Long-term Performance Assessment of Concrete Exposed to Acid Attack and External Sulfate Attack

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Abstract

This study aims to assess the degradation of below-grade concrete of nuclear power plants (NPP) in Japan, considering possible acid and sulfate attacks. A survey on the underground environments of several NPPs and residential buildings across the country was conducted, and their associated concrete performance was evaluated where concrete samples from core drillings were available. Moreover, acid and sulfate exposure tests on mortar specimens lasting for up to four years were carried out in the laboratory to simulate actual field situations. The effects of exposure conditions, such as solution concentrations, temperature, and immersion conditions, were examined. The surveyed environments were classified into non-aggressive or slightly aggressive environments. The concrete core samples investigated showed insignificant degradation and satisfactory strength after 40 years of exposure. The laboratory test results showed that the accelerated tests using highly concentrated solutions could exacerbate the extent of decalcification and even alter the degradation mechanism for magnesium sulfates. Therefore, a close-to-reality concentration is preferred for reproducing field situations. The carbonation/neutralization depth was used as an indicator to estimate the degradation extent. The measured values in the laboratory using low-concentration solutions correlated well with the field results, suggesting that the below-grade concrete’s degradation in the NPPs investigated may be less than 10 mm after 60 years of exposure.

1. Introduction

Reinforced concrete (RC) structures in service are often exposed to various types of aggressive environments. For example, foundations and below-grade concrete in direct contact with sulfate-bearing soils and groundwater may be subject to sulfate attacks, and sewage pipes and structures near hot springs suffer sulfuric acid-induced degradation (JSCE 2014). The ingress of the reactive ions from external environments can change the hardened cement paste’s microstructure, leading to cracking, softening, and disintegration (Skalny et al. 2002). Although a suitable mix design ensuring sufficient resistance to certain exposure conditions can be determined with laboratory tests, it is essential to assess concrete performance in the field after long-term exposure.

For deciding the severity of exposure conditions, several durability design codes specify environmental exposure classifications. The quantities of the aggressive species in water and soils define the degree of environmental aggressivity. A summary of these codes can be found in the state-of-the-art report of RILEM TC 211-PAE (2012). For nuclear power plants (NPP), the ageing management program (AMP 306) of the International Generic Ageing Lessons Learned Report (IGALL) issued by the IAEA (IAEA 2018) has recommended routine monitoring of groundwater chemistry (pH, chlorides, and sulfates) for evaluating its impact on below-grade structures. Groundwater/soil with pH < 5.5, chlorides > 500 ppm or sulfates > 1500 ppm can be deemed aggressive (IAEA 2018).

Concerning the long-term performance of concrete under aggressive environments, simulation tests by immersing concrete specimens in attacking solutions are commonly conducted in laboratories to investigate their chemical resistance. Several case studies of field concrete situations can also be found in the literature. Regarding chloride attacks, Bader (2003) reported about evaluating the concrete performance exposed to the highly concentrated chloride and sulfate environments in the Arabian Gulf, and Li et al. (2018) about investigating the chemical alterations of concrete in underground tunnel structures in China. As for sulfate attacks, Hobbs and Taylor (2000) studied the formation of sulfate-bearing mineral thaumasite in concrete in the UK and Marchand et al. (2002) numerically investigated the performance of concrete slabs exposed to sulfate-bearing soils in the US. In Germany, Bellmann et al. (2012) targeted sulfate related mining areas, and in Spain Menéndez et al. (2019) reviewed the incidence of sulfate attack. In Japan, chemical sulfate attacks on concrete structures near hot springs or old coal-mining areas have been reported (Tokumitsu and Matsushita 1979; Matsushita et al. 2010). Yoshida et al. (2010) investigated several deterioration cases of concrete foundations of...
residential buildings due to physical sulfate attacks and indicated that such cases are spread widely across Japan. Whereas these studies are of great importance, a question arises on how to link laboratory test results with various field situations.

Meanwhile, there is still a lack of standardized methods for calculating the degradation process, although the abovementioned codes have provided specifications on how to design concrete to withstand a given aggressive environment. Menéndez et al. (RILEM TC211-PAE 2012) used applied thermodynamics to analyze the reaction between Portland cement and sodium sulfate, revealing the resulting phase changes. Miura et al. (2017) developed a sophisticated numerical approach for evaluating mortar's expansion and cracking behavior subjected to external sulfate attack. Despite these approaches, for engineering purposes, a simplified tool is required to interpret laboratory test results and estimate the degradation extent of concrete within its service life. As both the reaction of penetrated acids or magnesium ions with hydrated products and the migration of hydroxide ions outwards when concrete is exposed to sodium sulfate solutions (Skalny et al. 2002) induce a decrease of the pH within concrete, the carbonation/neutralization depth is a promising indicator for assessing the degradation extent.

