

1 Long-term use of modern Portland cement concrete: change in
2 strength due to reaction between aggregate and cement paste

3

4 Ippei Maruyama^{a,b,*}, Abudushalamu Aili^a, Shohei Sawada^c, Kazuhiro Yokokura^d, Yoshito
5 Umeki^e

6

7 a: Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan

8 b: Graduate School of Engineering, The University of Tokyo, Tokyo, Japan

9 c: Nuclear Power Department, Kajima Corporation, Tokyo, Japan

10 d: Civil & Architectural Engineering Department, Hamaoka Nuclear Power Station, Chubu
11 Electric Power Company Incorporated, Shizuoka, Japan

12 e: Civil & Architectural Engineering Department, Chubu Electric Power Company
13 Incorporated, Nagoya, Japan

14 *: corresponding author, i.maruyama@bme.arch.t.u-tokyo.ac.jp

15

16 Abstract

17 Experimental measurements on samples cored from thick concrete walls of existing
18 building structures whose age was ~50 years at most showed that concrete strength
19 increased after long-term use due to chemical reactions between aggregate and cement
20 hydrates. Chemical compositions of reacted aggregate were analyzed by comparing the
21 oxide composition of cement paste with that of original cement based on inductively
22 coupled plasma atomic emission spectroscopy (ICP-AES) measurement. The results
23 provide indicators to determine the dissolving aggregate minerals as well as the reaction
24 degree of aggregate. A model was proposed to simulate the progress of reaction degree
25 over time in coupling with moisture transport and temperature in concrete. The
26 mechanism of strength increase was discussed by analyzing the gel-space ratio
27 estimated from XRD-Rietveld analysis and that estimated from the thermodynamic
28 simulation of the reaction. Finally, the strength prediction model was proposed for the

29 aging management of building structures.

30

31 Keywords: Concrete (E), Aggregate (D), Reaction (A), Long-term performance (C)

32

33 Highlights:

34 ● Minerals dissolving from aggregate were quartz, albite, and chlorite.

35 ● The dissolution rate of aggregate was modeled, considering the coupling with
36 moisture transport in concrete.

37 ● Strength increases due to the reaction between aggregate and cement paste can be
38 regarded as a result of space-filling, i.e., an increase in gel space ratio.

39

40

41 1 Introduction

42 The long-term use of concrete structures is one of the significant options to reduce the
43 CO₂ emissions from the concrete sector [1]. For this goal, aging management, including
44 structural performance evaluation in the current and future, is necessary. However, the
45 long-term alteration of concrete properties, especially compressive strength, is a
46 significant challenge to predict because there are many scenarios according to the
47 corresponding materials and exposed environments.

48 The long-term operation of nuclear power plants is also a crucial issue in our society, and
49 carbon neutrality is required to attain a sustainable society. Currently, the building of
50 new-generation nuclear reactors and small modular reactors is under planning, and such
51 a process will take a relatively longer time than that of ordinary structures because of
52 safety regulations and social acceptance. Nuclear energy is considered an important
53 base-load energy in Japan. Therefore, the long-term operation of existing nuclear power
54 plants is promising. Compressive strength is the primary index for the safety evaluation
55 of concrete structures, especially for seismic performance. However, evaluating
56 compressive strength in long-term used concrete members is difficult because of the
57 thickness of the member and different phenomena that affect the compressive strength.

58 To develop a method to evaluate and predict the compressive strength of the aged

59 concrete structures exposed to the specific environments of nuclear power plants, we
60 investigated decommissioning plants deeply. During the decommissioning process of the
61 Hamaoka nuclear powerplant in Shizuoka prefecture in Japan, it was found that the
62 strength and Young's modulus of concrete increased after long-term use [2]. In a
63 previous study, it was confirmed that, in unit 1 of the power plant, the aggregates in the
64 concrete dissolved and reacted with hydrates in cement paste based on Rietveld analysis
65 of X-ray diffraction (XRD) data and that the increase of strength was attributed to the
66 "aggregate-paste reaction" [2,3]. The reaction scheme was analyzed using X-ray
67 microdiffraction and energy dissipative X-ray spectroscopy (EDS) to understand the
68 formation of Al-tobermorite (i.e., the crystal form of calcium aluminum silicate hydrates
69 (C-A-S-H)) which was a rare case [4]. Furthermore, similar reactions and strength
70 increases were found to be time-evolving when we analyzed other decommissioning
71 concrete walls constructed at different decades but using aggregates of similar origin.
72 Such field data showing a time-dependent relation of aggregate reaction and
73 compressive strength, measured on harvested samples from real structures with various
74 ages (from ~48 years to ~17 years), cannot be obtained in laboratory experiments and
75 hence precious for long-term performance evaluation of structures. The primary
76 objective of the work is to present these valuable in-situ data and to put forward
77 underlying common phenomena.

