Scientific paper

Long-term Material Properties of a Thick Concrete Wall Exposed to Ordinary Environmental Conditions in a Nuclear Reactor Building: the Contribution of Cement Hydrates and Feldspar Interaction

Jiří Rymeš¹, Ippei Maruyama²*, Ryu Šhimamoto³, Atsushi Tachibana⁴, Yoshihito Tanaka⁵, Shohei Sawada⁶, Yoshikazu Ichikawa⁷, Osamu Kontani⁸

Received 19 December 2018, accepted 23 April 2019  doi:10.3151/jact.17.5.195

Abstract

A variation of material properties with depth is observed in a massive, seismic-resistant internal wall of Unit 1 of the Hamaoka Nuclear Power Plant (NPP) 45 years after its construction. The maximum values are attained in the center of the structural element and gradually decrease towards the surface, while still well exceeding the required performance. It is found that this trend can be mostly attributed to the reaction between cement hydrates and rock-forming minerals of a feldspar group, which releases silica and alumina oxides into the pore solution, where they react with portlandite to form new hydrates. No evidence of expansive distress similar to the alkali-silica reaction (ASR) is found in the material, owing to this reaction. Possible implications for the aging management of existing concrete structures are discussed.

1. Introduction

Investigations of real concrete structures several decades old may reveal phenomena that are difficult to capture in short-term laboratory experiments. Lessons learned from such investigations are valuable not only for understanding the fundamental processes in concrete, but also for further developing structural maintenance tools. This paper presents a comprehensive set of experimental data obtained from an internal concrete wall of Unit 1 of the Hamaoka Nuclear Power Plant (NPP), which is currently in the process of being decommissioned.

In the nuclear industry, high structural robustness requirements demand the use of concrete elements of large cross-sections. While assessing the material properties of thick concrete elements, an obvious question arises: can we consider a constant distribution of material properties or is there any variation with depth? In a long-term experiment, a convex-shaped distribution of compressive strength was observed in a 1.3-m-thick concrete wall (Ozaki et al. 2001). In ten years of monitoring, the lowest compressive strength values were repeatedly measured in the center of the specimen while the strength increased towards both surfaces. It is worth mentioning that the material, initially cured for 13 weeks, showed a substantial increase in compressive strength for a 2-year period before stabilizing. This increase was uniform throughout the entire depth of the member, and can be explained by the different temperature history throughout the depth of the member. At an early age, the hydration heat creates a concave temperature distribution and the resulting increase in curing temperature decreases the final strength of the material. This is due to microstructural defects in the concrete matrix induced by differential thermal expansion (Lawrence 1998), as well as due to densification of calcium-silica-hydrate (C-S-H) resulting in a coarse and porous microstructure of hardened cement paste (HCP) (Gallucci et al. 2013).

To answer the above-stated question, the possibility of development of an opposite trend of compressive strength shall be considered. This trend might be a result of aging phenomena, which, through various mechanisms, decrease the material performance characteristics. Since these mechanisms originate from the external environment, the physical properties would be affected from the surface of the structural element. Drying in both heated and ordinary environmental conditions reduces the strength and Young’s modulus of concrete,
owing to different volumetric changes of HCP and aggregates (Maruyama et al. 2014a). In a laboratory experiment for a shear wall, a decrease in stiffness has been shown when, the initial stiffness was reduced by almost half (Sasano et al. 2018). Data collected by Maruyama (2016) document such a mechanism for real concrete structures on a time scale of more than a decade.

Similarly to drying, any change in temperature induces volumetric change. For applications in the nuclear industry, data of concrete affected by temperature has been collected by the United States Nuclear Regulatory Commission (Naus 2010). A general feature of this data is insufficient resolution in the low-temperature range, which makes their application difficult for structural elements subjected to milder drying gradients. Such conditions can be represented by drying in environmental conditions or under temperatures up to 65°C, which is the maximum allowable design temperature in case of Japanese NPPs (Maruyama et al. 2017). Moreover, for massive concrete members, due to the low permeability of concrete, the internal porous system slowly equilibrates with the external environment. Consequently, any change in surface conditions affects only a limited part of the material, such that the majority of the cross-section, especially under stable conditions inside a reactor building, is not subjected to any cyclic loading. This illustrates the need for data measured on equilibrated samples rather than those that focus on the length of exposure to a given condition.

It is worth mentioning that excessive drying at an early age may result in an uneven degree of hydration (DoH) since the clinker in the surface region would not be fully hydrated, thus the compressive strength would increase from the surface towards the center throughout an affected depth of a certain thickness. Based on the Japanese standard JASS 5 valid at the time of the construction, the demolding of wall elements was conducted at the age of at least 7 days (AIJ 1969). Finally, if the impacts of excessive drying and concave distribution of temperature during the hydration period are both considered, the resulting trend of compressive strength would reflect both of those phenomena and may change from increasing to decreasing between the surface and center of the element.

Apart from structural elements subjected to ordinary environmental conditions, concrete structures in NPPs, and in industrial operations in general, are exposed to specific conditions. To successfully elucidate the impacts of different factors on material characteristics for applications in the nuclear industry, concretes placed in both ordinary and specific conditions need to be investigated. As the first step of doing so, this paper presents data obtained on an internal structural element with a primary load-bearing function that has been subjected to mostly ordinary environmental conditions during its service life.

This paper is divided into three sections: experimental techniques and results obtained from a seismic-resistant internal wall of the reactor building Unit 1 of the Hamaoka NPP, identification of feldspar HCP interaction as the dominant mechanism responsible for the concave distribution of material properties, and implications for the aging management of NPPs.

2. Materials and methods

2.1 Background of specimens

Data from the reactor building of Unit 1 of the Hamaoka NPP, Shizuoka Prefecture, Japan, are reported. Commercial operation ran from 1976 to 2009, and the unit is currently undergoing decommissioning while simultaneously being subjected to research investigations. The data from an internal wall of thickness of 1500 mm, which was constructed in November 1971, are used in this paper. During the service life, the relative humidity of the surrounding environment is assumed to be approximately 40 – 50% and temperature approximately 23 – 28°C. A schematic of the structure is shown in Fig. 1 (left) and the characteristics of the concrete mixture are given in Table 1.

The core sampling took place in July 2016. Due to the significant thickness of the member, the coring was performed from two opposite sides of the wall ($\phi$ 100 × ~900 mm and $\phi$ 100 × ~700 mm). Three different coring methods were employed: a wet coring method (W), a dry coring method with high heat impact (DA), and a dry coring method with low heat impact (DB). For method W, water was used as a coolant for the heat generated from coring while the coring bit was cooled using air in methods DA and DB. For methods W and DA, the full length of the core drill was sampled at once, which, in the case of dry coring, generates heat, which may influence the material properties of the obtained specimens. Method DB reduces this impact by incrementally coring sections approximately 250 mm in length. The temperature at the surface of the core drill was measured immediately after drilling conducted. The coring speed was 10 – 20 mm/min for all methods. A schematic illustration of the core-sampling method and a quick overview of sample types for different analyses are shown in Fig. 1 (right).
2.2 Experimental techniques

(a) Compressive strength, static elastic modulus, Poisson's ratio, and bulk density

The compressive strength, static elastic modulus (hereafter simply elastic modulus), and Poisson’s ratio were measured simultaneously according to Japanese standards JIS A 1107 and JIS A 1149 (JSA 2012, 2017) on samples of dimensions φ100 × 200 mm. Strains in the longitudinal and lateral directions were measured using polyester strain gauges (Tokyo Measuring Instruments Laboratory Co.). Bulk density was measured on the same samples.