The current study was conducted to assess the extent of ageing degradation of below-grade concrete structures of nuclear power plants (NPP) in Japan, considering possible acid and external sulfate attacks. A survey targeting both NPP facilities and residential RC buildings was carried out to investigate the underground exposure conditions and the concrete's performance under such conditions, where concrete samples from core drillings were available. Moreover, based on the survey results, laboratory tests on mortars were conducted to study the effects of exposure conditions, cement type, and water-to-binder (w/b) ratio on the chemical deterioration, while aiming to reproduce the field observations.

2. Field survey

The survey on NPPs reported herein covered 11 plants (denoted A to K) across the country. Sampling and testing groundwater in the vicinity of the below-grade concrete were performed, and the results were compared with the classification of exposure types suggested by BS EN 206 (2013). In addition, below-grade concrete samples originating from seven RC buildings, five in Tokyo, one in Hiroshima, and one in Fukuoka, were examined along with the associated exposure conditions. These buildings were more than 40 years old and expected to be demolished. Concrete samples from these buildings were obtained by core drillings at their underground peripheral walls, directly in contact with the groundwater/soil.

2.1 NPP facilities

2.1.1 Groundwater sampling and analysis

A series of groundwater samples were collected from sub-drains on both the land side and marine side in consideration of the geographic characteristics of each plant investigated. A sub-drain system is a group of wells installed near reactors and turbine buildings to reduce flowing groundwater. To study the ion concentrations' annual variations, at plant A, the groundwater was sampled three to four times a year from each of six sites, of which four sites were located at the land side. For the other NPPs, two samples per plant were tested at most. The chemical analyses of the groundwater samples were conducted following JIS K0101 (JIS 1998). Table 1 summarizes the methods adopted for different items/components.

| Item/Component | Method                        |
|----------------|-------------------------------|
| pH             | pH glass electrode            |
| SO\(_4\)^2⁻, Mg\(^{2+}\), NO\(_3\)^⁻, Na\(^+\), K\(^+\), Ca\(^{2+}\), Cl\(^{-}\) in mg/L | Ion chromatography        |
| NH\(_4\)^+ in mg/L | Indophenol               |
| Free carbonic acid H\(_2\)CO\(_3\) in mg/L | Titration                |

Table 1: Investigated items/components of groundwater and adopted methods.

2.1.2 Analysis results

The box-and-whisker plot in Fig. 1 shows the ion concentrations of the groundwater samples taken from the plant A. The concentrations of NH\(_4\)^+ are not plotted in the figure as they were smaller than 0.3 mg/L. The groundwater samples on the land side mainly contained sodium sulfates, and the ion contents showed minor annual fluctuations (see the dispersion in the data). On the other hand, the samples collected on the marine side contained a high number of chlorides with increased sulfate contents, and the annual changes were significant. Although these results draw attention to the interaction with seawater, their large variability is deemed to be due to the limited sample size. For clarification, more monitoring is required in the future.

The ion concentrations in the samples of different NPPs are compared in Table 2, where the values of the plant A are the average values. Some of the results are

Fig. 1 Measured ion concentrations of groundwater at plant A.
also plotted in Fig. 2. The figure includes the exposure classes for chemical attacks as suggested by BS EN206 (2013), (see Table 3). All groundwater samples showed a pH value larger than 6.5, suggesting a negligible risk of acid attack. Samples taken on the land side of the plants E and F were found to have sulfate ion concentrations marginally larger than 250 mg/L (< 250 ppm), which is a slightly aggressive environment (XA1 class). Nevertheless, the values are significantly lower than the criteria of 1500 ppm suggested by IGALL (IAEA 2018).

In comparison to the samples taken on the land side, substantially higher ion concentrations were observed on those taken on the marine side, with part of the test results showing similar levels to those of seawater. The degradation due to the seawater attack is out of this study’s scope. Some studies (Mehta 1999; Thomas 2001)

Table 2 Measured ion concentrations of groundwater.

| Plant No. | A | B | C | D | E | F | G | H | I | J | K |
|-----------|---|---|---|---|---|---|---|---|---|---|---|
| **pH**    | 8.5| 7.9| 8.1| 7.8| 7.9| 7.9| 7.9| 7.8| 7.7| 8.2| 7.4|
| **SO₄²⁻** | 111| 69 | 63 | 124| 252| 278| 25 | 156| 13 | 25 | 9 |
| **Mg²⁺**  | 8  | 9  | 21 | 19 | 47 | 22 | 7  | 112| 9  | 8  | 3 |
| **Cl⁻**   | 45 | 21 | 37 | 56 | 133| 27 | 70 | 1110| 40 | 18 | 29 |
| **H₂CO₃** | 10 | < 5| 8  | 20 | 6  | < 5| < 5| < 5 | < 5| < 5| 17 |

Fig. 2 Comparison of groundwater’s chemical components with exposure classes specified in EN 206.
have indicated that the formed ettringite is typically non-expansive in the presence of excessive amounts of chloride ions. Furthermore, Yamaji (2011) measured the ion concentration profiles of the concrete cores extracted from seven marine structures and found that the magnesium ions' ingress depth was less than 10 mm after 40 years of exposure. Hence, the below-grade concrete on the marine side studied herein may have had little degradation due to seawater attack.

