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Development of Soundness Assessment Procedure for Concrete Members Affected by Neutron and Gamma-Ray Irradiation

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Abstract

In 2008, Nuclear and Industrial Safety Agency (NISA) (currently integrated to the Nuclear Regulatory Authority) launched a project to develop a soundness assessment method for concrete members subject to a radiation environment. Presently, the soundness of concrete members subject to radiation is evaluated based on whether the predicted fast neutron fluence and gamma-ray dose values are lower than specific reference values in Japan, which are $1 \times 10^{20}$ n/cm$^2$ and $2 \times 10^5$ kGy, respectively. These reference values were determined based on report by Hilsdorf et al. This project begins by reviewing Hilsdorf et al.’s report, and we find that the scientific evidence for the current reference values is weak. We thus conclude that new experimental research is required to assess the current reference values and to propose a new alternative soundness assessment procedure if needed. We quantitatively evaluated the influence of neutrons, gammarays, and the resultant heating and drying processes on the strength of concrete as well as their underlying mechanisms. The irradiation experiments confirmed the degradation mechanism of concrete due to neutron irradiation. The main reason for this degradation is the metamictization of rock-forming minerals, which, in turn, leads to aggregate expansion. Due to aggregate expansion, cracks around aggregates form, which reduce the compressive strength and Young’s modulus of concrete. Among the rock-forming minerals, α-quartz is the most sensitive to neutron radiation. $^{60}$Co gamma-ray irradiation experiments demonstrated that concrete strength increased as the gamma-ray dose and gamma-ray flux does not have a dose-rate impact on the first radiolysis of evaporable water in cement paste within the present study. The effect of gamma-ray irradiation on the properties of concrete is equivalent to that of heating and drying. Concrete strength alteration due to heating and drying is attributed to the colloidal and porous nature of hardened cement paste and crack formation around the aggregate due to a mismatch in the volume changes of the mortar and aggregate. In addition, a numerical analysis code called DEVICE (Damage EValuation for Irradiated ConcretE) is developed to harness knowledge obtained from concrete samples to predict the distribution of the physical properties in concrete members and their changes over time. From these fundamental studies, we propose a new soundness assessment procedure for concrete members subject to radiation. We also recommend a new radiation-induced strength-degradation reference value of $1 \times 10^{19}$ n/cm$^2$ for fast neutron.

1. Introduction

1.1 Background

Concrete structures in nuclear power plants may undergo undesirable changes because of loads and environmental conditions. Since concrete structures in nuclear power plants are seldom replaced, predicting their aging phenomena as well as evaluating their current and future soundness is crucial. The widespread use concretes for buildings and civil engineering structures has led to a solid understanding of their numerous degradation phenomena. Nevertheless, there is a lack of knowledge regarding the high-temperature (~90 °C) and radiation environments specific to nuclear power generation facilities because such conditions are rarely encountered in more common structures. Several nuclear power plants in Japan that are being considered for operating periods exceeding 40 years are expected to surpass neutron irradiation fluence levels of $1 \times 10^{19}$ n/cm$^2$ (fast neutron, > 0.1 MeV). Researchers have claimed that concrete exposed to such fluence levels would deteriorate (Hilsdorf et al. 1978). Table 1 summarizes the maximum expected fast neutron fluence and gamma-ray dose of boiling water reactors (BWR) and pressurized water reactors (PWR) in Japan over an operating period of 60 years. Figure 1 shows typical
concrete members subjected to irradiation.

According to the Review Manual for Aging Management Technical Evaluation (Japan Nuclear Energy Safety Organization 2013), “the mechanism of the decrease in concrete strength due to neutron irradiation and gamma-ray irradiation is not sufficiently clarified, but it is known that substances subjected to neutron irradiation and gamma-ray irradiation generate heat, and it is highly possible that moisture escapes from the concrete, which may lead to a decrease in the strength of the concrete due to drying shrinkage-induced multiscale cracks.” Therefore, drying is listed as one of the main causes of concrete degradation. In the Review Manual, the integrities of concrete structures under gamma-ray and neutron radiation were evaluated based on whether the forecast values of gamma-ray dose and neutron fluence after a 60-year period exceeded the “reference level” at which the deteriorated concrete strength becomes problematic. If the radiation levels did not exceed the reference values of $1 \times 10^{19}$ n/cm$^2$ and $2 \times 10^8$ kGy for neutron fluence and gamma-ray dose, respectively, then the concrete was evaluated as sound. The reference values were prescribed according to the figures shown by Hilsdorf et al. (1978). In their conclusion, however, Hilsdorf et al. pointed out that the fluence level of $1 \times 10^{19}$ n/cm$^2$ was the threshold at which the alteration of concrete appeared, and that the influence of gamma-rays was not particularly significant. The reference level does not reflect such findings.

In addition, a careful investigation of the original literature cited in Hilsdorf et al.’s paper (Price et al. 1957; Batten 1960; Alexander 1963; Dubrovskii et al. 1966; Houben 1969; Van De Schaaf 1969; Stoces et al. 1970; Elleuch et al. 1972) confirmed that there was a discrepancy between the concrete used for light water reactors (LWR) and the samples and test conditions used in experimental studies found in literature, such as cement type, temperature conditions, and so on. The results of these studies are presented in Table 2 and Table 2. In Fig. 2, the data points enclosed by red frames are presumed to have been obtained at conditions largely different from actual LWR conditions. Table 2 lists all the neutron irradiation experimental conditions, whereby shaded entries signify experiments that did not meet the LWR conditions. Furthermore, the gamma-ray irradiation experiments by Sommers (1969) were conducted in deionized water, and calcium leaching must have occurred during the experiment. These results demonstrate that the Japanese reference levels need to be better informed by scientific studies and experimental results.

While the operating temperatures of LWR are less than 65 °C and hence have negligible influence on the strength of hardened cement paste (hcp), Maruyama et al. (2013) re-reviewed neutron irradiation experiments and developed the graph presented in Fig. 3. It confirms that the Fe/Cu ratio (ratio of strength of irradiated specimen to strength of non-irradiated specimen) decreases monotonically above $1 \times 10^{19}$ n/cm$^2$, and thus further scientific investigation is necessary to establish a
reference level. It is worth mentioning that the Oak Ridge National Laboratory team collected irradiation experimental data and reached a similar conclusion during this project (Field et al. 2015).

The above results reveal many uncertainties regarding the validity of the present reference values, and thus it is necessary to conduct further experimental studies. In addition, the neutron irradiation environment is always affected by (secondary) gamma-rays, which themselves are associated with gamma heating. Therefore, the effects of neutrons, gamma-rays, and heating and drying on the physical properties of concrete and their mechanisms are essential to establishing a valid reference level. It is also necessary to clarify environmental degradation conditions, their mutual interactions with the constituent materials in concrete, and the resultant change in the physical properties of the materials and concrete.

### Table 2 Experimental conditions found in papers referred by Hilsdorf et al. (Kontani et al. 2010). Conditions with gray hatching are considered to be different from those for LWR.

| Author       | Property Measured | Cement Type | Specimen Size (mm) | Irradiation Conditions                                      | Neutron Energy Level & Fluence (n/cm²) |
|--------------|-------------------|-------------|--------------------|-------------------------------------------------------------|----------------------------------------|
| Alexander    | Comp.             | OPC         | 51x51x51           | Temperature (deg C) 20 to 100                                | Neutron Thermal Neutron 0.29x10¹⁹ to 2.3x10¹⁹ |
| Batten       | Comp.             | OPC         | 51x51x203          | Not Available                                               | No Information 5.0x10¹⁹                 |
| Dubrovskii   | Comp.             | Liquid glass| φ15x15 cylinder    | 200 to 550                                                  | No Information 2.0x10¹⁹ to 2.4x10¹⁹     |
| Elleuch      | Comp.             | Aluminous cement | 25x25x50           | 210                                                        | Fast Neutron 2.6x10¹⁹ to 11.1x10¹⁰      |
| Houben Schaaf| Comp.             | OPC         | 8x8x70             | 150 to 200                                                  | Fast Neutron 3.0x10¹⁹ to 8.0x10¹⁹       |
| Price        | Bending           | OPC         | 51x51x203          | 50                                                         | Thermal Neutron 0.5x10¹⁹ to 7x10¹⁹      |
| Stoces       | Comp.             | OPC         | φ50x70 cylinder    | <80                                                        | Fast Neutron 4.2x10¹⁸                    |

OPC : Ordinary Portland cement

Fig. 2 Relationship between neutron fluence (left), gamma-ray dose (right), and strength ratio (Fc/Fco). Fc is the compressive strength after irradiation and Fco is the compressive strength of reference (Kontani et al. 2010).

Fig. 3 Relationship between concrete strength ratio (Fc/Fco) and neutron fluence of concretes satisfying the LWR conditions (Maruyama et al. 2013).
Concrete is a multi-scale composite comprised of various constituent materials. When concrete is subject to radiation, the neutrons, gamma-rays, and resultant energy deposition alter the concrete constituents, which, in turn, alter the macroscopic performance of the concrete. We interviewed domestic and foreign experts, reviewed literature, and compiled knowledge about how neutrons and gamma-rays affect the constituent materials within concrete. We compiled our results in Table 3.

### Table 3 Possible phenomena and impacts of neutrons and gamma-ray on concrete and concrete constituent materials.

| Cement paste | Water | - Drying due to radiation decomposition and gamma heating might change properties of cement paste. - Hydrogen peroxide and radicals generated in irradiation process might react with hydration products to alter properties of cement paste. |
|--------------|-------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Solid        | Solid | - Cement paste shrinks due to gamma heating. - Some hydrates are decomposed due to heating. - Physical properties change according to drying effect. - Si-O-Si bond and other covalent bonds are deformed by radiolysis impact and ballistic impact by electron. - Oxide atom in the Si-O-Si bond and other covalent bonds are knocked out by electron. - If the defects of crystal is formed, abundant water heals this defects by solution-precipitation process. |
| Aggregate    | Water | - Crystal water is removed due to gamma heating. - Adsorbed water is evaporated due to gamma heating. - Shrinkage of clay minerals and other layered structures occur due to drying. |
| Solid        | Solid | - Si-O-Si bond and other covalent bonds show metamictization, and volume change occurs. - Some deformation and metamictized state are healed by thermal effect. - Secondary electrons cause knock out some atoms in crystals. |
| Concrete     |       | - Crack in mortar around aggregate occur due to drying or heating. - Unreacted cement reacts under elevated temperature caused by gamma heating. - Strength changes by colloidal and porous material nature of hardened cement paste and cracking due to difference in volume change between mortar and aggregate. - Young’s modulus decreases due to crack opening. |
|              |       | - Expansion occur due to expansion of aggregate caused by metamictization. - Mortar or cement paste in concrete shrinks and crack in paste or mortar is produced due to restraint by aggregates. - Strength and Young’s modulus is reduced according to crack formation and crack opening due to expansion of aggregates. |

### 1.2 Working hypotheses

Concrete consists of water, cement, fine aggregate (sand), coarse aggregate (gravel), admixtures, and additives. The sizes of cement, fine aggregate, and coarse aggregate particles are ~10 μm, ~2 mm, and ~15 mm, respectively. The cement paste formed via a hydration reaction between cement and water serves as an adhesive between aggregates. The numerous types of hydrate produced by this hydration reaction have structural units ranging from several nanometers to several micrometers in size. Therefore, concrete is a multi-scale composite comprised of various constituent materials.

When concrete is subject to radiation, the neutrons, gamma-rays, and resultant energy deposition alter the concrete constituents, which, in turn, alter the macroscopic performance of the concrete. We interviewed domestic and foreign experts, reviewed literature, and compiled knowledge about how neutrons and gamma-rays affect the constituent materials within concrete. We compiled our results in Table 3.
In other words, when isolating the impact of neutrons via neutron irradiation experiments, supplemental reference experiments that consider heating and drying effects, as well as gamma-rays, are necessary to ensure completeness.

We begin by discussing the heating and drying effects accompanying neutron and gamma-ray irradiation, which exert the greatest influence over concrete modification. Because ordinary concrete uses excess water for the hydration reaction of cement in order to ensure workability, the matured concrete retains a large amount of excess water. Therefore, evaporation of internal moisture occurs under exposure to the general environment. Figure 5 compares the relationship between the strain (length change isotherm) of aggregate and hcp and the relative humidity (RH) at room temperature.

As shown here, the cement paste experiences a large shrinkage of roughly 3000 µm/m even under 60% RH, which is the average humidity in Japan. Commonly used sandstone, for example, may undergo a drying shrinkage strain of ~1000 µm/m at most if it contains a high proportion of clay minerals that shrink readily. On the other hand, since aggregates often consist of rocks stabilized underground for over tens of thousands of years, aggregates experience shrinkage of not more than several hundred micrometers per meter (generally ~150 µm/m). This is especially true of limestone produced in Japan: the high purity of calcite ensures that the limestone hardly shrinks. In either case, the cement paste and aggregate found in concrete undergo different volume changes during drying, resulting in the formation of many fine cracks within the concrete. These internal cracks bring about changes in the strength and stiffness of concrete. Our discussion so far has identified two important factors regarding the radiation environment: 1) differing degrees of volume change between the constituent materials, and 2) changes in the strength of the constituent materials themselves, especially the strength of the hcp.

Next, we derive factors that strongly influence radiation-induced concrete modification. Previous experimental studies have confirmed that, even while cement paste irradiated with neutron shrinks, its strength does not change (Elleuch et al. 1972). The calcium silicate hydrate (C-S-H) responsible for the strength of the cement paste has a small crystal unit, and this small unit is composed of a basic calcium oxide (CaO) layer structure with dimeric silicate chains (Si₂O₇²⁻) attached (Richardson 2014). When Si₂O₇²⁻ integrates into the CaO layer, the surface of this mono-C-S-H layer is negatively charged. This negative surface charge is balanced with a cation, such as Ca⁺² under high pH conditions, resulting in the compilation of the mono-C-S-H layer. However, when an imbalanced Si₂O₇²⁻ integration into the CaO layer occurs, the CaO layer becomes inflectional, causing limited crystal growth in the compilation direction (Gartner 1997; Gartner et al. 2000). Crystal deformations (triggered by gamma-ray-induced electron excitation) and crystal defects (produced by neutron flaring) exert minimal influence over the physical properties of hcp. The curved structure of C-S-H is simply insensitive to such influences. In addition, when water is present in the periphery, the crystal structure is rapidly healed by the dissolution-precipitation process. Therefore, the physical properties of hcp experience little to no change, so it is unlikely that the effect of radiation surpasses that of heating and drying.

From a previous study (Hobbs et al. 1994), it is known that ionic bonds are resistant to neutron irradiation, whereas covalent bonds resist it poorly, with their bond angles readily changing under exposure. Rock-forming minerals with high covalent bond content have poor neutron resistance. One major component of aggregate, α-quartz (hereafter “quartz”), is composed solely of covalent bonds and is highly dense: its poor resistance to radiation and consequent large volume changes make it highly sensitive to any radiation-induced stress.
expansion make it the aggregate component that is perhaps most harmful to concrete stability. Actually, it has been well established, through experimental studies, that quartz expands as a result of neutron irradiation (Wittels and Sherrill 1954; Primak et al. 1955; Primak 1958). When exposed to neutron radiation, quartz expands by 16–18% in volume and lengthens by 5–6% (Bykov et al. 1981). These changes are accompanied by a structural transformation to a metamictic structure, so that no definitive crystal structure can be confirmed. Other studies have found that metamictization occurs by electron irradiation, and it is therefore possible that gamma-rays have the same effect as electron irradiation. This metamictization process is produced by both radiolysis and ballistic impacts. In the case of quartz exposed to electron irradiation, an electron produced by a lower acceleration voltage exhibits a higher radiolysis efficiency, which speeds up the metamictization process. Electrons accelerated at voltages greater than 1500 keV, on the other hand, demonstrate ballistic impacts (Inui et al. 1990). A recent study reported that quartz subject to 100-keV electrons expands by only 4%, which is markedly smaller than the 16–18% expansion caused by neutron irradiation. Thus, the mechanism of neutron metamictization is different from that of the electron-induced metamictization (Maruyama and Muto 2016).

Nevertheless, gamma-rays and electrons possess the ability to cause rock-forming minerals to expand. This implies that neutron and gamma-ray irradiation will provoke rock-forming minerals, such as quartz, to undergo a structural transformation into the metamict state. This, in turn, will cause the aggregate to expand, creating cracks in concrete and thereby deteriorating its physical properties. The aggregate will thus decrease in strength and stiffness. However, since the cement paste, which is the main matrix of concrete, has already sustained significant damage due to aggregate expansion, the weakening of the aggregate’s properties does not alter the concrete’s strength and stiffness to any appreciable extent.

Numerous groups have studied quartz as an expanding rock mineral (Wittels and Sherrill 1954; Primak et al. 1955; Primak 1958; Weissmann and Nakajima 1963; Lell et al. 1968; Bykov et al. 1981; Inui et al. 1990; Eby et al. 1992; Bonnet et al. 1994; Douillard and Durand 1996; Bolse 1999; Ewing et al. 2000). Yet, the rate of metamictization and the final expansion strain of other rock-forming minerals are also important topics for research. It is particularly important to elucidate the behavior of the feldspar group (mostly covalent bonding) and the behavior of limestone (mostly ionic bonding), since radiolysis affects covalent bonds more than ionic bonds.

The preceding findings lead us to develop the working hypotheses for this work, which is summarized in Table 4. We established a research plan based on the factors relevant to understanding the modification of concrete exposed to a radiation environment.

1.3 Objective

In this study, our objective is to develop a methodology to evaluate the soundness of concrete structures exposed to gamma and neutron radiation, specifically concrete structures providing shielding and supporting functions. To do so, we determine the mechanism of radiation-induced concrete degradation and evaluate the Japanese reference levels through experimental studies. Since there are many types of aggregates, cements, and concrete mixture proportions used in Japanese LWR buildings, it is necessary to understand how gamma-rays and neutrons affect concrete components. This, in turn, will enable us to develop a comprehensive evaluation system for the soundness of concrete and its components.

Currently, soundness evaluation of concrete members is based on the reference values discussed earlier. Assuming that the current soundness evaluation method is successful, we develop a new soundness evaluation procedure to address the case in which the fast neutron fluence and/or gamma-ray dose surpasses the reference level (see Fig. 6). This tentative evaluation process is also used for gap analysis.

The soundness evaluation process consists of 1) evaluating the reference values for neutrons and gamma-rays, 2) evaluating the required concrete strength, and 3) evaluating the structural and shielding performance of the concrete member(s) partially affected by a one-sided radiation condition. In order to render items 2) and 3) feasible, we rely on a numerical analysis method to model the physical properties of concrete. The numerical model extrapolates the data

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1 The word amorphization is also sometimes used, but amorphous is most often used to refer to a glass state, in which atoms are oriented completely randomly. The atomic-level reorientation caused by neutron irradiation results in reduced density, but Si atoms still retain local structures such as six-atom rings. Therefore, the term metamictization is preferentially used in this report.
obtained by experimental investigations, yielding the distribution of the physical properties of concrete members and their changes over time under a one-sided radiation exposure environment. In the framework of this project, we developed a numerical calculation program DEVICE (Damage Evaluation for Irradiated Concrete) (Maruyama et al. 2016a), which can quantitatively evaluate the influence of environmental factors (neutrons, gamma-rays, temperature, and humidity) on the distribution of physical properties of concrete members. DEVICE was developed based on a concrete physical-property-prediction program known as the Computational Cement-Based Material Model (CCBM) (Maruyama and Igarashi 2015).

The structure of this paper is briefly introduced here. In chapter 2, results of neutron irradiation experiments are shown. The objective of chapter 2 was to clarify the mechanism by which concrete deteriorates in radiation environments and to experimentally verify the proposed working hypothesis for this degradation mechanism. A secondary objective was to acquire data for use in developing prediction techniques and soundness assessment methods for performance of concrete members in radiation environments. Chapter 3 shows results of gamma-ray irradiation experiments. In this chapter, impact of gamma-ray irradiation on radiolysis of evaporable water in hcp and physical properties of concrete, aggregates, andhcp are shown. The effects of dose-rate are also evaluated. Chapter 4 shows the results of experiments for heating and drying. The objective of this chapter is to clarify how the concrete properties are altered by volumetric stability of components and changing of calcium silicate hydrate (C-S-H) formed in hcp under the first drying and heating processes. Chapter 5 introduces a developed numerical code to evaluates time and spatial changes of physical properties of concrete in massive concrete member under heating, drying, and irradiation. The experimental data obtained in chapter 2, 3, and 4 are taken into account as various functions to represent behaviors of concrete and concrete components under such conditions. This code is necessary for evaluating the soundness of the target member in future. Chapter 6 proposes soundness assessment procedures of concrete members under radiation environments. Finally, chapter 7 discusses the limitation of the obtained results and issues to be solved in successive researches. Summary and conclusion are shown in chapter 8.

### 2. Impact of neutron irradiation

#### 2.1 Implementation outline

It is hypothesized here that aggregate expansion is a major cause of concrete degradation as considered in this research. Neutron radiation is hypothesized to cause metamictization in quartz, causing it to reduce in density, expand, and lead to cracking in the surrounding concrete.

The primary data of this research are changes in the physical properties of concrete. Yet, gamma radiation is also emitted in a neutron radiation environment, and gamma heating also affects concrete through heating and drying effects. With the intention of separating the effects of aggregate expansion from the effects of heating and drying, it was decided to also measure physical-property changes in non-irradiated specimens heated over time according to the temperature profile observed in irradiated concrete specimens. Data of concrete samples sealed at room 20 °C were also measured. A series of tests were conducted to comprehensively assess physical property changes in a radiation exposure environment, in which the properties of specimens exposed to ideal, heating/drying, and radiation-environment conditions were selectively compared.

The direct effects of neutron radiation include interactions due to secondary gamma radiation. Confirming the extent to which these interactions are involved in the decomposition of hydrates and water in cement paste, and especially the role of chemically bound water in

| Table 4 Working hypothesis for understanding concrete behavior subject to a radiation environment. |
|-----------------------------------------------|
| Cement paste | Gamma-rays | Neutrons |
| Water | -Gamma ray irradiation enhance the drying of cement paste. | - Neutron irradiation enhance the drying of cement paste. |
| Solid | - Impact of gamma-ray on cement paste is same as that of heating or drying. | - Impact of neutron on cement paste is comparable to that of heating or drying. |
| Aggregate | Water | - Impact of gamma-ray on aggregate is same as that of heating and drying in the realistic dose range, while the metamictization should occur due to irradiation theoretically. |
| Solid | - Aggregate expands due to metamictization. |
| Concrete | - Impact of neutron on cement paste is similar to that of heating or drying. |
| | - Compressive strength and Young’s modulus of concrete decreases due to crack opening caused by expansion of aggregates. |

| Solid | - Strength and Young’s modulus change due to gamma-ray irradiation are almost comparable to those due to heating or drying. | - Concrete expands due to expansion of aggregate. |

| Solid | - α-quartz is the most sensitive to neutrons and α-quartz content of aggregate is the major factor of expansion rate and ratio of aggregate in the realistic fluence range. | - Concrete expands due to expansion of aggregate. |

| Solid | - Aggregate expands due to metamictization. |

The primary data of this research are changes in the physical properties of concrete. Yet, gamma radiation is also emitted in a neutron radiation environment, and gamma heating also affects concrete through heating and drying effects. With the intention of separating the effects of aggregate expansion from the effects of heating and drying, it was decided to also measure physical-property changes in non-irradiated specimens heated over time according to the temperature profile observed in irradiated concrete specimens. Data of concrete samples sealed at room 20 °C were also measured. A series of tests were conducted to comprehensively assess physical property changes in a radiation exposure environment, in which the properties of specimens exposed to ideal, heating/drying, and radiation-environment conditions were selectively compared.

The direct effects of neutron radiation include interactions due to secondary gamma radiation. Confirming the extent to which these interactions are involved in the decomposition of hydrates and water in cement paste, and especially the role of chemically bound water in
their decomposition, represents an important step for the stability of cement paste.

As for aggregates: $\alpha$-quartz is already known to expand, and is believed to be a primary cause of concrete degradation. Concrete’s expansion, in both size and speed, should therefore change noticeably according to the $\alpha$-quartz content of its aggregate. The first step to confirm this hypothesis by establishing the existence of aggregate-dependent degradation. In conjunction, the existence of aggregates that lack radiation risk was confirmed by irradiating limestone - a structure that mostly contains ionic bonds.

Two kinds of tests were performed: interaction tests (IT), which focus on the radiolysis of water in cement paste, and physical property tests (PPT), which focus on physical changes in concrete, cement paste, and aggregate. PPT also included heating tests (HT) and cold tests (CT), in which specimens were not exposed to radiation, to isolate factors other than neutron radiation that cause physical changes. Table 5 shows the complete process for all neutron irradiation tests.

In addition to gathering these experimental data, radiation conditions were quantitatively evaluated. The radiation environment was measured in terms of fast-neutron- and gamma-heating-related data using monitoring equipment, but it is impossible to analyze the data while accounting for all conditions surrounding the capsule. Therefore, it was decided to estimate capsule conditions and heating conditions using MCNP5 (X-5 Monte Carlo Team 2003) when evaluating the experimental data. MCNP5 is code for calculating radiation transport using a Monte Carlo method, developed by the Los Alamos National Laboratory, United States.

2.2 Experiment  
2.2.1 Reactor selection

In advance of the experiments, the specifications and conditions at several domestic and foreign research reactors were reviewed (Japan Atomic Energy Research Institute 2004). Since a number of reactors were scheduled for decommissioning, only domestic and foreign reactors expected to be operational in the future were selected. After interviews with professionals affiliated with the reactors, the reactors’ respective suitability for concrete radiation testing was examined. Significant gamma heating is generated in most reactors, creating the risk of considerable temperature increase in concrete specimens. In real reactors, concrete is restricted to kept below 65°C, and it is considered that this condition does not change the concrete properties. Thus similar temperature condition is favorable for our experiment.

The facilities, Belgian Reactor 2 (BR2) and Halden Boiling Water Reactor (HBWR), perform irradiation tests at high neutron flux levels, making them poorly suited to neutron irradiation tests under temperature-controlled conditions. Concrete irradiation tests have been performed successfully with the Japan Materials Testing Reactor (JMTR), using an O-2 irradiation hole (Fujiwara et al. 2009). However, using the JMTR would require an estimated exposure time of three years. The
The JEEP II reactor at Norway’s Institute for Energy Technology (IFE) has a low output power, and is available for use for fundamental physics experiments. This reactor was promising for another reason: as a heavy water reactor, only low levels of gamma radiation are generated by neutron deceleration. This characteristic—low levels of gamma heating in proportion to fast-neutron flux levels—is another characteristic that makes conditions in JEEP II well-suited for concrete irradiation tests. Selecting a suitable chamber within the reactor can guarantee a fast neutron flux of approximately $2.0 \times 10^{12}$ n/cm$^2$/s, even if gamma heating was restricted to 0.04 W/g; the irradiation tests could be concluded in two years even with only 50% reactor up-time.