(b) Ultrasonic wave velocity

Ultrasonic wave velocity was measured on core specimens (ESP – 10 and Elsonic, Toyoko Elmes Co., Ltd.) and the dynamic elastic modulus was calculated. Based on the Japanese standard JIS A 1127 (JSA 2010), the following relationship was used:

\[ E_d = 4.0 \times 10^3 \cdot L \cdot \rho \cdot \left( \frac{V_p}{\lambda} \right)^2 \] (1)

where \( E_d \) is the dynamic elastic modulus (MPa), \( L \) is the specimen length (mm), \( \rho \) is the bulk density (kg/mm³), \( V_p \) is the ultrasonic pulse velocity (m/s), and \( \lambda \) is the wavelength used for measurement (0.224 m).

(c) Permeability

The permeability of the concrete samples was measured using a Cenbureau-type apparatus with nitrogen gas (purity 99.999%) at 20 ± 2°C. The samples were subjected to a nitrogen flow for several minutes prior to each measurement to stabilize the volume flow rate. At least three measurements were taken for each sample. The permeability was calculated for a flow of compressible fluid combining Darcy’s law and the Hagen–Poiseuille equation (Kollek, 1989):

\[ K = \frac{2 \cdot Q_{N2} \cdot P_{in} \cdot L \cdot \eta}{A \cdot (P_{in}^2 - P_{out}^2)} \] and

\[ Q_{N2} = \frac{dV}{dt} \approx \frac{V_{out} - V_{in}}{t_2 - t_1} \] (3)

where \( K \) is the permeability (m²), \( Q_{N2} \) is the volume flow rate of nitrogen (m³/s), \( P_{in} \) and \( P_{out} \) are the inlet and outlet pressures (Pa), respectively, \( L \) is the sample thickness (m), \( A \) is the cross-section subjected to the nitrogen flow (m²), \( V_i \) and \( t_i \) are the measured volume (m³) and time (s), respectively, and \( \eta \) is the dynamic viscosity of nitrogen at 20°C taken as 17.57 \times 10^{-6} \text{ Pa·s} (Cole and Wakeham, 1985).

(d) Water contents

For measuring physically bound water, approximately 1500 g of sample was roughly crushed to a particle size

![Fig. 1 (left) Schematic of Unit 1, Hamaoka NPP, with the position of the investigated wall indicated, (right) An outline of the experimental techniques. The sample labelling is based on cardinal directions of the coring surface and depth beneath the surface. The depth corresponds to the center of the sample.](image-url)
of 10 – 20 mm, and then dried at 105°C under a nitrogen flow (100 ml/min) until a constant mass was reached. The evaporable water was calculated by:

\[ w_e = \frac{m_{105} - m_{int}}{m_{105}} \]  

(4)

where \( w_e \) is evaporable water (g/g), \( m_{int} \) is the initial mass (g), and \( m_{105} \) is the dried mass at 105°C (g). Using approximately 800 g of the same sample, the chemically bound water was calculated based on the amount of water (recovered as condensate) released from 105°C to 850°C. The chemically bound water is defined as:

\[ w_{cb} = \frac{m_{H2O;850} - m_{105}}{m_{105}} \]  

(5)

where \( w_{cb} \) is chemically bound water (g/g), and \( m_{H2O;850} \) is the cumulative mass of condensed water between 105 and 850°C (g).

(e) Equilibrium relative humidity measurement
The equilibrium relative humidity (RH) was measured using a water activity meter by AquaLab 4TE (METER Group, ±0.3) at 20 ± 0.2°C (Rymeš et al. 2018). Approximately 10 g of material was chipped from the inner part of a DA sample after a compression test, immediately sealed into an aluminum–coated polyvinyl bag, and roughly crushed. The particle size was not controlled in order to reduce any additional drying during sieving. Since coring-induced drying has a negligible impact on the material in the center part of a core drill and since only a small sample in comparison to a relatively large core specimen was needed for the measurement, the type of dry coring technique had a negligible impact on the measured data.

(f) Alkali content
The total alkali content was determined using the water-soluble technique with a particle size below 50 μm (Ministry of Construction 1989). A sample of 10 g was dissolved in 100 ml of water at 40°C for 30 minutes and, after filtration of the solution, concentrations of Na and K were measured using atomic adsorption spectrometry. The total alkali content is expressed as a sodium equivalent as follows:

\[ Na_2Oeq = w_{NaO} + 0.658 \cdot w_{K_2O} \]  

(6)

where \( Na_2O_{eq} \) is the sodium equivalent (mg/g), and \( w_{NaO} \) and \( w_{K_2O} \) are the mass concentrations of sodium and potassium oxides, respectively (mg/g).

(g) Image analysis for aggregate content
The area proportion of coarse aggregates was calculated based on image analysis (NS2K-Pro software, Nano Systems, Inc.) using color scans of the surface of the core drills. Binary images were obtained based on different color tones of the aggregates and HCP. Then, grains with the major axis greater than 5 mm were defined as coarse aggregate and their combined ratio to total area was taken as the coarse aggregate area. The size of the surface scan was 2180 × 1353 pixels with a resolution of 200 dpi.

(h) Total porosity
Porosity was measured using the water evaporation technique on samples of \( \phi \) 100 × 10 mm. The samples were first saturated in water under vacuum conditions for one hour (vacuum level 0.1 Pa) and then kept in the water bath while their mass was periodically measured every 24 hours until the difference between two subsequent measurements became less than 0.1 g. Water on the surface was wiped dry before each measurement. Apparent density was measured simultaneously using the Archimedes method. The dry state was achieved by vacuum-drying for one hour (vacuum level 0.1 Pa), followed by oven-drying at 105°C. Carbonation was prevented by a nitrogen flow (100 cm³/min). Porosity was calculated by:

\[ p_s = \frac{\rho_s \cdot (w_s - w_e)}{\rho_e \cdot w_s} \]  

(7)

where \( p_s \) is the porosity (-), \( w_s \) is the saturated mass (g), \( w_e \) is the dry mass (g), \( \rho_s \) is the apparent density (g/cm³), and \( \rho_e \) is the liquid water density (0. 998 g/cm³).

(i) Carbonation depth
The carbonation depth was measured according to the Japanese standard JIS A 1152 (JSA 2018) using the phenolphthalein method. The core specimens were split in the longitudinal direction and approximately 5 mm of the material was removed from both longitudinal sides of the core before measuring.

(j) SEM analyses
Unhydrated clinker content was quantified based on analysis images taken by scanning electron microscope in the backscattered electrons mode (SEM-BSE) (Wong et al. 2009) using the Nano Hunter NS 2 K-pro (Nano System Co., Ltd.). For each sample, twenty images of the microstructure were obtained (SU-5000, Hitachi High-Technologies Corp.) at an accelerating voltage of 15 kV. Furthermore, the typical microstructure was observed using SEM-BSE (TM4000Plus, Hitachi High-Technologies Corp.) and the atomic composition was measured on one sample from the inner part and one sample from surface part of the wall by SEM-EDS (JSM-7500FE JEOL, Ltd.). Polishing of the specimens was conducted using silicon carbide papers followed by diamond paste suspensions up to a fineness of 1 μm.

(k) Chemical analyses
Fine powder samples were prepared for multiple analyses. First, the coarse specimens were coarsely crushed.
and the visible aggregate removed. The remaining material (hereafter referred to as mortar) was finely crushed to pass a 90 μm sieve and subsequently equilibrated in an 11% RH desiccator. The aggregate content of the mortar was determined using the dissolution technique. Approximately 1 g of mortar sample was weighted and dissolved in dilute hydrochloric acid (1:100). The insoluble residue was then oven-dried at 1000°C and weighed, and the ratio of dried residue to original mortar mass was taken as the aggregate content.

