the early stages and by the inflow of groundwater. The concentrations of 90Sr, 134Cs and 137Cs are varied 6.9×10^2 to 6.7×10^4 Bq/cm^3, respectively. These values would equal to Sr: 0.023 to 23 ppb and Cs: 0.26 to 460 ppb in case converting into the elemental concentration based on Table 10 and supposing the 10 years-decay of the radionuclides based on Table 11.

c) Seawater composition

Typical elemental concentrations (JSAC 2004) and pH (JMA 2014) of seawater are listed in Table 14. The pH at the surface is 8.1. The concentrations of Cs and Sr are 0.31 and 7800 ppm, respectively. The elemental concentration of Cs in the stagnant water from the damaged fuel would be 0.26 to 460 ppb as explained in the preceding section and much higher value than in the typical seawater. Thus, the effect of seawater contamination can be neglected. On the other hand, the elemental concentration of Sr in the stagnant water from the damaged fuel would be 0.023 to 23 ppb and much lower value than in the typical seawater. Even if it is assumed that the Cl concentration in Table 13 did not change from the seawater injection into the stagnant water, the concentration of Sr derived from the seawater would be 28 to 1134 ppb based on Sr/Cl ratio in Table 14 and Sr derived from the damaged fuel is still higher than from the seawater.

d) Groundwater composition

Typical compositions of groundwater samples collected from groundwater observation boreholes and wells in a study by TEPCO are shown in Table 15 (TEPCO 2016). The pH, Cl concentrations, and the Mg, Ca, SO_4^2-, and radioactive material concentrations in some samples were analyzed. Radionuclides were detected in the samples, especially $^3$H, 134Cs and 137Cs. The elemental concentrations of Sr and Cs were not analyzed in the TEPCO report.
(iii) Subjects to be considered
i) Types of concrete structures and stagnant water
The buildings that contain stagnant water are the reactor building (R/B), turbine buildings (T/B), centralized waste treatment plant (Centralized RW), process main building (PM/B), and high temperature incinerator building (HTI/B). In addition to the R/B building concrete, there is in-core concrete in the PCV, so the main contact between the liquid phase and the concrete is assumed to be the stagnant water in the PCV and the PCV in-core concrete, the R/B stagnant water and the R/B building concrete, the T/B stagnant water and the T/B building concrete, and the concentrated RW water and the concentrated RW building concrete. The water in the spent fuel pool is also contaminated, but the inner surface of the spent fuel pool is lined with stainless steel, preventing contact between the concrete and the water. Therefore, the spent fuel pool can be excluded from this analysis.

ii) Time periods to be considered
We considered three periods, which correspond to changes in radionuclide concentrations.

a) Early phase of the accident
The initial period of the accident was the most severe and is considered to have the greatest impact on concrete contamination. The decontamination of the water began after June 2011.

b) Between the beginning of the decontamination process and the completion of initial stagnant water treatment
This is a transitional period during which the concentrations of elements and nuclides in the stagnant water decreased as the various water treatment facilities began operation, and the treated water was circulated as core cooling water.

c) From then until now (2018)
To estimate the long-term effects, we used data from the post-stabilization period. Although the plant parameters have changed over time, we used the most recent values available as of 2018 in this report.

(iv) Example composition of contaminated water
Based on the information described above, we reported the concentrations of Cs, Sr and Pu (α-nuclide) which should be considered for the reaction with concrete, in Table 16. The concentrations of the nuclides (Bq/cm³) and the elemental concentrations converted from these concentrations (ppb) are also listed. Based on these concentrations, we prepared a simulated solution to test concrete immersion. However, because these concentrations are extremely low, it is necessary to set up an experimental test under conditions that allow for analysis. For example, when testing α-nuclides, a higher concentration is required for analysis because the lower limit of quantification is 3.7 Bq/ml for conventional total α-radioactivity analysis, and it would be difficult to analyze the composition of the stagnant water. Since the reaction may be different between high and low concentrations, we decided to set the concentration according to the needs of the experiment. The pH of the simulated solution should be between 7 and 8. The temperature of the simulated liquid is expected to be high in the PCV at the beginning of the accident but is mostly normal in the building.