### 2.2 Residential RC buildings

The second survey aimed to add information on the long-term performance of below-grade concrete structures to correlate laboratory and field results. The examined buildings are outlined in Table 4. Note that the buildings 2, 6, and 7 were in direct contact with groundwater. Buildings 3 and 4 were located at the same site, and the underground peripheral walls of the building 5 were provided with asphalt waterproofing. The specified strength of concrete ranged from 18 to 21 MPa. Unfortunately, despite an extensive search, the information on concrete mixture could not be found.

#### 2.2.1 Concrete core drilling and testing

Concrete core samples with a diameter of 100 mm were extracted from the peripheral walls from inside of the buildings according to the procedures of JIS A1107 (JIS 2012). The number of cores and the drilling locations are summarized in Table 4. As drilling below the groundwater level can cause submersion of the underground space, all core samples were extracted above the groundwater level. Compared with the concrete in direct contact with groundwater, the extracted core samples were expected with moderate degradation due to a lower concentration of deleterious ions in the soils.

Each core sample was divided into two parts. One part facing the interior and having a length of about 180 mm was tested for compressive strength and Young’s modulus following JIS A1108 (JIS 2018) and JIS A1149 (JIS 2017), respectively. The remaining part facing the interior and having a length of about 180 mm was tested for compressive strength and Young’s modulus following JIS A1108 (JIS 2018) and JIS A1149 (JIS 2017), respectively. The core samples of the building 6, however, were found to contain seashell aggregates. Hence, the acid-soluble silica content was measured by inductively coupled plasma mass spectrometry (ICP) to estimate the cement amount, as Yoshida et al. (1990) suggested.

Area analyses by EPMA were carried out to determine the concentration distributions of Cl, S, Ca, and Si. For the sample preparation, 15 mm thick samples with a cross-section of 80 × 80 mm² were cut from the concrete cores starting from the side facing the exterior. These samples were firstly subjected to methacrylic resin impregnation to strengthen their brittle structure and reduce gas emissions in a high vacuum. Then, the surfaces to be examined were polished using SiC abrasive powder and deposited with carbon to provide electrical conductivity. An electron probe of 50 μm in diameter scanned the sample surface at an interval of 0.1 mm within a period of 40 ms. The accelerating voltage was 15 kV, and the probe current was 200 nA. The characteristic X-ray intensities corresponding to the target elements were recorded at each square area of 0.1 mm side. They were converted afterward to elemental concentrations using the theoretical correction method. The standard samples, as suggested by JSCE-G-574-2005 (JSCE 2005), were adopted for correction.

#### 2.2.2 Groundwater/soil sampling and analysis

The groundwater samples were collected using a pumping device, and the buildings 2 and 6 that were in direct contact with groundwater were investigated. After drilling concrete cores, the soils adjacent to them were sampled (see Fig. 3). Soil sampling for the building 5 was not possible due to the tight construction schedule, besides the presence of the asphalt waterproofing on the exterior side of walls making the interaction with the groundwater/soil unlikely. The ion concentrations of the groundwater/soil samples were measured following JIS K0101 (JIS 1998) and JGS-0241-2009 (JGS 2009). Specifically, the soil samples' water-soluble components were extracted, and the concentrations of cations and anions were determined using atomic absorption spectroscopy and ion chromatography, respectively. The investigated items/components for a soil sample are given in Table 5. As for the groundwater samples, refer to Table 1. Note that only one groundwater/soil sample per building was tested.
Table 4 Summary of investigated buildings.

