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Impact of gamma-ray irradiation on hardened white Portland cement pastes exposed to atmosphere

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ABSTRACT

Samples of matured hardened cement paste were exposed to an environment with gamma-ray irradiation, which induces a natural carbonation process. After a dose of approximately 5×10^4 kGy, the physical properties, microstructure, and phase composition of the irradiated hardened cement paste samples are compared with those of reference samples exposed to an identical environment without gamma-ray irradiation. Experiments confirm that aragonite and vaterite are preferentially formed under irradiation and that the bending strength is dramatically increased after gamma-ray irradiation. Based on field-emission scanning electron microscopy observations, X-ray scattering profiles, and water vapor sorption isotherm data, it is concluded that vaterite formed on C–S–H plays a role in strengthening the structure of C–S–H via pseudomorphs.

1. Introduction

Concrete structures in nuclear power plants may undergo undesirable changes as a result of loads and environmental conditions. Since these structures can rarely be replaced, predicting their aging behavior and evaluating their current and future soundness are crucial for long-term operation. In Japan, several nuclear power plants that are expected to have operating periods exceeding 40 years are currently being considered to extend their life. Researchers have reported that concrete exposed to radiation fields will deteriorate [1]. According to the Review Manual for Aging Management Technical Evaluation [2], “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.” In the Review Manual, the soundness of concrete structures under gamma-ray irradiation was evaluated based on whether the forecast values of gamma-ray doses after a 60-year period exceeded the reference level of 2×10^5 kGy, at which the degradation of concrete strength becomes problematic.

In previous research into the effects of gamma-ray irradiation on hardened cement paste (hcp) or concrete, it was found that the radiolysis of water in hcp accelerated the drying process [3,4] and, in some cases, caused the production of unstable calcium peroxide during irradiation [5]. The concrete's compressive strength decreased [6], while the hcp's strength increased when it was accompanied with a carbonation process [4]. Unfortunately, the results of gamma-ray irradiation experiments are always affected by gamma-ray heating and by the drying process when the sample is exposed to ambient air. Hence, drying or heating themselves have a large impact on the microstructural changes and physical properties of hcp [7–20], so the impact of gamma-ray irradiation on hcp must be evaluated separately from the effects of drying or heating.

For this purpose, in this research, matured hcp samples, of which the effects of drying have been reported elsewhere [18–20], were exposed to environments both with and without gamma-ray irradiation to clarify which phenomena occur under gamma-ray irradiation.

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Table 1
Chemical composition of white Portland cement through X-ray fluorescence elemental analysis.[a]

Ig. loss (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	MnO (%)	Cl (%)
2.93	22.43	4.67	0.16	65.69	0.98	2.51	0.00	0.07	0.17	0.03	0.00	0.00

[a] Conducted by Taiheiyo Cement Corporation.

2. Experiment

2.1. Materials and specimens

White Portland cement, whose chemical composition is shown in Table 1, was used to produce the specimens. The aim of this research was to clarify the physical property changes and chemical changes in hcp. For this purpose, nuclear magnetic resonance (NMR) spectroscopy with magic angle spinning (MAS) is considered to be a promising technique to clarify the changes in C–S–H and other phases. Therefore, in this research, it was decided to use a cement containing a smaller amount of ferrite than ordinary Portland cement. A paste (10 L) with a water-to-cement ratio of 0.55 was prepared by mixing in a 20-L Hobart mixer for 3 min, and remixing for a further 3 min after scraping the paste from inside the mixer. To minimize segregation, the paste was remixed every 30 min for 6 h. After obtaining a creamy consistency, the paste was placed into molds and covered with polyvinylidene chloride wrap and wet paper to prevent water loss from the specimens. The molds were stored in a thermostatic chamber at a temperature of 20 ± 1 °C. The specimens were demolded after 4 days and immediately immersed in lime-saturated water, where they were kept for 180 days at 20 °C. After this long curing period, the specimens were considered almost fully hydrated; the results of the degree of hydration have been reported elsewhere [18]. They were then placed in various relative humidity (RH)-controlled chambers (11, 20, 30, 40, 50, 60, 70, 80, and 90, at 20 ± 1 °C) controlled by different concentrations of sodium hydrates [18,21] and allowed to dry slowly for ~2 years. Some of the samples were continuously kept in lime-saturated water at 20 ± 1 °C. In this experiment, samples dried under 50% RH and cured in lime-saturated water were used. Specimens were 3 mm × 13 mm × 300 mm slabs, which can obtain equilibrium with the surrounding RH fairly efficiently. The resulting samples equilibrated slowly at, for example, XX% RH are denoted as "SDSXX". The details of specimen preparation are provided in refs. [18,19].