| Table 15 Groundwater composition from 30 April 2015 to 15 February 2016 (TEPCO 2016). |
|----------------------------------------|----------------|------------------|
| pH                                    | Average       | Minimum          |
| Cl                                    | 7.15          | 6.0              |
| Mg                                    | 1140 ppm      | 6 ppm            |
| Ca                                     | 52 ppm        | 2 ppm            |
| SO₄²⁻                                  | 50 ppm        | 9 ppm            |
| Total β                                | 184 ppm       | 124 ppm          |
| H⁺ ions                                | 3.02×10⁵ Bq/L | 11.2 Bq/L        |
| Cl⁻                                    | 2.47×10³ Bq/L | 5.44 Bq/L        |
| Sr⁺                                     | 3.79×10² Bq/L | 5.14×10¹ Bq/L    |
| Cs⁺                                     | 7.99×10¹ Bq/L | 7.72×10⁰ Bq/L    |
| Cs⁺                                     | 2.78×10¹ Bq/L | 2.78×10⁰ Bq/L    |
| Total β                                | 3.02×10⁵ Bq/L | 11.2 Bq/L        |
| H⁺ ions                                | 2.47×10³ Bq/L | 5.44 Bq/L        |
| Cl⁻                                    | 3.79×10² Bq/L | 5.14×10¹ Bq/L    |
| Sr⁺                                     | 7.99×10¹ Bq/L | 7.72×10⁰ Bq/L    |
| Cs⁺                                     | 2.78×10¹ Bq/L | 2.78×10⁰ Bq/L    |

Table 16 Example composition of stagnant water.

| As shown in nuclide concentration (Bq/cm³) | As shown in element concentration (ppb) |
|------------------------------------------|----------------------------------------|
| ²³⁸Pu                                    | ²⁹⁰Sr                                   |
| ¹³⁴Cs                                    | ¹³⁷Cs                                   |
| Early phase of accident*                 | Present**                                |
| 5.7×10⁻³                                 | 9.9×10⁻¹                                |
| 8.9×10⁸                                 | 1.6×10⁴                                |
| 2.3×10⁹                                 | 1.7×10⁴                                |
| 2.1×10⁹                                 | 1.4×10⁴                                |
| 5.9×10⁻⁴                                 | 7.4×10⁻²                               |
| 300                                     | 5.8                                     |
| 1700                                    | 240                                    |

*The values of early phase of accident are the values from Table 10.
**Present values are,
²³⁸Pu: The value in PCV stagnant water in Unit 3 (see Table 12).
²⁹⁰Sr and ¹³⁴Cs: Arithmetic average of the current analysis values (see Table 13).
Cs: Average value of ¹³⁴Cs and ¹³⁷Cs shown in the left column.
Table 17 Example mixture proportion for concrete used in F1NPS buildings.

| Material       | W/C | S/C | Unit amount (kg/m³) | Volume of AE agent |
|----------------|-----|-----|---------------------|--------------------|
| Mortar         | 0.55| 2.39|                     |                    |

Table 18 Properties of the materials used for preparing the mortar specimens.

| Material       | Notation | Information                  |
|----------------|----------|------------------------------|
| Cement         | OPC      | Ordinary Portland cement (Density: 3.16 g/cm³, Specific surface area: 3140 cm²/g) |
| Fly Ash        | FA       | JIS class II (Density: 2.37 g/cm³, Specific surface area: 4210 cm²/g) (ASTM C 618 Class C) |
| *Fine aggregate| LS       | Limestone crushed sand (excluding fine particles less than 0.15 mm) |
| Admixture agent | AE       | AE agent was created using diluted pulverized Vinsol resin (Yamaso Chemical Co. Ltd.) |

*The maximum size of fine aggregates is 2.5 mm.

(4) Summary of Boundary conditions for radionuclide concentrations

To estimate contamination, several concrete characteristics, including the cement type, aggregate type, mixture proportions, the current condition and environmental exposure history must be considered. As shown in Fig. 11, the position of the concrete structure also affects the boundary conditions because of differences in surface coating, exposure to rainfall, the temperature during operation, moisture levels and carbonation depth from varying exposures to atmospheric CO₂. After the accident, a diverse set of changes occurred in the concrete at different positions, including the new contact with seawater after the tsunami and with the contaminated water from the troubled reactor. Additionally, the ratios of nuclide concentrations varied according to these changes and positions. The most important nuclides to consider for radiation exposure and disposal are Cs, Sr and α-nuclides. Additionally, because of the nature of the accident, the contamination levels for the vaporized Cs are significantly different from those of the less vaporized Sr and α-nuclides.