| Building No. | Description                  | Age (years) | Groundwater level (m) | Ground type | Exposure (soil) | Exposure (groundwater) | Core drillings |
|--------------|------------------------------|-------------|-----------------------|-------------|-----------------|------------------------|-----------------|
| 1            | Steel framed reinforced concrete, Eight stories above ground and three underground | 40          | About 20              | Fill materials (~10 m) | SO\(_4^{2-}\) = 15 mg/kg pH = 8.3 | 20m, Two cores 30cm long | 2~4m Two cores 45cm long |
| 2            | Steel framed reinforced concrete, Ten stories above ground and one underground | 50          | 2 - 3                | Fill materials silt (~3 m) | SO\(_4^{2-}\) = 36 mg/kg pH = 8.5 | 2.5m Ten cores 30cm long | Groundwater 1.6~2.8m |
| 3            | Steel framed reinforced concrete, Six stories above ground and two underground | 40          | About 25             | Fill materials (~6 m) | SO\(_4^{2-}\) = 40 mg/kg pH = 6.9 | 2.5m Four cores 30~55cm long | 25m Four cores 30~55cm long |
| 4            | Steel framed reinforced concrete, Seven stories above ground and two underground | 55          | About 25             | Fill materials (~6 m) | SO\(_4^{2-}\) = 383 mg/L pH = 10.0 | 25m Eight cores 30~55cm long | 25m Eight cores 30~55cm long |
| 5            | Steel framed reinforced concrete, Eight stories above ground and two underground | 85          | No data available    | No data available | (soil) SO\(_4^{2-}\) = 16 mg/kg pH = 9.6 | 3.3m Four cores 25cm long | 3.7m Four cores 25cm long |
| 6            | Steel framed reinforced concrete, Four stories above ground and two underground | 40          | 3.3                  | Fine sand (~3m) | (soil) SO\(_4^{2-}\) = 53 mg/kg pH = 6.9 | 2.5m Eight cores 25cm long | 2~3m Two cores 25cm long |
| 7            | Reinforced concrete          | 70          | 3.7                  | Fill materials (~8 m) | (soil) SO\(_4^{2-}\) = 43 mg/L pH = 7.3 | 2.5m Eight cores 25cm long | 0.5m 16 cores 25cm long |

Table 5 Investigated items/components of soil samples and adopted methods.

| Item/Component | Method       |
|----------------|--------------|
| pH             | pH glass electrode |
| Na\(^+\), K\(^+\) in mg/kg | Atomic absorption spectrometry |
| Ca\(^{2+}\) in mg/kg | ICP-OES |
| Mg\(^{2+}\), Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\) in mg/kg | Ion chromatography |

Fig. 3 Soil sampling from peripheral walls of RC buildings.
### 2.2.3 Analysis results

**Table 6** shows some of the measured ion concentrations in the groundwater and soil. It was found that the buildings 3 and 4 were within weakly acidic grounds (pH ≈ 6.5). Building 6 was in contact with a groundwater containing 383 mg/L sulfate ions, classified as a slightly aggressive environment (XA1 class) following BS EN206 (2013). The environments of the other buildings investigated were considered non-aggressive chemical environments.

**Table 7** presents the estimated mixture proportions, compressive strengths, and carbonation depths of the concrete taken from the core samples facing the exterior. It was found that the water to cement (w/c) ratios ranged from 0.44 to 0.65. The compressive strengths ranged from 27 to 50 N/mm², satisfactorily higher than those specified in the design. All measured values of the carbonation depth were below 10 mm, and part of the concrete cores showed no signs of carbonation. For the building 6, considering the construction year and the specified design strength of concrete, the estimated w/c ratio of 0.44 was somewhat low. Yoshida et al. (1990) reported that the ICP method might yield an error of ±15 kg/m³ for cement amount and a more considerable inaccuracy in the water content. Assuming a water content of 175 kg/m³ that is the median of the other buildings’ data, the w/c ratio could be from 0.47 to 0.52 when considering the error of ±15 kg/m³ for the cement amount.

**Figure 4** compares the concentration distributions of CaO and SO₃ obtained by the EPMA area analysis of the concrete taken from the core samples facing the exterior of the buildings. For the buildings exposed to non-aggressive chemical environments (buildings 2 and 7), no trace of calcium leaching could be found, and the ingress of sulfate ions was minor (< 1.8 mm for the building 2), revealing the soundness of the concrete under such environments even after several decades of exposure. On the other hand, regions of leaching (3.0 to 6.0 mm) were observed in the buildings 1, 3, and 4, the latter cases of which could be related to the slightly acidic ground. Still, no signs of ettringite or gypsum precipitation were found due to a low sulfate content in the environments. In comparison to the buildings 1, 3, and 4, the building 6 had a 0.3 mm thick layer rich in CaO, and a calcium leaching zone of about 2.1 mm thickness was found beneath. Besides, the sulfate contents were higher than those of the other cases, suggesting a slight degradation. As for the building 5, as expected, no signs of degradation were found, owing to the waterproofing effect.