For quantitative X-ray diffraction (QXRD) analysis, 10% of internal standard (α-Al₂O₃) was thoroughly mixed with the powder mortar sample. X-ray profiles were obtained by a D8 ADVANCE X-ray diffractometer (Bruker AXS) using a Cu-Kα X-ray source at 40 kV and 40 mA from 2θ = 2–65° in increments of 0.02° with a speed of 0.5°/min. At least three replicas were prepared from each sample. A quantitative Rietveld analysis was performed in Topas 4.2 (Bruker AXS). The identified phase and distinct peak positions of each are summarized in Table 2. Thermogravimetry was conducted on the same samples and the amount of portlandite was evaluated based on the peak of the differential thermogravimetric (dTG) curve above 430°C (Lothenbach et al. 2016).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for chemical analysis of the paste dissolved in acid/alkali solvents. First, the mortar powder was dissolved in dilute hydrochloric acid (1.65 mol/L) for 20 minutes at room temperature and then further dissolved in dilute potassium hydroxide (0.2 mol/L) for 60 minutes at 60°C. Concentrations of Si, Ca, Si, Al, Fe, Mg, SO₄, Na and K were measured and then converted into concentrations of their respective oxides. To correct for soluble aggregate content, separately collected aggregate was dissolved in acid/alkali solvents and the solution was measured. Then, the oxide contents proportional to the acid/alkali soluble part were subtracted from the results based on the ratio of insoluble residues of mortar to separately measured aggregates.

(I) Sorption experiments
The mortar powder samples without 11% RH conditioning were used for sorption measurements. Using the Brunauer–Emmett–Teller (BET) theory, specific surface areas were calculated based on measurements of water vapor sorption isotherms at 20°C (VSTAR, Quantachrome Instruments) and nitrogen sorption isotherms at -196°C (BELSORP-miniII, MicrotracBEL Corp.). Mortar powder samples of approximately 25 ± 1 mg and 75 ± 5 mg were used for water vapor sorption and nitrogen sorption, respectively. In order to prevent temperature-induced destabilization of cement hydrates and associated microstructural alternation (Zhang and Scherer 2011), the samples were vacuum-dried at room temperature and the dry state was typically achieved within one hour for water vapor sorption samples and within four hours for nitrogen sorption samples. For BET calculations, the cross-sectional area of a water molecule was taken as 0.114 nm² (Mikhail and Selim 1966) and 0.162 nm² for nitrogen (Livingston 1944). Since the specific surface area of aggregate is much smaller than HCP (Imamoto and Arai 2008), the calculated specific surface areas mainly originate from the paste, therefore, the results were normalized to the dry mass of paste determined by the dissolution technique, and by vacuum drying at 105°C at the end of each measurement. This allows comparison between different samples throughout the wall.

3. Experimental results

3.1 Distribution of material characteristics
The data presented in this paper are in addition to the results published previously (Yokokura et al. 2017) and

Table 2 Summary of phases used for QXRD.

| Phase name                  | Chemical composition | Distinct peak positions: 2θ (°) |
|-----------------------------|----------------------|---------------------------------|
| Portlandite                 | CH                   | 18.1                            |
| Monosulphate                | C₂A₃H₁₂               | 10.1                            |
| Ettringite                  | C₆A₃S₃H₁₂             | 9.2, 15.9, 23.0                  |
| Hydrogarnet                 | C₃AH₆                 | 17.6, 40.0, 45.2                 |
| Hemicarboaluminate          | C₄A₃S₉H₁₂             | 11.0                            |
| Calcite                     | C₇                         | 29.5                            |
| Alite                       | C₃S                  | 32.3                            |
| Belite                      | C₃S                  | 31.3, 31.6                      |
| Ferrite                     | C₂AF                 | 33.9                            |
| Aluminate                   | C₃A                  | not found                        |
| Amorphous halos             | C-(A)-S-H, C₃AH₁₃     | ~29.4, ~11.5                     |

Cement notation: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, H = H₂O, T = CO₂, S = SO₄
were obtained on samples from a different element. Compressive strength and elastic modulus as a function of wall depth are shown in Figs. 2 and 3, respectively. Regardless of the coring method, a concave trend attaining a maximum value in the center of the element can be observed. The maximum value of compressive strength is approximately 50 MPa in the center, and falling to 32 – 42 MPa at depths of 100 mm in the case of methods W and DB. Similarly, the elastic modulus is approximately 37 GPa in the center, while decreasing to 25 – 29 GPa at the surfaces. It is worth mentioning that the design compressive strength of the concrete was 22.5 MPa and the lowest measured value at a depth of 100 mm exceeds this design strength by more than 30%. Furthermore, the maximum measured value in the center part of the wall is approximately 37 – 60% larger than the lowest value close to the surfaces. A similar trend was measured for elastic modulus, where the increase of the center part varies between 45 – 63% compared to the surface of the wall.

The distribution of Poisson’s ratio by wall depth is plotted in Fig. 4. Methods W and DB gave values of approximately 0.2 in the center of the element, with only a slight decrease to approximately 0.16 – 0.18 towards the surfaces. The maximum value obtained by method DA is similar, however, a more pronounced reduction can be observed towards surfaces where a Poisson’s ratio of approximately 0.12 was measured.

The well-known relationship between compressive strength and elastic modulus is plotted in Fig. 5 for different coring techniques, showing a generally high correlation coefficient.

Bulk density distribution is shown in Fig. 6. A steady value of approximately 2.34 g/cm³ was obtained by method W for all depths of the member. For the dry methods, this same value was measured for the center samples, but decreases to 2.28 and 2.29 at depths of 100 mm.
The ultrasonic measurement results as a function of wall depth are shown in Fig. 7 for ultrasonic wave velocity (UWV) and in Fig. 8 for dynamic elastic modulus (DEM). With one exception, samples cored by method W yielded the highest results with a maximum UWV of 4630 m/s measured in the center (800 mm depth), compared to 4350 and 4150 m/s at the surfaces (100 mm from the surfaces). For samples cored by method DB, 4550 m/s was the maximum value in the center (800 mm depth) and 4140 and 3900 m/s were the lowest values at the surfaces. The overall lowest values were given by method DA, with a maximum UWV of 4410 m/s in the center (500 mm depth), and 4050 and 3930 m/s at the surfaces. Similarly, a maximum DEM value of 40.6 GPa was obtained for a sample from the center of the element cored by method W, and 34.9 and 31.8 GPa were measured for surface samples cored by this method. For method DB, 39.7 GPa was the maximum value in the center (500 mm depth), which decreases to 32.4 and 26.5 GPa at the surfaces. As in the previous case, the lowest results were measured by method DA with a maximum DEM value of 37.2 GPa in the center (500 mm depth) and the lowest values of 29.5 and 25.2 GPa at the surfaces. The trend of results using the ultrasonic technique is consistent with the concave distribution of mechanical properties such as compressive strength and elastic modulus.

To examine the possible impact of nonhomogeneous aggregate distribution on the mechanical properties, an image analysis was conducted. The original and binary images used for estimating the area proportional to the coarse aggregate are shown in Fig. 9 and the distribu-
tion through the wall is shown in Fig. 10. Coarse aggregate area varies from 30 to 37% through the member with no apparent trend. Similarly, porosity results show no apparent trend with values ranging from 0.137 to 0.152 cm$^3$/cm$^3$, as plotted in Fig. 11.

Since the compressive test results vary by coring technique, a short note on the matter is placed here. While methods W and DB give higher values for both compressive strength and elastic modulus, method DA shows a reduction of approximately 9 MPa for compressive strength in the center of the element, and an average reduction of approximately 4 GPa in the measured elastic modulus. It is assumed that wet coring is the least harmful technique for obtaining specimens for the compressive strength test and since there is no significant difference between methods W and DB, it is concluded that method DB is a comparably applicable method for coring specimens for the compressive test as well as for other experimental techniques. The temperature at the surface of the core sample is approximately 40°C in method W and in the range of 40 to 70°C in methods DA and DB (Ichikawa et al. 2017). The significance of the low-heat-impact method lies in the reduction of exposure time, since the time for which the surface is heated is shortened to approximately 50% or even 25% in the case of method DB compared to DA.

Establishing a dry, low-heat-impact coring method is crucial, especially for water-related characteristics since additional water supplied to the material during coring would impact experimental results.