In this project, the concrete that experienced significant thermal effects is not considered to be salvageable, since the damage is expected to be severe, and the radionuclide penetration is significant.

3. Materials and curing conditions for the mortar specimens (Nagoya University 2018)

The materials used for this study were gathered according to the construction data for the FNPS site, and one mixture proportion (Table 17) was selected from the record (Kaburagi 1969). In this study, we used Class I fly ash according to the Japan Industrial Standard JIS A 6201 (JSA 1999). The material properties and mixture proportions are shown in Tables 18 and 19, respectively.

The chemical composition of ordinary Portland cement and fly ash powder was determined using XRF (X-Ray Fluorescence) technique, as shown in Table 20. The phase composition of powdered samples of raw ordinary Portland cement and fly ash was determined using X-ray diffraction (XRD) (D8 Advance, Bruker AXS) and the Rietveld analysis software (TOPAS), as shown in Tables 21 and 22, respectively. Rietveld analysis was done with the initial crystal structures’ parameters basically listed by Aranda et al. (2012), and each code in ICSD (NIST 2018) and in PDF database (Gates-Rector and Blanton 2019) are shown in the tables. The non- or low-crystalline phases (glass phase and minor components not showing any well-peaks) are quantified by the internal standard method with corundum (α-Al₂O₃).

Table 23 shows the chemical composition of fine aggregates. Based on the polarized micrography and XRD measurements, the minerals found in the samples are
The mortar was mixed using a Hobart mixer. Each mixture batch had a volume of 4 L. The mortar was placed in a mold with a cross-section of 50×50 mm². The specimens were cured at 40°C in moist air for three months, and then were cut into 20×20×50 mm³ pieces using a diamond precision saw and used for the experiment. The specimens were cured in a humid condition at 40°C for 3 months or at 20°C for a year as the pre-curing step. Then, the specimens were distributed according to different curing/deterioration conditions, as summarized in Table 25. The samples were placed into each condition after coating five surfaces with epoxy resin and the other one keeps bare except for the drying conditions. For

listed in Table 24.

Table 19 Mix design for mortar specimens.

| Mixture ID | Water to binder ratio W/B | FA (%) | The measured value for 4 L mixture (g) | OPC | LS | RS | AE agent (ml) |
|------------|---------------------------|--------|--------------------------------------|-----|----|----|---------------|
| OPC-LS     | 0.55                      | 0      | 1136                                 | 2064| -  | -  | 4936          |
| OPC-RS     |                           | 15     | 1756                                 | 308 | -  | -  | 4936          |
| FAC-LS     |                           |        |                                      |     |    |    | 160.0         |
| FAC-RS     |                           |        |                                      |     |    |    | 80.0          |

Notes:
(1) Gypsum was added to adjust the total SO₃ content in powder to 2.5%.
(2) The AE agent was used by diluting Vinsol (Yamuna Chemical Co., Ltd.) 100 times. The amount of AE agent amount added corresponds to the targeted air amount of 7.0±1.0% (the measured amount of AE agent is expressed as the amount of the solution diluted 100 times).

Table 20 Chemical composition determined by XRF analysis (mass %).

| Cement  | LOI  | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | SO₃ | Na₂O | K₂O | TiO₂ | P₂O₅ | MnO  | SrO  | Total |
|---------|------|------|-------|-------|------|------|-----|------|-----|------|------|------|------|-------|
| OPC     | 2.26 | 20.54| 5.18  | 2.92  | 64.30| 0.90 | 2.04| 0.35 | 0.32| 0.31 | 0.57 | 0.08 | 0.05 | 99.82 |
| FA      | 2.41 | 56.23| 30.89 | 3.05  | 1.66 | 0.92 | 0.23| 0.36 | 1.24| 1.67 | 0.49 | 0.02 | -    | 99.17 |

Table 21 Mineral composition of OPC cement determined by XRD/Rietveld analysis (mass %).