Table 6 summarizes the characteristics of the reactors examined. Based on the characteristics shown here, it was decided to conduct the irradiation tests using the JEEP II reactor.

Next, specimen height was established based on the environment in the irradiation holes of the reactor. Figure 7 shows the positions of the irradiation holes used in this study within the reactor, Figure 8 shows neutron flux distributions for holes #52 and #36.

### 2.2.2 Specimen size
While it is true that the gamma heating value is low for the JEEP II reactor, limiting the size of the specimens was inevitable. In general standards, compressive strength has been evaluated using concrete specimens of φ100×200 mm and a maximum aggregate diameter of 20 mm, but it is difficult to perform irradiation tests on specimens of this size. Pre-irradiation tests was performed to determine a suitable test specimen size that would limit gamma heating.

Mortar specimens (φ50×100 mm) were used for the pre-irradiation tests and the results are shown in Figure 9. As shown, the specimen’s core reached approximately 83°C, while its surface reached 58°C, which is equivalent to the temperature of the reactor’s cooling water. The frequent temperature fluctuations in the figure are...
because the reactor was repeatedly and frequently shut down for other experiments.

The surface and core of the φ50-mm specimen differ by 26°C. Assuming the tensile strength of 4 MPa and a Young’s modulus of 20 GPa for normal concrete, cracks begin to appear if tensile strain reached to 200 μ. If a thermal expansion coefficient of 10 μ/°C is assumed, cracks could form in the concrete at the surface. Therefore, it was decided to minimize the core–surface temperature differential such that the corresponding strain differential was kept below 200 μ. In Fig. 10, setting specimen diameter to φ40 mm greatly reduced the appearance of the cracks attributable to a high core–surface temperature differential. Consequently, it was decided to test φ40-mm specimens in order to reduce the confounding effects of gamma heating over a wide internal-temperature distribution.

Figure 11 shows a vertical cross-section of the irradiation holes with an installed capsule equipped with a monitoring apparatus. As shown here, the reactor core is 90 cm in height, and a neutron flux distribution exists within the irradiation hole in the vertical direction. Neutron flux varies over a ~60-cm region spanning ±30 cm of the hole’s center; it changes maximally by ~20%, and becomes smaller at the ends of the region. This constitutes local differences in the radiation environment. This 60-cm region was adopted as the irradiation range for the experiments while still trying to meet two conditions: placing as many test specimens in the chamber as possible due to their small dimensions, and avoiding major disparities in irradiation conditions between specimens. The average neutron flux in this range was 3.6×10^{12} n/cm²/s: a measurement shared by both chambers. In addition, establishing the temperature environment within the radiation environment was indispensable for evaluating the experimental data. Therefore, in addition to the loading test specimens, temperature monitoring specimens also needed to be placed into the capsule. Based on these conditions, the range was divided into 10 sectors, each containing one 6-cm-height
specimen. A temperature monitoring specimen was inserted in the uppermost space, small aggregate and paste specimens in the lowermost space, and eight concrete specimens into the region in between.

Specimen size of $\phi 40 \times 60$ mm was determined, but this height–diameter ratio is unusual for research practices in Japan. JIS A 1132:2014 specifies that specimens should have a height–diameter ratio of 2, and that their diameter be at least three times the maximum dimension of the aggregate used. Therefore, it was decided to set the maximum aggregate diameter to 13 mm. The height–diameter ratio was maintained at 1.5 in the experiments: it is still possible to properly measure compressive strength in specimens with this ratio (Kosaka 1974). Preliminary experiments—loading tests with $\phi 40 \times 60$-mm specimens—damage due to compression shear from diagonal cracks was confirmed. Therefore, loading tests can be performed appropriately for specimens with a 1.5 height–diameter ratio. The number of specimen for each condition was set to $n=4$. The obtained conclusions were mainly derived from the compressive strength ratio ($F_c/F_{co}$), which is the ratio of concrete strength to the concrete strength of the sealed condition. Normalization should reduce the height-diameter influence.

Initially, it was feared that the damage surrounding the aggregates within the concrete would be underestimated due to aggregate size. This is because damage to the mortar are relatively minimized for large ratios of depth of interfacial transition zone to aggregate diameter (detailed in Chapter 4). However, in contrast to normal concrete, the damage in concrete containing this aggregate size was almost the same under heated and dry conditions (Maruyama and Sasano 2014; Lin et al. 2015). As a result, aggregate size was not a major problem in this research, where aggregate expansion reached a few percent (as will be shown later).

### 2.2.3 Capsule

The capsule consists of a double tube made of aluminum. Cement-paste and concrete specimens are enclosed in the cylinder, separating them from the cooling water to provide some clearance. Cooling water flows in from the bottom of the outer cylinder and out from the top of the outer cylinder. This structure allows cooling water to flow between the outer surface of the inner cylinder and the inner surface of the outer cylinder, removing the heat generated in the specimens. A tube connects the inner cylinder to a measurement system outside the reactor to capture the gas and water vapor generated by radiation. The tube is equipped with a helium-based flushing system to eliminate any clogging.

The capsule is constructed from aluminum. In the planning stages, the risk was discussed of alkali corrosion reactions during the experiments between condensed water vapor and calcium hydroxide leached from the concrete and the aluminum. Nonetheless aluminum was adopted, for the following reasons:

1. High thermal conductivity. Concrete has low thermal conductivity: temperature in a concrete specimen’s core rises if heat cannot escape the surface quickly. A temperature differential between the surface and core risks producing cracks in the specimen. Aluminum’s thermal conductivity is over 10 times that of stainless steel thus it can help to reduce a specimen’s core temperature by allowing heat to escape quickly.

2. Softness: Concrete specimen expansion was taken into consideration by setting a clearance measuring 1% of the specimen diameter, assuming a maximum fast neutron fluence of $6.0 \times 10^{17}$ n/cm$^2$. However, cases of even greater expansion following neutron irradiation at this fluence have also been observed in past experimental data. Selecting an aluminum container would likely prevent damage to the specimen by accommodating for its expansion on the inner surface of the capsule. Aluminum therefore was selected to account for potential cases of maximum fluence producing excessive expansion.

### 2.2.4 Concrete specimens (PPT)

As this study concerns highly aged concrete, the water-to-cement ratio of concrete should be within the normal strength range. Concrete used at nuclear power plants is usually based on Portland cement, plain or with added fly ash (Architectural Institute of Japan 2013). The pozzolanic reaction of Japanese fly ash (low CaO content)
with Portland cement is slow. Therefore, it was unfeasible to test sufficiently hydrated fly-ash concrete within the scope of this research. Alite and belite have little effect on the chemical composition of C-S-H produced in a reaction system that uses sufficiently hydrated Portland cement (Richardson 2004), meaning it should be easy to isolate the effects of neutron irradiation on aged concrete here.

In addition, many un-reacted cements undergo accelerated hydration in a radiation environment due to the effects of radicals. It was undesirable for specimens to undergo accelerated hydration in this study, as this phenomenon is irrelevant to conditions in real reactors. Therefore, it was decided to use a high-early-strength cement (notation: H) with a water-to-cement ratio of 0.50 to stabilize hydration as much as possible over a preparation period of one year, with the aim of avoiding hydration-induced strength development appearing in the irradiation tests. The properties of the cement used are presented in Table 7, Table 8 and Fig. 12.

The influence of bleeding in the concrete was minimized in the mixing step. Concrete was mixed by using high-performance twin-screw mixer for 120 s.

Another objective of this study was to observe variation in the properties of concrete containing aggregates of different rock types, when exposed to identical fluence. Therefore, two kinds of concrete were prepared with different constituent aggregates: Aggregate A (GA), the aggregate shown in Chapter 4 with the highest quartz content (Table 35, aggregate A), or Aggregate B (GB) (Table 35, aggregate C), which has usage data from commercial nuclear power plants. With the aim of focusing on the effects of coarse aggregates, the concrete specimens contained the same volume of coarse aggregate, as well as the same amount of mortar prepared at the same mixture proportion. Table 9 and Table 10 show the materials used in the concrete and their mixture proportions.

In addition, Table 12 (GA, GB, and the used sand (S)) and Fig. 13 show the mineral compositions and grain size distributions of the aggregates used.

### Table 7 Chemical composition of used cement. (H: high early-strength ordinary portland cement)

| Cement Type | Density (g/cm³) | Blaine value (cm²/g) | Chemical Composition (mass%) | Total |
|-------------|----------------|---------------------|-----------------------------|-------|
| H           | 3.14           | 4340                | C: 61.8±1.8, Belite: 17.6±1.2, Aluminate: 8.2±0.4, Ferrite: 6.8±0.6, Periclase: 0.79±0.22, Bassanite: 3.15±0.22, Gypsum: 0.9±0.58, Calcite: 0.79±0.26 | 100.03 |

### Table 8 Mineral composition of used cement. (H: high early-strength ordinary portland cement)

| Alite | Belite | Aluminate | Ferrite | Periclase | Bassanite | Gypsum | Calcite | Total |
|------|--------|-----------|---------|-----------|-----------|--------|---------|-------|
| H    | 61.8±1.8 | 17.6±1.2  | 8.2±0.4 | 6.8±0.6   | 0.79±0.22 | 3.15±0.22 | 0.9±0.58 | 100.03 |

### Table 9 Properties of used materials.

| Materials | Notation | Specification | Density (g/cm³) |
|-----------|----------|---------------|----------------|
| Water     | W        | Tap water     | —              |
| Cement    | C        | High-early-strength cement, produced by Taiheiyo cement Corp. | 3.14 |
| Find aggregate | S | Land sand, sandstone, produced in Shizuoka prefecture | 2.61 |
| Coarse aggregate | GA | Altered tuff crushed aggregate (Notation A, in Chap. 4), Aggregate size 5~13 mm, produced in Aichi prefecture | 2.66 |
| GB | Sandstone gravel (Notation C, in Chap. 4), Aggregate size 5~13 mm, produced in Shizuoka prefecture | 2.64 |

### Table 10 Mixture proportions of concretes.

| Notation | Aggregate type | W/C (%) | s/a (%) | Unit mass (kg/m³) |
|----------|----------------|---------|---------|-------------------|
| S        | GA, GB, and the used sand (S) | 50 45 | 183 366 799 995 — | — 1057 |

2.2.5 Hcp specimens and aggregate specimens

In the IT, the same cement and water-to-cement ratios used to prepare the concrete specimens are used to create hcp specimens. Two-step mixing was used for better mixing performance. To avoid bleeding, additional mixing was performed every 30 min until the mixture reached consistency. The specimen size was the same as
under nitrogen gas flow.

In order to evaluate the expansion levels of aggregates with varying α-quartz content, irradiation tests were performed on five kinds of siliceous rocks (sandstones) from Japan, including GA and GB. Limestone was used as a representative rock with high ionic bond content. Information about the aggregates used, including region of origin and mineral composition, are presented in Table 11 and Table 12. Aggregate specimens had dimensions of φ10×10 mm: there were six rock types, and six specimens were prepared for each exposure condition.

2.2.6 Measurements during irradiation tests

Neutron flux and gamma heating were measured using equipment installed inside the irradiation capsule, as shown in Fig. 11. Specimen temperature was measured using thermocouples placed on the specimen in the uppermost area of the capsule.

No carrier gas was used in the neutron irradiation tests. The capsule vented the gas generated by radiolysis of pore solution in concrete when the pressure in the capsule reached the trigger pressure (1.1 ~ 1.4 bar). The released gas was connected to a water vapor condensation system and gas collecting branch. Water was separated from the gas in the moisture collection tank. The dehydrated gas was then sampled, and subjected to composition analysis using gas chromatography.

Gas was generated by neutron irradiation (H₂ and O₂) in a closed region of the system, extending from the capsule to a release valve, which increased the internal pressure. The release valve opened once pressure reached the trigger pressure (1.1 ~ 1.4 bar), relieving the pressure. The amount of gas produced was measured using a flow meter, and evaluated via calculations based on pressure and internal system volume. In addition, a helium-gas flash line was installed to accommodate adverse situations: for example, condensation inside the capsule obstructing the smooth discharge of gas, or condensed water in the system’s piping worsening the flow of gas and water vapor.

Initially, it was planned to evaluate released water amount using a humidity gauge, via the same technique as that for the gas. However, it was found that the humidity inside reached 100%, making it impossible to accurately measure released water amount. Therefore, the system was updated by installing a container to condense water vapor by cooling the system at 2~3 °C (“condenser” hereafter) to collect most of the released

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### Table 11 Type of used aggregate for irradiation experiment.

| Notation | Rock type          | Type of aggregate | Site of production | Notation in Chapter 4.3 |
|----------|--------------------|-------------------|--------------------|-------------------------|
| GA       | Altered tuff*      | Crushed aggregate | Aichi prefecture   | A                       |
| GB       | Felsic sandstone   | Crushed aggregate | Shizuoka prefecture | C                       |
| GC       | Felsic sandstone   | Crushed aggregate | Tokyo              | F                       |
| GD       | Felsic sandstone   | Crushed aggregate | Shizuoka prefecture | G                       |
| GE       | Felsic sandstone   | Crushed aggregate | Saitama prefecture | J                       |
| GF       | Limestone          | Crushed aggregate | Oita prefecture    | P                       |

*One of the project advisor concluded based on a polarization micrograph that the quarry is located within the mesozoic accretionary complex (i.e. marine sedimentary rocks) composing high contents of tuffaceous sediments and the origin of quartz (silica) is more likely from the altered tuff-rich sediments hydrothermally.

that for concrete, i.e. φ40×60 mm.

In the PPT, the whitehcp used in Section 4.2 was used. The water-to-cement ratio was 0.55; the cement’s chemical composition, properties, and mineral composition are shown in Table 32 and Table 33 (symbol: W). Specimens were aged for more than 1 year, cured under lime-saturated water at 20±1 °C. Six φ10×10 mm cement paste specimens were cut from a φ50×100 mm specimen and prepared. Before installation, specimens were dried at 75 °C in thermostatic chamber for 1 week

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### Table 12 Phase composition of used aggregates determined by XRD/Rietveld analysis.

| Minerals (mass%) | Chlorite | Illite | Sericite | Biotite | Pyrite | Microcline Orthoclase | Anorthoclase | Anorthite | Albite | Dolomite | Calcite | Quartz | Amorphous SUM |
|-----------------|----------|--------|----------|---------|--------|----------------------|--------------|------------|--------|----------|---------|--------|----------------|
| GD               | 3.42±0.4 | 4.4±0.63 | 6.67±1.38 | 2.79±0.9 | 4.13±0.4 | 29.06±0.94 | 7.21±1.18 | 23.59±0.44 | 47.13±1.08 | 100     |
| GC               | 3.6±0.8  | 6.67±1.38 | 2.83±0.35 | 3.71±1.44 | 3.13±0.63 | 2.93±0.43 | 29.06±0.94 | 7.21±1.18 | 23.59±0.44 | 47.13±1.08 | 100     |
| GB               | 3.42±0.4 | 4.4±0.63 | 6.67±1.38 | 2.79±0.9 | 4.13±0.4 | 29.06±0.94 | 7.21±1.18 | 23.59±0.44 | 47.13±1.08 | 100     |
| GE               | 11.43±0.47 | 12.79±1.1 | 6.67±1.38 | 2.79±0.9 | 4.13±0.4 | 29.06±0.94 | 7.21±1.18 | 23.59±0.44 | 47.13±1.08 | 100     |
| GF               | 3.91±0.98 | 4.32±0.64 | 6.67±1.19 | 2.79±0.9 | 4.13±0.4 | 29.06±0.94 | 7.21±1.18 | 23.59±0.44 | 47.13±1.08 | 100     |

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**Fig. 13 Particle size distribution of used coarse aggregates.**
Table 13 Cross sections of nucleus for neutron in monitoring wire.

| Isotope | Reaction | Reaction cross section for thermal neutron (E<0.625 eV) [barn] | Reaction cross section for fast neutron (E>1 MeV) [barn] |
|---------|----------|---------------------------------------------------------------|----------------------------------------------------------|
| 54Fe    | (n,γ)    | 1.48 - 1.41                                                   |                                                          |
| 54Fe    | (n,p)    | 0.122 – 0.103                                                 |                                                          |
| 54Mn    | (n,γ)    | 7.54 – 7.20                                                   |                                                          |
| 59Co    | (n,γ)    | 28.2 – 31.5                                                   |                                                          |
| 60Co    | (n,γ)    | 1.39 - 1.42                                                   |                                                          |
| 58Ni    | (n,p) 70.82d |                                                       |                                                          |
| 58Ni    | (n,p) total | 0.099 – 0.115                                                |                                                          |
| 58Co    | (n,γ)    | 149 – 163                                                     | 1620 – 1833                                               |
| 58mCo   | (n,γ)    | 80500 – 83000                                                | 108100 - 111600                                           |
| 58mCo   | (n,p)    | 27500 – 28600                                                |                                                          |

Table 14 Properties of monitoring wires for neutron irradiation experiments.

| Type of monitoring wire | Fe | Co/Al | Ni |
|------------------------|----|-------|----|
| Specification          |    |       |    |
| EC-NRM 524             |    |       |    |
| 0.1 mm foil            |    |       |    |
| 0.5 mm wire            |    |       |    |
| IRMM-572 Mn            | EC-NRM 521 |     |
| 0.1 mm foil            | Al 1.0 mm wire | 0.5 mm wire |
| Co 0.5 mm wire         | IRMM-528 | 0.5 mm wire |
| IRMM-528 Al 1.0 mm wire | 0.5 mm |    |
| EC-NRM-502             |    |       |    |
| 0.1 mm foil            |    |       |    |
| 0.5 mm wire            |    |       |    |
| Reaction for measurement | 54Fe(n,p) | 54Mn | 59Co(n,γ) | 60Co | 58Ni(n,p) | 58mCo |
| Sensitivity of neutron energy | 2 – 20 MeV | < 10 eV | 2 – 20 MeV |
| Target isotope         | 54Mn | 60Co | 58Co |

Figure 14 shows the water vapor collection system after improvements. The upper portion of the condenser was an aluminum block, which raised its cooling efficiency; the intake and exhaust pipes were connected to this part. A glass tube connected to a relief valve was attached to the bottom of the block; this structure allowed the amount of condensed moisture to be measured. Most of the moisture then condensed in the condenser, but the relative humidity downstream of the condenser was still about 30–40%. Therefore, a water vapor adsorption container was installed to capture the moisture that was unable to condense on the condenser, and a hygrometer was installed to measure the relative humidity and temperature of the gas went through the vapor adsorption container. The amount of released water was calculated based on the trapped mass in the condenser and vapor absorber and the vapor mass evaluated by measured humidity and flow rate.

In the neutron irradiation tests with the JEEP-II reactor, the fluence received by specimens was quantified by evaluating the radioactivation of monitoring wires (Table 13). Using this method, neutron fluences were back-calculated from how activated the monitoring wires were by the neutron irradiation, according to several specific neutron-related reactions. Preparing several monitoring wires consisting of different elements allowed the total fluence from neutrons of various energies to be determined, based on those elements’ respective sensitivities to radioactivation by neutrons of various energies.
The kinds of monitoring wires used in the study are summarized in Table 14. Three kinds of monitoring wires were used in this study, made respectively of Fe, Co/Al or Ni. The activation processes for each of these elements are shown in Fig. 15, as are the decay processes for the generated daughter nuclides (denoted in bold in the figure). Monitoring wires were attached, as shown in Fig. 16, parallel to the length of the specimens placed in the irradiation rig.

Since activation creates daughter nuclides that emit gamma radiation as they decay, the daughter nuclides can be quantified by measuring these gamma-rays. Quantifying the daughter nuclides allowed cumulative doses to be calculated by using the known pre-activation quantities of these elements and their activation cross-sections. The cumulative fluence can be determined separately for neutrons of different energies because each element’s activation cross-section differed according to neutron energy.

Equation (1) represents the activated radioactivity of daughter nuclides immediately after irradiation.

\[
A = f \sigma N \left(1 - \left(\frac{1}{2}\right)^{t/T}\right)
\]

Here, \(f\) is neutron fluence, \(\sigma\) is the activation cross-section, \(N\) is the number of atoms of the element pre-activation, \(t\) is exposure time, and \(T\) is the half-life of the daughter nuclide.

However, neutron fluence, as calculated above, corresponds to the dose received by the monitoring wire. This value must be converted in order to determine the actual dose received by the specimens. For conversion, the ratio of the fluence rate at the monitoring wire to the fluence rate at the specimen, obtained using HELIOS code (Wemple et al. 2008), was used

\[
\phi_s = \left(\frac{\phi_{sw}}{\phi_w}\right) \phi_w
\]

Equation (2) converts the neutron fluence received by the monitoring wire \(\phi W\) into fluence received by the specimen \(\phi S\). \(\phi S/\phi W\) denotes the fluence rate ratio between the monitoring wire and the specimen, obtained using HELIOS code.

### 2.2.7 IT

Cement paste specimens were encapsulated in a pressure vessel and irradiated with neutrons, and the water vapor and hydrogen gas generated were measured. To determine the decomposition behavior of water, IT were run with three conditions (levels) of cement paste moisture content while keeping neutron flux and temperature constant. It was originally planned to include fast neutron flux as a parameter to determine dose-rate effects. However, it was found that neutron flux cannot be varied by using shielding material because such a procedure would affect conditions in other holes. Table 15 shows the experimental parameters for the IT. As shown, specimens with different moisture contents were irradiated for approximately two months, during which their gas and water vapor production were measured.

**Table 15 Experimental parameters (IT).**

| Notation | Capsule | Water content       | Neutron flux   | Temperature | Irradiation period |
|----------|---------|---------------------|----------------|-------------|--------------------|
| IT-A1    | IFA-758 | Dried at 75 °C      | ~3.6E+12 n/cm²/s | Constant    | ~2 months          |
| IT-A2    | IFA-759 | Dried at 120 °C     |                |             |                    |
| IT-A3    | IFA-760 | Sealed condition    |                |             |                    |
| IT-A4    | IFA-761 | Sealed condition    |                |             |                    |

**Fig. 15** Activation processes for elements used in monitoring wires, and decay processes for daughter nuclides post-activation.

**Fig. 16** Longitudinal (top) and radial (bottom) placement of each monitoring wire (red) in the irradiation rig.
Irradiation. As shown here, the gas generated by four specimens was measured. While the irradiation container can hold five φ40×60 mm specimens, neutron flux is lower at the container’s ends than at its center. Because of this, the three central specimens were designated as true specimens, the uppermost specimen for temperature measurements, and the lowermost specimen as a dummy specimen (made of Al).

Insufficient water vapor was collected for specimen IT-A3. Therefore, another IT was performed with IT-A4, which was another sealed specimen prepared to have the same moisture content. Only mass change and dimension changes were measured in a corresponding post-irradiation experiment (PIE). For specimen dimension measurements, diameter was measured as the mean of five measurements taken at the vertical midpoint of the specimen, and height was measured as the mean of three measurements taken at different locations shown in Fig. 18. Measurements had a precision of 0.001 mm (i.e. 1 μm).

2.2.8 PPT
In the PPT, specimens were irradiated using the setup shown in Fig. 19. Specimens consisted of two kinds of concrete (each with a different kind of coarse aggregate), cement paste, and six kinds of aggregates. One concrete specimen was placed at the top of the capsule for measuring temperature. The various components of concrete were irradiated as small specimens (φ10×10 mm), held inside an Al holder at the bottom of the capsule. Specimens were irradiated at four levels of neutron fluence, as shown in Table 16. At the beginning of the experiment, the maximum fluence was set at 6.0×10^{19} n/cm^2: the expected maximum fluence in a representative Japanese commercial nuclear reactor (Mihama Unit 2) over 60 years of operation. However, an advisory council involved in the project proposed a maximum fluence of even higher than this value: the maximum fluence was accordingly increased to 1.0×10^{20} n/cm^2.

Based on the original maximum fluence, the clearance between each specimen and the internal surface of the capsule was set at 1% of sample diameter.

After irradiation and before the PIE, all concrete and cement-paste specimens were heated and dried at 76±1°C in a chamber under nitrogen gas (99.6% purity) flow at 100 ml/min. The applied temperature history is shown in Fig. 20. The degree to which HCP dries in

| Notation | Capsule | Water content | Target fast neutron fluence | Neutron flux | Expected irradiation period* |
|----------|---------|---------------|----------------------------|--------------|-----------------------------|
| PPT-B    | IFA-753 | Sealed        | 0.75 x 10^{19} n/cm^2      | ~3.6E+12 n/cm^2/s | 1 month                    |
| PPT-C    | IFA-752 |               | 1.5 x 10^{19} n/cm^2       | ~3.6E+12 n/cm^2/s | 2 months                   |
| PPT-D    | IFA-751 |               | 3.0 x 10^{19} n/cm^2       | ~3.6E+12 n/cm^2/s | 7 months                   |
| PPT-E    | IFA-750 |               | 6.0 x 10^{19} n/cm^2       | ~3.6E+12 n/cm^2/s | 17 months                  |

*including outage periods.
concrete varies according to irradiation time, and alters its strength as well. (Details are described in Chapter 4.) Accordingly, strength changes due to aggregate expansion alone cannot be quantitatively evaluated between specimens if the degree of drying varies among them.

In the PIE, the mass change, length change, compressive strength (via compression tests), and Young’s modulus (via a compressometer) of concrete specimens were measured. In a preliminary experiment, standard specimens were measured at three different institutes, which all confirmed they had the same compressive strengths (±2.5%). Compressive strength was measured for a loading speed of 0.6 MPa/s using a Matest E161N device. Length and mass change were measured using the same technique as in the IT.

Before the compressive strength test, Young’s modulus was measured using an INSTRON EZ50 device, according to JIS A1108:2006. A customized compressometer (base length = 40 mm) using three linear variable differential transformers (LVDTs) was developed for this test. Loading speed was set at 0.6 MPa/s.

In addition to mass change and length change, the Vickers hardness of cement paste specimens was measured. To measure Vickers hardness, specimens were subjected to a 2.942 N force (300 gf) using a Future-TECH FM-100 device for 15 s, then the indentation was observed and measured via optical microscope. Aggregate specimens were measured in terms of mass change, length change, and using X-ray powder diffraction.