Results of permeability measurements are shown in Fig. 12. A convex trend with the lowest permeability value of $1.08 \times 10^{-17}$ m$^2$ in the center part at a depth of 700 mm was observed. From the center, the permeability increases towards the surface samples where values of $2.37 \times 10^{-16}$ and $3.42 \times 10^{-16}$ m$^2$ were measured.

Measurement results for evaporable water throughout the depth of the element are plotted in Fig. 13. In the center of the element, methods W and DB gave comparable results of 4.8%, while this value is reduced to 4.4% for method DA. Towards the surfaces, the amount of physically bound water is reduced to approximately 2.3 – 2.5% for the dry coring methods, while the concave trend diminishes in method W, due to adsorption of the cooling water into the material during coring. The trend in Fig. 6 is reasonably explained by Fig. 13, namely, that the evaporable water content (which is affected by the coring method) determines the nominal density of concrete. The chemically bound water, shown in Fig. 14, has a constant distribution of approximately 4% throughout the entire depth profile regardless of the coring method used.

The measurement results for equilibrium RH in Fig. 15 show a concave trend corresponding to the water
content measurements shown in Fig. 13 (Rymeš et al. 2018). The highest equilibrium RH value of 82.4% was obtained at a depth of 500 mm, which gradually decreased to 63.2% and 65.9% at the surfaces.

A concave distribution for alkali content is shown in Fig. 16. Maximum values of approximately 1.50 mg/g are attained in the center, while total alkali contents of 1.09 and 1.18 mg/g were measured 100 mm from the surfaces. As the trend suggests, this is closely related to the distribution of mechanical properties as will be discussed later.

The depth of carbonation can be seen in Fig. 17. The average depths are 3.1 mm and 3.4 mm for the two surfaces, with maximums of 6 mm and 10 mm, respectively.

The results for BET-specific surface area detected by water vapor and nitrogen are shown in Fig. 18. For water vapor, the maximum value of 235 m²/gHPC was obtained in the center and values of 101 and 83 m²/gHPC.
were measured 5 mm from the surfaces, showing more than a 50% reduction. The maximum value obtained using nitrogen as a probe was 37.7 m²/gHPC while values of 12.4 and 9.8 m²/gHPC were measured 5 mm from the surfaces. The trends of both measurements show a decrease at the surfaces, which can be attributed to the impact of drying (Maruyama et al. 2014a, 2014b). However, while relatively high BET-specific surface areas were measured at all depths of the wall except at the surfaces in case of water vapor, the decrease from the center towards the surfaces is more gradual for the nitrogen sorption results. The data for water vapor and nitrogen sorption isotherms are shown in the Appendix.

3.2 Chemical analyses results

Representative XRD patterns are shown in Fig. 19 for different positions in the element. The distribution of amorphous phases found from QXRD shows a trend resembling the distribution of mechanical properties, as shown in Fig. 20. A maximum amorphous content of more than 88% per gram of paste was attained in the center of the wall, decreasing to 82% and 84% at the two surfaces. This trend is inverse to the distribution of portlandite, with contents of 1.8% and 1.6% at the surfaces, which gradually decreases towards the center where portlandite is completely absent. An important insight from QXRD is that the total amount of unhydrated clinker does not vary significantly by depth and is less than approximately 5% per gram of paste, as shown in Fig. 21.

For supplementary data, SEM analysis was conducted. Using 3.15 g/cm³ for the density of clinker and assuming the bulk density of the paste to be approximately 1.80 g/cm³, the mass distribution of unhydrated clinker through the wall was calculated from the SEM-BSE image analysis results. The calculated image analysis results show smaller values compared to those from QXRD. The origin of this discrepancy might lie in the...
quantification of the paste content which is necessary for normalizing the results of the two techniques. Samples from a depth of 5 mm below the surfaces show 3.40% and 5.46% unhydrated clinker, though this amount was lower elsewhere. This can be attributed to rapid moisture loss in shallow depths and subsequent termination of the hydration process. However, this seems to only occur close to the surfaces since the amount of unhydrated clinker elsewhere is lower and generally uniform. Based on QXRD, it can be concluded that the distribution of mechanical properties cannot be attributed to the differing DoH throughout the element. This is further supported by the uniform distribution of chemically bound water.

Distributions of the remaining constituents of the paste are plotted in Fig. 22, with most showing a slight decrease in the center part of the wall compared to at the surfaces. Since the measured amount of calcite is uniform, it is assumed to originate from aggregate in the concrete batch and not from carbon dioxide diffusing into the concrete microstructure. This agrees with experimental data for carbonation depth determined by the phenolphthalein method. Furthermore, the peak on the XRD profiles around 11.5° is a sign of C4AH13, which is known to be unstable in the presence of calcite in HCP (Adu-Amankwah et al. 2017).

The absence of portlandite in the center of the element was confirmed by dTG curves, where the typical portlandite peak above 400°C (Lothenbach et al. 2016) is completely absent for samples S500, N700, and N500 mm, as shown in Fig. 23. Comparing quantification of portlandite with both techniques, higher values were obtained from dTG, which can be explained by the presence of finely intermixed amorphous calcium hydroxide within the low-density areas of C-S-H, which allows them to remain hidden from the X-ray in the amorphous structure (Taylor 1997). Furthermore, the dTG curves show a continuous mass loss up to almost 700°C with only a few clear peaks, suggesting overlapping and continuous decomposition of several phases of similar thermal stability.

The mechanical properties as a function of amorphous phase content are plotted in Figs. 24, 25 and 26. Based on the relatively high correlation of these, especially for mechanical properties, it is concluded that the different amounts of amorphous hydrates are the dominant mechanism behind the distribution of mechanical properties.
Fig. 25 Elastic modulus (W) as a function of amorphous content evaluated by QXRD.

\[ y = 1.9392x - 133.66 \]
\[ R^2 = 0.7627 \]

Fig. 26 Permeability as a function of amorphous content evaluated by QXRD.

\[ y = -5E-17x + 4E-15 \]
\[ R^2 = 0.5961 \]

Fig. 27 Typical microstructures observed using SEM-BSE. Magnification varies from ×200 to ×400. Intact as well as disturbed aggregate grains can be observed throughout the thickness of the wall.
The absence of portlandite in the center of the element suggests some form of interaction between the hydration products and rock-forming minerals present in the aggregate batch. Detailed observation of the microstructure using SEM-BSE images showed severe disturbances of certain aggregate grains, as shown in Fig. 27. This is not the case for all minerals since some grains appear to be affected while others remain intact. Surprisingly, the presence of disturbed grains is not characteristic for the center or surface part, but can be found in every observed specimen.

To further examine this, the atomic composition of aggregates was examined using SEM-EDS for the N700 sample and the resulting measurements are shown in Fig. 28. Quartz grains represented by measurement points 1, 4, 6, 8, 10, 11, 14, and 19 show an intact structure as well as albite grains at points 2, 16, 17, and 25. Analyses close to the boundaries of the paste and aggregates show the presence of calcium at points 3, 7, 9, 12, 13, and 15. Severe deterioration can be observed in alkali feldspars containing both potassium and sodium in their structure at measurement points 3, 18, 21, 22, 23, and 24. Measurement point 5 represents a grain with a low Al/Si ratio and uneven surface color, however, its structure was not disturbed as in the case of other feldspar grains. Measurement point 20 shows the composition of orthoclase with an intact structure that gradually becomes disturbed. A certain amount of iron was detected at measurement points 12, 13, 15, 18, 23, and 24, and a significantly large iron content was observed at measurement point 26.

Based on the observations of the disturbed structure of fine aggregates based on measurements of atomic composition using SEM, it is concluded that fine aggregates of a feldspar group interacted with the HCP. It seems reasonable to assume that coarse aggregate of the same origin would also undergo this same process.