Specimens were irradiated with gamma rays in an irradiation room of the Cobalt Irradiation Facility at the Takasaki Advanced Radiation Research Institute (TARRI; Gunma Prefecture, Japan). Two gamma rays with energies of 1.17 and 1.33 MeV were emitted from ^{60}Co sources. Alanine dosimeters (Amino Gray dosimeters, developed by JAERI and JMACS Japan Co., Ltd.; diameter 11 mm, height 50 mm) were attached to the surfaces of the specimens prior to irradiation and after every ~4 months for 1 h to measure the dose rate. Specimens were uniformly irradiated by the ^{60}Co sources for ~10 months such that the deposited energy would reach 5×10^4 kGy. The temperature and RH of the room were recorded using a type-T thermocouple and a humidity sensor (SPF-54, Tateyama Kagaku Group). Specimen temperature was also measured over time using type-T thermocouples attached to the specimens' surfaces. The ventilation system of the experimental room was connected to atmospheric air and, therefore, the samples were exposed to atmosphere in which the CO_2 concentration was approximately 405 ppm according to the Japan Meteorological Agency [22].

Meanwhile, reference samples were placed in the same room but in a location where there was no radiation. In the analysis, samples before irradiation (denoted as -Ini), samples after irradiation (denoted as -Irr), and the reference samples (denoted as -Ref) were all used.

2.2. Analysis

The phase compositions of the hcp specimens were analyzed using powder X-ray diffraction (XRD) and Rietveld analysis. All the hcp specimens were submerged in acetone for 6 h and dried in a vacuum for several minutes with a vacuum pump. The specimens were stored at 11% RH and 20 °C for 2 weeks. The specimens were ground in a ball mill, and corundum powder (10 wt%) was added to the sample powder as a standard reference. The XRD (D8 Advance, Bruker AXS) parameters were as follows: tube voltage 50 kV, tube current 250 mA, 2θ scan range of 5–65°, step width 0.02°, and scan speed 2°/min. The software used for Rietveld analysis was TOPAS Ver. 4.1 (Bruker AXS). In the Reitveld analysis, the quantified phases were gypsum, bassanite, anhydrate, portlandite, periclase, calcite, vaterite, aragonite, ettringite (Ett), monosulfate calcium aluminate (Ms), monocarbonate calcium aluminate (Mc), hydrogarnet (C_3AH_6, Hg), and calcium aluminate hydrate (C_4AH_{13}), as well as typical cement minerals such as alite, belite, cubic-C_3A, orthorhombic-C_3A, and ferrite phase (C_4AF). Structural models for the minerals (alite, belite, cubic-C_3A, orthorhombic-C_3A, and C_4AF) were taken from an NIST Technical Report. Those for periclase, calcite, vaterite, aragonite, gypsum, bassanite, anhydrite, portlandite (CH), Ett Ms, Mc, hydrogarnet, a calcium aluminate hydrate, and corundum were taken from the ICSD database. The halo pattern of the amorphous phase was refined as a background function. The samples were measured three times for each set of experimental conditions.

Thermogravimetry (TG) analyses were conducted under N_2 gas flow at 10 °C/min using TG differential thermal analysis instruments (2000SA, Bruker AXS). The results were evaluated using differential TG (DTG). In addition to these TG analyses, TG analyses coupled with differential scanning calorimetry (DSC) and gas chromatography (GC) were conducted for SDS100-Irr and SDS100-Ref to confirm the decomposition phases. The temperature range was from 40 to 1000 °C and the rate of temperature increase was 10 °C/min. He gas was used as a carrier gas. For gas chromatography (GC), the scan range was 2–1000 Da (1 scan/s), applied voltage was 1000 V, and the capillary size was φ0.32 × 5 mm. The instruments for the DSC TG and the GC were STA 449F1 (NETZSCH) and JMS-Q1050GC (JEOL), respectively.

Spectra of ^{29}Si dipolar-decoupling MAS NMR were collected using a Bruker Avance 300 MHz spectrometer equipped with a 9.4-T widebore magnet. Samples were packed into 7-mm ZrO_2 rotors and rotated at MAS rates of up to 5 kHz using a standard cross-polarization (CP)–MAS probe. A recycle delay of 60 s was used and the number of scans was 5000. All spectra were recorded at room temperature and referenced using a hexacyclotrisiloxane peak at −9.55 ppm relative to tetramethylsilane (run separately).

Spectra of ^{27}Al MAS NMR were collected on an ECA700 spectrometer (JEOL; magnetic field of 16.4 T) using a CP-MAS probe with an outer diameter of 4.0 mm and ZrO_2 rotors at a spinning frequency of 15 kHz. A recycle delay of 0.5 s was used and the total accumulation time was 6400 s. The ^{27}Al chemical shifts were referenced using $AlK(SO_4)_2 \cdot 12H_2O$ as the external reference (0 ppm).

Fourier-transform infrared spectroscopy (FT-IR) with attenuated total reflection (ATR) of the samples was performed using ALPHA (Bruker Biospin). Diamond ATR was used for the measurement. The number of scans was 128. The CO_2 peaks of the background were canceled by a blank measurement, and the scan range was from 450 to 3800 cm^{-1}.

Water vapor sorption measurements were conducted using the