In general, the below-grade concrete of the buildings examined has been exposed to non-aggressive or slightly aggressive chemical environments for more than 40 years. Although calcium leaching regions and possible phase alterations in the building 6 were noticed, the affected regions’ thicknesses were smaller than 5 mm, and

### Table 6 Measured ion concentrations of groundwater/soil samples.

| Item/Component | 1 | 2 | 3 | 4 | 6 | 7 |
|----------------|---|---|---|---|---|---|
| pH             | 8.3 | 8.5 | 6.9 | 6.2 | 10.0 | 9.6 |
| SO₄²⁻ (mg/kg)  | 15 | 36 | 53 | 40 | 76 | 16 |
| Mg²⁺ (mg/kg)   | 1 | 3 | 4 | 3 | 1 |
| NO₃⁻ (mg/kg)   | 5 | 2 | 59 | 8 | 5 | 5 |
| CI⁻ (mg/kg)    | 9 | 2 | 18 | 15 | 21 | 9 |
| Water content  | % | | | | | |
| SO₄²⁻ (mg/L)   | / | 45 | / | 383 | / | / |
| Mg²⁺ (mg/L)    | / | 8 | / | / | 2 | / |
| NO₃⁻ (mg/L)    | / | <1 | / | / | 3 | / |
| CI⁻ (mg/L)     | / | 4 | / | / | 194 | / |
| H₂CO₃ (mg/L)   | <5 | / | / | / | / | / |
| H₂CO₃ (mg/L)   | / | / | / | / | / | / |

() indicates the standard deviation.

### Table 7 Estimated mixture proportion, compressive strength, and carbonation depth.

| Estimated mixture proportion | Building No. | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|------------------------------|--------------|----|----|----|----|----|----|----|
| w/c ratio                    | 0.62         | 0.65 | 0.60 | 0.54 | 0.63 | 0.44 | 0.51 |
| Cement (kg/m³)               | 282          | 306 | 307 | 314 | 280 | 354 | 331 |
| Water (kg/m³)                | 176          | 198 | 185 | 171 | 177 | 157 | 167 |
| Compressive strength (N/mm²) | 39.7 (5.9)   | 40.2 (5.1) | 41.1 (6.2) | 38.4 (9.3) | 31.1 (3.9) | 29.0 (2.7) | 36.0 (8.1) |
| Elastic modulus (10⁵N/mm²)   | 2.70 (0.57)  | 2.66 (0.19) | 2.40 (0.37) | 2.59 (0.44) | 2.65 (0.41) | 2.20 (0.30) | 2.50 (0.37) |
| Carbonation depth (mm)       | 3.4 (2.1)    | 2.0 (1.2) | 3.3 (2.1) | 1.8 (2.1) | 2.3 (2.7) | 1.4 (1.2) | 2.1 (1.8) |
the concrete performance, such as strength, was satisfactory. To simulate the field situations and predict the degradation extent due to acid attack and external sulfate attack, laboratory studies considering various exposure conditions were carried out.

3. Laboratory studies

3.1 Experimental program

To the best of authors’ knowledge, there is no standardized test addressing acid attacks on cement-based materials. As for assessing the sulfate resistance of concrete, accelerated tests are widely adopted. Specimens are continuously immersed in high-concentration sulfate solutions following ASTM C1012/C1012M-13 (ASTM 2013) or exposed to drastic drying-wetting cycles (Nehdi and Hayek 2005). These test conditions, however, do not necessarily reflect actual underground conditions. Moreover, highly concentrated sulfate solutions will favor gypsum precipitation, while frequent drying may lead to physical sulfate attack involving salt crystallization (Whittaker and Black 2014).

Therefore, in this study, first, tests on mortars were conducted to investigate the effects of exposure conditions, such as the pH in an acid attack, the sulfate concentration for external sulfate attack, and immersion conditions. Then, the resistance of different cements or binders and the effect of the w/b ratio were examined. These tests aimed to correlate laboratory results with field observations and explore a proper method of predicting degradation. The variations of mass and length of the mortar specimens were measured at regular intervals up to four years of exposure to aggressive environments. On the other hand, the carbonation depths were decided and used to assess the degradation.

3.1.1 Materials

The moderate-heat Portland cement (M, low C₃A content: 2.5%), usually applied for mass concrete of the nuclear facilities in Japan, was used for assessing the effects of exposure conditions along with a binary binder (MF) containing 20% fly ash (FA). In addition, the ordinary Portland cement (N, high C₃A content: 9.5%) and one blended with 20% FA designated as NF were considered to examine the effect of binder type.

Table 8 Oxide composition of binder materials (% weight).

| Material       | M cement | N cement | Fly ash |
|----------------|----------|----------|---------|
| SiO₂            | 23.58    | 20.91    | 55.34   |
| Al₂O₃           | 3.61     | 5.45     | 29.70   |
| Fe₂O₃           | 4.21     | 2.94     | 4.40    |
| CaO             | 63.62    | 65.18    | 2.20    |
| MgO             | 0.98     | 1.54     | 0.78    |
| SO₃             | 2.06     | 2.08     | 0.28    |
| Na₂O            | 0.29     | 0.27     | 0.85    |
| K₂O             | 0.41     | 0.53     | 0.70    |
| Density in g/cm³| 3.21     | 3.16     | 3.20    |
| Blaine fineness in cm²/g | 3220 | 3440 | 3820 |

Table 9 Clinker content of cement (% weight).

| Phase   | C₃S  | C₃A  | C₄AF |
|---------|------|------|------|
| M cement| 43.6 | 34.8 | 2.5  |
| N cement| 59.6 | 15.1 | 9.5  |

Table 8 Oxide composition of binder materials (% weight).