### 3.3 Interaction between paste and aggregate

Properties of the resulting paste surrounding the reactive...
aggregate grains were further studied using the SEM-EDS technique and compared with paste in the neighborhood of unreacted aggregates. The line scans were close to unreacted quartz grains on the S100 sample, and close to reacted feldspars on the N700 sample. At different locations on each of these samples, thirteen line scans with 256 measurement points were taken, and a ternary system of Ca-Si-Al (strictly speaking pseudoternary) was measured. A typical measurement outcome is shown in Fig. 29. Clear differences can be observed in the composition of the surrounding paste. A Ca-rich area surrounds unreacted quartz grains, while Si-rich paste can be found in proximity to reacted feldspars.

This shift in atomic composition is evident when the measurement results of all line scans are plotted on a ternary diagram, as shown in Fig. 30. The cluster of measurement points shifts towards the silica vertex of the diagram in the case of a feldspar reaction, while the alumina content is stable approximately 10% or slightly increased for both. The exact nature of the phase is unknown and it does not seem to represent a single phase. This is supported by the dTG results showing significant mass loss from 105 – 400°C. This range is often attributed to various alumina hydrates (Lothenbach et al. 2016) and continuous mass loss without any distinguished peak, suggesting a rather heterogeneous and variable composition. The contribution of aggregate to the mass loss in dTG was checked on the residue after acid dissolution. The results showed only negligible mass loss throughout the entire temperature range.

The oxide mass concentrations measured by ICP-AES are plotted in Fig. 31. The composition of ordinary Portland cement (OPC) from the literature (Nakao 1968) is shown for comparison when the concentrations of Na₂O and K₂O are taken as 0.3 and 0.4, respectively (JCA 2013). The increase in silica concentration with respect to presumed OPC composition and the subsequent shift towards a lower Ca/Si ratio due to the feldspar reaction were confirmed by the results. Furthermore, the concave trend of silica distribution agrees with the assumption of an uneven rate of the feldspar reaction throughout the wall depth. A Ca/Si ratio of approximately 1.58 – 1.61 is attained in the center of the wall.
samples, gradually increasing to 1.76 and 1.84 for samples at depth of 100 mm.

Based on the ICP-AES results, the concentration of silica in the paste increased to 48 – 61% depending on the depth while the concentration of alumina increased to 2.5 – 8.4% when compared with the presumed OPC. Since it is unlikely that any oxide would become insoluble, the changes in the concentration are due to the dissolution of oxides from aggregates.

Assuming that all CaO originates from OPC only, the proportion of OPC hydrates to all hydrates in the paste, including the additional products due to the reaction between HCP and rock-forming minerals, was calculated based on the ratio of CaO in OPC and its quantity measured by ICP-AES. This allows estimation of the amount of reacted aggregate and calculation of the degree of aggregate reaction based on the original mixture proportions of the concrete. The calculated reaction rate of the aggregates displays a concave trend throughout the depth of the wall, varying from 3.0% and 2.6% at the surfaces to approximately 3.8% in the center, as plotted in Fig. 32. In Fig. 33, the degree of reaction is correlated with compressive strength, giving a correlation coefficient of 0.74. The details of the calculations are shown in the Appendix.

4. Discussion

4.1 Reaction of hardened cement paste and feldspar minerals

Feldspars are a group of rock-forming minerals with an aluminosilicate structure that is supplemented by mainly calcium, sodium and/or potassium. Calcium and sodium are characteristic of plagioclase feldspars, while sodium and potassium distinguish alkali feldspars. Their interaction with calcium hydroxide was first addressed in the studies of van Aardt and Vissel (1977b, 1977a, 1978). The process was described as a reaction of feldspar-containing rock aggregates in a saturated calcium hydroxide solution (pH ≈ 12.5, temperature-dependent), which results in a release of sodium and potassium oxides from the feldspars into the pore solution, and the formation of new hydration products. The leaching of oxides from feldspars, namely albite, was also confirmed at room temperature and ordinary pH (Knauss and Wolery 1986). The primary hydration products have been identified as C-(A)-S-H, hydrogarnet, C₄AH₁₃ and, in some cases, 11 Å tobermorite. The formation of these is evidence that, apart from alkalis, silica and alumina are also liberated from the crystal structure of feldspars and subsequently react with portlandite supplied by cement paste resembling alumina-blended supplementary cementitious material (SCM) systems.

Initially, this phenomenon was examined with regards to possible formation of expansive gel, which may distress the material similarly to ASR, however, in plentiful calcium hydroxide conditions, no such behavior was observed (Way and Cole 1982). Nonetheless, as a consequence of alkali oxides leaching into the pore solution, the increased alkali content may lead to destabilization of other silicates in the aggregate. This has been confirmed for a system of HCP–feldspars–calcined flint (Constantiner and Diamond 2003). For this mixture, the increase in alkali concentration over time was slower than for a HCP–feldspars mixture, thus confirming alkali consumption through the formation of ASR gel. As described in the previous section, the increase in the total alkali content can be confirmed as well as local presence of phases rich in silica outside of aggregate grains, however, no swelling-induced cracks were observed in the microstructure nor any disruption of quartz grains.

To the authors’ knowledge, only one study deals with the possible contribution of additional hydrates to compressive strength (Harada and Hagiwara 1984). In this accelerated experiment conducted at 80 ± 3°C, the mixtures undergoing reaction between HCP and feldspar aggregate continuously increased in compressive strength within 180 days of the experiment, while non-reactive mixtures showed no change in strength. This behavior was confirmed for a real concrete structure several decades old, and through the use of ICP-AES measurements, the reaction rate of aggregates could be calculated. Regarding a possible reaction mechanism, a
useful analogy can be found in the studies of SCM, which forms a chemically similar system. C-(A)-S-H resulting from the hydration of metakaolin of a given Si/Al ratio would differ in the Ca/Si ratio based on the calcium hydroxide content (de Silva and Glasser 1993). In conditions of plentiful calcium hydroxide, C-(A)-S-H with Ca/Si above 1.5 is formed while Ca/Si less than 1.0 is attained if there is a scarcity of calcium hydroxide. Therefore, it seems reasonable to assume that the increase in strength would have a different rate over time determined by decreasing portlandite content, and an upper limit corresponding to its total amount supplied from cement.

It is assumed that the reaction gradually terminates from the surfaces as the water leaves the porous system. However, if enough water remains in the porous system, then the dissolution of feldspar will continue even after all portlandite has reacted. In the above-mentioned studies, feldspar reacted in a calcium-rich environment, which may be favorable for the formation of a basic calcium-oxide (Ca-O) structure, and by incorporating dissolved silica the reported C-(A)-S-H is created. Once calcium becomes scarce, the conditions may become favorable for the formation of highly hydroscopic alkali silica gel whose expansive nature is reduced through subsequent incorporation of Ca and cross-linking of the silanol (Si-OH) groups (Ichikawa 2009). Therefore, at this moment, the harmful impact of feldspar dissolution would depend on the mobility of residual calcium hydroxide in the pore solution and on the dissolution of other Ca-bearing cement hydrates. The latter would likely depend on temperature, pH, and alkalinity of the pore solution.

Based on the ICP-AES results, the overall lowest Ca/Si ratio of the paste is 1.58, which is higher than the 0.83 of tobermorite (Taylor 1993), demonstrating a sufficient amount of Ca for formation of a basic Ca-O backbone of the C-S-H hydrates. The required calcium can be dissolved from C-(A)-S-H or from other cement hydrates such as ettringite (Lothenbach et al. 2017). Locally, the Ca/Si ratio of the products as measured by SEM-EDS can be lower, but the formation of such phases does not manifest in a harmful way. This may be related to the sufficient mobility of the silica-rich compound and its limited swelling property, as described later.