### 2.2.9 HT and CT

In the HT, specimens were heated and dried without radiation exposure to create reference data for isolating the effects of radiation. The parameters of HT were summarized in Table 17. During the PPT, the internal temperature of the specimen located at the top of the capsule (i.e., the temperature monitoring specimen) was measured. Internal temperature was considered the maximum temperature inside the specimen, and average temperature was calculated by considering the gamma heating and heat diffusion as shown in Fig. 10. These two temperature histories were applied to HT specimens.

As in the PPT, the initial moisture conditions of all specimens was sealed curing condition. The capsule was immersed in a water bath, the temperature of which was controlled according to the measured and calculated temperature data from the corresponding neutron irradiation test (including outage periods). As Fig. 21 shows, water temperature followed the original temperature history with high precision.

In addition, in order to confirm that the compressive strength of sealed specimens at 20 °C had not been changed dramatically during the irradiation tests, the compressive strength and Young’s modulus of the concrete were measured three times during the irradiation period. These experiments are referred to as “cold tests (CT)”, and their data used for reference.

### 2.2.10 Quantitative evaluation of radiation environment using MCNP calculations

In order to quantitatively determine the effects of the neutron and gamma radiation to which specimens were exposed, the exposure conditions in the 3D space inside the JEEP II reactor were simulated for each specimen and energy level using MCNP5 code for calculating radiation transport with a Monte Carlo method (Brown et al. 2002). The geometrical shape and composition of all components of the neutron irradiation tests—i.e. the JEEP-II reactor, irradiation rig, capsule, and specimens—were configured according to equipment technical drawings, measurement conditions, and observed values. Details are presented in Figs. 22 and 23, and Table 18.

Table 19 shows the MCNP5 analysis conditions as configured for this analysis. Output was calculated in terms of neutron and gamma-ray fluence and deposition energy in order to estimate specimen radiation effects and heating values.

| Notation | Capsule | Water content | Corresponding PPT test | Temperature | Heating period |
|----------|---------|---------------|-------------------------|-------------|---------------|
| H1-3     | IFA-757.1 | Sealed content | PPT-B                  | Maximum temperature of concrete sample | 1 month |
| H1-6     | IFA-757.2 |              | PPT-C                  |             | 2 months     |
| H1-12    | IFA-757.3 |              | PPT-D                  |             | 7 months     |
| H2-24    | IFA-756   |              | PPT-E                  |             | 17 months    |
| H3-3     | IFA-755.1 |              | PPT-B                  |             | 1 month     |
| H3-6     | IFA-755.2 |              | PPT-C                  | Average temperature of concrete sample | 2 months |
| H3-12    | IFA-755.3 |              | PPT-D                  |             | 7 months     |
| H4-24    | IFA-754   |              | PPT-E                  |             | 17 months     |
Because physical quantities are calculated in MCNP on a per-neutron basis, normalization is necessary in order to simulate a real-world test. Although it is possible to theoretically perform the normalization based on the outputs of the furnace etc., the measured values of neutron flux and gamma-ray flux were used for the normalization so that model conditions conformed with actual conditions.

As shown in Fig. 8, each specimen in the capsule receives a different neutron fluence, which means that heat generation due to radiation also varies in the vertical direction. Furthermore, since cooling water flows outside the capsule, the temperature of a specimen differs between its center and its surface. Heat generation in each specimen was determined based on the deposition energy calculated by MCNP5, and heat transfer analysis was carried out to determine the center and surface temperatures of each specimen by simulating the test environment using the finite element analysis code NX Nastran (Siemens PLM Software, USA).

The parameters and analytical conditions necessary for conducting the heat transfer analysis were set according to measured values and literature values (Table 20).

The analysis was run as a steady heat transfer analysis, based on the assumptions that levels of heat-

---

Table 18 MCNP 5 Model Composition of Neutron Irradiation Test Object.

| Structure          | Concrete specimens | Cement Paste specimens |
|--------------------|--------------------|------------------------|
| Fuel enrichment   | Aggregate F        | Aggregate F            |
| 3.5%UO₂            | 5.144E-03          | 3.298E-02              |

Table 19 Analysis Conditions.

| Analysis code      | MCNP5              |
|--------------------|--------------------|
| Cross-section library | ENDF/B, continuous energy ACE format |
| Number of history | PPT test: 118000000 / IT test : 38000000 |
| Number of batch    | 6000               |
| Number of skip     | 100                |
| Analysis domain    | Cylindrical configuration (radius 110cm, height 180cm) |
| Boundary condition | Vacuum interface   |

---

Fig. 22 MCNP5 model of the JEEP II reactor (left: top view, center: front view, right: magnified view of fuel assembly).

generating irradiation and cooling water temperature would not change drastically over time. Since the actual temperature measured was almost constant immediately after the irradiation, the assumption of a steady heat transfer analysis seems valid. Specimens were modeled using cylindrical elements, according to their shape. A two-dimensional, axisymmetric model was used because the position of the fuel assembly and flow of the cooling water were parallel to the specimens’ axis, and so heat transfer in and from specimens can be regarded as almost isotropic in the radial direction.

Only the specimens were set as elements in the model. In order to perform a complex analysis, it would be necessary to simulate the aluminum capsule on the outside of the specimens and set a heat transfer coefficient at the boundary between the capsule and the cooling water. Although ideal literature values exist for heat transfer coefficients from aluminum to water outside a cylinder, the actual capsule in this case has fine irregularities due to heat dissipation, and therefore its heat transfer behavior is expected to be different from the ideal state. Since the heat transfer coefficient of the test environment here was not measured, the heat transfer coefficient with respect to cooling water required for the analysis was set in the element boundary as an effective value, assuming that the aluminum on the outside of the speci-

Table 20 Parameters and Conditions for Heat Transfer Analysis.

| Heat Transfer Coefficient | Concrete specimen | PPT test 200 [W/m²/K], IT test 100 [W/m²/K] |
|---------------------------|-------------------|-----------------------------------------------|
| Thermal Conductivity      | Cylindrical object was modeled as two-dimensional axial symmetry |
| Analysis Code             | Analysis type     | Steady heat transfer analysis |
| Analysis model            | Element: CQUADX4 (Square, axisymmetric element), 5mm×5mm |
| Heat generation           | It was set for each specimen based on deposition energy of fluence analysis |

Fig. 23 MCNP5 models of the irradiation rig (left: PPT, right: IT).
mens has the same temperature distribution as the cooling water temperature. More specifically, a preliminary analysis was performed by changing the thermal conductivity from 100 W/m²/K by 50 W/m²/K, to set the value that could reproduce the center temperature of the measured specimens. In addition, the thermal conductivity of the concrete specimens was set in reference to literature values (JSME Data Book 2009), and the thermal conductivity of the cement paste specimens was set in reference to an experimental report (Maruyama and Igarashi 2014). The ambient temperature was set as a linear distribution in the axial direction, based on the temperatures measured at the cooling water inlet and the cooling water outlet. Since the difference of temperatures between the cooling water inlet and the outlet was as low as 5 °C and not more than 10% of the cooling water temperature, it was decided that linear temperature distribution would be an appropriate approximation.

2.3 Experimental results

2.3.1 Irradiation environments

Table 21 shows the total neutron fluences for whole specimens in the PPT and IT, as calculated by converting the neutron fluences received from the monitoring wires. The values in the table indicate the maximum fluence measured across all specimens in the noted condition.

Radiation data calculated based on monitoring wire and monitoring system data are summarized for each irradiation condition in Table 22.

In this analysis, neutron fluence was normalized by assuming the observed value at the center of the reactor core among test specimens was equal to the fast neutron fluence as determined by the monitoring wire in Table 21 and to the neutron fluence per neutron as calculated by MCNP5. Since thermal neutrons are more influenced by scattering than fast neutrons and uncertainties of their origins are significant, it was inappropriate to use thermal neutron data to attempt to normalize the analysis results of monitoring wires and MCNP5.

Table 23 shows the fluence received by each PPT specimens and their calorific values and temperatures due to irradiation. In addition, data obtained for visualizing the dose-rate distribution in the capsule are summarized in Fig. 24.

| Test ID | Thermal neutron fluence [n/cm²] | Fast neutron fluence [n/cm²] |
|---------|--------------------------------|-----------------------------|
| PPT-B   | 3.41×10¹⁹                     | 8.13×10¹⁵                   |
| PPT-C   | 7.47×10¹⁹                     | 1.48×10¹⁵                   |
| PPT-D   | 2.41×10²⁰                     | 4.77×10¹⁹                   |
| PPT-E   | 4.25×10²⁰                     | 9.60×10¹⁹                   |
| IT-A1   | 7.24×10¹⁹                     | 1.62×10¹⁹                   |
| IT-A2   | 8.60×10¹⁹                     | 2.00×10¹⁹                   |
| IT-A3   | 1.11×10²⁰                     | 2.61×10¹⁹                   |
| IT-A4   | 8.35×10¹⁹                     | 1.86×10¹⁹                   |

Fig. 24 Neutron flux distributions for each PPT.
Table 22 Irradiation Results of Neutron Irradiation Test

| Test ID | Container ID | Irradiation hole | Irradiation period (full-power days) | Fast neutron (E > 0.1MeV) | Thermal neutron (E < 0.625eV) |
|---------|--------------|------------------|-------------------------------------|---------------------------|-------------------------------|
|         |              |                  | Target fluence (n/cm²)               | Average fluence (n/cm²)   | Neutron flux (n/cm²/s)       |
|         |              |                  | (n/cm²)                             | (n/cm²)                   | Neutron flux ratio            |
|         |              |                  | Dose rate (kGy)                     | Dose rate ratio           |                               |
|         |              |                  | (kGy/h)                             |                           |                               |
|         |              |                  | Center of specimen (°C)             |                           |                               |
| IT-A1   | IFA-758      | #36              | 50.32                               | 1.61E+19 1.62E+19 3.72E+12 | 1.034 6.00E+19 6.83E+19 1.57E+13 0.978 |
| IT-A2   | IFA-759      | #36              | 60.66                               | 1.75E+19 2.00E+19 3.63E+12 | 1.008 7.90E+19 8.38E+19 1.60E+13 0.995 |
| IT-A3   | IFA-760      | #36              | 80.83                               | 2.34E+19 2.60E+19 3.60E+12 | 1.000 9.60E+19 1.06E+20 1.52E+13 0.948 |
| IT-A4   | IFA-761      | #36              | 56.42                               | 1.83E+19 1.88E+19 3.80E+12 | 0.955 7.60E+19 8.15E+19 1.67E+13 1.041 |
| PPT-B   | IFA-753      | #52              | 25.19                               | 7.09E+18 8.10E+18 3.57E+12 | 0.990 2.80E+19 3.20E+19 1.47E+13 0.916 |
| PPT-C   | IFA-752      | #36              | 45.26                               | 1.27E+19 1.48E+19 3.61E+12 | 1.004 5.90E+19 6.98E+19 1.78E+13 1.111 |
| PPT-D   | IFA-751      | #36              | 155.59                              | 4.09E+19 4.78E+19 3.37E+12 | 0.934 1.92E+20 2.24E+20 1.67E+13 1.039 |
| PPT-E   | IFA-750      | #52              | 299.39                              | 8.17E+19 9.62E+19 3.52E+12 | 0.978 3.70E+20 4.04E+20 1.56E+13 0.972 |
| Average |              |                  |                                     |                           |                               |
|         |              |                  | 3.60E+12                            |                           |                               |

Table 23 Fluence, calorific values, and temperatures of each specimen obtained from the results of MCNP5 and monitoring wire.

| Test ID | Container ID | Irradiation hole | Radiation dose (kGy) | Dose rate (kGy/h) | Dose rate ratio | Temperature Center of specimen (°C) | JEEP II operating rate (Excluding planned suspension period) | Moisture condition |
|---------|--------------|------------------|----------------------|-------------------|----------------|-------------------------------------|-------------------------------------------------------------|-------------------|
| IT-A1   | IFA-758      | #36              | 4.80.E+05            | 397.3             | 1.104          | 72.5                                | 0.769 75°C dried                                            |                   |
| IT-A2   | IFA-759      | #36              | 5.59.E+05            | 384.2             | 1.067          | 71.0                                | 0.809 120°C dried                                           |                   |
| IT-A3   | IFA-760      | #36              | 7.23.E+05            | 372.5             | 1.035          | 75.0                                | 0.776 sealed curing                                        |                   |
| IT-A4   | IFA-761      | #36              | 5.79.E+05            | 427.3             | 1.187          | 73.0                                | 0.848 sealed curing                                        |                   |
| PPT-B   | IFA-753      | #52              | 1.99.E+05            | 328.5             | 0.913          | 71.0                                | 0.855 sealed curing                                        |                   |
| PPT-C   | IFA-752      | #36              | 3.20.E+05            | 294.9             | 0.819          | 69.5                                | 0.765 sealed curing                                        |                   |
| PPT-D   | IFA-751      | #36              | 1.15.E+06            | 308.2             | 0.856          | 70.0                                | 0.789 sealed curing                                        |                   |
| PPT-E   | IFA-750      | #52              | 2.63.E+06            | 366.6             | 1.018          | 74.0                                | 0.757 sealed curing                                        |                   |
| Average |              |                  | 359.9                |                   |                | 74.0                                | 0.796 sealed curing                                        |                   |

Table PPT-B

| Axis level (mm) | Specimen ID | Description | Neutron fluence (n/cm²) | Calorific value (W) | Specimen temperature (°C) |
|-----------------|-------------|-------------|-------------------------|---------------------|--------------------------|
| 570             | A54         | Concrete specimen w/ thermocouple | 6.77E+18 | 2.67E+16 | 2.80E+19 | 2.47E+16 | 5.48E+00 | 64.7 | 59.6 |
| 510             | B13         | Concrete specimen | 7.19E+18 | 2.77E+16 | 3.01E+19 | 4.44E+16 | 5.91E+00 | 65.0 | 59.6 |
| 450             | A13         | Concrete specimen | 7.61E+18 | 2.85E+16 | 3.20E+19 | 4.57E+16 | 6.27E+00 | 65.3 | 59.5 |
| 390             | B14         | Concrete specimen | 7.91E+18 | 2.90E+16 | 3.31E+19 | 4.65E+16 | 6.51E+00 | 65.4 | 59.4 |
| 330             | A14         | Concrete specimen | 8.10E+18 | 2.94E+16 | 3.38E+19 | 4.67E+16 | 6.81E+00 | 65.5 | 59.3 |
| 270             | B15         | Concrete specimen | 8.13E+18 | 2.95E+16 | 3.39E+19 | 4.71E+16 | 6.74E+00 | 65.1 | 58.9 |
| 210             | A15         | Concrete specimen | 8.05E+18 | 2.93E+16 | 3.37E+19 | 4.68E+16 | 6.61E+00 | 64.6 | 58.6 |
| 150             | B16         | Concrete specimen | 7.80E+18 | 2.88E+16 | 3.28E+19 | 4.63E+16 | 6.45E+00 | 64.0 | 58.1 |
| 90              | A16         | Concrete specimen | 7.45E+18 | 2.82E+16 | 3.15E+19 | 4.54E+16 | 6.18E+00 | 63.2 | 57.6 |
| 30              |             | Small specimen (aggregate, cement paste) | 7.01E+18 | - | 2.96E+19 | - | 5.03E+00 | 53.3 | 53.3 |
| Average value (8, excluding small specimen and specimen w/ thermocouple) | 7.78E+18 | - | 3.26E+19 | - | 6.43E+00 | 64.7 | 58.9 |
| Axis level (mm) | Specimen ID | Description | Neutron fluence (n/cm²) | Calorific value (W) | Specimen temperature (°C) |
|----------------|-------------|-------------|-------------------------|---------------------|---------------------------|
|                |             |             | Fast neutron | Thermal neutron | Center | Surface |
|                |             |             | E > 0.1 MeV | E < 0.625 eV | Median value | 1σ | Median value | 1σ | Median value | 1σ |
| 570            | A53         | Concrete specimen w/ thermocouple | 1.23E+19 | 5.23E+16 | 5.51E+19 | 8.66E+16 | 9.36E+00 | 70.9 | 62.2 |
| 510            | B05         | Concrete specimen | 1.31E+19 | 5.42E+16 | 5.96E+19 | 9.04E+16 | 1.04E+01 | 72.0 | 62.5 |
| 450            | A05         | Concrete specimen | 1.38E+19 | 5.56E+16 | 6.31E+19 | 9.24E+16 | 1.10E+01 | 72.6 | 62.6 |
| 390            | B06         | Concrete specimen | 1.44E+19 | 5.67E+16 | 6.54E+19 | 9.48E+16 | 1.11E+01 | 72.7 | 62.5 |
| 330            | A06         | Concrete specimen | 1.47E+19 | 5.72E+16 | 6.67E+19 | 9.54E+16 | 1.15E+01 | 72.9 | 62.4 |
| 270            | B07         | Concrete specimen | 1.48E+19 | 5.76E+16 | 6.72E+19 | 9.58E+16 | 1.15E+01 | 72.6 | 62.1 |
| 210            | A07         | Concrete specimen | 1.46E+19 | 5.70E+16 | 6.62E+19 | 9.48E+16 | 1.14E+01 | 72.1 | 61.7 |
| 150            | B08         | Concrete specimen | 1.42E+19 | 5.64E+16 | 6.47E+19 | 9.42E+16 | 1.10E+01 | 71.2 | 61.2 |
| 90             | A08         | Concrete specimen | 1.36E+19 | 5.51E+16 | 6.23E+19 | 9.24E+16 | 1.04E+01 | 70.1 | 60.5 |
| 30             | Small specimen (aggregate, cement paste) | 1.28E+19 | - | 5.85E+19 | - | 1.00E+01 | 53.3 | 53.3 |
| Average value (8, excluding small specimen and specimen w/ thermocouple) | 1.41E+19 | - | 1.41E+19 | - | 1.10E+01 | 72.0 | 61.9 |

| Axis level (mm) | Specimen ID | Description | Neutron fluence (n/cm²) | Calorific value (W) | Specimen temperature (°C) |
|----------------|-------------|-------------|-------------------------|---------------------|---------------------------|
|                |             |             | Fast neutron | Thermal neutron | Center | Surface |
|                |             |             | E > 0.1 MeV | E < 0.625 eV | Median value | 1σ | Median value | 1σ | Median value | 1σ |
| 570            | B54         | Concrete specimen w/ thermocouple | 3.97E+19 | 1.69E+18 | 1.78E+20 | 2.81E+17 | 8.71E+00 | 69.9 | 61.8 |
| 510            | B09         | Concrete specimen | 4.25E+19 | 1.75E+18 | 1.92E+20 | 2.92E+17 | 9.64E+00 | 70.8 | 62.0 |
| 450            | A09         | Concrete specimen | 4.51E+19 | 1.80E+18 | 2.03E+20 | 2.99E+17 | 1.03E+01 | 71.5 | 62.2 |
| 390            | B10         | Concrete specimen | 4.64E+19 | 1.83E+18 | 2.12E+20 | 3.06E+17 | 1.06E+01 | 71.8 | 62.1 |
| 330            | A10         | Concrete specimen | 4.77E+19 | 1.86E+18 | 2.16E+20 | 3.07E+17 | 1.09E+01 | 71.9 | 62.0 |
| 270            | B11         | Concrete specimen | 4.77E+19 | 1.85E+18 | 2.18E+20 | 3.11E+17 | 1.09E+01 | 71.6 | 61.7 |
| 210            | A11         | Concrete specimen | 4.73E+19 | 1.85E+18 | 2.14E+20 | 3.06E+17 | 1.06E+01 | 70.9 | 61.2 |
| 150            | B12         | Concrete specimen | 4.60E+19 | 1.82E+18 | 2.10E+20 | 3.05E+17 | 1.03E+01 | 70.1 | 60.7 |
| 90             | A12         | Concrete specimen | 4.38E+19 | 1.77E+18 | 2.01E+20 | 2.97E+17 | 9.79E+00 | 69.0 | 60.1 |
| 30             | Small specimen (aggregate, cement paste) | 4.12E+19 | - | 1.88E+20 | - | 9.12E+00 | 53.3 | 53.3 |
| Average value (8, excluding small specimen and specimen w/ thermocouple) | 4.58E+19 | - | 2.08E+20 | - | 1.04E+01 | 70.9 | 61.5 |

| Axis level (mm) | Specimen ID | Description | Neutron fluence (n/cm²) | Calorific value (W) | Specimen temperature (°C) |
|----------------|-------------|-------------|-------------------------|---------------------|---------------------------|
|                |             |             | Fast neutron | Thermal neutron | Center | Surface |
|                |             |             | E > 0.1 MeV | E < 0.625 eV | Median value | 1σ | Median value | 1σ | Median value | 1σ |
| 570            | B53         | Concrete specimen w/ thermocouple | 7.92E+19 | 3.16E+17 | 3.30E+20 | 5.05E+17 | 9.16E+00 | 70.6 | 62.1 |
| 510            | B01         | Concrete specimen | 8.55E+19 | 3.28E+17 | 3.55E+20 | 5.24E+17 | 9.97E+00 | 71.4 | 62.3 |
| 450            | A01         | Concrete specimen | 9.02E+19 | 3.38E+17 | 3.77E+20 | 5.39E+17 | 1.06E+01 | 72.0 | 62.4 |
| 390            | B02         | Concrete specimen | 9.33E+19 | 3.43E+17 | 3.91E+20 | 5.50E+17 | 1.10E+01 | 72.4 | 62.4 |
| 330            | A02         | Concrete specimen | 9.56E+19 | 3.48E+17 | 4.00E+20 | 5.54E+17 | 1.13E+01 | 72.6 | 62.3 |
| 270            | B03         | Concrete specimen | 9.60E+19 | 3.48E+17 | 4.02E+20 | 5.58E+17 | 1.13E+01 | 72.3 | 62.0 |
| 210            | A03         | Concrete specimen | 9.49E+19 | 3.46E+17 | 3.99E+20 | 5.53E+17 | 1.11E+01 | 71.7 | 61.5 |
| 150            | B04         | Concrete specimen | 9.22E+19 | 3.41E+17 | 3.88E+20 | 5.49E+17 | 1.07E+01 | 70.7 | 61.0 |
| 90             | A04         | Concrete specimen | 8.80E+19 | 3.32E+17 | 3.72E+20 | 5.37E+17 | 1.02E+01 | 69.8 | 60.4 |
| 30             | Small specimen (aggregate, cement paste) | 8.25E+19 | - | 3.50E+20 | - | 9.98E+00 | 53.3 | 53.3 |
| Average value (8, excluding small specimen and specimen w/ thermocouple) | 9.20E+19 | - | 3.86E+20 | - | 1.08E+01 | 71.6 | 61.8 |
Table 24 Comparison of neutron flux and gamma-ray dose between actual member conditions and irradiation test conditions.

|                   | Actual equipment condition *1 | Irradiation test condition |
|-------------------|-------------------------------|-----------------------------|
| Fast neutron flux | n/cm²/s                       | JEEP II                     |
|                   | 4.4×10¹⁰                     | (times 82)                  |
| Gamma-ray dose rate | kGy/h                        | 3.0×10⁻⁸⁻4.3×10⁻⁸          |
|                   |                               | (times 590⁻840)             |

*1 Fukuya, K., H. Nakata, K. Fuji, I. kimura, M. Ohmura, H. Kitagawa, T. Itoh and K. Shin (2002).
*2 Radiation Field Analyses in Reactor Vessels of PWRs. INSS Journal 9 153-161.

Table 24 shows the irradiation conditions of actual members in a commercial plant and the irradiation environments of neutrons and gamma-rays in this study. As shown here, the accelerated test in the JEEP II reactor had a fast neutron flux that was (at maximum) 82 times greater than conditions in the commercial plant, and a gamma-ray dose-rate of (at maximum) 840 times greater. Gamma-ray dose-rate was greater than that in the gamma-ray irradiation test environment shown in Chapter 3. As will be described later in the discussion section, aggregates are less likely to be affected by gamma-rays, because gamma-ray dose is two orders of magnitude smaller than the dose to make quartz metamictized by gamma-ray. In addition, the results of PIE of cement paste confirmed that the effects of gamma-ray irradiation on hcp during the neutron irradiation test were negligible.

2.3.2 IT

In this section the results of the IT are primarily presented, and the findings examined as they relate to the interactions of neutrons and gamma-rays with water in cement paste. Nuclear reactor output across conditions (IT-A1–IT-A4) ranged from 1.9–2.2 MW. In addition, reactors were turned on and off relatively frequently to simulate reactor output, and neutron output was 82 times greater than conditions in the commercial plant, and a gamma-ray dose-rate of (at maximum) 840 times greater. Gamma-ray dose-rate was greater than that in the gamma-ray irradiation test environment shown in Chapter 3. As will be described later in the discussion section, aggregates are less likely to be affected by gamma-rays, because gamma-ray dose is two orders of magnitude smaller than the dose to make quartz metamictized by gamma-ray. In addition, the results of PIE of cement paste confirmed that the effects of gamma-ray irradiation on hcp during the neutron irradiation test were negligible.

Fast neutron flux during the neutron irradiation tests was 3.73–3.86×10¹⁰ n/cm²/s, and gamma-ray flux was 372.5–427.3 kGy/h. Gamma heating values were 0.11–0.12 W/g (Table 22, unit is converted from dose rate value.), and temperature increase was seen over time due to a reduction in specific heat as the specimens dried. The gas measurement system in these tests was operated according to the following settings: when internal capsule pressure rose to 1.25 bar, the release valve opened and released the pressure, and when it subsequently fell to approx. 1.0 bar, the valve closed again. A1 and A2 tested cement paste specimens dried at 75 °C and 120 °C and released very little water vapor, reaching relative humidities of 20–30% and ~10%, respectively. There was little moisture content in A1 and A2, minimally affecting water decomposition and making pressure rise very slowly. Gas sampling and composition analysis were performed before gas pressure reaches 1.25 bar in these cases. Measurements for A3 and A4 were made according to the expected settings. The intervals between release valve openings grew longer over time: this was because gas production became less efficient as the moisture content decreased.

A3 used a cement paste specimen in a sealed condition that contained a lot of free water and it released very little water vapor before the IT experiment. As the condenser was not installed prior to the improvements to the water vapor collection system, it was impossible to accurately determine the water vapor amount because the relative humidity reached 100%, condensing much of it. Measurements were again conducted for A4, which, similar to A3, used a cement paste specimen of a sealed curing condition that contained much free water. As a result of the improved vapor collection system with an equipped condenser, the relative humidity of the gas dropped to below 5%, allowing measurement of moisture content that passed through the condenser based on the humidity and flow rate. The results of IT-A4 are presented in Fig. 25, taking it as a representative example for the IT.