Fig. 4 Elemental distributions by area analysis of EPMA.
having a ratio of 0.45 or 0.65 were also fabricated. They were cast in prismatic steel molds (40 × 40 × 160 mm³) at 20°C. The fresh mortar's air content was set to 4.0 ± 1.0% by adjusting the chemical admixture dosage. After 24 hours, the specimens were demolded and then cured in water at 20°C for 90 days to minimize the influence of maturity on the resulting degradation. All mortar mixtures were confirmed to have a compressive strength of about 50 N/mm² at 91 days. The specimens were further cut in half for the exposure tests (40 × 40 × 80 mm³). The damage in prisms tends to be localized at the corners, where the concentrations of harmful ions that have migrated from the external environment are higher. Hence, for each prism, two parallel surfaces (40 × 80 mm²) were tested, while the other four surfaces were protected with epoxy resin. The original mass in the saturated surface dry state and the length were measured before the exposure tests.

Table 10 lists the exposure conditions. The concentrations of the test solutions were determined according to the exposure classes of BS EN206 (2013) and the field survey results. Figure 5 shows a comparison of some results, in which the worst scenarios found in the survey correspond to the mildest test conditions. For acid attacks, the solution pH was automatically maintained through titration during the test period. In the meantime, the solution was slowly circulated to make the acid distribution uniform. Figure 6 presents the monitoring results of the sulfuric acid solutions used. The pH values agree with our test targets. In the external sulfate attacks, the specimens were immersed in spacious ponds (see Fig. 7); the solutions were renewed once every week until six months and once every two weeks after that.

As ground environments are relatively stable with a steady temperature of 18°C, full immersion experiments at 20°C were performed as a control test. Considering that the temperature at a ground's surface layer is likely to be affected by seasonal fluctuations and solar radiation and the moisture content may be influenced by ground-water movement and rainfalls, temperature history and

| Exposure level | pH of H₂SO₄ and HNO₃ solutions | Concentration of SO₄²⁻ of Na₂SO₄ solutions (mg/L) | Concentration of Mg²⁺ of MgSO₄ solutions (mg/L) | Immersion regimes       |
|---------------|---------------------------------|-----------------------------------------------|-----------------------------------------------|------------------------|
| Low           | 2                               | 1000                                         | 250                                           | Full immersion at 20°C |
| Intermediate  | 4                               | 10000                                        | 2500                                          | Full immersion at 20°C, full immersion with a temperature history, drying-wetting cycles |
| High          | 6                               | 50000                                        | 12500                                         | Full immersion at 20°C |

![Fig. 5 Comparison of solution concentrations with EN exposure classes and survey results.](image1)

![Fig. 6 Monitoring results of pH of sulfuric acid solutions.](image2)

![Fig. 7 Full immersion in sulfate solutions.](image3)
drying-wetting cycles were employed in the study, respectively. The temperature was maintained at 5°C for 90 hours and then raised to 40°C at the rate of 5°C/hour. It was maintained for 64 hours and cooled to 5°C afterward. Such a cycle lasting one week had the same accumulated temperature as that of the control test. The drying-wetting cycles consisted of one-day drying twice a week, during which the specimens were dried in a room at 20°C and 60% RH.

At regular testing intervals, one or two specimens for each test case were taken out of the solutions, and their mass variations and degradation depths were determined (see Fig. 8). Firstly, any salt efflorescence appearing at the surface was removed by water. The length \( L_i \) of each specimen was then measured with a caliper having a resolution of 0.01 mm and compared with the original length \( L_0 \) to determine the length change \( L_{loss} \). The specimen was then immersed in demineralized water for more than 48 hours, and the mass variation relative to the initial one was measured. After that, the specimen was cut along the penetration direction, and the carbonate depth \( L_c \) was measured by the phenolphthalein test. Finally, the weak surface layers were carefully removed using a nylon brush, and the thickness of the weak zone was determined by measuring the remaining length \( L_c \).