| Phase     | C₃S  | C₃A  | C₄AF | Periclase | Basanite | Gypsum | Calcite | Total               |
|-----------|------|------|------|-----------|----------|--------|---------|---------------------|
| Value     | 50.35±1.22 | 23.27±2.07 | 8.79±0.30 | 10.10±0.37 | 0.38±0.12 | 1.90±0.155 | 0.16±0.04 | 5.01±0.39 | 99.96 |
| Crystal system | Monoclinic | Monoclinic | Cubic | Orthorhombic | Cubic | Monoclinic | Rhombohedral |  |
| ICSD codes | 64759 | 8196 | 1841 | 9197 | 9863 | 79528 | 151692 | 80869 |
| PDF codes  | 01-085-1378 | 01-086-0398 | 01-070-0839 | 01-071-0667 | 01-071-1176 | 01-083-0438 | 33-0311 | 01-086-0174 |

Table 22 Mineral composition of fly ash determined by XRD/Rietveld analysis (mass %).

| Phase     | Quartz | Mullite | Magnetite | Hematite | Calcite | Rutile | Glass* | Total               |
|-----------|--------|---------|-----------|----------|---------|--------|--------|---------------------|
| Value     | 8.71±0.32 | 26.42±0.54 | 0.11±0.05 | 0.27±0.06 | 0.64±0.14 | 0.33±0.26 | 63.49±1.03 | 99.97 |
| Crystal system | Rhombohedral | Orthorhombic | Cubic | Rhombohedral | Rhombohedral | Tetragonal |  |
| ICSD codes | 41414 | 74008 | 49549 | 82904 | 80869 | 16636 |
| PDF codes  | 46-1045 | 01-082-0037 | 01-077-1545 | 01-087-1166 | 01-086-0174 | 01-072-1148 |

*The glass phase is quantified by the internal standard method with corundum (α-Al₂O₃).

Table 23 Chemical composition of fine aggregates.

| LOI  | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | SO₃ | Na₂O  | K₂O | TiO₂ | P₂O₅ | MnO  | Total |
|------|------|-------|-------|------|------|-----|-------|-----|------|------|------|-------|
| RS   | 1.03 | 79.51 | 8.75  | 3.30 | 1.85 | 1.45| 0.01  | 1.86| 1.69 | 0.35 | 0.05 | 99.95 |
| LS   | 41.66| 5.35  | 0.72  | 0.26 | 47.03| 4.57| 0.02  | 0.04| 0.15 | 0.03 | 0.03 | 99.86 |

Table 24 Observed minerals in fine aggregates.

| Quartz | Plagioclase | Orthoclase | Chlorite | Mica | Amphibole | Calcite | Dolomite |
|--------|------------|------------|----------|------|-----------|---------|----------|
| RS     | X          | X          | X        | X    | X         | X       |          |
| LS     | X          |            |          | X    |           |         |          |
saturation conditions, we immersed the sample into water and induced suction for 12 hours. We also tested two drying conditions: in the first, the sample was placed in an oven at 105°C, while in the second, the sample was exposed to circulating moisture-controlled nitrogen air at 20°C and 40% RH remained constant. The samples exposed to the drying condition were coated with an epoxy resin according to the same protocol described above. For the carbonation condition, we used an enforced carbonation chamber with a controlled CO₂ concentration of 5% for 3 months. After the carbonation process, some specimens were used in the original condition, while others were immersed in water before use. For the leaching conditions, we submerged the samples in deionized water for 3 months. The deionized water was replaced twice per week.

4. Radionuclide behavior

4.1 Cesium and strontium (Yamada et al. 2021b)

(1) Factors examined

Several factors that must be clarified experimentally are summarized in Table 26. Because the experiments require the use of radioisotopes (RI) for various conditions, it is preferable to reduce the quantity of RI as much as possible. Therefore, we used mortar instead of concrete for the experiments because the smaller aggregate size in the mortar reduces the specimen size needed to maintain homogeneity. The size and content of the aggregate affect the speed of ion ingress. Other factors are compared in Table 26.

In this study, we investigated several factors. We selected these factors and their levels according to their effect on the adsorption of ions in concrete, which is expected to affect the ingress of ions. For this study, these factors included the materials used in concrete; the conditions of the concrete including Ca-leaching, carbonation, and water suction in dried concrete; solution chemistry of the ion concentrations and coexisting ions; and the combination of effects, which may compete for adsorption.