Figure 26 compares the amounts of gas produced in each IT. Sealed specimens emitted a lot of gas during neutron irradiation, but the specimens that were dried at 75 °C and 120 °C generated almost no gas (IT-A1 and IT-A2). This is because water vapor production and water decomposition due to radiation almost completely ceased as water became less likely to evaporate from within the specimen. Figure 27 shows the gas composition ratio data for the gas collected periodically during irradiation. Effects of He on gas analysis were observed for the 75°C and 120°C specimens (Fig. 27 (a) IT-A1 and (b) IT-A2), as the He that was used for preliminary leak checks had remained inside the capsule. In short, it was observed that the volume of gas produced did not exceed the air volume inside the capsule. As shown here, the H₂O₂ ratio was maintained at 2:1 as water under-
went radioactive decomposition (radiolysis) when there was sufficient evaporable water present (Fig. 27 (c) IT-A3 and (d) IT-A4). However, it was also observed that H₂ levels rose and O₂ levels dropped as drying proceeded. In case of Fig. 27 (d), red line showing O₂ starts to decrease at 40 days and thin blue line starts to increase. This is likely because O₂ was consumed by a precipitation of calcium peroxide octahydrate.

Clarifying the interactions between radiation and the cement paste provides a fundamental basis for making soundness assessments.

H₂ generation G-values (molecules of hydrogen formed per 100 eV of energy absorbed) for gamma-rays and neutrons were calculated (Table 25). The obtained value is irrespective to the phases of protons, such as...
evaporable (free) water, physically or chemically adsorbed water, or chemically bound water. The sum of the absorbed neutron and gamma-ray doses (kGy) were obtained by MCNP5 calculation. H2 generation rates due to gamma radiation during the neutron irradiation experiment were estimated based on the H2 generation G-value data for gamma-rays (see Fig. 28.), which will be shown in detail in the next chapter. The generation rate of H2 by neutrons was calculated by subtracting the generation rate of H2 by gamma rays from the experimental generation rate of H2.

The results are shown in Fig. 29. The H2 generation G-value was negative when water content was nearly 0, leading to a high H2 generation G-value for gamma radiation being calculated based on the gamma irradiation tests. This is possibly explained by the fact that the gamma-ray flux in the neutron irradiation tests was extremely high: approx. 10–100× higher than the flux (i.e. dose-rate) in the gamma irradiation tests, and the H2 generation G-value for gamma-rays was overestimated.

### Table 25 Obtained data for calculation process of H2 generation G value due to neutrons and gamma-rays.

| Case   | IT-A1 | IT-A2 | IT-A3 | IT-A4 |
|--------|-------|-------|-------|-------|
| Sample shape | | | | |
| Cement paste φ4×6 cm | | | | |
| Drying condition | Dried at 75 °C | Dried at 120 °C | Sealed condition | Sealed condition |
| Neutron dose rate (kGy/h) | 69.4 | 69.4 | 64.8 | 64.8 | 107 | 107 | 109 | 109 |
| Gamma-ray dose rate (kGy/h) | 88.4 | 88.4 | 91.2 | 91.2 | 94.2 | 94.2 | 96.1 | 96.1 |
| Sum of neutron and gamma-ray dose rate (kGy/h) | 157.8 | 157.8 | 156.0 | 156.0 | 201.2 | 201.2 | 205.1 | 205.1 |
| Mass of sample (g) | | | | |
| (1) | 116.9 | 117.1 | 114.4 | 114.2 | 140.6 | 118.5 | 141.3 | 119.5 |
| (2) | 116.4 | 116.9 | 113.9 | 114.7 | 140.7 | 118.0 | 142.1 | 120.6 |
| (3) | 116.6 | 117.0 | 114.0 | 114.8 | 141.1 | 118.7 | 141.0 | 119.0 |
| Water mass (g) | 15.4 | 16.8 | 5.1 | 7.0 | 111.9 | 22.4 | 114.7 | 27.7 |
| Water content (g/g-dried hcp) | 0.03 | 0.04 | 0.01 | 0.02 | 0.25 | 0.05 | 0.25 | 0.06 |
| Total water mass including chemically bound water (g) | 95.8 | 97.2 | 85.5 | 87.4 | 192.3 | 102.8 | 195.1 | 108.1 |
| Rate of H2 gas generation (μmol/h) | 150 | 30 | 120 | 10 | 4490 | 240 | 4920 | 450 |
| H2 gas generation G value for neutron and gamma-ray | 0.10 | 0.02 | 0.09 | 0.01 | 1.12 | 0.11 | 1.19 | 0.20 |

Fig. 27 H2:O2 composition ratios of gas generated from IT specimens.
in this high dose-rate. Therefore, in Fig. 29, the theoretical upper limit H\textsubscript{2} generation G-value for neutrons is also shown (specifically, the maximum theoretical G-value), assuming G = 0 for gamma-rays. The difference of G value between each plot (circle) and bar corresponds to the G-value calculated by gamma-ray. The H\textsubscript{2} generation G-values for neutrons was 1.7–2.3 when specimens contained a lot of water. This value is large: 2–5× larger than the value for hydrogen generation from bulk water by gamma radiation alone (G=0.45) or neutron (G=1.0) (Elliot et al. 1990, Kasten 1991, Joseph et al. 2008, Butarbutar et al. 2014). This value can be 0.04 when there was almost no free water. This indicates that chemically bound water degrades no more than 1–2% in response to the neutron fluence received over 60 years.

2.3.3 CT

Compressive strength data obtained in CT to serve as reference concrete trends are shown in Fig. 30. Con-A showed an almost constant value after irradiation experiment, while Con-B showed a gradual increase. It is possible that water in GB—the water adsorption ratio of which is higher than that of GA—diffused into the cement paste matrix to create additional hydration during this period. However, these results are satisfactory as reference values for irradiation experiments. Mean values of compressive strength and Young’s modulus for concretes during the irradiation period are used as reference.

2.3.4 PPT: Concrete

Figure 31 contains measurement data of PPT-E taken to determine the irradiation conditions during measurements in the PPT. Nuclear reactor output during the PPT was approximately 2.0 MW (Fig. 31 (a)). In addition, the reactors were turned on and off relatively frequently to replace materials (Fig. 31 (a)). The cooling water temperature was controlled at 52°C outside the reactor and rose to 57 °C while cooling the reactor after being piped in. After being sent out of the reactor, it was...
cooled back to 52°C by cooling equipment (Fig. 31 (d)). Gamma heating values of 0.09–0.10 W/g were measured based on data from the monitoring wires (Fig. 31 (c)). Concrete specimens located at the top of the capsule had core temperatures of 71–75 °C (Fig. 31 (b)).

Internal capsule pressure was controlled during irradiation by a release valve, which opened to relieve pressure when the pressure level reached 1.25 bar, and closed again when the pressure fell to 1.0 bar. Gas collection and analysis were performed periodically (Fig. 31 (e)). The absolute humidity showed almost saturated state at the first duration, and then gradually decreased (Fig. 31(f)), and consequently, the calculation of released water was not correct in this experiment.

The fast neutron flux during irradiation was $3.37 - 3.61 \times 10^{12}$ n/cm$^2$/s, while gamma flux was 295–367 kGy/h (Table 22).

Figure 32 compares the gas volumes captured from each capsule during irradiation between PPT conditions. The initial conditions were identical for all specimens,
but gamma flux differed. A trend of high evaporation rates was observed from specimens exposed to high gamma-ray fluxes (Table 22). Only the case of PPT-E alone breaks this trend: above fast neutron fluence of $1.0 \times 10^{19}$ n/cm$^2$, the collected water content dropped lower than those measured in PPT-B and D, despite the high gamma flux and the high specimen temperature of PPT-E. Captured water amounts are also summarized in Fig. 33, but because the water collection system was inconsistent across test conditions, those data cannot be compared directly.

Next, some of the issues encountered are discussed. The first is evident on the surface of specimens. Many pock-marks were confirmed on the lateral surfaces of specimens (see Fig. 36). This was not observed on the top and bottom surfaces of specimens, which were immediately adjacent to the surfaces of other specimens. Powder found in the capsule was collected and weighed, but the mass loss of specimens due to such pock-marks was negligible in comparison to the mass change of the sample due to drying. Based on a SEM-EDS analysis, Fe and Mg were confirmed at the center of pock-marks, but a detailed mechanism for their appearance has not been clarified.

Another issue was encountered with the specimens tested in PPT-E. For PPT-E, the capsule was originally designed with the objective of a fast-neutron fluence of $6.0 \times 10^{19}$ n/cm$^2$. The distance between the inner wall of the capsule and the specimen affects the heat transfer properties of the specimen, and should thus be kept to an absolute minimum. Based on previous irradiation reports (Dubrovskii et al. 1967; Elleuch et al. 1972; Hilsdorf et al. 1978), it was concluded that a gap of 1% specimen diameter would be sufficient, since the concrete was expected to expand due to radiation. However, after a discussion with advisors on this project, the target fluence was raised to $1.0 \times 10^{20}$ n/cm$^2$ to ensure the safety assessment would be performed properly. The result was that the specimen broke the capsule during irradiation, water flooded into the capsule, and the reactor experienced a system shut-down.

Afterwards, the capsule was removed from the reactor, and the specimens were extracted by cutting the rig along its longitudinal (i.e. vertical) axis. PIE were conducted on the extracted specimens. The experienced stress in the specimens was calculated based on design blueprints and rig strength, which yielded a circumferential stress of 24.5 MPa and a longitudinal stress of 35.1 MPa in concrete. Figure 34 shows the fractured capsule, while Fig. 35 shows a specimen extracted from it. Some specimens showed increased mass with respect to the start of irradiation. For the PIE, the same drying procedure shown in Fig. 20 after irradiation was performed, but this accident still created some inconsistencies in the data.

Figure 36 shows visual observation data for representative specimens post-irradiation. Here, PPT-D and PPT-E specimens are presented, because their conditions involved high cumulative fluences. As shown, various cracks were observed on the surface of the sample, both large and small, on all sides. In addition, many pop-outs are also confirmed on the surface of specimens. This must be a result of expansion of aggregates near surfaces. As will be discussed later, the concrete itself also expanded, appearing to support the hypothesis that the cracks were a product of aggregate expansion.

Figure 37 shows the measurement data for the PIE. The mean wire-measured fast-neutron fluences in PPT-B, PPT-C, PPT-D, and PPT-E were $7.76 \times 10^{18}$, $1.41 \times 10^{19}$, $4.52 \times 10^{19}$, and $9.11 \times 10^{19}$ n/cm$^2$, respectively, and MCNP5-calculated fast neutron fluences in PPT-B, PPT-C, PPT-D, and PPT-E were $7.78 \times 10^{18}$, $1.41 \times 10^{19}$, $4.58 \times 10^{19}$, and $9.20 \times 10^{19}$ n/cm$^2$ respectively. Mass decreased by 3.5% for both Con-A and Con-B specimens, as depicted in Fig. 37 (a). This is because specimens were dried at 76°C in all tests, in order to match the dried condition.

Figure 37 (b) shows changes in specimen length. Diameter length changes could not be measured properly because of pock-marks and deposits on the surfaces of specimens (see Fig. 36), so it was decided to examine changes in vertical length (i.e. height). Expansion was
greater for Con-A than for Con-B. The former contained tuff, which has high quartz content, whereas the latter contained river gravel, which has about half of tuff’s quartz content. This finding supports this study’s working hypothesis: that quartz metamictization causes expansion and damage in concrete. But obviously, the strain difference around $9.20 \times 10^{19} \text{n/cm}^2$ did not reflect the exact quartz content, therefore, a contribution of other rock-forming minerals is possible.

In the data of PPT-E, fluence and expansion magnitude were inversely correlated in the specimens. It is suspected that this occurred due to the compaction of concrete (Sereda et al. 1966) that was constrained by the capsule.

Figure 37 (c) shows the relationship between the compressive strength of concrete and fast-neutron fluence. As shown here, a trend of decreasing strength with increasing fluence in PPT-B, PPT-C, and PPT-D was

Fig. 35 Removed specimen. (Specimen diameter and length are 4 and 6 cm respectively.)

(a) Longitudinal crack across grooves
(b) Peripheral crack shown in groove

Fig. 34 Cracked capsule. (The distance of grooves of the capsule is 10 mm.)

(a) PPT-D A11
(b) PPT-D B11

(c) PPT-E A03
(d) PPT-E B03

Figure 36 Representative irradiated specimens: Visual observation data.
observed. Considering this finding in combination with the data in Fig. 37 (b) and the cracks in Fig. 36, it is concluded that aggregate expansion causes damage to concrete, reducing its strength.

In PPT-E, strength was found to decrease on average for Con-B, but to slightly increase for Con-A: this was interpreted, as previously stated, to be an effect of compaction. To summarize: since Con-A expanded more, it experienced greater compaction and was thus put under heavy stress inside the capsule. As a result, the cement paste fraction of the concrete was put under pressure from both the aggregates and the capsule. Consolidation of the cement paste fraction, which acts as a binder, caused the stress to increase. In addition, this figure reveals that the amount by which strength decreases varied depending on the degree to which the component aggregate expands (as deduced from the degree to which the concrete expands), even for otherwise identical concretes given the same fluence. Thus, it was identified that the concrete’s strength reduction on aggregate expansion depends on the expansion of the aggregate itself, data which are discussed later. In addition, the strength of the specimens subjected to neutron irradiation was reduced to approximately 50% that of non-irradiated, non-heated specimens.

Figure 37 (d) shows the relationship between Young’s modulus and fluence. As shown here, Young’s modulus decreases with increasing fluence; however, a slight increase in Young’s modulus was observed for PPT-E, relative to PPT-D. This trend can also be explained by the compaction of cement paste. It was confirmed that a Young’s modulus was significantly reduced to as low as 30% that of non-heated, non-irradiated specimens. Furthermore, both damage caused by aggregate expansion and resultant Young’s modulus reductions were found to depend on aggregate type.

2.3.5 HT: Concrete

HT (non-irradiated) were performed to determine the effects of neutron irradiation. These were conducted outside the reactor, with all conditions kept identical to all irradiation tests except for the irradiation. Figure 38 shows the data collected for H2-24 (IFA-756, PPT-E:

![Graphs showing results of concrete specimens of PPT.](image-url)
maximum temperature); Fig. 38 (a) shows the temporal changes in the core temperature of the concrete specimen; Fig. 38 (b) shows the temporal changes in internal capsule pressure due to helium flushing; Fig. 38 (c) shows the temporal changes in gas flow rate due to helium flushing; and Fig. 38 (d) shows the temporal changes in absolute humidity in the humidity gauge tank due to helium flushing. These figures appear to show that while heating causes specimens to emit water vapor, it quickly reaches equilibrium inside the capsule. The same absolute humidity was always observed, despite performing helium flushing with the same timing as the corresponding irradiation experiment. This can be attributed to insufficient drying of the specimen due to sole heating process, as evidenced by Fig. 39. In this figure, a gradual decrease of specimen’s mass was shown in HT specimens.

Figure 40 shows the results of the HT. The horizontal axis here is not heating time, but fast-neutron fluence. The data are placed according to the fast-neutron fluence they would have received at their position inside the capsule if they had been irradiated. Specimens exhibited slight shrinkage, as shown by the length changes in Fig. 40 (a); this was in the range of normal drying shrinkage (Maruyama 2016). Figure 40 (b) shows com-

![](image1)

Fig. 38 Measurement data during HT (H2-24).

![Fig. 39 Mass change in specimens immediately after HT and PPT. (HT data are associated with corresponding fluence of PPT data.)](image2)
pressive strength data. The concretes exhibited slight strength reductions due to heating; in particular, Con-B’s strength was reduced to 85% of its original strength, while Con-A’s was reduced to 90%. Figure 40 (c) shows Young’s modulus data. As shown here, Young’s modulus decreased the most over the drying period corresponding to PPT-B, but showed slight recovery thereafter. These data suggest that temperature cycling within the range of the present study is not harmful to concrete.

2.3.6 PPT: hcp

Here, the results of irradiating white cement paste are shown. The fluences received by white cement paste are presented in Table 26, calculated based on monitoring wire data and MCNP5 computational results. Figure 41 shows the results of PIE. Mass increases were observed in PPT-B (Fig. 41(a)). This finding was due to the fact that the lower specimens within the capsule were immersed in water due to the condensation inside the capsule, and due to insufficient drying when each sample in the holder was dried at 76 °C. PPT-C and PPT-D specimens decreased in mass due to the elimination of condensation inside the capsule and to more-complete drying.

Mass increases were again observed in PPT-E: a result of capsule flooding due to capsule fracture. Chemical deposits were observed over the surface of these specimens due the early submersion under condensed water in the capsule and consequent dissolution/precipitation reactions, thus, the related diameter data (Fig. 41 (c)) is lacking in reliability. On the other hand, no deposits were observed in the longitudinal direction Fig. 41 (b), giving related measurements high reliability. Based on the observed length changes, PPT-B specimens exhibited swelling behavior due to moisture absorption in the early period. Shrinkage was observed to accompany drying in PPT-C and PPT-D, and the swelling in PPT-E was due to the capsule fracture. When cement paste has high water content, hydrates like C-S-H reach solubility equilibrium with the pore solution, and so its crystalline structure does not accumulate damage due to neutron radiation. In addition, its high resistance to radiation is attributable to constituent ionic crystalline structures, including portlandite, which strongly resist radiation even after drying. Moreover, ionic bonding is also present in the CaO layer in C-S-H. Cement paste strength was enhanced by radiation, as can be seen in the Vickers hardness test data shown in Fig. 41 (d), and this finding also suggests that cement paste has high resistance against neutron radiation.

| Notation | Fast neutron fluence (×10¹⁹ n/cm²) | Thermal neutron fluence (×10²⁰ n/cm²) |
|----------|-----------------------------------|--------------------------------------|
| PPT-B    | 0.70                              | 0.30                                 |
| PPT-C    | 1.28                              | 0.59                                 |
| PPT-D    | 4.12                              | 1.88                                 |
| PPT-E    | 8.25                              | 3.50                                 |

Fig. 40 HT results. (HT-MAX: HT test using maximum temperature history at the center of concrete specimen. HT-AV: HT test using averaged temperature distribution in the concrete specimen.)
2.3.7 PPT: Aggregates

Aggregate specimens were irradiated under the identical conditions to hcp specimens. The radiation fluences received at each position in the capsule were the same as those presented in Table 26. The results of PIE are summarized in Fig. 42. In all cases, masses increased somewhat, and, in the case of GA, it increased greatly. These results suggest the possibility that the metamictized quartz in GA absorbed water after a large proportion had metamictized and transformed to silica gel with water (Ichikawa and Koizumi 2002).

GA showed the greatest expansion in terms of diameter and height changes. This suggests that quartz, with the lowest neutron irradiation resistance among the components tested, readily expanded in volume upon metamictization. Deposits resulting from condensed moisture occurred along the circumference of specimens (Fig. 43), but their effect on the expansion amount in PPT-E was comparatively small, with the expansion observed to be isotropic. Limestone (GF) has an ionic crystalline structure and does not contain quartz, and, in contrast, it hardly expanded.

Figure 44 shows the XRD data for GA. The diffraction peaks grew smaller and shifted to the small-angle region with increasing fluence. These shifts to the small-angle region are a manifestation of increased structural periodicity and widened atomic spacing. The peak-height reductions signify that the number of periodic structures per unit mass had decreased, indicating that metamictization had caused structural collapse. In summary, neutron radiation resulted in the collapse of periodic structure, metamictization, and expansion in aggregates.

2.4 Discussion

2.4.1 Expansion of aggregate

Several questions regarding the aggregate expansion mechanism should be discussed. 1) Does quartz have a dominant role in aggregate expansion, with its known behavior of metamictizing and swelling? 2) Is it possible that other rocks and minerals metamictize to contribute to expansion? 3) Given that in this experiment neutron flux and temperature were higher than in commercial reactors, should any of the findings be interpreted differently under commercial reactor conditions?

First, the results presented in Fig. 42 are re-evaluated in terms of the aggregates’ quartz content, focusing at the role of quartz. These new data are presented in Fig. 45. As shown, expansion strain can largely be explained by quartz content for fast-neutron fluences as large as $4.12 \times 10^{19}$ n/cm$^2$. In addition, GA, with its largest quartz content among aggregates, expanded the greatest amount at all fast-neutron fluences, even as high as $8.25 \times 10^{19}$ n/cm$^2$. However, expansion strain did not follow the same trend at $8.25 \times 10^{19}$ n/cm$^2$, with some aggregates expanding greater than other aggregates that had expanded to a lesser extent than for other fluences. This finding demonstrates that the expansion of
covalently bonded minerals in feldspar also contributes to aggregate expansion. In addition to these findings, authors also suspect the impact of texture or grain size in aggregate on the bulk density change of aggregates, because cracks in aggregates were found after irradia-

tion (Fig. 43) and this elucidates the significance of texture which has large influence on crack propagation and resultant crack opening conditions. Limestone whose major component is calcite, on the other hand, did not expand at all. The calcite, an ionic bonded mineral, did...
not experience expansion over the range of irradiation conditions here. These findings indicate that concrete made with limestone aggregate has a very low risk of degradation due to neutron irradiation.

Next, the influence of temperature, one of the irradiation conditions in this study, is discussed. Bykov et al. compiled and discussed the earlier literature on the temperature dependence of quartz metamictization due to neutron irradiation (Bykov et al. 1981). They found that the temperature of the irradiation environment significantly affects the degree of quartz metamictization. First, the test findings here are evaluated for their consistency with prior research. Bykov et al. discuss their data with fast-neutron fluence for neutrons of ≥0.01 MeV on the horizontal axis. The volume expansion of quartz is calculated from the data of GA. In this calculation, it is assumed that the quartz content of GA was 92% and only quartz expanded in the aggregate. Further, the aggregate expansion behavior is modeled based on nucleation and growth theory (Avrami 1941; Weber 1990; Harbsmeier and Bolse 1998). This model’s suitability and validity is discussed in Bolse’s paper, where such behavior is expressed with good precision (Harbsmeier and Bolse 1998).

Figure 46 was constructed with the objective of evaluating temperature effects in the model: it contains an Arrhenius plot of the natural logarithm of fluence once half the final expansion volume is reached versus the inverse of temperature during irradiation. The obtained activation energy is approximately 16 kJ/mol.

The nucleation and growth model theory can be expressed by the following equation:

\[
e_{\text{quartz}}(n) = e_{\text{quartz},\infty} \left(1 - \exp\left(-\frac{n}{K(T)}\right)^d\right)
\]

Here, \(e_{\text{quartz},\infty} : 18\%\), the maximum expansion volume of quartz; \(n\) = fast-neutron fluence (n/cm\(^2\)); \(K(T)\) = fast-neutron fluence when expansion reaches half the maximum expansion volume (n/cm\(^2\)); \(T\) = absolute temperature (K); and \(d\) : dimensional coefficient (known to range from 2–5 based on previous studies on metamictization: 2.38 is adopted here according to Field et al. (2015)).

At this time, \(K(T)\) was calculated using the following equation.

\[
K(T) = 0.45 \times 10^{20} \times \frac{\text{Exp}(2000/298)}{\text{Exp}(2000/T)} \cdot (4)
\]

The quartz expansion data obtained from GA results are looked at for comparison. Figure 47 contains data from Bykov’s paper: a nucleation and growth model that incorporates temperature dependence, and quartz expansion data from GA. As can be seen here, the expansion behavior of quartz in GA obtained in this study is in accordance with the previous research, meaning that it can essentially be assessed using the nucleation and growth model proposed above.

The trends of temperature dependence presented in Bykov et al. indicate that expansion behavior tends to slow with increasing temperature. This indicates that...
thermal vibrations which is higher in higher temperature, generate protective effects due to thermal healing if the neutron damage accumulated per unit time is constant. The temperature effects in the Bykov data would be reversed if the quartz had the kind of expansion mechanism seen in metals (i.e. void generation whereby ready bond migration and higher temperature promote the accumulation of defects and the formation of voids). It is thus clear that natural rock minerals, in particular quartz, do not expand according to the void-generation mechanism. Metals’ weak susceptibility to radiation effects means that their degradation mechanism is due to effective clustering, which is attributable to balancing the generation rate of elements in matrix and the diffusion time of these dissolved elements. However, in the context of the expansion behavior of natural rock minerals shown here, the speed and quantitative balance of thermal healing and defect formation are problematic. This means that, in terms of dose-rate effects, thermal healing is relatively enhanced under low-fluence conditions, and appears to reduce the degree of expansion.

Given this analysis, it was attempted to interpolate a model proposed in the past research that explicitly incorporates thermal healing in a real-world reactor setting (Nakano et al. 2005; Maruyama and Muto 2016). This was a three-layer model that includes a crystalline phase, an intermediate phase, and a metamictized phase, and which differs from the nucleation and growth model.

\[ R = R_1C_1 + R_2C_2 + R_3C_3 \]  
\[ C_1 + C_2 + C_3 = 1 \]  
\[ \frac{dC_1}{dt} = -\phi_1\sigma_1C_1 + bC_2 \]  
\[ \frac{dC_2}{dt} = \phi_2\sigma_1C_1 - \phi_2\sigma_2C_2 - bC_2 \]  
\[ \frac{dC_3}{dt} = \phi_3\sigma_2C_2 \]  

\[ C_1, C_2, \text{ and } C_3 \] are the respective mass composition ratios in the crystalline, intermediate, and metamictized phases in rock; \( R_1, R_2, \text{ and } R_3 \) are their respective densities; \( \phi \) is neutron flux (n/cm²/s); and \( \sigma_1 \) and \( \sigma_2 \) are the equivalent cross section areas for each phase change (1.0×10⁻⁵ cm²/n, 1.5×10⁻⁵ cm²/n respectively). Here, the thermal healing parameter is \( b = 4×10^{-6} \text{ s}^{-1} \) at 50 °C, a value determined by Primak (1958). In the calculation process, a neutron flux of 1.9×10¹⁴ n/cm²/s during testing, and of 2×10¹¹ n/cm²/s in a commercial reactor are assumed (Fukuya et al. 2002). The results are shown in Fig. 48. This figure shows the possibility of avoiding aggregate expansion when thermal healing is explicitly accounted for and when fluence is low. The role of thermal healing in natural rock minerals such as quartz must be clarified in future.

2.4.2 Concrete degradation

Here the mechanism is discussed by which neutron radiation deteriorates concrete. The phenomena of aggregate and concrete expansion have already been reported (Dubrovskii et al. 1967; Elleuch et al. 1972; Hilsdorf et al. 1978). In this study, aggregate expansion, shrinkage of cement paste, concrete expansion, and crack formation following irradiation were confirmed. Consistency in the experiments is validated using the composite law for concrete, which can be applied to estimations of concrete volume changes based on the components properties.

Presuming expansion only occurs in quartz in aggregate, it was assumed that aggregate expansion strain is determined by the proportion of quartz in the aggregate, and decided to estimate the averaged strain for total concrete based on expansion strain in coarse aggregate using the composite law.