### 3.2 Results

#### 3.2.1 Effect of exposure conditions

**Figure 9** shows the mass variations resulting from sulfuric acid and nitric acid attacks, respectively. The test cases are named by binder type-, w/b ratio-, solution type-, concentration-, and exposure conditions. For example, M55-S6-Full represents an M-cement-made specimen with a w/b of 0.55 fully immersed in a sulfuric acid solution (pH = 6). The penetrated sulfuric acid reacts with portlandite and calcium aluminate hydrate to form gypsum and ettringite, resulting in expansion of mortar/concrete, which can cause cracking and peeling of the surface layer. On the other hand, when exposed to nitric acid, calcium nitrate is formed instead, which is a highly water-soluble material that can leach out, leading to a mass loss (Zivica and Bajza 2001; Goyal et al. 2009). Such a mass loss behavior characterized the tests with highly concentrated acid solutions (pH = 2) in this study, in which the mass loss was more than 1.5% after one year of exposure. However, in the cases with higher pH solutions, the mass gain was first observed up to 24 weeks, and then the mass remained almost constant. The absorption of acids was considered to cause the initial mass gain. Although the acids slowly reacted with the mortar matrix constituents, the matrix alterations seem minor.

**Figure 10** compares the length loss, the thickness of the weak zone, and the carbonation depth after 208 weeks of exposure to the acids between different pHs. For the cases with higher pH solutions, no evident length changes were found, and the weak zone due to the dissolution of the hydrated phases was thinner than 0.5 mm. As for the sulfate attacks, the mass variations are plotted in **Fig. 11**, whereas **Fig. 12** compares the degradation depths after 208 weeks of exposure between different cases. Negative values of length loss were taken as representing an expansion behavior. The specimens exposed to sodium sulfate with different concentrations showed a similar behavior characterized by a mass increase and some expansion. As the C_3A contents of the cement (M and MF) were small, the main reaction products were supposed to be gypsum that had filled micro pores resulting in a mass gain and expansion (Naik et al. 2006). In the case of magnesium sulfate, the specimens exposed to a low level of Mg\(^{2+}\) (250 mg/L)
yielded a similar mass increase and expansion behavior due to the generation of brucite and gypsum. However, with the increasing concentration of Mg$^{2+}$, significant mass loss and surface layer spalling occurred (see M55-Mg5-Full and MF55-Mg5-Full). As other studies indicated (Santhanam et al. 2001; Neville 2004), when concrete is exposed to a high level of Mg$^{2+}$, the conversion of C-S-H to M-S-H becomes dominant, leading to a great decalcification. This can explain the drastic mass loss observed in this study.

Figure 13 shows the mass variations due to the exposure to sulfuric acid (pH = 4) under different immersion regimes. The degradation depth after 208 weeks of exposure for each test case is shown in Fig. 14. It appears that the temperature history adopted accelerated the sulfuric acid attacks on both M and MF cements producing more mass gains and roughly double-thick weak zones when compared with the control tests (M55-S4-Full and MF55-S4-Full), although the extents of carbonation were similar (see Fig. 14). On the other hand, when drying-wetting cycles were included in the test, the behavior of mass loss and length decrease was
observed soon after the test’s start, while carbonation developed more slowly than that under the other two immersion regimes. These behaviors can be attributed to physical attacks induced by salt crystallization.

The test results using Na$_2$SO$_4$ solutions (10000 mg/L SO$_4^{2-}$) with different immersion conditions are shown in Fig. 15 (mass variation) and Fig. 16 (degradation depth after 208 weeks of exposure). Similar to the findings on the sulfuric acid attack, the results of the sodium sulfate attack also showed that the temperature history exacerbated the chemical phase transformation, while the physical attack occurred in the tests applied with drying-wetting cycles.

The tests on the effects of exposure conditions reveal that the accelerated tests, such as those with highly concentrated solutions and increased temperature, drastically aggravate the extent of decalcification and produce a pronounced weak zone at the specimen’s surface layer. It is unclear if such a degree of degradation may eventually occur after a more extended exposure period to the actual environments with low concentrations of aggressive agents. Moreover, in the magnesium sulfate attack, the degradation mechanism depends on the concentration of Mg$^{2+}$. These differences make it challenging to correlate the results of the accelerated tests with field situations. Hence, full immersion in a low-concentration solution with a stable temperature is preferred for evaluating the long-term performance of below-grade concrete.

### 3.2.2 Effect of cement type

After 208 weeks of exposure to the four different solutions (acids of pH = 4 or sulfates with 10000 mg/L SO$_4^{2-}$), the degradation depths are compared between different cement types (see Fig. 17). In the acid attacks, the N cement showing reduced weak zones performed better than the M cement and those blended with fly ash. It appears that, without sufficient calcium hydroxide in the matrix, the acids directly reacted with C-S-H and produced more significant surface weakening.

It is well known that using the cement with a low C$_3$A content can provide good resistance concerning sodium sulfate attack. The test results showed that the N-cement-made specimens had the most extensive expansion when exposed to the sodium sulfate solution, leading to cracking and surface layer spalling. In comparison to the N cement, the M cement with a lower C$_3$A content and those blended with fly ash yielded better resistance as the amount of formed ettringite reduced. It
is, however, not the case for exposure to the magnesium sulfate solution. The thicknesses of the weak zones in the M cement or binary cement made specimens were approximately twice that of N cement, which is attributed to the direct attack on C-S-H induced by Mg\(^{2+}\). Therefore, the pH and the concentration of Mg\(^{2+}\) in the exposure environments of concrete should be considered when determining an appropriate cement type.