Furthermore, it is well known that aluminum-containing SCM systems are efficient for the mitigation of ASR (Kawabata and Yamada 2015). There is not a complete agreement about the exact acting mechanism, however, two possible explanations have been suggested. First, the decrease in Ca/Si for blended cements and the incorporation of aluminum to the bridging site of C-(A)-S-H creates an alkali sorption site of higher capacity, as well as enhancing the binding capacity of silanols sites (Hong and Glasser 2002). The other hypothesis suggests that aluminum decreases the dissolution of silica through adsorption on the surfaces of ASR-reactive aggregate grains (Chappex and Scrivener 2012). Finally, it should be noted that the scope of ASR studies is usually limited to the dissolution of silicates, such that no information can be obtained regarding the behavior of systems that release both alumina and silica oxides, such as in the case of reactive feldspars. Zeolite phases may potentially be formed, due to availability of alumina in the system supplied by either feldspar dissolution or by the destabilization of cement hydrates such as hydrogarnet. The possibility of formation of such phases has been recently reported for cement-like systems composed of C-S-H and ettringite in the presence of albite (Lothenbach et al. 2017).

The mechanism behind the formation of silica-rich phases originating from continuous feldspar dissolution, and in particular why the presence of silica-rich phases does not result in harmful distress in the material matrix, will now be discussed based on the ASR model suggested by Ichikawa (2009; Ichikawa and Miura 2007). It suggests that the lack of harmful distress in the material matrix is related to the ability of the released silica oxide to leave the inner perimeter and precipitate outside of the original aggregate grain. If an aggregate grain is tightly sealed with newly formed calcium alkali silicate or C-(S)-A-H of sufficient strength and low permeability, then the released oxides consequently become entrapped and their precipitation has the potential to crack the surrounding aggregate grain. On the other hand, if the compound can be freely released outside of the grain perimeter, then the resulting product precipitates in available pores of the concrete matrix thus having no harmful impact on the properties of the material. Generally, there is plentiful calcium around aggregates in the first stage of feldspar dissolution since portlandite precipitates in the interfacial transition zone (Larbi and Bijen 1990), forming a calcium-rich zone around the reactive aggregates. If the concrete mixture contains a certain amount of fine reactive particles such as pozzolans or, as in this case, reactive feldspars in the form of fine aggregate and dust particles, these would preferably react with the dissolved calcium from portlandite, owing to their large specific surface area, and form hardened material. Additionally, in the case of feldspar dissolution, the dissolved alumina would also contribute to the consumption of calcium from portlandite through the formation of calcium aluminate hydrates such as hydrogarnet (Rajabipour et al. 2015). The larger grains react later, and thus would not be sealed in a thick layer of solid impermeable product meaning that any potential alumina and silica gel can be released to the empty pores of the concrete matrix where they react with calcium slowly dissolved from cement hydrates other than portlandite. Such a mechanism, therefore, does not result in expansive distress, but rather contributes to mechanical properties through densification of the microstructure.

The identification of HCP-feldspar reaction, which affects the concrete as discussed above, relies mainly on
three independent experimental techniques, which all revealed the same trend. The QXRD results showing the concave trend of the amorphous phase, which is inverse to the distribution of portlandite as plotted in Fig. 20, the ICP-AES results showing the decrease in the relative content of CaO due to the increase in contents of the oxides, which were dissolved from feldspars, as shown in Fig. 31. Knowing the initial mixture proportions, the later technique also allows quantification of the degree of aggregate reaction plotted in Fig. 32. The last evidence of the reaction is the concave trend of total alkali content as shown in Fig. 16. A supporting argument of the feldspar reaction is the direct observation of the microstructure combined with measurements of atomic composition using SEM-EDS. All of the above-mentioned experimental techniques use a relatively small amount of sample, however, as they all yielded to the same conclusion, the reliability of the presented data is proven.

The trends of evaporable water content and equilibrium RH, that are shown in Figs. 13 and 15, respectively, explain the gradual termination of the HCP-feldspar reaction from the surface of the wall due to evaporation of water from the porous system. The different degree of aggregate reaction then explains the observed distribution of mechanical properties. On the other hand, characteristics, which may also affect the mechanical properties, such as total porosity or distribution of coarse aggregate, were shown not to vary throughout the element.

4.2 Implications for aging management of NPPs
Safe, long-term, and reliable serviceability of existing concrete structures is one of the essential tools for sustainable development. To ensure this, their structural performance needs to be evaluated and future trends predicted, which is especially crucial for structures of strategic importance, such as those that form energy containment systems. From the results provided, it is apparent that the negative impact of hydration heat is overturned by the reaction of feldspar minerals which then becomes the dominant factor in the distribution of material properties.

The beneficial trend of the feldspar reaction is certainly not universal, but it can be relevant for many concrete structures. In such a case, this tendency needs to be considered in order to provide reasonable inputs for structural models. Similarly, a representative value shall be provided for judgement of structural safety by national regulatory bodies for structures subject to licensing procedures. In this case, the real performance of the entire structure would be underestimated based on the value of compressive strength at the surface. The distribution of compressive strength and elastic modulus through the depth of the member creates a series of parallel springs that together transfer the load. Therefore, the average measured value or average value of a fitted concave trend seem to be a reasonable approach. This is not only the case for a distribution originating from a reaction between cement paste and aggregate, but is a generally applicable approach for other possible disproportionate effects such as surface drying, and uneven DoH, or as an alternative to the effective thickness approach for considering severe surface deterioration.

The overall mechanism of feldspar dissolution is still poorly understood. Several factors need to be investigated in order to predict the rate of dissolution. It has been shown that the rate of albite dissolution increases with temperature and pH (Knauss and Wolery 1986). At a pH of 12 – 13 the rate is approximately 2 – 3 magnitudes faster than at a neutral pH (Savage et al. 1992). The mechanism of oxide release from feldspars possibly depends more on microstructural characteristics (Locati et al. 2010) and crystal defects than on chemical composition of the mineral.

The interaction between concrete and rock-forming minerals has been studied in related engineering fields as well. In recent years, the possible interaction between cement paste and bedrock has been examined for the design of deep geological repositories for nuclear waste. In clays, an interface of high porosity originated from calcium hydroxide dissolution when HCP and clayey rock were in contact (Dauzeres et al. 2010). This would have a negative impact on the material’s properties. It
may be explained by the different mechanisms of both processes. In the case of feldspar, it has been suggested that the oxides are liberated through a dissolution process rather than ion exchange (Savage and Rochelle 1993).

A common feature of most published studies is an experimental period of up to one or two years at most. One exception is a 15-year-long experiment (Moyce et al. 2014) that suggested a two-stage mechanism where, C-S-H is produced as a result of calcium–feldspar inter-action in the first phase, followed by the second phase when carbon-bearing dolomite undergoes dedolomitization, the released CO₂ carbonates the initially formed C-S-H. In their experiment, the second stage occurred some time after the 15th month of the experiment. Based on the results presented in this paper, a certain amount of calcite was observed using QXRD and dTG, which suggests possible carbonation of C-(A)-S-H through the dissolution of calcite, which was possibly presented in the aggregate batch to some extent.

5. Conclusion

A gradual increase in material performance characteristics from the surface towards the center was observed in a thick internal wall of a Japanese nuclear power plant after the end of its operational cycle. Comparing the surface and center parts, an increase of more than 50% in compressive strength was observed while still well-exceeding the design value by at least 30%. Such variation combined with the still high material performance suggests the involvement of a more influential mechanism than solely material degradation. This is supported by the fact that the investigated element was not subject to any intense degrading factors related to the operation of nuclear facilities or external environmental conditions.

An interaction between HCP and rock-forming minerals of a feldspar group was identified as a reason for the concave distribution of material performance characteristics in a thick concrete wall 45 years after its construction. Al₂O₃ and SiO₂ oxides were dissolved from the structure of the minerals and subsequently reacted with portlandite in the HCP, primarily forming amorphous C-(A)-S-H hydrates. The resulting hydrates have a low Ca/Si ratio similarly as observed for SCM. This reaction could be observed throughout the entire depth of the examined wall structure, however, the degree of reaction is higher in the center, establishing a concave trend of mechanical properties. It is concluded that the dominant factor responsible for termination of the reaction towards the wall surfaces is the absence of water in the porous system. This finding emphasizes the role of drying for evaluation of massive concrete members.