The Hobbs model is adopted for evaluation (Hobbs 1974). The Hobbs model predicts concrete shrinkage based on aggregate shrinkage, aggregate Young’s modulus, matrix shrinkage, matrix Young’s modulus, and their volume ratios in concrete. In this paper, this model was adapted to predict concrete expansion based on aggregate expansion.

![Fig. 47 Comparison of obtained data with Bykov data. The quartz expansion due to metamictization is calculated from the expansion data and quartz content of GA. The nucleation and growth model is plotted.](image)

![Fig. 48 Predicted expansion of aggregate by considering thermal healing role in the condition of commercial plant.](image)
\[ \varepsilon_c = n + (2mn - n - 1)\varepsilon_{agg} \]

\[ n = E_{agg} / E_m \]

\[ m = \varepsilon_{agg} / \varepsilon_m \]

\[ e_{agg, irr} = \varepsilon_{agg, irr} \]

\( \varepsilon_c \) is concrete strain, \( \varepsilon_m \) is matrix strain, \( n \) is Young’s modulus ratio (i.e. the ratio of the aggregate’s Young’s modulus \( E_{agg} \) to the mortar’s Young’s modulus \( E_m \)), \( m \) is the strain ratio (i.e. the ratio of aggregate strain \( \varepsilon_{agg} \) to matrix strain \( \varepsilon_m \)), \( e_{agg, irr} \) is strain due to aggregate irradiation, and \( V_{agg} \) is the volume ratio of aggregate in the concrete. In this assessment, our observed values for expansion strain, and a Young’s modulus that was 1/3 of the value estimated for real cement paste which is cracked due to expansion of aggregate were used. This value was adopted from Hansen and Nielsen (1965).

Figure 49 compares the concrete strain calculated using the composite law with observed values for concrete strain. As can be seen, the estimated values are slightly greater than the experimental values, but the expansion behavior of concrete was estimated fairly successfully. In summary, it can be concluded that concrete expansion is dependent on the expansion of aggregate, in particular quartz, in aggregate.

Next discussion is the consistency of the data obtained here with the phenomenon shown in earlier research of concrete strength reduction due to neutron irradiation. Figure 50 shows the relationships between strength ratio to the concrete strength of CT (\( F_{c, F_{co}} \)), Young’s modulus ratio to the concrete Young’s modulus of CT (\( E_{c, E_{co}} \)), and fast-neutron fluence in the neutron irradiation tests. Figure 51 shows the relationship between the \( F_{c, F_{co}} \), \( E_{c, E_{co}} \), and heating time in the HT. Strength and Young’s modulus both fell in the HT, consistent with the known effects of heating and drying. The maximum strength reduction observed was 15% and this tendency was also observed in Con-B specimens in the tests here. Heating and drying were inextricably responsible for the strength reductions in the neutron irradiation tests. Evaluating heating and drying effects while also accounting for the final value for strength ratio (\( F_{c, F_{co}} \)) would help provide an understanding of the regions in reduced-strength concrete where neutron effects are especially significant.

Figure 52 was created to examine this strength reduction due to fast neutrons, by dividing the strength ratio in the irradiation tests by \( F_{c, F_{co}} \). As can be seen here, strength is barely reduced by neutron radiation-induced aggregate expansion. Even in Con-A, which contained an aggregate with high quartz content, strength did not fall in response to fast-neutron fluences greater than \( 1.40 \times 10^{19} \text{ n/cm}^2 \). However, the strength reductions caused by the expansion behavior of (quartz within) aggregate may have been underestimated, as irradiation tests were conducted in a 76 °C environment. To address this concern, the total neutron fluence necessary to cause the same expansion at 55 °C (the assumed temperature of concrete in a radiation environment in actual reactors) was estimated using Eq. (4), and the results compared with literature values for other concretes. The

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**Figure 49** Comparison of calculated expansion of concrete by composite law with experimental data.

**Figure 50** \( F_{c, F_{co}} \) and \( E_{c, E_{co}} \) as a function of neutron fluence.
results are shown in Fig. 53. Based on the existing literature values and the scope of the present study, $1.0 \times 10^{19}$ n/cm$^2$ seems to be an acceptable estimate of the fast-neutron fluence necessary to cause strength reductions. This finding is consistent with the conclusion of Hilsdorf et al. (1978).

In a similar manner, Fig. 54 was made to evaluate the relationship between total neutron fluence and $F_c/F_{co}$. In this figure, this study’s data were added to previously compiled data from concrete irradiation tests (Maruyama et al., 2013). As can be seen, the data here for compressive strength ratio’s relationship with total neutron fluence are largely consistent with preceding research. The figure shows that strength reduction due to neutron radiation occurred at total neutron fluences of over $6.0 \times 10^{19}$ n/cm$^2$. However, it is necessary to include the caveat that no corrections have been made for temperature in this figure.

Furthermore, if the physical properties of concrete depend on aggregate expansion, there should be a correlation between the strain and the $F_c/F_{co}$ because the crack opening spaces (= damage in concrete) should be almost linear to the concrete expansion strain. To examine this relationship, this study’s data were plotted along with literature values for length changes and corresponding $F_c/F_{co}$. These data are shown in Fig. 55. PPT-B, PPT-C, and PPT-D specimens exhibited the lowest strength ratios among experiments. The data appears to

![Fig. 52 Strength ratio ($F_{c,irr}/F_{c,he}$) due to neutron irradiation by considering the strength reduction of heating.](image)

![Fig. 53 Fast neutron fluence versus strength ratio ($F_c/F_{co}$) for a 55 °C environment.](image)

![Fig. 54 Relationship between total neutron fluence and $F_c/F_{co}$.](image)

![Fig. 55 Data points for compressive strength ratio.](image)
indicate the presence of a lower limit in conditions where specimens accumulate damage due to aggregate expansion while unconstrained physically - this lower limit is indicated with a line in the figure. On the other hand, PPT-E specimens lie above this lower limit line. Strength enhancement can be observed under its conditions, when the specimen was constrained and the cement paste was compacted. Moreover, data from preceding research that is located higher than this lower limit line seem to reflect the effects of physical constraint. The effects of physical constraint can also be confirmed from other specimens’ data: Dubrovskii’s specimens expanded to the greatest extent and had large physical constraint by the capsule, and were the highest above the lower limit line (Dubrovskii et al. 1967). Consequently it appears that the application of this lower limit line is restricted to specimens with an expansion strain of up to ~2%.

2.5. Summary
It was confirmed that the cement paste did not reduce in strength when exposed to fast-neutron (>0.1 MeV) fluences of up to \(8.09 \times 10^{19} \text{n/cm}^2\), and that it shrunk in volume. For aggregates, it was confirmed that quartz, with its high covalent bond content, has poor neutron resistance and expanded, while limestone, which contains ionically bonded calcite, did not expand for fast-neutron fluences of up to \(8.09 \times 10^{19} \text{n/cm}^2\). It was newly confirmed that aggregates containing quartz expanded more with increasing quartz content. Examining the results of X-ray powder diffraction, it was confirmed that neutron radiation induces increases in the lattice constants and loss of periodicity in crystalline structures in natural rock minerals, causing metamictization.

Concrete specimens were exposed to fast-neutron fluences up to a maximum of \(9.6 \times 10^{19} \text{n/cm}^2\) in irradiation tests. It was observed that when aggregates expand, concrete also expands, cracks form in the concrete, and its strength and Young’s modulus fall as a result. It was observed that two kinds of concrete, which contained aggregates with different quartz content, exhibited different expansion amounts, strength reduction ratios, and Young’s modulus reduction ratios after exposure to the same total neutron fluence. In summary, it was newly confirmed that the degree to which an aggregate expands depends on its mineral composition, and accordingly, that concretes containing different aggregates incur different levels of damage even following exposure to identical neutron fluence.

Data on length changes for aggregate and for concrete were obtained. By evaluating these data based on the composite law for dimensional change of concrete, it was found that experimental data could largely be predicted by using reduced Young’s moduli while taking into account matrix cracks. In addition, it was newly found that concrete strength increased when concrete specimens were physically constrained as their constituent aggregates expanded. An equation for the relationship between expansion strain and strength ratio in concrete under conditions without such a constraint was proposed, where concrete strength reduces as aggregates expand.

Confirmatory findings were obtained that quartz’s expansion behavior in aggregate due to neutron radiation is highly temperature-dependent; related observations were supported with findings from the literature. A model was proposed for calculating the activation energy for this process, as well as for expressing the temperature dependence of expansion behavior. Using this model, corrections were made for the effects of radiation environment temperature in this study and in previous research, and it was estimated that strength reductions begin to occur at a fast-neutron fluence of \(1.0 \times 10^{19} \text{n/cm}^2\) in 55°C concrete: a typical condition for radiation environments in nuclear reactors. This finding is consistent with Hilsdorf et al.’s conclusion that using this reference value allows soundness assessments to be performed on a more-scientific basis.

Aggregate expansion behavior was found in acceler-
ated tests and there is no data of aggregate expansion for neutron flux in commercial reactor. And thermal healing effects were explicitly accounted for using a three-phase phenomenological model. It was suggested based on the model that aggregate does not expand when accumulated damage due to neutrons is balanced out by thermal healing effects.

The variety and rates of expansion behavior of rock-forming minerals, and their respective roles in thermal healing roles, are key factors to incorporate into soundness assessment. More-extensive data should be obtained for long-term operation of nuclear power plants.

3. Impact of gamma-ray irradiation

3.1 Introduction

The direct effects of gamma radiation include radical generation. Confirming the extent to which this process is involved in the decomposition of hydrates and water in cement paste, and especially the role chemically bound water plays in their decomposition, is also an important step for confirming the stability of cement paste.

For the aggregate, the effects of gamma radiation-induced electrolytic dislocation of oxygen atoms in covalent bonds is understood (Hobbs 1995). And the dose to cause metamictization of rock-forming minerals is higher than that for 60-year operation of commercial reactors (Ichikawa and Kimura 2007). It was therefore decided to perform irradiation tests on aggregates and evaluate their properties in order to confirm this knowledge.

These experiments included interaction tests (IT), which focused on radiolysis within cement paste due to gamma radiation, and physical property tests (PPT), which focused on examining the properties of exposed concrete and its constituent materials. Heating tests (HT) and reference cold tests (CT, which is identical to that of neutron irradiation) were also planned to elucidate impacts of sole gamma-ray on concrete and concrete components. Specimens were gamma-ray-irradiated in an irradiation room of the Cobalt-60 Irradiation Facility at the Takasaki Advanced Radiation Research Institute (TARRI; Gunma Prefecture, Japan). The parameters as well as the complete testing process are summarized in Table 27.

In principle, it is necessary to examine gamma-ray of various energy levels, but it was difficult to perform irradiation tests using monochromatic gamma radiation at different energy levels; thus, it was decided to perform gamma-ray irradiation tests using cobalt-60 ($^{60}$Co, two gamma rays with energies of 1.17 and 1.33 MeV are emitted). In addition, it is impossible, in principle, to determine whether the obtained data can be applied to commercial reactors without assessing the effects of dose-rate (It was unfeasible to do so in the neutron irradiation tests). Therefore, it was decided to run gamma-ray irradiation tests for different dose-rates in this investigation. The quantities of energy deposited by radiation when it hydrolyzed the water in cement paste was evaluated using alanine dosimeters.

3.2 Experiment

3.2.1 IT

With the objective of evaluating the decomposition behavior of water in cement paste exposed to gamma radiation, experiments on cement-paste specimens were performed by measuring their temperature and the quantities of gas and moisture generated by them during exposure. Irradiation tests were conducted for two months, under three conditions for gamma dose-rate, two for water content, and three for irradiation temperature. The parameters are summarized in Table 28.

Cement paste was made using tap water and ordinary Portland cement (Type I cement, density: 3.16 g/cm$^3$, Blaine value: 3210 cm$^2$/g), mixed at a water-to-cement ratio of 0.30. Cement paste was mixed using a mortar mixer (capacity: 20 L). After being put in the mixer vessel, cement was mixed by low-speed rotation for 60 s, during the first 30 s of which water was added. Next, the mixer was stopped for 30 s while the contents were scraped off its interior, after which the contents were mixed by high-speed rotation for 90 s.

Cement paste was then poured in two layers into a disposable tin-metal mold with dimensions of $50 \times 100$ mm (Summit Mold, Inc.), and specimens were formed using a push rod and table vibrator. After pouring, the mold and its contents were immediately covered with a plastic sheet and sealed in a plastic (vinyl) bag. Specimens were cured for four weeks in a temperature-controlled room at 20 °C, and then removed from their molds, their surfaces ground smooth, and their dimensions and mass measured. Except for those designated to have their strength measured in this initial condition, specimens were dried in a thermostatic chamber. The drying period differed according to drying temperature conditions; specimens were dried for 14 d at 40°C or for 7 d at 120 °C. 40 °C was selected to simulate a reactor environment, and 120 °C was chosen to evaluate the decomposition of chemically bound water.

Specimens were irradiated for approximately 61 d in total. The gas measurement apparatus was configured to perform 24-h continuous measurement, while water content was measured nine times over the irradiation period. The gas and water collection system consisted of a moisture measurement apparatus, a 12-channel concentrator, a gas injector, and a gas chromatograph. Gas measurements were automated under electronic control. Figure 56 shows the layout of the plumbing and wiring used for gas measurements. Carrier-gas cylinders and the gas measurement system were placed outside the irradiation room. Figure 57 shows the set-up of specimens in the irradiation room.

Each moisture measurement apparatus contained a moisture collector: a GL-45-type glass container (volume=250 ml) filled with magnesium perchlorate.
(Mg(ClO₄)₂: ~170 g). Moisture was carried in Ar gas discharged from the stainless-steel container, and captured upon entering the vessel: moisture weight was measured separately for each glass vessel.

The carrier gas (Ar) was continuously piped into the stainless-steel container at a flow rate of 100 ml/min (0 °C, 1 atm) and was released into the air after passing through the moisture collector. After the moisture collector, the gas was analyzed using the gas chromatograph after passing through the 12-channel concentrator.

Table 27 Experimental schedule for gamma-ray irradiation experiments.

| Drying condition (Notation) | Temperature (°C) | Target dose rate (kGy/h) | Actual dose rate (kGy/h) | Capsule number |
|----------------------------|-----------------|--------------------------|--------------------------|---------------|
| Drying at 40 °C for 14 days (D40) | 60              | 10                       | 7.05                     | #1            |
|                              | 5               | 5                        | 3.84                     | #3            |
|                              | 1               | 1                        | 0.87                     | #5            |
|                              | 40              | 5                        | 3.84                     | #7            |
|                              | 1               | 1                        | 0.87                     | #9            |
| Drying at 120 °C for 7 days (D120) | 25              | 1                        | 0.87                     | #11           |
|                              | 60              | 10                       | 7.05                     | #2            |
|                              | 5               | 5                        | 3.84                     | #4            |
|                              | 1               | 1                        | 0.87                     | #6            |
|                              | 40              | 5                        | 3.84                     | #8            |
|                              | 25              | 1                        | 0.87                     | #10           |
|                              | 1               | 1                        | 0.87                     | #12           |
and gas injector. A gas chromatograph (GC-8A1T, Shimadzu Corp.) was used. Each channel required 8 min for measurements: 6 min for the measurement itself, and 2 min to vent the sampled gas from the sample loop after measurements in the channel upstream were finished. Some specimens were designated for temperature measurements during the irradiation tests: their surface temperature was recorded along with the air temperature of the irradiation room every 5 min using a type-T thermocouple.

Alanine dosimeters were attached to the sides of specimens before irradiation commenced and after it concluded (Amino Gray dosimeters, developed by JAERI and JMACS Japan Co., Ltd.: diameter=11 mm, height=50 mm) for 1 hour to measure dose rate. As gamma rays are physically attenuated by the specimen itself, the dose-rates received by specimens were determined as the average of two doses measured in two locations: immediately in front of and behind the capsule.

Specimen temperature during irradiation was set at

![Table 29 Experimental parameters (PPT).](image)

| Irradiation period | Dose rate |
|--------------------|-----------|
|                    | 10kGy/h   | 5kGy/h   | 2.5kGy/h | 1.25kGy/h |
| 4 months           | 2.5×10^4 Gy | —        | —        | —         |
| 8 months           | 5.0×10^4 Gy | 2.5×10^4 Gy | —        | —         |
| 16 months          | 1.0×10^4 Gy | 5.0×10^4 Gy | 2.5×10^4 Gy | —         |
| 32 months          | 2.0×10^4 Gy | 1.0×10^4 Gy | 5.0×10^4 Gy | 2.5×10^4 Gy |

![Fig. 56 Schematic of irradiation experiment (IT).](image)
three levels: 60, 40, and 25 °C. Specimens were placed at varying distances from the gamma-ray source to achieve target gamma dose-rates of 10, 5, and 1 kGy/h.

### 3.2.2 PPT

#### (1) Concrete

Identical specimens to those used in the neutron irradiation tests were used to separate the effects of neutrons and gamma rays on the physical property changes observed in the neutron irradiation tests. The water-to-cement ratio was 0.50, and two types of concrete containing different coarse aggregate were prepared. Con-A contains the altered tuff crushed coarse aggregate (GA), and Con-B contains sandstone gravel (GB).

The mixture proportions of concrete (Table 10), properties of used materials (Table 9), chemical composition of used cement (Table 7), phase composition of used cement (Table 8), particle size distribution of cement (Fig. 12) and coarse aggregate (Figure 13), and mineral composition of used aggregate (GA and GB in Table 12) are shown in Chapter 2.

With the aim of focusing on the effects of coarse aggregates, the concrete specimens contained the same volume of coarse aggregate, as well as the same amount of mortar prepared at the same mixture ratio.

Specimens were directly exposed to radiation, without being sealed in capsules. Dose-rate effects were assessed under several experimental conditions: four levels of gamma dose and two kinds of aggregate. Specimens were placed in the room for 4, 8, 16, or 32 mo. in locations where they were irradiated at respective dose-rates of 10, 5, 2.5, and 1.25 kGy/h, for respective doses of $2.0 \times 10^5$, $1.0 \times 10^5$, $5.0 \times 10^4$, and $2.5 \times 10^4$ kGy as they are summarized in Table 29. Irradiation periods were estimated to achieve the respective target doses: data were reviewed, as appropriate, to account for changes in dose-rate during the time frame due to the decay and replacement of the radiation source. Table 29 shows an overview of the test parameters and Fig. 58 shows a schematic of irradiation conditions.

The temperature and humidity of the room were measured by using a type-T thermocouple and a humidity sensor (SPF-54: Tateyama Kagaku Group). Specimen temperature was also measured over time using an type-T thermocouple stuck to their surfaces. After irradiation, mass changes, dimensional changes, compressive strength, Young’s modulus, free-water content, and chemically bound-water content were also measured.

#### (2) Hcp

The water-to-cement ratio of white cement (W) paste was 0.55; the chemical composition, properties, and mineral composition of the white cement paste prepared for the tests are shown in Table 32 and Table 33 (symbol: W). Hcp specimens were identical to the ones used
for PPT of neutron irradiation shown in Chapter 2 and in the experiments on the impact of heating and drying shown in Chapter 4.

Samples with two different moisture contents were investigated. One is denoted as SDS100 which was cured in saturated Ca(OH)$_2$ solution for ~3 yr. The other is denoted as SDS50 which was dried/moisture-conditioned for ~2.5 yr in a humidity-controlled desiccator (RH=50%) after 0.5 yr of curing under saturated Ca(OH)$_2$ solution. Thereafter, specimens were uniformly irradiated by 60Co for approx. 10 mo. such that the deposited energy would reach 5×10$^4$ kGy. Various analyses were performed on the specimens at Nagoya University thereafter, after sealing them in polyethylene-coated aluminum bags. Results of bending tests, equilibrium moisture content tests, X-ray powder diffraction (XRD)/Rietveld analysis, and water vapor sorption isotherm tests are shown in this report. Specimens were either irradiated specimens (Irr), reference specimens set aside in the same room where they were not exposed to radiation (Ref), or ‘initial’ specimens, having the same properties as before the irradiation tests (Ini).

(c) Aggregates
In order to verify alterations in aggregates with varying quartz content, irradiation tests were performed on three kinds of silicate rocks (sandstones) from Japan, including GA and GB. Limestone (GF) was also used for this measurement as a representative rock with a high ionic bond content. Information about the aggregates used are compiled in Table 11, Table 12, and Table 30. Specimen size was φ45×90 mm and five specimens were used for each condition. Target doses were 2.5×10$^4$, 5.0×10$^4$, and 1.0×10$^5$ kGy with a dose rate of 10 kGy/h. After the irradiation, compressive strength, Young’s modulus, mass change, and length change were measured.

3.2.3 HT
(a) Concrete
In order to reproduce the heating and drying experienced by specimens exposed to gamma radiation, unsealed specimens were subjected to equivalent histories of temperature and humidity in a thermo-hygrostat chamber. Specimens were heated for one of four different lengths of time: 4, 8, 16, or 32 mo., corresponding to the irradiation periods in the gamma-ray irradiation tests. Humidity was maintained at one of two levels, simulat-
ing the temperature and humidity received by specimens in the 1st and 4th rows (corresponding to dose-rates of 10 and 1.25 kGy/h, respectively) in the gamma irradiation tests. Table 31 shows an overview of the test parameters. In addition, Fig. 59 shows the temperature and humidity profiles each thermo-hygrostat was configured to follow.

Temperature and humidity were set in one-week intervals, adopting the average of the respective values observed each week over the irradiation tests. For temperature, the average of the temperatures measured by thermocouples on the surfaces of irradiation test specimens were used, calculated separately for the 1st and 4th rows. For humidity, the relative humidity with respect to the irradiation room temperature (psychrometer equivalent) was converted to the relative humidity with respect to the irradiation test specimen surface. However, if the mass lost by the heated specimen exceeded the mass lost by the corresponding irradiation test specimen before the testing period concluded, specimens were sealed in an aluminum pack and heat-cured while ensuring moisture could not dissipate. After heating, mass changes, dimensional changes, compressive strength, Young’s modulus, free-water content, and bound-water content were measured via physical tests.

(b) Aggregate

Heating tests were performed on the aggregate specimens. The same procedure as that for concrete was adopted. Temperature equivalent relative humidity of irradiated samples were measured. Temperature and humidity were set in one-week intervals, adopting the average of the respective values observed each week over the irradiation tests. Compressive strength, Young’s modulus, mass change, and length change were measured.

3.3 Experimental results

3.3.1 IT

Specimen temperature and irradiation room temperature during the irradiation tests are shown in Fig. 60. In all cases, specimen temperature was successfully controlled to within ±1°C of the respective target temperature. H2O generation rates and cumulative totals are shown in Fig. 61. H2O generation rate peaked immediately after irradiation onset, and decreased monotonously thereafter. The higher the specimen temperature, the more water was produced; however, total water production showed little dependency on irradiation dose-rate. Moreover, very little water was produced from the D120 series of specimens, pre-dried at 120 °C.

H2 generation rates for D40 and D120 specimens are shown in Fig. 62 and Fig. 63, respectively. H2 generation rates peaked immediately after irradiation onset, but tapered off thereafter. The higher the dose-rate, the higher the H2 generation rate: at irradiation onset, the H2 generation rate was almost proportional to the dose-rate. In addition, H2 generation rates were almost completely unaffected by specimen temperature. The specimens’ H2 generation rate fell more sharply over the course of the irradiation period the higher their temperature. However, this was due to decreased water content resulting from the high levels of water lost by such specimens. D120 specimens, which had been pre-dried at 120°C, were found to produce very little hydrogen. O2 and N2 levels were below the lower detection limit, while CO2 was undetectable. The mechanism of unbalanced results of water radiolysis in cement paste is not solved completely, but probably, this is due to forming CaO2·8H2O in the system during irradiation (Bouniol and Aspart 1998).

The H2 generation G-value was calculated based on the data obtained in this test. Figure 64 displays the changes in G-value as calculated over the irradiation period for D40. At the start of irradiation, G-value
ranged from 0.3–0.4, somewhat below the G-value for bulk water (0.45 (Kasten 1991)), and declined as exposure continued. This trend could have been attributable, in part, to the moisture content of the cement paste: to confirm, the \( \text{H}_2 \) generation G-value was re-plotted against water content as shown in Fig. 65. Indeed, G-value decreased as the water content was reduced. In addition, G-values for D120 specimens, which had been pre-dried at 120°C, stayed around 0.05 throughout the irradiation period, indicating that chemically bound water in the paste was hardly decomposed at all in a realistic time span.

### 3.3.2 PPT and HT

(a) Concrete

The temperature/humidity environment of the gamma-ray irradiation room is shown in Fig. 66, while specimen temperatures are shown in Fig. 67. The room’s temperature annually varied between roughly 10 - 30 °C, while its humidity could be broadly averaged at around 50% RH. Specimen temperature rose as a result of gamma heating effects, to a maximum of 45°C. The results of the gamma-ray irradiation tests are shown in Fig. 68 and Fig. 69. In terms of compressive strength, the sealed Con-A specimens had nearly identical values throughout the 32-mo. testing period, whereas a slight increase in strength was observed for...
the sealed Con-B specimens (Fig. 30). A tendency for the strength of gamma-ray-irradiated specimens to increase the longer they were irradiated was observed for both Con-A and Con-B specimens. Similarly in the heating tests, a tendency was observed for the speci-

![Temporal changes in H₂ generation G-value](image1)

**Fig. 64** Temporal changes in H₂ generation G-value (D40).

![Temperature and humidity of irradiation room](image2)

**Fig. 66** Temperature and humidity of irradiation room.

![Relationship between H₂ generation G-value and completely water content](image3)

**Fig. 65** Relationship between H₂ generation G-value and completely water content. (Water content of 0 represents the dried condition at 120 °C.)

![Temperature of concrete specimens (PPT)](image4)

**Fig. 67** Temperature of concrete specimens (PPT).

![PIE results of Con-A (PPT)](image5)

**Fig. 68** PIE results of Con-A (PPT).
mens’ strength to increase the longer they were heated. Young’s modulus was unchanged by gamma-ray irradiation. In the heating tests, Young’s modulus was found to gently increase over time in Con-A specimens, while barely changing in Con-B specimens. The specimens’ water content fell from an initial ~4% to ~1% in their first four weeks of drying, but decreased gradually thereafter. Loss-on-ignition (LOI) values tended to increase over time, but this could have been a result of carbonation in the concrete (Fig. 70).