3.2.3 Effect of water-to-binder ratio

Figure 18 shows the effect of the w/b ratio on the degradation depth after exposure to the four different test solutions (acids of pH = 4 or sulfates with 10000 mg/L SO\(_4^{2-}\)) for 208 weeks. In the acid attacks, reducing the w/b ratio increased the acid resistance of the mortar specimens due to their lower porosity and permeability. As for the sulfate resistance, the carbonation depth also decreased as the w/b ratio reduced. On the other hand, it was found that when expansive products such as ettringite, gypsum, or brucite are generated, the lower porosity yielded by a small w/b ratio can result in more significant expansion behavior after a long-term exposure to sodium and magnesium sulfates.

4. Discussion on the prediction of degradation extent

For predicting the degradation extent of concrete exposed to aggressive environments, simulation tests using close-to-reality concentrations of aggressive agents can capture the actual deterioration process (RILEM 2012). However, within a reasonable test period, such a test method may only reproduce the early stage of the degradation, which requires an extrapolation of the test results. The commonly measured mass variations of mortar/concrete specimens are difficult to extrapolate as the acid and sulfate attacks involve both mass gain and loss. As for the length change, the expansion of specimens is followed by their length decrease due to cracking and surface scaling. In the present study, progressive carbonation/neutralization was confirmed in all test cases beyond the weak zones of the mortar specimens. Therefore, the carbonation depth was used as an indicator to correlate the test data and the survey results.

The test results of carbonation depths are plotted against the square root of time in Fig. 19. A linear relationship reflecting diffusion phenomena was found despite the distinct forms of chemical attacks. The larger fitting coefficient for the more concentrated solution...
reveals the acceleration effect, but the underlying reactions may alter, as discussed before. It should be borne in mind that this indicator just roughly gives which area is affected by penetrated acids or sulfates and does not suffice to characterize the degradation type.

Figure 20 shows the comparison of carbonation depths between the field observations and some of the laboratory tests under similar exposure conditions. The effect of aggregates on the chemical degradation was neglected here because the field concrete contained non-limestone aggregates. The carbonation depths found in the field concrete were comparable to the predictions based on the laboratory tests. Regarding the acid attacks, the less carbonation in the concrete of the buildings 3 and 4 compared with the prediction curves is likely due to no-direct contact with groundwater and to drying at the top surface of soils. Given that the groundwater of the NPPs examined in this study has a pH larger than 6.5 and an $\text{SO}_4^{2-}$ concentration marginally greater than 250 mg/L, the carbonation depth of a normal-strength below-grade concrete may be smaller than 10 mm after 60 years of exposure. Hence, the degradation may merely reside in such a shallow surface area.

5. Conclusions

This paper investigated the underground environments of several NPPs and residential RC buildings across Japan for potential attacks by acid and external sulfate attacks. The performance of below-grade concrete exposed to such environments was examined where concrete samples from core drillings were available. Furthermore, long-term exposure tests on mortars were carried out in the laboratory using acid and sulfate solutions with various concentrations to examine the effects of exposure conditions, cement type, and w/b ratio. The following conclusions were drawn:

1. For the NPPs examined, the groundwater on the land side contained mainly sodium sulfates with a pH greater than 7.0, classified as a non-aggressive or slightly aggressive environment according to BS EN206. In contrast, the groundwater on the marine side contained a large amount of chlorides.

2. Parts of the buildings examined have been exposed to...
slightly aggressive environments (pH = 6.5, SO₄²⁻ > 350 mg/L). However, the concrete cores extracted showed little degradation after 40 years of exposure; only leaching zones with a thickness of less than 6.0 mm were found.

(3) Laboratory test results indicated that the highly concentrated solutions used for accelerated tests could exacerbate the extent of decalcification and even alter the degradation mechanism for magnesium sulfate, making it difficult to correlate with a field situation.

(4) Compared with ordinary Portland cement, the cement with a low C₃A content or blended with fly ash showed good resistance to sodium sulfate but performed poorly against acids and magnesium sulfate. The effect of lowering the w/b ratio was twofold; the penetration of harmful ions was restrained due to the low porosity of mortar, while in case of forming expansive products, it caused more expansion.

(5) The carbonation depths measured in the laboratory test using low-concentration solutions were correlated with the field results, allowing a rough estimation of the degradation extent. The results suggested that the below-grade concrete in the NPPs examined may have a degradation of less than 10 mm after 60 years of exposure.

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