(2) Effects of material used in concrete

To assess the nuclide penetration in concrete experimentally, we fabricated mortar samples that are representative of the materials at F1NPS as mentioned in Section 3. These samples contained two types of cement, ordinary Portland cement (OPC), fly ash blended cement (FAC); and two types of aggregate, washed limestone crushed sand, river sand, clay in aggregate. For this study, these factors included the materials used in concrete; the conditions of the concrete including Ca-leaching, carbonation, and water suction in dried concrete; solution chemistry of the ion concentrations and coexisting ions; and the combination of effects, which may compete for adsorption.

| Cement type | Aggregate | Pre-curing | Condition after pre-curing |
|-------------|-----------|------------|----------------------------|
|             |           | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X |
|             |           | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X |
| OPC         | Limestone | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X |
|             |           | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X |
| River sand  | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X |
|             |           | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X |
| FAC         | Limestone | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X |
|             |           | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X |
| River sand  | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X | 40°C for 3 months | X |
|             |           | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X | 20°C for a year | X |

Table 26 Factors investigated by immersion experiments.

| Factor                      | Range of experiments                                      |
|-----------------------------|----------------------------------------------------------|
| Material used in concrete   | Cement type: Ordinary Portland cement (OPC), fly ash blended cement (FAC) |
|                             | Clay in aggregate: Washed limestone crushed sand, river sand |
| Condition of concrete       | Degradation: Ca-leaching, carbonation                     |
|                             | Water suction: Water saturated, dried under 105°C         |
| Solution chemistry          | Ion concentration: 100 nM to 100 mM                        |
|                             | Coexisting effects of ions: Cs/Sr                         |
| Combined effects            | Degradation and ion concentration, water suction and ion adsorption |
procedures previously described in the literature (Nagoya University 2019; Yamada et al. 2020). The results of these measurements are shown in Fig. 12. For Cs, the penetration depths in the OPC and FAC mortars were about 7 and 2 mm, respectively; the aggregate type did not have a significant effect on penetration. The penetration depth of Sr was about half that of Cs for every combination of cement and aggregate. In solutions containing coexisting Cs and Sr, the ions behave independently, particularly in water saturated OPC+LS mortar. In this condition, the ion concentration had almost no effect on ion ingress in the range of 10 μM to 100 mM.

(3) Cs and Sr ingress in dried carbonated mortar

Other findings relating to the ingress of Cs and Sr in dried mortar have been reported elsewhere (Yamada et al. 2020). In the study, dried mortar made of limestone without clay was placed in a 100 nM solution of Cs and Sr. After 6 hours, the penetration depths for Cs and Sr were 6 and 3 mm, respectively. For the RS mortar sample, the penetration depths were 3 and 3 mm, respectively. The results indicate that the rate of Sr penetration increased in dry conditions compared with water-saturated conditions. Cs penetration could be influenced by material adsorption in the water-suction process, while Sr was unaffected. The coexistence of Cs and Sr did not have any observable effects on the penetration behavior of individual species.

A previous study done by Haga et al. (2019) suggested that Ca leaching and carbonation could result in the formation of an aluminosilicate hydrate geopolymer in concrete and these altered materials could adsorb Cs and Sr at rates several orders of magnitude higher than materials in baseline conditions (Haga et al. 2019). Figure 13 shows the penetration profiles of Cs and Sr in OPC cement paste in 0.5 M chloride solutions during a seven-day experiment. The profiles include several characteristic regions. In the non-carbonated sound paste, sharp peaks for Cs could be observed near the sample surface. After these sharp peaks, the plot became a characteristic diffusion profile. Sr penetration was significantly lower in this sample. In the carbonated sample, the sharp Cs peak increased (the peak is overlapped by “Sr sound”) and the Sr peak was pronounced. During the penetration phase, Ca leaching is likely, and other cations including Cs and Sr can be adsorbed to the material. Both Cs and Sr displayed plateaus in the carbonation region, which had a depth of 4 mm. After this plateau, Cs had a clear diffusion profile, but the depth was greater than that of the carbonation depth, indicating that Cs quickly moved through the carbonated region. The penetration depths were greater than those shown in Fig. 12 because these experiments were conducted on samples with no aggregates.