Acknowledgment

This project is supported by the “R&D of the safety improvement of nuclear facilities” project of the Minis-

try of Economy, Trade and Industry (METI) in Japan. A part of the experimental works was supported by Tai-heiyo Consultant, and the authors would like to express their thanks to Mr. Masahito Shibata. The authors acknowledge the helpful feedback provided by Professor Hitoshi Hamasaki of Shibaura Institute of Technology, Associate Professor Noriyuki Takahashi of Tohoku University, and Associate Professor Yo Hibino and Assistant Professor Atsushi Teramoto of Hiroshima University.

References

van Aardt, J. H. P. and Visser, S., (1977a). “Calcium hydroxide attack on feldspars and clays: Possible relevance to Cement-aggregate reactions.” Cement and Concrete Research, 7(6), 643-648.

van Aardt, J. H. P. and Visser, S., (1977b). “Formation of hydrogarnets: Calcium hydroxide attack on clays and feldspars.” Cement and Concrete Research, 7, 39-44.

van Aardt, J. H. P. and Visser, S., (1978). “Reaction of Ca(OH)₂ and of Ca(OH)₂ + CaSO₄.2H₂O at various temperatures with feldspars in aggregates used for concrete making.” Cement and Concrete Research, 8(6), 677-681.

Adu-Amankwah, S., Zajac, M., Stabler, C., Lothenbach, B. and Black, L., (2017). “Influence of limestone on the hydration of ternary slag cements.” Cement and Concrete Research, 100, 96-109.

AUI, (1969). “Japanese Architectural Standard Specification JASS 5 Reinforced Concrete Work.” 4th ed. Tokyo, Architectural Institute of Japan. (in Japanese)

Chappex, T. and Scrivener, K. L., (2012). “The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction.” Cement and Concrete Research, 42(12), 1645-1649.

Cole, W. A. and Wakeham, W. A., (1985). “The viscosity of nitrogen, oxygen, and their binary mixtures in the limit of zero density.” Journal of Physical and Chemical Reference Data, 14(1), 209-226.

Constantiner, D. and Diamond, S., (2003). “Alkali release from feldspars into pore solutions.” Cement and Concrete Research, 33(4), 549-554.

Dauzeres, A., Le Bescop, P., Sardini, P. and Cau Dit Cournes, C., (2010). “Physico-chemical investigation of clayey/cement-based materials interaction in the context of geological waste disposal: Experimental approach and results.” Cement and Concrete Research, 40(8), 1327-1340.

Gallucci, E., Zhang, X. and Scrivener, K. L., (2013). “Effect of temperature on the microstructure of calcium silicate hydrate (C-S-H).” Cement and Concrete Research, 53, 185-195.

Harada, M. and Hagiwara, Y., (1984). “Experimental study on the reactivity of aggregate in concrete.” Bulletin of the International Association of
Engineering Geology, 30(1), 235-239.
Hong, S.-Y. and Glasser, F. P., (2002). “Alkali sorption by C-S-H and C-A-S-H gels: Part II. Role of alumina.” Cement and Concrete Research, 32(7), 1101-1111.
Ichikawa, T., (2009). “Alkali-silica reaction, pessimum effects and pozzolanic effect.” Cement and Concrete Research, 39(8), 716-726.
Ichikawa, T. and Miura, M., (2007). “Modified model of alkali-silica reaction.” Cement and Concrete Research, 37(9), 1291-1297.
Ichikawa, Y., Maruyama, I., Wada, H., Yokokura, K., Ishikawa, S. and Saito, G., (2017). “Soundness evaluation method for concrete structures based on the data obtained from decommissioning Hamaoka nuclear power plant Part 3: Investigation on core sampling method.” In: Summaries of technical papers of annual meeting. Hiroshima, 31 August - 3 September 2017. Tokyo, Architectural Institute of Japan, 1259-1260.
Imamoto, K. and Arai, M., (2008). “Specific surface area of aggregate and its relation to concrete drying shrinkage.” Materials and Structures, 41(2), 323-333.
JCA, (2013). “Common Sense of Cement.” Toyko: Cement Association. (in Japanese)
JSA, (2010). “Methods of test for dynamic modulus of elasticity, rigidity and Poisson’s ratio of concrete by resonance vibration (JIS A 1127).” Tokyo: Japanese Standards Association. (in Japanese)
JSA, (2012). “Method of sampling and testing for compressive strength of drilled cores of concrete (JIS A 1107).” Tokyo: Japanese Standards Association. (in Japanese)
JSA, (2017). “Method of test for static modulus of elasticity of concrete (JIS A 1149).” Tokyo: Japanese Standards Association. (in Japanese)
JSA, (2018). “Method for measuring carbonation depth of concrete (JIS A 1152).” Tokyo: Japanese Standards Association. (in Japanese)
Kawabata, Y. and Yamada, K., (2015). “Evaluation of alkalinity of pore solution based on the phase composition of cement hydrates with supplementary cementitious materials and its relation to suppressing ASR expansion.” Journal of Advanced Concrete Technology, 13(11), 538-553.
Knauss, K. G. and Wolery, T. J., (1986). “Dependence of albite dissolution kinetics on pH and time at 25°C and 70°C.” Geochimica et Cosmochimica Acta, 50(11), 2481-2497.
Kollek, J. J., (1989). “The determination of the permeability of concrete to oxygen by the Cembureau method-a recommendation.” Materials and Structures, 22(3), 225-230.
Larbi, J. A. and Bijen, J. M. J. M., (1990). “Effects of water-cement ratio, quantity and fineness of sand on the evolution of lime in set portland cement systems.” Cement and Concrete Research, 20(5), 783-794.
Lawrence, D. C., (1998). “Physicochemical and mechanical properties of Portland cement.” In: P. C. Hewlett Ed. Lea’s Chemistry of Cement and Concrete, 4th ed. London, Arnold, 343-419.
Livingston, H. K., (1944). “Cross-sectional areas of molecules adsorbed on solid surfaces.” Journal of the American Chemical Society, 66(4), 569-573.
Locati, F., Marfil, S., Baldo, E. and Maiza, P., (2010). “Na₂O, K₂O, SiO₂ and Al₂O₃ release from potassic and calcic-sodic feldspars into alkaline solutions.” Cement and Concrete Research, 40(8), 1189-1196.
Lothenbach, B., Bernard, E. and Mäder, U., (2017). “Zeolite formation in the presence of cement hydrates and albite.” Physics and Chemistry of the Earth, 99, 77-94.
Lothenbach, B., Durdziński, P. and De Weerdt, K., (2016). “Thermogravimetric analysis.” In: K. L. Scrivener, R. Snellings, and B. Lothenbach Eds. A Practical Guide to Microstructural Analysis of Cementitious Materials. Boca Raton, CRC Press, 177-211.
Maruyama, I., (2016). “Multi-scale review for possible mechanisms of natural frequency change of reinforced concrete structures under an ordinary drying condition.” Journal of Advanced Concrete Technology, 14(11), 691-705.
Maruyama, I., Kontani, O., Takizawa, M., Sawada, S., Ishikawa, S., Yasukouchi, J., Sato, O., Etoh, J. and Igari, T., (2017). “Development of soundness assessment procedure for concrete members affected by neutron and gamma-ray irradiation.” Journal of Advanced Concrete Technology, 15(9), 440-523.
Maruyama, I., Nishioka, Y., Igarashi, G. and Matsui, K., (2014a). “Microstructural and bulk property changes in hardened cement paste during the first drying process.” Cement and Concrete Research, 58, 20-34.
Maruyama, I., Sasano, H., Nishioka, Y. and Igarashi, G., (2014b). “Strength and Young’s modulus change in concrete due to long-term drying and heating up to 90°C.” Cement and Concrete Research, 66, 48-63.
Mikhail, R. S. and Selim, S. A., (1966). “Adsorption of organic vapors in relation to the pore structure of hardened cement pastes.” In: T. C. Powers Ed. Symposium on Structure of Portland Cement Paste and Concrete. Washington D.C., Washington Highway Research Board, Division of Engineering, National Research Council, National Academy of Sciences-National Academy of Engineering, 123-134.
Ministry of Construction, (1989). “Comprehensive technological development project report: Measurement of water-soluble alkali metal elements in concrete (Draft).” Ver. 02, Tokyo, Ministry of Construction, Japan. (in Japanese)
Moyce, E. B. A., Rochelle, C., Morris, K., Milodowski, A. E., Chen, X., Thornton, S., Small, J. S. and Shaw, S., (2014). “Rock alteration in alkaline cement waters over 15 years and its relevance to the geological disposal of nuclear waste.” Applied Geochemistry, 50, 91-105.
Nakao, T., (1968). “Characteristics of Japanese cement (especially comparison with those of foreign cement).” Cement and Concrete, 253, 27-39. (in Japanese)