(b) Hcp

Figure 71 contains post-irradiation and reference data for the bending strength cement paste. The blue points are corresponding the bending strength of hcp sample after long-term conditioning under different RHs. Thus, these blue points shows the sole drying impact. Orange points indicates the PIE results. After long-term gamma-ray irradiation, the strength was increased in both cases. The increased strength after irradiation was almost the same disregards to starting equilibrium RH in the samples. On the contrary, green points which indicate the samples set in the same irradiation room but not irradiated, show almost consistent trend with blue points. Therefore, based on the difference between the orange points and the green points, it seems that there exists a
mechanism for gamma-ray-induced strength enhancement.

To investigate this potential mechanism, differential thermal gravimetric (DTG) analysis was performed to investigate alterations in cement in the testing environment. The results for saturated specimens (i.e. SDS100) in three conditions are shown in Fig. 72. As can be seen here, gamma-ray irradiation caused peak reductions around 100 °C and 420 °C, but peak increases in the vicinities of 600 °C and 730 °C. It is clear that carbonation accompanied the drying: the 100 °C and 420 °C peaks correspond to evaporable water and portlandite, respectively, while the 600 °C and 730 °C peaks indicate calcium carbonation (CaCO₃) decomposition. Specifically, the peak at 600 °C is associated with aragonite and vaterite, distinct from the 730 °C peak for calcite (Wu and Ye 2015). To confirm this suspicion, CaCO₃ was quantified in the specimens using XRD and the Rietveld analysis method: the results are shown in Fig. 73. As is clear from this figure, large quantities of vaterite and aragonite are deposited in samples exposed to gamma radiation, whereas the majority of deposits in the absence of radiation take the form of calcite. This finding suggests that vaterite and aragonite formation are involved in the observed strength enhancement.

Water-vapor sorption isotherm test at 293 K using a volumetric method to evaluate the microstructure of cement paste specimens: the results are presented in Fig. 74. As shown, the amount of water vapor adsorbed decreased significantly with drying (Maruyama et al. 2014a). The major difference between SDS100-Irr and SDS100-Ref was the presence of a kink (sudden drop) in the desorption line near 40% RH for the former. This kink is believed to originate from the layered structure of C-S-H, 2016b). Specifically, it appears that carbonation in a gamma-ray radiation environment causes aragonite and vaterite to form while maintaining the C-S-H layered structure, whereas carbonation in an ordinary indoor environment destroys the C-S-H layered structure, or else creates Q₃ sites in silica atoms in the C-S-H layers like tobermorite. Either way, carbonation would account for the absence of a kink in the water vapor sorption isotherm in an ordinary indoor environment. It is concluded that inter-C-S-H structures bind suitably and contribute to strength enhancements when C-S-H’s layered structure is maintained and vaterite and aragonite form.

\(\text{(c) Aggregates} \)

Figures 75 and 76 respectively show dimensional and strength changes evident in the gamma-ray irradiation and heating tests. Aggregates tested were naturally occurring: specimens showed wide variation due to joints inside the aggregates. It is unclear why the dimensions of aggregates (except limestone) instead expanded. An expansion strain value of 4% for quartz has been reported in past research following electron irradiation-induced metamictization (Maruyama and Muto 2016), but the data obtained here did not reach this value. Taking into account the large variation and the little differ-
ences from the heating tests, it appears that gamma radiation’s effects on aggregates in terms of volume changes are unremarkable.

Great variation also appeared in the strength data. Generally speaking, aggregate strength does not significantly differ following heating versus following gamma-ray irradiation, and it can be concluded that any changes did not have a large impact on concrete physical properties during the compression tests.

3.4 Discussion

The findings of these experiments are as follows. Aggregates did not exhibit any special expansion behavior after exposure to gamma-ray doses of up to $1.0 \times 10^5$ kGy received from a $^{60}$Co source; volume changes in this range were within the scope attributable to heating and drying effects. Gamma radiation doses around $5.0 \times 10^4$ kGy from a $^{60}$Co source preserved the layered structure of C-S-H and enhanced strength in cement paste under conditions where they caused vaterite-carbonation. Similarly, concrete strength was unaltered by gamma-ray radiation doses of up to $2 \times 10^5$ kGy from a $^{60}$Co source in the present study: strength was maintained or enhanced to the same degree attributable to heating and drying effects. To examine this tendency further, the effects of gamma-ray radiation with the effects of heating and drying were compared in terms of resulting mass loss.

Figure 77 shows the relationship between Fe/Cfo and the mass reduction ratio for Con-A. With respect to the mass reduction rate, the Fe/Cfo of gamma-ray-irradiated specimens and heat-dried specimens exhibit quite similar behavior. There was almost no difference between the gamma-ray-irradiated and heat-dried specimens exposed to conditions under which carbonation typically proceeds; all gamma-ray-irradiated specimen data was within the range of heat-dried specimen data. When supplemental drying tests under non-CO$_2$ conditions were performed, however, the strengths of those specimens quickly fell as the mass reduction rate increased, faster than the strengths of gamma-ray-irradiated and heat-dried specimens. This tendency was almost identical to that observed for heating and drying tests performed in Chapter 4 (data indicated in gray in the figure).

Figure 78 shows the relationship between Fe/Cfo and the mass reduction ratio for Con-B. As can be seen here, there were some gamma-ray-irradiated specimens that exhibit higher strengths with respect to the mass reduction ratio than did heat-dried specimens. Moreover, gamma-irradiated specimens exhibited an inverse relationship between strength and the mass reduction rate, growing strong while losing mass; in contrast, heat-dried specimens tended to decrease in strength as they
lost mass. In addition, specimens dried in non-CO$_2$ conditions in supplemental tests exhibited lower strength ratios than comparable specimens that were heat-dried in carbonating conditions: this trend was almost identical to that observed in the heating and drying tests in Chapter 4.

These findings lead to the conclusion that while exposure to a carbonating environment confers greater strength enhancement compared to a non-carbonating environment, the effects of gamma radiation in this context are barely apparent.

**Fig. 76** Compressive strength changes of aggregates due to gamma irradiation (error bar=1σ).

**Fig. 77** Relationship between the compression-strength ratio and the mass change (Con-A).
4. Impact of Heating and Drying

4.1 Introduction

There is no definite knowledge as to what kind of phenomena occur in concrete under initial drying conditions and how the physical properties of concrete change as a result of drying and heating. However, studies have reported that hcp undergoes irreversible shrinkage after the first desorption process (Helmuth and Turk 1967; Maruyama et al. 2015), indicating the occurrence of an irreversible reaction accompanied by a physical property change after drying. This irreversible reaction has been studied using various procedures, including nitrogen BET surface-area measurements (Hunt et al. 1960; Parrott et al. 1980; Litvan and Myers 1983; Maruyama et al. 2014a), water-vapor BET surface-area measurements (Tomes et al. 1957; Maruyama et al. 2014a), and surface area and C-S-H structures obtained by small-angle X-ray or neutron scattering (Bayliss 1973; Winslow and Diamond 1974; Kropp et al. 1985; Vökl et al. 1987; Thomas et al. 1998, 2008, Chiang et al. 2012, 2013), among other techniques and interpretations (Feldman and Sereda 1968; Wittmann 1968, 1973, Parrott et al. 1980; Parrott and Young 1981; Beaudoin 1982; Jennings 2008; Beaudoin et al. 2010; Maruyama 2010; Muller et al. 2013). However, research efforts have largely ignored the strength of hcp and concrete during the initial drying and heating process. This calls for studies that report data on hcp, aggregate, and concrete properties in equilibrium with drying conditions and the homogeneous moisture distribution inside the specimen. Very few reports of this nature have been published (Pihlajavaara 1974, Kishitani et al. 1982), which is in contrast to the large number of papers on concrete behavior under elevated temperature (Naus 2010).

In this study, we first quantitatively evaluate the strength and Young’s modulus of hcp after drying and heating. We also investigate changes in the microstructure of cement paste through experimental observations and then discuss corresponding mechanisms. These studies are also extended to other cement cases. Secondly, we discuss the volume stability of a key aggregate found in concrete. We collect and investigate sandstone and limestone aggregates sourced from across Japan. Finally, we study the physical properties of dried or heated concrete composed of different coarse aggregates and with water-to-cement ratios. The mechanisms governing the changes in strength and Young’s modulus are subsequently identified. In addition, we examined the influence of aggregate type on the occurrence of microscopic damage around aggregate particles.

4.2 Hcp

In order to elucidate the mechanism governing changes in hcp properties due to drying and heating, thin specimens of hcp were prepared and dried under different RHs and temperatures for more than 1 year. The bending strength, Young’s modulus, and water vapor sorption isotherm were subsequently investigated.

White cement (W), high-early-strength Portland cement (H), and moderate-heat Portland cement replaced by fly ash at 20 wt% (MF) were used. The chemical compositions, obtained via X-ray fluorescence (XRF) analysis, and the physical properties of the cements are shown in Table 32. Table 33 outlines the mineral composition of the cements obtained through XRD and quantitative Rietveld analysis. Table 34 shows the composition of fly ash.

Since W does not contain ferrite, it is suitable for...
analyses that use a magnetic field, allowing the extensive evaluation of various properties. For this reason, we used W as a central sample for elucidating the mechanism behind changes under the first desorption process. The water-to-cement ratio was 0.55; this value was selected as a representative example of general strength. The samples were cured under a saturated calcium hydroxide solution at 20±2 °C for 6 months and dried the samples afterwards.

Cement paste samples were prepared with H using water-to-cement ratios of 0.55, 0.40, and 0.30, which allowed us to evaluate the impact of the water-to-cement ratio on the alteration process arising from heating and drying. Similar to W, we cured the samples for 6 months before commencing the drying process.

For MF, we conducted experiments that were representative of the typical low heat cement used in Japanese LWR buildings. The cement structures of nuclear power plant facilities have large cross-sectional dimensions, as well as countermeasures that suppress cracking due to the hydration heat of cement. Water-to-cement ratios were set to 0.40 and 0.55. The wet curing period before starting the drying process was 9 months.

We used a paddle mixer to mix the various types of cement paste. For water-to-cement ratios of 0.4 and 0.55, additional re-mixing in intervals of 30 min was necessary to halt bleeding and ensure a good consistency. The size of the specimen was 3 × 13 × 300 mm in order to promote rapid drying and to eliminate uneven water content and strain distributions in the cross section during testing. After mixing, the cement paste was poured into steel formworks with dimensions of 3 × 13 × 300 mm. Demolding was carried out at an age of 1 to 4 days. After demolding, wet curing in a saturated calcium hydroxide solution was carried out in a thermostatic chamber (20±2 °C) until the start of the drying process.

The length and mass of each sample were measured prior to drying. Samples were dried under different RHs of 95, 90, 80, 70, 60, 50, 40, 30, 20, and 11% in a thermostatic chamber at 20±2 °C. The RHs were controlled using a sodium hydroxide solution at different concentrations (Stokes and Robinson 1949; Maruyama 2010). The samples were dried for 12 months (W and H series) and 24 months (MF). After 3 months of drying, a portion of the samples dried under 11% RH were heated to 40, 50, 60, 70, 80, and 90±1 °C for 9 months. Heat drying was carried out in a container connected to a CO₂ adsorbent in an environment approximately equal to ambient conditions, c.a. 20 °C and 60% RH.

Bending-load experiments were conducted using three-point flexural loading. The span used was 60 mm, and at least five samples were tested for each target condition. The bending strength was evaluated according to: $f_b = \frac{P l h}{8 I}$, where $f_b$ denotes the bending strength of hcp (N/mm²), $P$ is the maximum load (N), $l$ is the span (mm), $h$ is the thickness of the sample (mm), and $I$ is the geometrical moment of inertia (mm⁴).

Water vapor sorption measurements were conducted using the volume method with a water vapor sorption analyzer (Hydrosorb 1000, Quantachrome) to examine microstructural changes. Using the volume method to determine the water vapor sorption isotherm is more convenient than the mass method in quickly measuring the equilibrium adsorption isotherm. This is because gases other than water molecules are removed from the system before measurements. Preliminary experiments revealed that the relative error with respect to the Brunauer–Emmett–Teller (BET) theory surface area ($S_{BET}$) is 0.5% (Maruyama et al. 2014a).

A sample (~20 mg) was used for each measurement at 20 °C, with a pressure tolerance of 0.05 mmHg and a time tolerance of 120 s. The measurement points on the adsorption and desorption branches were divided into intervals of $p/p_0 = 0.05$ up to 0.95, terminating at 0.98 (RH = 98%). BET theory was used to calculate the BET surface area ($S_{BET}$) of the adsorption branch with a water molecule section of 0.114 nm². The samples were ground in a ball mill, yielding powders 25–75 μm in diameter. As a pre-treatment step, samples were dried using a vacuum pump (theoretical minimum pressure of 6.7×10⁻² Pa; observed maximum pressure of 50 Pa) and heated them to 105 °C on a heating mantle for 30 min.

The water absorptions of each of the samples were measured. The samples were pulverized to a size of ~3 mm each, then water was absorbed using vacuum suction for a duration of 5 minutes. The surfaces of the samples were then wiped to ensure that their surfaces were in a dry and saturated state. After measuring the sample mass, the samples were dried in a nitrogen environment at 105 °C for 24 hours. The samples were weighed, and the difference in weight corresponded to the saturated moisture content. At least three sample sets were tested for each condition. The relative error in the saturated moisture content measurements was less than 1%.

In addition to water sorption experiments, results from nitrogen sorption isotherms, solid-state ²⁹Si magic angle spinning (MAS) dipolar decoupling (DD), nuclear magnetic resonance (NMR), solid-state ²³⁷Al MAS NMR, ultrasonic pulse velocity measurement, low-temperature differential scanning calorimetry (DSC), length-change isotherms, Fourier transform infrared spectroscopy (FTIR), ¹H-NMR relaxometry, dynamic thermal gravimetry (TG), conventional thermal gravimetry, small-angle X-ray scattering (SAXS), and field-emission
scanning electron microscopy (FE-SEM) have all been collected in this project, some of which have been reported. Figure 79 illustrates the relationship between the degree of drying and the bending strength of W55 (here, W55 represents the hcp sample using W with a water-to-cement ratio of 0.55). Figure 80 displays the bending Young’s modulus in relation to the degree of drying. As shown here, the bending strength of the cement paste displays a complex behavior with respect to the drying condition. Starting from a saturated state, the bending strength increases as the RH decreases to 80%. From this point on, the strength decreases with decreasing RH until 40%, at which point the strength increases once again with stronger drying. Given that the trend observed for the bending strength reverses at 11% RH and 40 °C, it can be considered that heating at 40 °C is comparable to drying under 20% RH at 20 °C.

When heat drying at 90 °C or less, the bending strength decreases slightly as the temperature increases. One explanation for this behavior is that the friction between the internal hydrates decreases because the expansion pressure of ettringite, which becomes unstable at a high temperatures, decreases (Lothenbach et al. 2007). Similar trends are observed for the Young’s modulus with respect to the drying and heating conditions.

Figure 81 presents typical water vapor sorption isotherms obtained from W55 samples. In general, the degree of sorption at 98% RH decreases with decreasing RH (i.e., stronger drying). Furthermore, mesopores decreased rapidly from 40 °C to 90 °C and adsorption in the region under 30% RH decreased as the sample was dried at less than 70% RH.

Figure 82 summarizes the values of $S_{H2O}$ obtained by sorption isotherms. Figure 84 displays the microstructural changes from the viewpoint of water vapor sorp-
tion of hcp as a function of the degree of drying.

It is considered that adsorption within the 40 to 95% RH range (dW_{0.40}) takes the form of water molecules adsorbing between C-S-H monolayers, which move relatively freely. This sorption amount corresponds to several nanometers in scale (Maruyama et al. 2015). Water adsorbed in the region below 40% RH (dW_{0.0}) is thought to be mainly adsorbed between stable C-S-H layers, which reflects part of the C-S-H crystal structure (Feldman and Sereda 1968; Maruyama et al. 2015). In the high RH region, capillary condensation occurs but this RH region appears to be very small in the data obtained using the volume method. Consequently, water absorption of the samples is obtained in parallel to confirm the presence of residual pores (dW_{95–100}). In this series of experiments, a threshold value of 95% RH was set to distinguish the capillary pores detected by capillary condensation (macropores) from nanometer-scale pores (mesopores).

The decrease of dW_{0.40} shown in Fig. 84 represents a reduction of water adsorption sites in the stable C-S-H layers due to drying. This is due to the dehydration of water molecules hydrated with Ca ions on the surface of C-S-H and the generation of Si-O-Ca-O-Si bonds that stabilize the interlayer between mono-C-S-H layers (Gartner et al. 2017). This mechanism is considered to be an irreversible process involving C-S-H during the first drying step. Ca ions in the tightly stabilized C-S-H layers contain several Si-O-Ca-O-Si bonds and, consequently, the space available for further water adsorption is restricted. This trend is more or less consistent with the $S_{H2O}$ trend shown in Fig. 82. At 40% RH, the degree of desorption drops abruptly (Maruyama et al. 2015; Maruyama et al. 2016b), causing a change in the average distance between C-S-H interlayers (Bayliss 1973; Maruyama et al. 2016b). This observation is likely linked to the formation of Si-O-Ca-O-Si bonds in C-S-H and the ensuing increase in the bending strength of hcp. Schematic of C-S-H views of different size is summarized in Fig. 83.

In Fig. 84, dW_{95–100} represents the capillary pores outside the aggregation structure of C-S-H layers. The dW_{95–100} increased because capillary tension, acting on pore water, caused C-S-H sheets to coagulate. We believe that an increase in capillary pores increases the occurrence of stress concentrations under loading, which, in turn, lowers the strength of hcp. And, for dW_{0.40} above 40% RH, it cannot be concluded that the bending strength is not increased because there is no large difference in dW_{0.40}. Thus, it is clear that the volume and number of capillary pores have a direct impact on the strength of hcp in this region.

The complex trends exhibited by the bending strength and Young’s modulus under drying and heating can be explained by both the colloidal behavior (increase of strength of the solid due to drying) and porous behavior (strength as a function of pore size and volume of pores) of hcp.

The strength increase from 100% to 80% RH can be explained by the following scenario: the hydrates floating in the coarse pores coagulate while drying, owing to capillary tension acting on pore water. The hydrates are chemically combined, via bridging formations, with calcium and silicate ions that precipitate out of the pore.
water. This phenomenon was confirmed by ultrasonic S-wave pulse velocity measurements carried out by Maruyama et al. (Maruyama et al. 2014a).

Two kinds of C-S-H exist in the Portland cement paste system: low-density C-S-H (LD C-S-H) and high-density C-S-H (HD C-S-H) (Thomas et al. 1998; Tennis and Jennings 2000; Constantinides and Ulm 2004; Jennings 2008). LD C-S-H is not, strictly speaking, the same as outer-product C-S-H (OP C-S-H) (Goto et al. 1976), which refers to C-S-H that has precipitated outside the boundary of the original cement grains, as shown in Fig. 85. However, other than the C-S-H by hollow-shell formation (Kjellsen et al. 1997), a large proportion of LD C-S-H is in fact OP C-S-H. Figure 86 displays an FE-SEM image of loosely precipitated LD C-S-H formed from CaO layers wound by attaching silicate dimers (Gartner 1997; Gartner et al. 2000) under Ca-super saturation state. Based on the backbone of CaO layer, the LD C-S-H forms fibrillar shape. It is in this LD C-S-H that irreversible processes occur during the first drying process. The mechanism can be explained by Gartner, Maruyama, Chen (GMC) model (Gartner et al. 2017). The GMC model presumes that dehydration of initially wet C-S-H occurs in discrete steps, in which oxygen atoms associated with water or OH ligands around the charge-balancing Ca cations are replaced by oxygen atoms bound to silicon in the silicate groups attached to the basal CaO layer. The irreversible shrinkage associated with this water loss is ascribed to the irreversible formation of $\equiv$Si-O-Ca-O-Si$\equiv$ bonds between adjacent basal sheets.

We proceeded to confirm whether the trends we observed with W55 were similar for different cement types with varying water-to-cement ratios. Figure 87 presents the bending strength results for high-early-strength cement pastes with different water-to-cement ratios due to drying and heating. Much like W55, the bending strength of high-early-strength cement with a water-to-cement ratio of 0.55 (H55) dipped to a minimum around 40% RH. Its bending strength then increased under stronger drying (in the range below 40% RH). In the cases of H40 and H30 (water-to-cement ratios of 0.40 and 0.30, respectively), however, their minimum bending strengths did not occur around 40% RH. In addition, we did not observe any appreciable change in strength from 100% RH to 70% RH; rather, their strength increased as the drying intensity increased. This is because the distance between the cement particles decreases as the water-to-cement ratio, as well as the amount of OP C-S-H, decreases as deduced from the
data by Tennis and Jennings (2000). Probably, this is the reason that we could not confirm that the strength of high-early-strength cement deteriorated as a result of OP C-S-H coagulation and an increase in porosity in those RH range. Further investigation is needed to determine why the strength of H30 is lower than that of H40 in the high-temperature region.

Figure 88 displays the bending strength results for MF55 and MF40. Their overall behavior was similar to W55 because the 9-month curing period was not sufficient for the hydration of fly ash. Thus, MF55 and MF40 exhibited small differences in behavior with respect to the water-to-cement ratio. MF55 and MF40 cements only exhibited a large bending strength at 100% RH, which is caused by continuous fly ash hydration in wet conditions.

We summarize this section as follows. The change in strength of hcp due to heating and drying within a temperature range of 20 to 90 °C is caused by 1) an increase in number and size of capillary pores due to OP C-S-H coagulation (from capillary tension acting on pore solutions) during drying, and 2) the stabilization of mono-C-S-H layers in OP C-S-H via the formation of Si-O-Ca-O-Si bonds due to water dehydration to Ca ions within interlayers during drying. The bending strength trends observed for cement types with the same water-to-cement ratios were similar, while cement types with different water-to-cement ratios exhibited different trends. In the case of lower water-to-cement ratios, the strength increase due to C-S-H stabilization is emphasized.

4.3 Aggregate

Aggregates have a large influence on concrete properties because they occupy roughly 65% of the volume of normal-strength concrete. Sandstone, which is frequently used for concrete, is stabilized by diagenesis. Therefore, it is unlikely that the strength and Young’s modulus of sandstone aggregates are greatly altered by general heating and drying processes. In addition, since the paste found in concrete has smaller tensile strength and larger shrinkage than those of aggregates, the aggregate constrains hcp shrinkage. This, in turn, causes crack formation in hcp. Therefore, based on these two considerations, we will not be discussing changes in the strength and Young’s modulus of aggregates here. Instead, we will discuss the changes in aggregate volume. Several studies have already found that the volumetric stability of aggregates against drying is a key factor causing the drying-induced shrinkage strain of concrete (Roper 1960; Fujiwara 2008; Maruyama 2016).

In this study, twelve natural sands of siliceous to felsic sedimentary rock aggregates (sold as sandstone) available in Japan and four limestone aggregates were collected. For them, we determined length-change isotherms, thermal expansion coefficients, and mineral compositions. Polarization microscope observations, XRF, and XRD/Rietveld analyses were conducted. Then the relationships between the mineral composition and volumetric stability of the aggregates were obtained.

XRF analysis was conducted to confirm the composition of oxides. Measurements were performed through the use of a glass bead using a wavelength dispersive-type fluorescent X-ray analyzer.

Powder XRD analysis coupled with quantitative Rietveld analysis was performed to identify the mineral components in the aggregates. Specimens subjected to XRD analysis were finely ground using a vibration pulverizer. As an internal standard, 50-wt% corundum (α-Al2O3) was mixed into the specimen. The XRD instrument (D8 Advance, BrukerAXS) employed an X-ray source of Cu-K with a 40-kV tube voltage, a 40-mA tube current, a scan field of 2θ = 5–65°, a 0.02° step size, and a 5°/min scan speed. The Rietveld analysis was performed using the software application TOPAS (ver. 4.2, BrukerAXS), and the effects of preferred orientation and particle size were optimized. The targeted minerals chosen were quartz, calcite, dolomite, albite, anorthite, microcline, orthoclase, chlorite, sericite, biotite, and illite, as well as the internal standard, corundum.

The length-change isotherm and thermal expansion coefficient of the aggregate were determined by a humidity-controlled thermo-mechanical analyzer (BrukerAXS TMA4000SA with HC9700) to study the volume changes of the aggregates. The resolution of the displacement meter was 2.5 nm, and a contact load of 0.098 N was applied. Cubic specimens (6 mm on each side) were cut out and changes in their length (three orthogonal directions) were measured while considering their anisotropy. The drying-induced shrinkage was measured under a controlled environment at RHs of 98, 80, 60, 40, 20, and ~0% (Nitrogen gas flow) at 20 °C for four hours. The reference length of the length-change isotherm was selected to be a specimen in equilibrium at an RH of 98%. A quartz glass rod was used as a standard specimen to cancel the thermal strains of the thermo-mechanical analyzer. Changes in the lengths of
specimens were determined by raising the temperature from 20 to 65 °C in four hours at an RH of nearly 0% under a nitrogen gas flow. Strains in three orthogonal directions were averaged in order to take the anisotropy of the specimens into account.

Polarization microscopy was performed to evaluate the shapes of the minerals and rock aggregate particles. Each sample was cut to a thickness of ~500 μm with a diamond cutter and then adhered to a glass plate with epoxy resin. The sample was then polished with abrasive paper and diamond powder to a thickness of ~25 μm.

The XRF results of oxide composition and loss of ignition (LOI) (by TG analysis) are summarized in Table 35. They reveal that the aggregate samples are quartz and/or feldspar group rich and containing a large amount of SiO₂. Table 36 shows the results of our cross-polarized microscopy observations. All the samples were confirmed as quartz and/or feldspar group rich sandstone aggregates, but a number of them are altered tuff, shale, siltstone, and mudstone. However, since these major minerals are all common, we can develop a unified interpretation for all the samples analyzed. Figure 89 presents the results of the aggregate mineral compositions obtained using XRD. Aggregate A contained the highest amount of α-quartz (more than 90%), while aggregate L contained the least. In addition, numerous other clay minerals and feldspar group minerals were identified in aggregate L.