Figure 14 shows the penetration behaviors of Cs and Sr in dried carbonated mortar (OPC and limestone) under
water suction conditions in a vacuum for 40 min. For these experiments, 10 μM of CsCl or SrCl₂ was used, and the carbonation depth of the mortar sample before the immersion tests was 3 mm. Most of the Cs and Sr was adsorbed in the carbonated region; however, both Cs and Sr penetrated more quickly. For the saturated conditions described above (Yamada et al. 2020), the penetration depths for Cs and Sr were 7 and 3 mm, respectively. However, in dry conditions, these depths were 20 and 10 mm, respectively. When water ceased to move through the concrete, the elements could rearrange within the pores throughout the samples. Studies of these behaviors require several months and are currently being conducted. The further experiments and discussions on the effect of elemental concentration on penetration depth are found in another publication (Yamada et al. 2021a).

4.2 Alpha nuclide (Aihara et al. 2020)

Alpha nuclides including Pu, Am, and Cm were detected in contaminated water in the basement of several buildings. To examine their penetration behaviors in concrete, OPC and FAC paste samples (sound, carbonated, and dried) were immersed in a model solution containing $1.1 \times 10^5$ Bq/mL of Pu-239 and $3.4 \times 10^4$ Bq/mL of Am-241. The distribution ratios of Pu and Am between the cement paste powder and the solution are shown in Fig. 15. For the sound paste, Pu and Am nuclides were not detected in the solution; this resulted in a large distribution ratio. In the carbonated paste, distribution to the paste decreased by two orders of magnitude. This may be attributed to a decrease in the pH of the immersed solution. To generate the penetration profiles of Pu-239, Aihara et al. (2020) immersed cuboid-shaped samples of sound, carbonated and dried paste. The samples were covered with epoxy, except for the sole surface in contact with the solution. As shown in Fig. 16, Pu was concentrated at the surface in every case; the results suggest that Pu may have precipitated as a hydroxide. At depths greater than 2 mm, Pu could only be detected on the protective resin, and no penetration within the paste could be observed.

5. Water suction and structure change of C-S-H (Kiran et al. 2020)

After the earthquake and subsequent tsunami and the associated need for fuel coolant, the dried concrete surface encountered the contaminated water, and nuclides in the solution could ingress into the concrete through an advection current resulting from suction in the concrete. After the accident at the nuclear power plant, a portion of the reinforced concrete members were exposed to higher temperature conditions relative to those under ordinary operation conditions. This temperature history could have a large influence on both the degree of drying in the concrete and on the nature of the solution, which is related to the suction behavior in concrete. To understand the impact of the materials used in concrete and the environmental conditions, Kiran et al. (2020) conducted several experiments.

First, moisture transport in the mortar specimens were investigated using the X-ray radiography method (Fig. 17) to understand the impact of cement type (ordinary Portland cement and the binder composed of ordinary Portland cement mixed with fly ash), sand type (aggregate used in F1NPS and limestone), pre-drying condition and temperature (20°C and 60°C).

Figures 18 and 19 show the penetrated water depth as
They showed that water transport displayed anomalous behavior; the relationship between the penetration depth and the square root of exposure time deviated from a linear relationship became nonlinear. Mortar containing fly ash (FAC mortar) showed a more linear trend as a function of the square root of exposure time [Fig. 18(a)]. One possible explanation is that the morphology of calcium silicate hydrate (C-S-H) is affected by the calcium-silicate ratio. The behavior of water in the OPC mortar was more anomalous than in FAC mortar [Fig. 18(a)]. The sorptivity became smaller, and the anomaly was significant when the pre-drying condition was mild [Fig. 18(b)]. At higher temperatures, the first slope was larger, while the second slope was smaller (Fig. 19). The second slope cannot be explained only by the changes in the surface tension and the viscosity of the pore solution; rearrangement of the C-S-H structure is the dominant factor in the slope change at elevated temperatures, as described later.

$^1$H-NMR relaxometry provides direct evidence that C-S-H undergoes dynamic microstructure changes under the water suction (Gajewicz et al. 2016; Zhou et al. 2017). In this project, the reproducibility of the behavior of C-S-H and the impact of temperature on hardened cement paste with water-to-cement ratios of 0.40 and 0.55 were investigated using $^1$H-NMR relaxometry (Kiran et al. 2020). The results show rapid dynamic microstructure changes in the higher temperature conditions (Fig. 20), with an activation energy of 35 kJ/mol. In the dried state, the C-S-H structure is shrunken, with large pores. When the water is introduced to the sample, it fills the large pores, which are connected and easy to enter. After C-S-H encounters the water, C-S-H will adsorb the water, resulting in an expansion that decreases the large pores. Narrowing the large pores by expanding the C-S-H structure can decrease the rate of water suction, and this phenomenon occurs more rapidly at higher temperatures, which can be confirmed experimentally in Fig. 19. Consequently, to evaluate the water suction and the resultant Cs and Sr transport due to advection, it is necessary to consider explicitly the dynamic microstructure change of C-S-H.