Naus, D. J., (2010). “A compilation of elevated temperature concrete material property data and information for use in assessments of nuclear power plant reinforced concrete structures.” No. NUREG/CR-7031, Oak Ridge, Oak Ridge National Laboratory.

Ozaki, M., Ooifuji, N., Kitagawa, T. and Ono, K., (2001). “On the long term properties of concrete.” AJJ Journal of Technology and Design, 7(13), 9-14. (in Japanese)

Rajabipour, F., Giannini, E., Dunant, C., Ideker, J. H. and Thomas, M. D. A., (2015). “Alkali-silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps.” Cement and Concrete Research, 76, 130-146.

Richardson, I. G., (2014). “Model structures for C-(A)-S-H(I).” Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials, 70(6), 903-923.

Rymeš, J., Maruyama, I., Wada, H., Yokokura, K., Kontani, O. and Sawada, S., (2018). “Soundness evaluation method for concrete structures based on the data obtained from decommissioning Hamaoka nuclear power plant Part 6: Measurement of equilibrium relative humidity.” In: Summaries of technical papers of annual meeting. Sendai, 4-6 September 2018. Tokyo, Architectural Institute of Japan, 1067-1068.

Sasano, H., Maruyama, I., Nakamura, A., Yamamoto, Y. and Teshigawara, M., (2018). “Impact of drying on structural performance of reinforced concrete shear walls.” Journal of Advanced Concrete Technology, 16(5), 210-232.

Savage, D., Bateman, K., Hill, P., Hughes, C., Milodowski, A., Pearce, J., Rae, E. and Rochelle, C., (1992). “Rate and mechanism of the reaction of silicates with cement pore fluids.” Applied Clay Science, 7, 33-45.

Savage, D. and Rochelle, C. A., (1993). “Modelling reactions between cement pore fluids and rock: implications for porosity change.” Journal of Contaminant Hydrology, 13, 365-378.

de Silva, P. S. and Glasser, F. P., (1993). “Phase relations in the system CaO-Al_2O_3-SiO_2-H_2O relevant to metakaolin - calcium hydroxide hydration.” Cement and Concrete Research, 23(3), 627-639.

Taylor, H. F. W., (1993). “Nanostructure of CSH: Current status.” Advanced Cement Based Materials, 1(1), 38-46.

Taylor, H. F. W., (1997). “Cement chemistry.” 2nd ed. London, Thomas Telford Publishing.

Way, S. J. and Cole, W. F., (1982). “Calcium hydroxide attack on rocks.” Cement and Concrete Research, 12(5), 611-617.

Wong, H. S., Matter, K. R. and Buendeld, N. R., (2009). “Estimating the water/cement (w/c) ratio of hardened concrete using backscattered electron microscopy.” In: 12th Euroseminar on Microscopy Applied to Building Materials. Dortmund.

Yokokura, K., Wada, H., Kontani, O. and Maruyama, I., (2017). “Concrete strength evaluation of massive concrete structures based on the data obtained from decommissioning nuclear power plant.” In: Transactions, SMiRT-24. Busan, 20-25 August 2017. Raleigh, International Association for Structural Mechanics in Reactor Technology, 209-218.

Zhang, J. and Scherer, G. W., (2011). “Comparison of methods for arresting hydration of cement.” Cement and Concrete Research, 41(10), 1024-1036.

Appendix

A.1 Sorption measurement data

Water vapor sorption data are shown in Fig. 34 and nitrogen sorption data in Fig. 35.

---

Wong, H. S., Matter, K. R. and Buendeld, N. R., (2009). “Estimating the water/cement (w/c) ratio of hardened concrete using backscattered electron microscopy.” In: 12th Euroseminar on Microscopy Applied to Building Materials. Dortmund.

Yokokura, K., Wada, H., Kontani, O. and Maruyama, I., (2017). “Concrete strength evaluation of massive concrete structures based on the data obtained from decommissioning nuclear power plant.” In: Transactions, SMiRT-24. Busan, 20-25 August 2017. Raleigh, International Association for Structural Mechanics in Reactor Technology, 209-218.

Zhang, J. and Scherer, G. W., (2011). “Comparison of methods for arresting hydration of cement.” Cement and Concrete Research, 41(10), 1024-1036.

Appendix

A.1 Sorption measurement data

Water vapor sorption data are shown in Fig. 34 and nitrogen sorption data in Fig. 35.
otherwise, the terms in the following equation represent weight contents. The relationships are as follow:

\[ m_{\text{sol,agg}}^{O^{2-}} = m_{\text{sol,agg}}^{O^{2-}} \frac{m_{\text{isol}}}{m_{\text{isol,ref}}} \quad \text{and} \quad \frac{m_{\text{agg}}^{O^{2-}}}{m_{\text{agg}}} = m_{\text{agg}}^{O^{2-}} - m_{\text{sol,agg}}^{O^{2-}} \quad (8) \]

where \( m_{\text{sol,agg}}^{O^{2-}} \) is the oxide contents corresponding to the soluble part of aggregates in the measured mortar sample, \( m_{\text{agg}}^{O^{2-}} \) is the oxide content measured after the acid/alkali treatment of the aggregate only, \( m_{\text{agg}}^{O^{2-}} \) is the corrected oxide contents in the paste, \( m_{\text{isol}} \) is the measured oxide contents of the mortar sample, and \( m_{\text{isol,ref}} \) are contents of insoluble residues in the mortar sample and in the aggregate reference sample.

The results for the paste include contributions of the HCP and the products of the aggregate reaction. Assuming that all CaO originates from cement clinker only, the portion of HCP was quantified by:

\[ \phi_{\text{HCP}} = \frac{m_{\text{CaO}}^{\text{HCP}}}{m_{\text{OPC}}} \quad (10) \]

where \( \phi_{\text{HCP}} \) is the HCP content in the total paste (-), and \( m_{\text{CaO}}^{\text{HCP}} \) and \( m_{\text{CaO}}^{\text{OPC}} \) are the CaO contents in the paste and in the cement clinker (JCA 2013), respectively. Furthermore, the total mass of the reacted aggregate was calculated by:

\[ m_{\text{agg,react}} = m_{\text{OPC}} \frac{1 - \phi_{\text{HCP}}}{\phi_{\text{HCP}}} \quad (11) \]

where \( m_{\text{agg,react}} \) is the total mass of reacted aggregates (kg), and \( m_{\text{OPC}} \) is the total mass of cement in the concrete (kg) based on the mixture proportion listed in Table 1. Finally, the degree of reaction of the aggregates was calculated as follows:

\[ \phi_{\text{agg,react}} = \frac{m_{\text{agg,react}}}{m_{\text{agg}}} \times 100 \quad (12) \]

where \( \phi_{\text{agg,react}} \) is the degree of reaction of the aggregates (%), and \( m_{\text{agg}} \) is the total aggregate content in the concrete mixture (kg), as listed in Table 1.