Figure 90 plots length-change isotherms taken from shrinkage strains averaged across the three orthogonal directions. Aggregate J shrunk the most, while aggregate A shrunk the least because of its high α-quartz content. A previous study pointed out that the presence of montmorillonite is a factor in the shrinking of aggregates (Sakota 1988), and that clay minerals are pre-

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### Table 35 Chemical composition of used aggregates by XRF analysis (mass%) and LOI (Igarashi et al. 2015).

|   | LOI | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | K₂O | TiO₂ | P₂O₅ | MnO | Total |
|---|-----|------|-------|-------|-----|-----|-----|------|-----|------|------|-----|-------|
| A | 0.61 | 91.21 | 2.86  | 1.9   | 0.46| 0.72| 0.61| 0.18 | 0.75| 0.29 | 0.03 | 0.11| 99.12 |
| B | 0.76 | 90.38 | 3.71  | 1.73  | 1.02| 0.24| 0.24| 1.19 | 0.15| 0.02 | 0.17 | 0.04| 99.5  |
| C | 1.73 | 71.85 | 13.48 | 3.89  | 2.72| 1.44| 0.41| 3.15 | 1.46| 0.32 | 0.06 | 0.04| 98.82 |
| D | 2.63 | 72.07 | 14.63 | 3.57  | 0.98| 0.95| 0.34| 2.42 | 3.22| 0.34 | 0.08 | 0.02| 98.62 |
| E | 2.43 | 75.05 | 12.23 | 2.95  | 1.73| 0.86| 0.3 | 2.65 | 2.15| 0.34 | 0.04 | 0.03| 98.33 |
| F | 3.55 | 71.79 | 12.05 | 2.3   | 4.49| 0.72| 1.02| 3.11 | 2.59| 0.28 | 0.03 | 0.03| 98.41 |
| G | 1.21 | 78.78 | 10.95 | 2.66  | 0.57| 0.4 | 0.27| 2.9  | 2.11| 0.14 | 0.01 | 0.03| 98.82 |
| H | 1.09 | 66.75 | 15.81 | 5.33  | 2.67| 1.68| 1.06| 3.04 | 2.39| 0.65 | 0.09 | 0.02| 99.49 |
| I | 1.92 | 70.26 | 14.65 | 3.7   | 1.53| 1.27| 0.35| 4.22 | 2.17| 0.41 | 0.07 | 0.09| 98.72 |
| J | 10.25 | 52.61 | 13.08 | 4.82  | 11.49| 2.03| 0.04| 3.18 | 1.48| 0.62 | 0.11 | 0.09| 99.8  |
| K | 6.44 | 60.5  | 16.37 | 5.82  | 7.1 | 2.51| 0.25| 2.84 | 2.27| 0.65 | 0.14 | 0.08| 98.53 |
| L | 5.09 | 64.32 | 15.44 | 6.47  | 4.09| 2.36| 0.49| 2.53 | 1.59| 0.59 | 0.09 | 0.14| 98.11 |

### Table 36 Results of cross-polarized microscopy observation of used aggregates after Igarashi et al. (2015). (The long side of the pictures has ~7 mm.)

| Agg. | A | B | C | D | E | F |
|------|---|---|---|---|---|---|
| Agg. | Thermally altered tuff | Shale | Sandstone | Sandstone | Sandstone | Sandstone |
| Grain size (mm) | 0.1–0.3 | ~0.1 | 1.0–3.0 | 1.0–3.0 | 0.5–3.0 | 2.0–5.0 |
| Image (crossed nicols) | | | | | | |

| Agg. | G | H | I | J | K | L |
|------|---|---|---|---|---|---|
| Agg. | Sandstone | Siltstone | Sandstone | Sandstone | Mudstone | Sandstone |
| Grain size (mm) | 1.0–3.0 | 0.5–1.5 | 0.5–1.5 | 0.5–1.5 | ~0.05 | 1.0–3.0 |
| Image (crossed nicols) | | | | | | |
assumed to be the main factor governing shrinkage.

Figure 91 plots the relationship between the chlorite content in aggregates and aggregate shrinkage at 60% RH. The findings reveal that chlorite, one of the clay minerals, has a large influence on the shrinkage behavior of these aggregates.

Figure 92 displays a representative example of a close-up cross-polarized microscopy image of aggregate D. In this figure, feldspars and quartz are present as grains (particles of rock forming minerals). Clay minerals form inside these grains, especially feldspar, through the elution of alkali metal ions, calcium, and silicate due to weathering. These substances were qualified by XRD as illite or other clay minerals. However, clay minerals that precipitate inside the feldspar or quartz grains are surrounded by stiff crystals, which prevent moisture transfer to the outside. Even if moisture transfer occurs, causing changes to the volume of minerals, the feldspar grain will not shrink. On the other hand, chlorite (precipitated by ion elution or recrystallization outside the quartz and feldspar grains) shrinks and thus shortens the distance between the grains. That is, the shrinkage of chlorite in the matrix (outside the grains) is likely to be a strong contributor to aggregate shrinkage. Therefore, it is more important to consider the relationship between the amount of clay minerals formed in the matrix and the shrinkage strain, rather than the whole clay minerals including those formed in grains in the aggregate.

Figure 93 plots the results of the thermal expansion coefficients of siliceous aggregates, which reveal large variation in their values. Among all the minerals shown in Fig. 89, quartz has the largest thermal expansion coefficient, which led us to plot the thermal expansion coefficient as a function of quartz content in Fig. 94. Here, we observe a strong correlation between the $\alpha$ -
quartz content and the thermal expansion coefficient.

It is now clear that the amounts of chlorite and α-quartz present in sandstone aggregate (which is widely used for concrete in Japan) are important factors governing its changes in volume: the amount of α-quartz is strongly correlated with the thermal expansion coefficient of the aggregate; and chlorite is strongly correlated with drying-induced shrinkage strain of aggregate particles. In order to develop a more comprehensive understanding of aggregate behavior, the authors advocate for further investigations into how changes in aggregate volume are influenced by grain size and the geometry of grains and matrix. Nevertheless, as a first approximation for concrete engineering, this work illustrates how shrinkage and thermal expansion coefficients are affected by mineral composition.

Secondly, limestone aggregates are addressed. Length-change isotherms and thermal expansion coefficients were collected for four limestone aggregates from different production areas using the same procedures as for siliceous to felsic sedimentary aggregates. In many cases, we observed small total shrinkage strains, as shown in Fig. 95. For instance, the maximum shrinkage was 60 μ under nitrogen flow. The results in Fig. 96 also show low thermal expansion coefficients (5 μ/°C or less). Although limestone is mainly composed of calcite, it tends to be mixed with dolomite and clay minerals, particularly for limestone produced in Europe. Limestone containing clay minerals will exhibit greater shrinkage (Roper 1960). However, since limestone aggregates used for concrete in Japan are likely to be crystalline and of a higher purity (calcite), they tend to exhibit low dry shrinkage strains and low thermal expansion coefficients.

Table 37 Kinds and properties of used aggregates (Maruyama et al. 2014).

| Notation | Properties | Agg. notation in 4.3 |
|----------|------------|----------------------|
| C-G1     | Limestone; max. size, 20 mm; density, 2.71 g/cm³; absorption, 0.24%; solid volume ratio, 62.3%; F.M., 6.65. | N |
| C-G2     | Felsic sandstone; max. size, 20 mm; density, 2.64 g/cm³; absorption, 0.89%; solid volume ratio, 62.5%; F.M., 6.70. | D |
| C-G3     | Altered tuff; max. size, 20 mm; density, 2.70 g/cm³; absorption, 0.65%; solid volume ratio, 61.3%; F.M., 6.68. | A |
| C-G4     | Altered tuff; max. size, 13 mm; density, 2.70 g/cm³; absorption, 0.57%; solid volume ratio, 59.8%; F.M., 6.25. | A |
| C-G5     | River gravel (felsic sandstone); max. size, 20 mm; density, 2.65 g/cm³; absorption, 0.90%; solid volume ratio, 64.3%; F.M., 6.76. | G |
| S        | River sand; density, 2.57 g/cm³; absorption, 2.51%; solid volume ratio, 68.3%; F.M., 2.60 | |

Fig. 94 Relationship between α-quartz content and thermal expansion coefficient.

Fig. 95 Length-change isotherms of limestone aggregates (average of strains in three orthogonal directions).

Fig. 96 Thermal expansion coefficients of limestone aggregates (average of strains in three orthogonal directions).
4.4 Concrete

4.4.1 Compressive strength and Young’s modulus

The compressive strength and Young’s modulus of concrete are known to vary with drying and heating (Naus 2010). However, the previous experimental data show large variation because samples did not attain equilibrium and because aggregates have a large impact on the properties of concrete. Cement pastes with colloidal components take a longer time to reach equilibrium than those containing aggregates. With regards to volumetric changes of concrete components, cement paste and mortar exhibit larger shrinkage than coarse aggregate particles. The thermal expansion coefficient of cement paste ranges from 15 to 30 μ/°C (Maruyama and Teramoto 2011; Maruyama and Teramoto 2013; Maruyama et al. 2014c), which is greater than that of aggregates (Johnson and Parsons 1944; Rosnnolrz and Surru 1949; Mukhopadhyay et al. 2007). Consequently, the mismatch in volume change between the paste/mortar and aggregates may result in concrete damage when heated.

In this study, concretes were prepared with different types of original rocks having the same volume of coarse aggregates. Aggregates were selected by considering their resistance to mortar shrinkage, aggregate shrinkage, and changes in aggregate size. The concrete samples were then dried under different RHs or heated at different temperatures to reach equilibrium. The changes in their physical properties were confirmed after drying or heating.

C-G1 is limestone, and a minute crystalline structure has been confirmed by cross-polarized microscopy observation (Fig. 97). C-G2 is sandstone with a grain size of ~2 μm for quartz and feldspars grains surrounded by a chlorite matrix. C-G3 and C-G4 are thermally altered tuff with quartz grains of ~0.1 μm. The maximum sizes of C-G3 and C-G4 were 20 mm and 13 mm, respectively. C-G5 is river gravel, whose original rock is sandstone. The constituent grains, chlorite content, and degree of shrinkage of C-G5 are larger than those of C-G2.

The results of the phase composition analysis of the aggregates according to the powder XRD/Rietveld analysis are shown in Fig. 98. Limestone (C-G1) and thermally altered tuff (C-G3 and C-G4) were very pure (> 90 wt%) in calcite and quartz, respectively. Feldspars, clay minerals, and mica were found in both C-G2 and C-G5 (sandstone specimens). Figure 99 plots the length-change isotherms and thermal expansion coefficients of each aggregate, while Fig. 100 compiles results for the Young’s modulus and Poisson’s ratio. The Young’s modulus and Poisson’s ratio are dynamic values obtained from ultrasonic pulse velocity measurements on the aggregates under surface dry and saturated condition.

Table 38 summarizes the mixture proportions of concrete (G1–G5) and mortar (M), as well as the results of the slump and air content test in a fresh state. The unit water, cement, and fine aggregate content were kept constant. The amount of air was adjusted by adding an air-entraining (AE) agent, yielding results that were

| Mixture | W/C (% | Slump (cm) | Air (%) | Unit mass (kg/m³) |
|---------|---------|------------|---------|-------------------|
| G1      | 55      | 15.0       | 3.6     | 160 291 853 1009 (C-G1) |
| G2      | 55      | 13.5       | 3.9     | 160 291 853 979 (C-G2) |
| G3      | 55      | 13.0       | 3.8     | 160 291 853 1013 (C-G3) |
| G4      | 55      | 9.5        | 3.7     | 160 291 853 1013 (C-G4) |
| G5      | 55      | 13.5       | 3.9     | 160 291 853 994 (C-G5) |
| G3H     | 40      | 9.7        | 4.3     | 175 438 635 1088 (C-G3) |
| M       | 55      | 24.5       | 6.5     | 256 468 1365 - |

Fig. 97 Cross-polarized microscopy observation for C-G1 (×100, The long side of the picture has ~7 mm.).

Fig. 98 Phase compositions of used aggregates obtained by XRD/Rietveld analysis.
approximately constant across all the concretes. High-
early-strength Portland cement paste (P) was used (Ta-
ble 39, the same as H in Section 4.2).

Concrete specimens φ50 × 100 mm³ in size were pre-
pared as the diameter of the cylindrical specimen
needed to be more than three times as large as the
maximum aggregate particle size. However, based on
data by Kishitani et al. (1982), we estimated that a
φ100-mm specimen would take over 300 days to reach
equilibrium. Due to this time limitation, the sample di-
meter was reduced to 50 mm to shorten the time taken
to attain equilibrium. Since this caused large variations
in our data, five replicates were used for each drying
and heating run.

Specimens were placed into disposable tin molds and
sealed with aluminum adhesive tape. The specimens
were stored in a thermostatic chamber kept at 20±2 °C
for 56 days. The samples were then dried under 80, 60,
40, and 20% RH at 20±2 °C in desiccators or heated at
40, 50, 60, 70, 80, and 90±1 °C in thermostatic cham-
bers. The experiments were carried out in an ordinary
laboratory environment with temperatures ranging from
20–25 °C and RHs from 30–70%. For temperature-
controlled runs, the air in the chamber would equilibrate
with ambient air.

In order to evaluate the effect of sample drying,
changes in the mass and length of two representative
specimens were collected for each drying condition.
Metallic wire gauges with a 30-mm reference length
were attached to the specimen surface and a total of four
points were measured and averaged.

In addition, four 5-mm-thick disc specimens were cut
out from each concrete specimen and stained their sur-
face with white and black spots. By capturing 16-bit
images using a digital camera before and after drying,
the maximum and minimum principal strain distribu-

| LOI (%) | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | Na₂O | K₂O | Cl⁻ | Total |
|---------|------|-------|-------|-----|-----|-----|------|-----|-----|-------|
| 2.3     | 20.04| 5.21  | 2.87  | 64.9| 1.46| 2.21| 0.14 | 0.34| 0.019| 99.489|

Table 39 Chemical composition of used cement (mass%) (Maruyama et al. 2014).

Fig. 99 Volume change properties of aggregates: (a) thermal expansion coefficient, and (b) length-change isotherm.

Fig. 100 Dynamic modulus of aggregates: (a) Young’s modulus, and (b) Poisson’s ratio.
tions were measured via a digital image correlation method (DICM). Through this analysis, damage in the concrete was calculated based on a maximum principal strain distribution provided by Maruyama and Sasano (2014).

The concrete specimens were dried for a period of 150 days. The results of concrete G3, which took the longest time to reach equilibrium, are examined as a representative case (Fig. 101). G3 reached equilibrium in all cases except under 20% RH. In this case, the change in specimen mass was evaluated by extrapolation using an exponential function, which confirmed that 97% of the specimen was dry.

Figure 102 presents the results of shrinkage (above) and the results of water content (below) of different concretes. The water content of concrete was almost identical for each drying or heating condition. Slight differences in the water content are believed to be due to the different water absorption capacities of the various types of aggregates used. Mortar experienced the greatest shrinkage strain, while concrete shrinkage of G2 and G5 (shown in Fig. 102 above) experienced larger strains than the other concrete cases. On the other hand, shrinkage of C-G1 and C-G3 underwent near-zero shrinkage (Fig. 99), but the shrinkage of concrete was different. The difference in shrinkage must be attributed to the difference of coarse aggregates. This arises from the formation of aluminates hydrates, such as monocalcium, at the surface of the C-G1 limestone aggregates. The densification of the interfacial transition zone (ITZ) reduces the shrinkage of concrete (Monteiro and Mehta 1986; Ping and Beaudoin 1992).

The DICM can quantify damage in the mortar matrix of concrete due to restriction of coarse aggregates subject to drying. Figure 103 displays an example DICM measurement of G5 heated at 70 °C. G5 contains river gravel, whose coarse aggregates exhibit non-uniform shrinking behavior. Some aggregate particles shrunk drastically, which, in turn, led to crack widening around those aggregates. The DICM can detect such non-uniform cracking behavior in concrete sections. Although not shown here, G2, whose aggregates shrunk more than those of G1 and G3, displayed cracks in the mortar matrix that were clearly small. This cracking...
trend in the concrete section was quantified using a cracking index defined by:

\[ D_c = \sum_i \varepsilon_i \Delta A_i > \sum_i \varepsilon_i \Delta A_i \]

(12)

where \( D_c \) is the cracking index, \( \varepsilon_i \) is the maximum principle strain of unit cell \( i \), \( \Delta A_i \) is the area of the DICM unit cell (which is a function of the step value and whose area is defined step × step), and \( n_i \) is the number of cells used in the DICM analysis. In our analysis, 1 pixel = 0.041 mm, and so \( \Delta A_i = 1.68 \times 10^{-3} \) mm².

Figure 104 presents the results of the damage index. From this figure, it is observed that damage to concrete occurred starting from the sealed condition to 60% RH. From that point on, the damage index did not increase until 20% RH. In the heating experiments, the damage index increased gradually from 40 °C to 70 °C, followed by a steep increase in damage from 70 °C to 90 °C. Only G5 exhibited a steep increase in its damage index from 50 °C to 90 °C. The damage indices of G5 and G2 were almost identical to that of M in drying conditions. Therefore, the damage sustained by G5 and G2 in concrete from the sealed condition to 40–60% RH was sufficiently small and comparable to that of M because of their shrinking aggregates.

The ratio of the compressive strength after drying or heating (Fc) to that of the initial sealed condition (Fco) is plotted to dried or heated conditions for evaluating the effects of aggregate type, aggregate size, and water-to-cement ratio on the strength change. Figure 105 displays the compressive strength ratios of the concrete specimens along with the W55 results (from the bending experiments discussed earlier) denoted as Fb/Fbo. In all cases, the compressive ratio dipped to a minimum of ~20% or 40% RH at 20 °C. Under stronger drying conditions, however, the strength of the concrete specimens recovered. Similarly, heating the specimens at 60 °C led several concrete samples to a complete recovery (relative to the initial strength at the sealed condition).

Figure 106 compares the concrete specimens containing aggregates with a maximum size of 20 mm and a water-to-cement ratio of 0.55. The strength of G2 and G5, which contain coarse aggregates that typically shrink, increased at 80% and 60% RH. On the other hand, G1 and G3, which contain typically non-shrinking coarse aggregates, showed a reduction in strength. Cement paste increased in strength as well. Consequently, owing to the lesser damage caused by shrinking aggregates, the strength of G2 and G5 increased, owing to the nature of the hcp. For G1 and G3, however, the damage due to a mismatch in volumetric change between coarse aggregates and mortar increased and exceeded the strength increase caused by the hcp. Therefore, a reduction in strength occurred. Our findings reveal that the property changes of concrete due to drying are strongly influenced by the volumetric stability of its aggregates.

From 60% to 20% RH, the strength of concrete decreased and the damage index did not increase significantly. Consequently, the impact of the reduction of hcp strength became dominant in this region. Further drying and heating resulted in an increase in concrete strength. The damage index and hcp strength both increased from 40 °C to 90 °C. Here, the strength of concrete increased.
by ~10%. Even though the damage index increased, the strength increase of hcp was still dominant. The rise in damage index was caused by crack opening under further mortar shrinkage, which, however, has a negligible effect on the stress passes bearing a compressive load. Therefore, the strength increase of hcp, which is located in the stress-bearing passes, has a dominant impact on the stress passes bearing a compressive load. The stress-bearing passes, determined by crack formation around aggregate particles under drying, remained almost fixed from 100% to ~60% RH.

**Figure 107** presents the results for G3 (Gmax = 20 mm), G4 (Gmax = 13 mm), and M (Gmax = 5 mm). The sample P was included to understand the impact of aggregate particle size on the strength change under drying and heating. As shown here, larger aggregate particle sizes are associated with a strength reduction in the sealed condition to 60% RH region. It is deduced that crack formation around aggregates is the dominant factor accounting for this decrease in strength. The strength ratio increased from a local minimum value to the heating condition at 60 °C, for which no significant differences was observed between G3, G4, and M (0.10, 0.11, and 0.12, respectively).

**Figure 108** summarizes the effect of the water-to-cement ratio on the strength change due to drying and heating. For G3H (water-to-cement ratio of 0.40 with coarse aggregates of C-G3), an increase in strength from sealed condition to 80% RH was observed. The local minimum value occurred around 40% RH (20% RH for a water-to-cement ratio of 0.55). The strength decreased continually as it was heated at higher temperatures. Although this may have been caused by a larger amount of hcp in G3H, the validity of this mechanism has not been confirmed. Further studies are needed to investigate cases with lower water-to-cement ratios.

Our findings are consistent with the a previous study by (Kishitani et al. 1982). They also observed a complicated trend for concrete heated from 50 °C to 300 °C over a period of 1000 days. The concrete strength increased initially but then decreased. It increased again and finally decreased monotonically. Based on the interrelationships between concrete, mortar, and paste strength in equilibrium, and the degree of drying and heating, it is concluded that the colloidal and porous material properties of hcp, as well as the damage created by the difference in volume change between the coarse aggregate and mortar, cause the strength of concrete to change. **Figure 109** presents a schematic depicting the mechanism governing the change in concrete strength due to drying and heating.

The results of this study have shown that, under high-temperature conditions, the strength of concrete drops by less than 15% (within a specific drying range be-
After considering the variation in data, we propose that a strength margin of 15% is adequate. This value is almost consistent with the strength criteria listed in ACI349-13 (American Concrete Institute 2013).

Next, the Young’s modulus of concrete is addressed. Figure 110 plots Ec/Eco (ratio of Young’s modulus after drying (Ec) and initial Young’s modulus (Eco) at the sealed condition) against the drying and heating conditions. The results demonstrate that the Young’s modulus of concrete decreased by 70% even under an RH of roughly 60% RH. G1 and G3, which contain non-shrinking aggregates, exhibited a large reduction ratio for the Young’s modulus. After drying, cracks in mortar form in the concrete, owing to the difference in volume changes between the mortar and aggregate. This leads to void formation in the concrete via shrinkage-induced crack opening, which, in turn, causes the nominal Young’s modulus to decrease, owing to a reduction in the solid stress-bearing area.

Because we only varied the type of coarse aggregate used in these experiments, this difference in coarse aggregates must account for the variations in Ec/Eco ratios that we observed. We introduce the concept of “gap strain” to account for the reduction in Ec/Eco based on the aggregates’ restraint role for mortar shrinkage. The gap strain refers to the strain difference between the shrinkage strain of mortar and concrete. It represents the pore volume caused by crack opening in the mortar due to the restraint of mortar shrinkage. The results are shown in Fig. 111, which demonstrate that drying and heating decreases the Young’s modulus of concrete through pore accumulation by crack opening in mortar. Large cross-sectional members gradually lose their stiffness, as indicated by a reduction in Young’s modulus.
modulus due to drying. This, among other reasons, causes changes in the natural frequencies of buildings (Maruyama 2016). More data is necessary, however, to properly understand this problem.

### 4.4.2 Tensile strength

The damage accumulated inside concrete, caused by a difference in the volume changes of mortar and aggregates under drying, also affects its tensile strength. Table 40 lists the materials used in this experiment and Table 41 outlines the formulations used for mortar and concrete as well as the results of a fresh property test.

Because aggregate size affects the length change and damage sustained around aggregates during drying, coarse aggregates with grain sizes of 5–10 mm, 10–15 mm, and 15–20 mm in equal proportions by mass were used. The concrete specimens are designated as LS-Mix for concrete with crushed limestone aggregate, and SS-Mix for concrete with crushed sandstone. The main different property of used aggregates is shrinkage behavior (Fig. 112). In order to evaluate the effect of coarse aggregate size, concretes containing coarse limestone aggregate (GL) with particle sizes of 5–10 mm, 10–15 mm, and 15–20 mm were prepared; these concrete specimens are designated as LS-S, LS-M, and LS-L, respectively. Concrete containing coarse sandstone aggregate (GS) of the same sizes as those for the LS series are designated as SS-S, SS-M, and SS-L.

The same volumetric proportions of coarse aggregate, water, cement, and fine aggregates were used for all concrete batches. Therefore, the slump and air content were not adjusted. We added, however, a viscosity agent to suppress bleeding in order to obtain uniform concrete. In addition to concrete, mortar (M) was prepared that had the same proportion of paste and fine aggregate in the concretes. The eight types of concrete (with different
types of coarse aggregates were poured into lightweight cylindrical molds ($\phi 100 \times 200$ mm) and demolded after two days. Standard water curing was carried out for up to one year in a saturated aqueous solution of calcium hydroxide at a constant temperature of $20 \pm 1 ^\circ$C. The $\phi 100 \times 200$ mm mortar and concrete cylinders were then cut with a diamond cutter to a thickness of 9 mm to produce $\phi 100 \times 9$ mm specimens. The specimens were dried at a constant temperature of $20 ^\circ$C and RHs of 95% RH, 80% RH, 60% RH, 43% RH, and 20% RH. The concrete specimens were also heated in a temperature-controlled chamber at 40 °C, 65 °C, and 90 °C. To eliminate the effect of carbonation during heating, we heated the sample in a closed system at room temperature in equilibrium with a saturated sodium hydroxide solution. When the mass of the specimen changed by 0.03% or less over 24 hours, it is assumed that the system reached equilibrium. The maximum drying or heating period lasted ~40 days.

Before conducting the splitting tensile strength (Brazilian test) experiments, the mass and diameter of each sample were recorded before and after the drying or heating steps. The resolutions of the mass balance and displacement meter were 0.001 g and 0.5 $\mu$m, respectively. For preliminary experiments, the thickness of the disk specimen did not affect the results of the splitting tensile strength tests (Lin et al. 2015). Five specimens were used for each test condition.

**Figure 113** plots the relationship between the shrinkage strain and the drying and heating conditions of the LS-Mix, SS-Mix, and M. The shrinkage strain of the SS-Mix was greater than that of the LS-Mix for each drying condition because GS is a shrinking aggregate. **Figure 114** presents the results of the splitting tensile strength tests of the LS series (LS-L, LS-M, LS-S, LS-Mix) and the SS series (SS-L, SS-M, SS-S, SS-Mix) with respect to different drying and heating conditions. The splitting tensile strengths of the concretes increased from the saturated condition to 80% RH, followed by a
I. Maruyama, O. Kontani, M. Takizawa, S. Sawada, et al. / Journal of Advanced Concrete Technology Vol. 15, 440-523, 2017

decrease in strength from 80% RH to 43% RH. Their tensile strength rose again from 43% RH to 11% RH. For the heating tests, the tensile strength of the LS series declined gradually from 40 °C to 90 °C, while the tensile strength of the SS series remained essentially constant from 40 °C to 90 °C.

Figure 115 displays the ratio of the splitting tensile strength (Ft) after drying to the splitting tensile strength at the saturated condition (Fto) of LS-Mix, SS-Mix, and M. As shown here, the Ft/Fto ratios of mortar and concrete diverge below 80% RH. The most important observation from Figure 115 is that the tensile strength reaches its maximum at 80% RH which is almost corresponding to the RH region in which hcp showed local maximum of bending strength. However, cement paste exhibits its maximum bending strength at heated conditions of around 50–60 °C while tensile strength of concrete showed gradual decrease as the temperature is increased. This trend is contrary to what we observed for compressive strength from the viewpoint of crack formation. It is reasoned that the crack opening process, rather than crack formation under drying, has a large impact on the splitting tensile strength.