6. Numerical modelling for Cs and Sr (Tomita et al. 2020)

6.1 Outline

In this project, the basics of numerical modelling were used to estimate the transport of Cs and Sr in water-saturated concrete. Figure 21 introduces the concept of the phase equilibrium/mass transport model. Various ions ingress into the concrete through pores saturated
with liquid by the diffusion low under the restriction of charge balance. During the movement of ions in the pores, ions interact with solid phases such as cement hydrates. The base model used for this study was a phase equilibrium/mass transport model, a reaction transport model. To understand the interaction between the solution and the solid, the study conducted thermodynamic phase equilibrium calculations using PHREEQC. Furthermore, to study the transport of various ions, a multi-species transport calculation based on the Nernst–Planck equation was adopted (Hosokawa et al. 2011, 2019).

To simulate the material transport of Cs and Sr in real concrete, this model must be extended for Cs and Sr, and information about the material and boundary conditions is required. The outline of the simulation study is shown in Fig. 22. The basic model was extended for Cs and Sr by considering the interaction of these ions with C-S-H having various Ca/Si ratios, degradation by carbonation and Ca-leaching and the strong ion adsorption phenomena on clays in aggregate through ion exchange mechanisms. The coefficients used in this new model were determined from adsorption experiments in various

Fig. 21 Schematic of the phase equilibrium/mass transport model.

Fig. 20 Water redistribution in pores of different sizes after rewetting dried concrete.

Fig. 22 Outline of the material transport simulation.
conditions, such as in samples with various Ca/Si ratios in the C-S-H, in wide concentration ranges, in the presence of various coexisting ions, in degraded cement paste, and in samples that used the same types of aggregate used in the original structures.

After the phase equilibrium/mass transfer model was constructed, the extended model was used in a trial to reproduce the Cs and Sr profiles, considering the exposure history of the concrete of the turbine pit. The model incorporated the information summarized in Section 2 as the concrete characteristics and boundary conditions.

### 6.2 Extension of the phase equilibrium/mass transport model for Cs and Sr

Historically, phase equilibrium/mass transport models have been developed to assess the risk of chloride corrosion of the reinforcing steel in concrete in marine environments. Therefore, the target ion was traditionally limited to chloride. However, in this project, the target ions are Cs and Sr. There are a limited number of studies investigating Cs and Sr transport models. However, it has been shown that the amount of Cs and Sr adsorbed depends on various factors such as concentration; the presence and concentration of coexisting ions; the type of cement hydrates, especially the Ca/Si ratio of C-S-H; and the presence of clays in the aggregate. Therefore, these effects were individually examined in experiments, except for the effects of the aggregate (Haga et al. 2019). To study the aggregate, a series of new investigations was conducted for the same type of aggregates used in the original structure.

The C-S-H dissolution equilibrium model by Nonat (2004) is versatile, and can be used in the model extension when considering various Ca/Si ratios in C-S-H and the competitive interactions between various ions such as Na, K, Cs, Ca, and Sr. The strength of the interactions can be described using a simple equilibrium constant for the fundamental reaction between each ion and the silanol in the silica tetrahedra of C-S-H. However, the interactions between silanol and ions are affected by Ca/Si ratio. Therefore, different equilibrium constants must be set to consider the Ca/Si ratio and its effect on the corresponding adsorption experiments.

After determining the equilibrium constants, we confirmed the applicability of the extended model by comparing various kinds of adsorption experiments in a wide range of concentrations, with concentrations ranging from 100 nM to 100 μM in the presence of C-S-H having various Ca/Si ratios ranging from 0.6 to 1.2. The phase equilibrium model was then applied to the adsorption results in various conditions such as different degradation conditions (washed, Ca-leached, and carbonated), different coexisting ion conditions (Cs only, Sr and Cs in the same concentrations, and 1M of Na and K), and different Cs concentrations (ranging from 100 nM to 100 μM). In every case, the experiments and calculations were consistent, as shown in Fig. 23. Therefore, the Cs and Sr adsorption model was successful.