Aggregate shrinkage influences the role of aggregates in restraining drying-induced mortar shrinkage in concrete. If the shrinkage of aggregate particles is small, then the ensuing damage to the concrete is large. This, in turn, impacts the splitting tensile strength. Since this scenario is equivalent to the Young’s modulus of concrete, the gap strain can be used to account for this behavior. Figure 116 plots Ft/Fto as a function of the gap strain. In both cases of LS-Mix and SS-Mix, the Ft/Fto ratios reveal similar trends. This indicates that the gap strain, which is representative of the pores created by crack opening (due to the role of aggregates in restraining drying-induced mortar shrinkage), is the main factor causing the decrease in Ft/Fto due to drying.

Similar to the compressive strength and Young’s modulus of concrete, the change in the splitting tensile strength due to drying and heating can be explained by the colloidal nature of hcp and the damage caused by the difference in volume change between the mortar and coarse aggregates.

5. Development of numerical code

5.1 Computational Cement-Based Material Model (CCBM)

This section is based largely on an article by Maruyama and Igarashi (2015).

The Computational Cement-Based Material Model (CCBM), developed by Nagoya University in 2005, is a computational simulation model used to predict the spatial and temporal changes to the physical properties of concrete members. The CCBM was created to evaluate the performance of an existing reinforced concrete member. The proposed simulation model includes models for the rate of hydration of cement minerals, phase composition, and hygro-thermomechanical properties of cement paste (i.e., compressive strength, Young’s modulus, Poisson’s ratio, thermal expansion coefficient, autogenous shrinkage, drying shrinkage, heat capacity, heat transfer coefficient, water vapor sorption isotherms, and water transfer coefficient). A structure of CCBM is shown in Fig.117. The spatial distribution and temporal changes in concrete properties are computed by coupling these models with heat and water transport equations. Maruyama and Igarashi (Maruyama and Igarashi 2015) validated these models with existing experimental data. The most advanced aspects of CCBM (models for moisture treatments, volume change, and concrete strength prediction) are briefly introduced here.

The sorption isotherm is one of the most important properties of hcp, which is determined by the C-S-H because of its large surface area and major hydrates of Portland cement. Previous research has demonstrated that different types of matured hcp with the same water-
to-cement ratios normalized by $S_{H_2O}$ exhibit nearly identical desorption isotherms (Maruyama 2010; Maruyama and Igarashi 2011). Furthermore, the adsorption branch process and sorption amount at 40% RH in the desorption process are correlated with $S_{H_2O}$. Consequently, the sorption isotherm of hcp is modeled as a function of $S_{H_2O}$ and total water absorption. As shown in Fig. 82, $S_{H_2O}$ is affected by long-term drying and heating. Fig. 118 displays a schematic of the isotherm model and Fig. 119 compares the model with the desorption isotherm of hcp under different temperature conditions.

Because capillary tension theory is unable to account for the hysteresis of drying-induced shrinkage strain, another theory was proposed. Previous studies found that the shrinkage strain of matured cement paste was a function of the incremental statistical thickness of ad-

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**Concrete physical properties**

![Concrete physical properties diagram](image)

**Fig. 117** Structure of CCBM (Maruyama and Igarashi 2015).

**Fig. 118** Schematic of water vapor sorption model of hcp.

**Fig. 119** Example of model of hcp under different temperature condition.
sorbed water films (Badmann et al. 1981), as shown in Fig. 120 (Maruyama 2016). Above 40% RH, the shrinkage associated with the first desorption process has a linear relationship with the incremental statistical thickness of adsorption. In addition, the slope of the linear trend for conditions under 40% RH is similar among specimens with different water-to-cement ratios. These findings indicate that the shrinkage strain of hcp under the first desorption step, which is inherently accompanied by irreversible C-S-H alteration, can indicate how much water is removed from C-S-H. These characteristics were used to predict the drying shrinkage of hcp. An example is shown in Fig. 121, where the model successfully reproduces the shrinkage strain hysteresis. The thermal expansion coefficient (TEC), which is also an important property for changes in hcp volume, is affected by the drying process (Mayer 1950). The change in TEC due to drying and heating can be predicted using a shrinkage model with the change in the statistical thickness of adsorption. Figure 122 compares the results obtained alongside experimental data.

The compressive strength of hcp is modeled according to the gel-space ratio, which was originally proposed by Powers and Brownyard (1946-1947). This model considers the density difference of C-S-H based on its formation temperature. An example of early-age strength development with and without elevated temperature is shown in Fig. 123 with calculation results.

Change in concrete strength under drying or heating can be predicted using this hcp strength model and by predicting the volume changes of the hcp and aggregate. The latter model receives the shrinkage and TEC as inputs. Figure 124 provides an example of Fe/Fco calculated using this model along with experimental results for concrete containing coarse limestone aggregate.

The original CCBM is able to model the concrete strength under the typical environmental conditions experienced by concrete structures. The CCBM can also evaluate the moisture transfer coefficient, heat capacity, and thermal conductivity. Since CCBM uses a finite-element method or finite-differential method, it can model the distribution of properties within a concrete
5.2 Damage Evaluation for Irradiated Concrete (DEVICE)

This section builds upon the work of Maruyama et al. (2016a). Considering the radiation conditions encountered by concrete, it was decided to employ a deterministic transport theory for the present study. In the ANISN code, originally developed in Oak Ridge National Laboratory (ORNL) (Engle Jr. 1967), the Boltzmann transport equation, which is an integro-differential balance equation for the conservation of radiative energy, was calculated using a discrete-coordinates (Sn) approximation by discretizing the spatial, angular, energy, and time variables. In this study, we coupled this 1-dimensional (1D) ANISN code with the 1D-FEM CCBM and named the resulting code “DEVICE” (for “Damage Evaluation for Irradiated Concrete”).

The neutron and gamma-ray flux distributions at the inner concrete surfaces are the inputs to the model. ANISN calculates the neutron and gamma-ray flux distributions in concrete members by using the spectra of radiation energy at the inner surface of the concrete and considering the cross-sections of the concrete members based on the material compositions and temperature. The calculations executed in ANISN involve the P3-S16 approximation (The PL represents that the L-th order Legendre polynomial is used to approximate the directional distribution of the scattering in the radiation transport equation. The SN means that N sets of Gaussian quadrature are used to discretize the angular term of the transport equation. For the P3-S16 approximation, we consider the Legendre expansion up to the third order for scattering angles, and discretize the transport equation by dividing an angle into 16 quadrature.) and the multi-group cross-section library V7-200N47G in SCALE6 with 200 neutron groups and 47 gamma-ray groups. Figure 125 presents a flowchart outlining how to introduce the ANISN to the CCBM, while Fig. 126 shows a schematic of the DEVICE calculation flow.

The impact of gamma rays is discussed based on the literature review presented in Table 3. Chapter 3 presents experimental results that illustrate the impact of gamma rays. Even though gamma radiation exceeding

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Fig. 125 Detailed process of introduction of ANISN-ORNL to CCBM.
~1.0 × 10^{12} \text{ Gy} affects the covalent Si-O bond (Douillard and Duraud 1996, Ichikawa and Kimura 2007), this value differs largely from the expected value in nuclear power plants (Table 1). Therefore, it is reasoned that concrete exposed to gamma rays can be treated as having undergone heating, drying, or both.

Gamma rays produce H₂ and O₂ gas from concrete via radiolysis of the pore solution, leading to gas pressure buildup in the pore system. This, in turn, may affect its vapor transfer properties. Furthermore, the gamma rays may enhance the solution-precipitation process of cement hydrates through radiolysis of the hydrates. This would enhance the healing and creep phenomena of the concrete system. However, having insufficient information, these aspects are not considered.

Since neutrons are electrically neutral, they do not exhibit any ionizing effects. Thus, neutrons always interact with a nucleus via scattering and absorption.

Cement hydrates always coexist with evaporable water in concrete exposed to the environmental conditions associated with LWRs. The cement hydrates are present in a state of equilibrium between dissolution and precipitation. Impinging neutrons can collide with atoms in the cement hydrates, displacing atoms from the hydrates. However, the dissolution-precipitation equilibrium plays a healing role in mitigating neutron damage in cement hydrates. In addition, C–S–H typically has a short-period recursive structure that cannot be detected through powder XRD in the layer-piling direction.

Therefore, structural defects may not significantly affect its physical properties. Radiation-induced changes in the strength of hcp have not been confirmed experimentally, as shown in Section 2.3 and relevant literature (Gray 1971; Elleuch et al. 1972).

As stated in the previous section, even while aggregates are well crystalized, there is evidence that quartz expands as a result of radiation. Previous neutron irradiation experiments on quartz revealed nearly identical densities in its final state (Wittels and Sherrill 1954; Primak et al. 1955; Primak 1958; Bykov et al. 1981; Bonnet et al. 1994), with a 15–18% reduction and a linear expansion of approximately 5–6%.

Damage accumulation and volume expansion of quartz are well described by the nucleation and growth model proposed by Avrami (1941) (Weber 1990, Harbsmeier and Böske 1998, Field et al. 2015). In the DEVICE, the equation (3) for predicting the quartz expansion is applied. In this case, threshold of fast neutron (E > 0.1 MeV) is considered, and equation (13) is used instead of equation (4). And based on the aggregate expansion considering the volumetric quartz content, concrete expansion strain is evaluated by using equation (8), while equation (14) and equation (15) are applied instead of equation (11).

\[ K(T) = 0.23 \times 10^{20} \times \frac{\text{Exp}(2000/298)}{\text{Exp}(2000/T)} \]  

(13)

![Fig. 126 Schematic of calculation flow of DEVICE and physical properties of concrete evaluated by DEVICE.](image)
\[
\varepsilon_{\text{agg}} = \varepsilon_{\text{agg,sh}} + \varepsilon_{\text{agg,T}} + \varepsilon_{\text{agg,ITZ}} + \varepsilon_{\text{agg,ITZ}}
\]

(14)

\[
\varepsilon_{\text{agg,ITZ}} = \frac{d_{\text{ITZ}}}{R_{\text{agg}}}
\]

(15)

where \(\varepsilon_{\text{agg,ITZ}}\): representative strain of the ITZ effect compensating the damage around the aggregates caused by drying (e.g., if the average radius of a coarse aggregate \(R_{\text{agg}}\) is 10 mm and the ITZ apparent thickness \(d_{\text{ITZ}}\) is 5 μm, then \(\varepsilon_{\text{agg,ITZ}}\) is calculated to be 500 μ);

\(\varepsilon_{\text{agg,sh}}\): drying shrinkage strain of the aggregates;

\(\varepsilon_{\text{agg,T}}\): thermal strain of the aggregates.

As previously discussed in 2.4.2, the expansion strain of the aggregate is considered as a damage index triggered by the expansion of the aggregate. We can apply the following lower boundary for the relationship between \(F_c/F_{co}\) and \(\varepsilon_c\):

\[
40.3 + 0.7 (1.4 \times 10^{-18} \varepsilon_c)
\]

(16)

The scatter in the data given in Fig. 54 is probably due to a confinement effect, which generally occurs in a section of the concrete structure. However, this confinement effect has not yet been quantitatively characterized, and hence the lower boundary above can be treated as a safety limit. In other words, the DEVICE model is able to calculate the worst-case scenario.

First, DEVICE was validated using experimental data from the decommissioned Japan Power Demonstration Reactor (JPDR), which was the first nuclear reactor that generated electrical power in Japan in 1963 (Idei et al. 1990). A simulation of the concrete biological shield (CBS) of JPDR was performed by considering internal heat, moisture, and radiation transport, as well as operation and decommissioning histories. The maximum fast neutron fluence was less than \(10^{18}\) n/cm\(^2\). Figure 127 presents a schematic of the CBS and the locations of the core sampling data. Figure 128 displays the simulation results of concrete strength as a function of fast neutron fluence with core-sampling data. As it is shown, the absolute value of strength distribution was well reproduced, while the deterioration due to neutron could not be confirmed because of the low level fluence.

The most important factors for soundness assessment were identified based on a parametric study on the CBS in a commercial PWR by DEVICE (Fig. 129). The first of the factors is the moisture transport on the surface of the CBS. If moisture on the CBS surface evaporates easily, then the loss of water will lead to stagnation in cement hydration. Exposure to drying conditions early on in the lifespan of concrete greatly affects the evolution of concrete strength in the inner section of the CBS. When a steel liner is present on the surface of the CBS, the concrete is sealed, allowing hydration to continue. However, if it is exposed to air or other drying conditions, then stagnation will occur, which, in turn, reduces the strength margin of concrete.

The second important factor is the temperature of the inner surface of the CBS. High temperatures cause a buildup in vapor pressure, allowing moisture to travel from the inside to the outside. This moisture movement alters the hydration process in the CBS. In addition, the temperature of the inner surface of the CBS has a large influence on the neutron-induced aggregate expansion rate. Higher temperatures accelerate thermal healing and reduce the rates of aggregate expansion. This slows down concrete degradation.
While DEVICE can shed light on how the concrete strength develops in CBS or other concrete members exposed to radiation, several limitations persist. Firstly, although the expansion of aggregates has been studied experimentally, the sensitivity of other rock-forming minerals, such as the feldspar group, lack quantitative characterization. This information is important for modeling aggregate expansion. Furthermore, the impact of thermal healing is still not understood and requires further investigation. The DEVICE model relies on concrete data obtained by accelerated irradiation experiments and it is thus possible that DEVICE overestimates aggregate expansion. Improved knowledge of aggregate expansion is needed to produce a more realistic evaluation of the expansion of aggregates. Secondly, the DEVICE model predicts the properties of concrete in a stress-free condition, which should produce the worst-case scenario. In real structures, however, concrete expansion in some parts of a member may cause additional cracking due to self-stress distribution in another part of the member. This risk is always kept in mind during safety evaluations. Finally, DEVICE is limited to predicting the strength of concrete and its Young’s modulus. However, bond behavior is very important when evaluating the performance of structural members, especially for shear walls. Therefore, further investigation of the concrete–rebar interface is necessary to evaluate structural performance. After the investigation, the expansion and strength of concrete may be used as key indices for the soundness evaluation.

6. Proposal for soundness assessment procedure

6.1 Soundness assessment procedure

Based on the experimental results presented in this project and the results of the parametric studies using DEVICE, we propose a soundness assessment procedure for concrete members subjected to a radiation environment. One of the aspects of this work focuses on validating the current reference values for neutron fluence and gamma-ray dose. Assessments based on these reference values are important as the dose and the fluence can both be predicted with high accuracy. It is also within the scope of this research to identify the various scales present within the soundness assessment process, such as the evaluations of concrete strength and member structural performance under radiation conditions that exceed the reference values.

With this in mind, we propose a new 3-step soundness assessment procedure in Fig. 130. The first step involves evaluating the current radiation conditions against the reference values. In the second step, the concrete’s compressive strength is evaluated against the required design strength. In the third step, the performance of the affected concrete member(s) is evaluated. Even if the structural performance does not satisfy the required performance, it is still possible to evaluate the structural performance by computing the structural performance of the structure. We will not, however, discuss this scenario here.

6.2 Reference value for strength degradation

The current reference values are $1 \times 10^{20}$ n/cm$^2$ for fast neutrons (> 0.1 MeV) and $2 \times 10^5$ kGy for gamma rays. Based on our experimental research, gamma rays do not cause concrete degradation. In fact, concrete exposed to gamma radiation increases in strength. Based on our experimental research, gamma rays do not cause concrete degradation. In fact, concrete exposed to gamma radiation increases in strength. In addition, the physical properties of hcp were increased, and those of aggregates did not change dramatically; rather, the observed changes were small enough that the properties of
concrete showed no degradation. Theoretically, gamma radiation causes metamictization in rock-forming minerals, but the required doses for metamictization differ greatly from the dose released during the lifetimes of nuclear power plants. Therefore, the reference value for gamma rays can be raised to a very large value, or even abandoned entirely. Before implementing this recommendation, however, it is necessary to verify the reproducibility of our experimental results.

In this study, it was confirmed that neutron fluence causes strength degradation in concrete. This is mainly due to aggregate expansion caused by the metamictization of rock-forming minerals. Among the rock-forming minerals, quartz was the most sensitive to neutrons. We also observed the evidences of expansion of feldspar-group minerals. In addition, hcp exhibited an increase in strength and shrinkage. Due to the mismatch in volume change, crack opening in the concrete causes the strength and Young’s modulus to deteriorate.

However, a threshold energy level was not established for neutron-induced metamictization, owing to limited knowledge on the metamictization process of rock-forming minerals. Therefore, we employed the de facto standard value of 0.1 MeV. In addition, as discussed in Section 2.4.1, the effects of thermal healing have not been elucidated. Therefore, there remains the possibility of overestimating the degree of aggregate expansion and the resultant degradation of concrete in the proposed value, which is based on accelerated irradiation experimental results.

Figure 131 plots $F_c/F_{co}$ against neutron fluence. The temperature effects on the rate of aggregate expansion are normalized at 55 °C by eq. (13). It is worth noting that the concrete strength drops by at most 15% when subject to drying or heating. If aggregate expansion is responsible for neutron-induced degradation, then this 15% strength reduction due to drying or heating must be excluded from the data obtained. Based on Fig. 131, the neutron fluence above which concrete degradation occurs is $1 \times 10^{19}$ n/cm², which is consistent with previous studies (Hilsdorf et al. 1978; Field et al. 2015). Therefore, we propose a new reference value of $1 \times 10^{19}$ n/cm² for fast neutron radiation (> 0.1 MeV).

### 6.3 Concrete strength evaluation

Limestone aggregate is relatively more stable under neutron irradiation than other rock-forming minerals with covalent bonds. However, concrete containing limestone aggregates will be deemed as “not sound” in...
the reference-value evaluation process. For this reason, we introduce the strength evaluation process. When the expansion strain of an aggregate is given, the degree of concrete expansion and concrete strength degradation can be calculated from equations (15), (8), and (3). Alternatively, DEVICE predicts the concrete strength considering the temperature, humidity, and radiation environment. The strength of concrete cored from a target structure or a cylindrical sample for quality control during construction are useful data for calibrating the concrete strength in DEVICE. These advanced methods should be used for strength evaluation. Since strength requirements sometimes change due to unforeseen circumstances (the possibility of an earthquake, for example), this process is a necessary component in the soundness assessment procedure.

6.4 Structural performance evaluation
For the member-level evaluation, it is, in principle, necessary to determine the required performance corresponding to dead loads and maximum shear strains of the member during an earthquake, while considering the portion exceeding the reference fluence. In past cases, concrete stresses due to the dead load were shown to have a sufficient margin, such as a stress-to-strength ratio of 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than $2.0 \times 10^{-3}$ (taken from Technical Guidelines for strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than 0.3 or less. In addition, if the maximum shear strain caused by an earthquake is the same as or less than the reference level was omitted in order to calculate the stiffness of the member and the stress of the concrete. These evaluation steps should be carried on to the new iterations of the soundness assessment flow.

It is also possible to use the finite-element method to evaluate structural performance in the event of earthquakes and under sustained loads by considering the volume change and physical property changes of concrete.

The bond behavior of concrete, which is affected by neutron irradiation, is important. As a first approximation, the bond behavior of concrete affected by the alkali–silica reaction (Graves et al. 2014) can be applied for the numerical analysis.

7. Issues in the future

7.1 Drying and heating impact
A strength reduction of 15% induced by drying or heating may occur in a specified drying range below 65 °C. Current regulations state that concrete is sound if it is under 65 °C, but this is not consistent with scientific knowledge. It is thus necessary to clarify how this possible strength reduction should be dealt with in regulations.

The degradation of concrete stiffness due to heating or drying is directly related to the earthquake response of buildings. This is significant and warrants further investigation to inform the design and maintenance of nuclear power plant buildings.

Changes in physical properties are brought about by moisture transfer. Moisture transfer is the dominant factor influencing the rate of stiffness change of large cross-sectional members. There is, however, insufficient data for validation of moisture transport under high temperatures or under a temperature gradient. The rate of C-S-H modification also affects the rate of moisture transport, and thus C-S-H variations due to drying or heating are needed to establish the long-term property changes of concrete.

The data we have presented here regarding drying- and heating-induced changes in concrete strength and Young’s modulus should be extended to different cement types and water-to-cement ratios. Data for concrete in its sealed condition under elevated temperatures are also needed. The compressive strength of concrete drops drastically in response to instantaneous temperature increases but recovers gradually with time. Understanding this mechanism of strength recovery is important.

7.2 Gamma-ray impact
Gamma rays enhance the dissolution/reaction process in unreacted cement. Therefore, systems with low water-to-cement ratios, fly-ash additives, or both, warrant further investigation. In general, Japanese fly ash has a low CaO content and resultant low rate of hydration, owing to its coal source and combustion type. This type of fly ash is frequently used for massive concrete members in nuclear power plants because it reduces the heat of hydration.

The dissolution/precipitation process of hydrates, which is accelerated by gamma radiation (Pignatelli et al. 2016a), requires further study to deliver a better understanding of long-term creep and the volume change of concrete.

Irradiation tests on quartz and other rock-forming minerals using high-energy gamma rays will help expand the data available to develop a thorough understanding of the metamictization process.

The findings reported in this work must be validated to ensure their reproducibility. Additional gamma-ray irradiation tests on concrete without carbonation are also desirable. After the validation, the reference values for gamma rays should be abandoned.

7.3 Neutron impact
Understanding the relationships between neutron fluence and the expansion strain of rock-forming minerals under different temperatures is necessary for many kinds of aggregates used in concrete for nuclear power plants. It is also important to grasp the metamictization process of quartz and other rock-forming minerals. The final expansion strain and the corresponding fluence of
rock-forming minerals are used for risk evaluation of concrete degradation. The data obtained at different temperatures are used to establish the role of thermal healing in the minerals. In addition, data from an actual plant in operation are also required to validate the role of thermal healing.

Another topic that warrants further study is the numerical modeling of concrete properties from aggregate size (Giorla et al., 2015, 2017; Le Pape et al., 2016). Numerical modeling of concrete should elucidate the cracking behavior and creep of mortar and/or paste. For example, such information will provide insight on why concrete that has expanded by 3% does not shatter into small pieces. In addition, we do not fully understand the behavior of mortar. The role of small aggregates with an interfacial transition zone has not yet been deeply discussed at length from a viewpoint of the change in physical properties of mortar and concrete. For neutron irradiation, the expansion of the small aggregates is also an important issue for meso-scale modeling.

The bond behavior of concrete is crucial for structural safety evaluation, but there remains a lack in understanding on how neutron radiation affects the bond behavior of concrete. Such data is necessary for evaluating the structural performance of concrete.

Finally, the possible risk of radiation-induced alkali–silica reactions (Ichikawa and Koizumi 2002; Ichikawa and Kimura 2007; Pignatelli et al., 2016b) is addressed here. The steel liner plate at the surface of the CBS should maintain the pore solution when subject to radiation. The metamatization of quartz and feldspar increases their solubility. Consequently, the risk of ASR inside the CBS increases, and the potential for its occurrence should be investigated by testing concrete from decommissioned plants.

8. Summary

This project, which was conducted over a span of eight years, sought to develop an soundness assessment flow for concrete members exposed to a radiation environment. The project was composed of four parallel sub-projects: 1) neutron irradiation experiment, 2) gamma-ray irradiation experiment, 3) experiments for the effects of heating and drying, and 4) numerical modeling. In the first three sub-projects, we investigated concrete and concrete components (aggregates and hardened cement paste (hcp)). The project yielded the following results:

1) The irradiation experiments established the degradation mechanism of concrete due to neutron irradiation. The main reason for this degradation is the metamatization of rock-forming minerals, which, in turn, leads to aggregate expansion. Due to aggregate expansion, cracks around aggregates form, which reduce the compressive strength and Young’s modulus of concrete. Among the rock-forming minerals, α-quartz is the most sensitive to neutron radiation. For siliceous rocks, the α-quartz content is a major factor governing the expansion of aggregates within the range of fluences encountered in nuclear power plants. On the other hand, the strength of hcp increased under neutron irradiation. In our accelerated irradiation experiments, the compressive strength and Young’s modulus of concrete dropped to 55% and 30% of their original values, respectively, when subject to radiation levels above $4.5 \times 10^{19}$ n/cm$^2$.

2) Our $^{60}$Co gamma-ray irradiation experiments demonstrated that concrete strength increased as the gamma-ray dose. The hcp also increased in bending strength when subject to radiation; this phenomenon is always associated with a carbonation of cement paste. Only when concrete is carbonated under irradiation will its strength increase through the formation of vaterite on C-S-H. Theoretically speaking, it is simply not possible to reduce the strength and Young’s modulus except through gamma heating. In other words, the effect of gamma-ray irradiation on the properties of concrete is equivalent to that of heating and drying. The regulation of gamma-ray irradiation on concrete degradation can be omitted after confirming reproducibility of the present results.

3) Concrete strength alteration due to heating and drying is attributed to i) the colloidal and porous nature of hcp and ii) crack formation around the aggregate due to a mismatch in the volume changes of the mortar and aggregate. In our study, the strength of concrete dropped by up to 85%, which corresponds to a non-shrinking coarse aggregate and a water-to-cement ratio of 0.55. The Young’s modulus of concrete decreased by up to 60% under intense drying. A cyclic temperature history does not have any impact on the physical properties of concrete.

4) We developed a numerical code called DEVICE (Damage EValuation for Irradiated ConcreteE) to harness the knowledge obtained from the concrete samples in order to predict the performance of concrete members and to model the distribution of the physical properties of concrete members and their changes over time. Based on our parametric study, the temperature at the inner surface (the portion nearest to the reactor core) of the concrete biological shielding and its surface condition with regards to humidity are the two most important factors governing concrete strength in the section in question. High temperatures introduce thermal healing to the metamatization process of aggregates and a loss of evaporable water causes a stagnation of concrete strength development, thereby reducing its strength margin.

5) We proposed a 3-step soundness assessment procedure for concrete members subject to neutron and gamma radiation. First, the radiation level encountered by the concrete member is evaluated against a neutron fluence reference value of $1.0 \times 10^{19}$ n/cm$^2$. Second, the required concrete strength is evaluated either by a core sample and estimated with $F_c/F_{co}$, or
by using DEVICE calibrated with concrete strength data from the actual site. Third, the structural performance of the concrete member is evaluated.

**Author contributions**

I. Maruyama, O. Kontani, and M. Takizawa designed the research and experiments, and wrote the manuscript with S. Sawada, S. Ishikawa, J. Yasukouchi, O. Sato, J. Etoh, and T. Igari. O. Kontani, S. Sawada, S. Ishikawa, M. Takizawa, and I. Maruyama carried out neutron irradiation experiments. O. Kontani, S. Sawada, J. Yasukouchi, and I. Maruyama carried out gamma-ray irradiation experiments. I. Maruyama carried out experiments for heating and drying. S. Igari and O. Sato conducted supporting calculations using MCNP5. I. Maruyama and T. Igari developed DEVICE code. All the authors contributed and discussed the results and provided inputs on the manuscript.

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