The aggregates were classified as one phase for the equilibrium calculations. In the model, the aggregate was immersed in a pore solution containing various Cs and Sr concentrations. From these adsorption experiments, we determined the equilibrium constants for the ion exchange reaction between the aggregate and the Cs/Sr.

### 6.3 Boundary conditions

Using the extended model, we conducted a trial in which the Cs and Sr transport processes occurred in concrete under the boundary conditions of the real reactor system. The target concrete in the trial was the lower part of the wall in the turbine pit. For the simulation, the variations in ion concentrations in the contaminated water in contact with the concrete must be defined. The outline of boundary condition variations is shown in Fig. 24.

After the earthquake and the subsequent tsunami, this section was saturated with seawater for one day. Therefore, the concrete was saturated with seawater at one point. Then, the concrete was exposed to highly contaminated water that leaked from the reactor container. Then, approximately one year later, several systems were introduced to remove the radionuclides with other stable ions, and the elemental concentrations decreased gradually over five years to reach groundwater levels for the stable elements in addition to some radionuclides. The behaviors of the decreasing concentrations are shown in Fig. 25.

Fig. 23 Comparison of adsorption amounts by experiments and by equilibrium calculations for Cs and Sr in various materials and ion conditions.
6.4 A trial estimation for Cs and Sr transports under real concrete conditions

As a trial, we estimated the Cs and Sr transport in the concrete wall under real concrete conditions using the numerical model. For this estimation, the material characteristics of the concrete and the boundary condition of the contacting solution are required. We used the information about the material used and the mixture proportion from the literature survey presented in Chapter 2. The factors relating to the pore structure that influence the effective diffusion coefficient were determined according to the literature (Hosokawa et al. 2011). In this trial, we assumed two different concrete conditions: non-carbonated concrete and concrete carbonated up to a depth of 30 mm. All samples were also assumed to be uncoated. The boundary conditions for the model are described in Section 6.3.

The results of the simulation are shown in Fig. 26. According to the simulation, concrete carbonation resulted in a small increase in Cs adsorption and a significant increase in Sr adsorption; for both species, the penetration depths decreased in carbonated samples. Because there are discrepancies between the results of the simulation and experiments, the model may be modified in future studies to include the rapid diffusion of species in carbonated regions and the intensive interactions between the carbonated cement paste and Cs. Haga et al. (2019) find from $^{27}$Al-NMR measurement that during carbonation in cement paste, alumina silica gel should be formed, and Cs is more likely to adsorb to the Al in this phase (Haga et al. 2019). However, we did...
not consider the formation of this phase in the current simulation system. We both intend to develop the model further and conduct the transport experiment with concrete in the future.

7. Summary

Before decommissioning the Fukushima Daiichi NPS, the extent of concrete contamination must be determined. The major results of the MEXT project investigating concrete contamination mechanisms are summarized below:

- From a literature survey, we determined boundary conditions such as the radionuclide concentration and the characteristics of the concrete at the reactor site.
- Through experiments in which the mortar was immersed in solutions containing realistic concentrations of Cs and Sr, we studied various material behaviors. In samples containing fly-ash blended cement, species penetration was much less significant than in OPC. Clays in aggregate increased the levels of adsorption but had no effect on the penetration depth. Cs penetrated much faster than Sr. Carbonation and Ca leaching in the cement paste increased the adsorption of Cs and Sr by two orders of magnitude. In dried carbonated concrete, the penetration depths were significantly greater than that in the water-saturated condition.

Concrete that increases the pH of its environment resulted in the formation of hydroxide at the material surface, which caused the precipitation of α-nuclides on the surface of the concrete.

- Water suction in dried concrete was examined using X-ray CR and 1H-NMR relaxometry. Different suction behaviors were detected at different temperatures, a phenomenon that could be explained by microstructural changes in the cement hydrates.
- We completed a preliminary simulation of the penetration of Cs and Sr in concrete, considering historical boundary conditions at the power plant site, such as the variation in radionuclide concentrations.

The objective of the next project is to estimate the contamination quantitatively using realistic concrete with cracks.

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