78 Dissolution of aggregate has been studied in the literature in many contexts, such as
79 alkali-silica reaction in cementitious materials [5] and in weathering of rocks in earth
80 science [6]. For main rock-forming minerals found in common aggregates, such as quartz,
81 albite, microcline, and chlorite, the main parameters impacting the dissolution rate are
82 summarized in [7,8] as moisture, temperature, ions in the water, including pH and
83 surface characteristics of the aggregate/mineral such as defects, crystallinity. For the
84 higher range of pH that corresponds to the pore solution in cementitious materials, the
85 effects of temperature, pH, and various ions were systematically studied in laboratory
86 experiments for quartz [9], amorphous silica [10], albite [11], chlorite [12,13] and illite
87 [14]. Experimental data on the long-term dissolution of in-situ aggregates, such as this
88 study, are scarce. Theoretical models accounting for the main factors of dissolution have
89 been established to predict the dissolution rate of minerals and used to estimate stability
90 against weathering [6]. Nevertheless, many complicated phenomena in the dissolution
91 of rock-forming minerals remain to be studied [15]. For instance, the composition of ions
92 released from feldspar during dissolution differs from stoichiometry and is known as
93 incongruent dissolution [16]. Another example of complexity is the formation of a
94 leached layer [15].

95 Based on these unique field data, the study aims to investigate the underlying common
96 phenomena, i.e., aggregate dissolution, reaction with cement hydrates, and increase of
97 compressive strength. At the same time, the study aims to elucidate the physical
98 mechanism behind the increase in strength and develop a universal methodology for
99 predicting long-term strength that can be promoted for broader use in engineering
100 practice.

101 The first necessary condition for the dissolution of aggregates in cementitious materials
102 is the pore water, which varies over time due to water transport by advection in liquid
103 form and by diffusion in vapor form. Time evolution of water content in mature concrete
104 can be modeled as a two-phase flow in porous media in a stricter manner [17] but for
105 application in real concrete, simplified models such as the Akita model proposed in [18]
106 can be enough, considering the complexity of boundary condition, variation of
107 microstructure and uncertainty of experimental data caused by coring and measurement
108 techniques. The composition of pore water, including pH values, can be measured
109 experimentally by extracting the pore water [19]. However, due to the difficulty in
110 extracting techniques, they have yet to be widely promoted. As alternatives,
111 thermodynamic simulation of hydration reaction [20,21] and mineralogical analysis of
112 cement hydrates may hint at the pH value. For instance, since portlandite is unstable at
113 a pH lower than 12.5, the presence of portlandite indicates that the pH value of the pore
114 solution is higher than 12.5 [19].

115 The compressive strength of concrete depends on various factors and is generally related
116 to mixture proportion and microstructure. One of the relevant descriptors of
117 microstructure is gel-space ratio, initially proposed in [22,23] as the volume ratio of
118 amorphous calcium silicate hydrates (C-S-H) to the original space, i.e., the sum of
119 volumes of cement clinker and water. Later, it was found that it is not only the volume of
120 C-S-H gel but the total volume of all hydrates that contributes to the strength
121 development [24]. The definition of gel-space ratio was modified to include the volume
122 of all hydrates, with experimental evidence showing a good relation between such gel-
123 space ratio and the strength of concrete [25–28]. Connecting gel-space ratio to
124 mechanical performance in literature was limited mainly to cement pastes and mortars,
125 even less to concrete with non-reactive aggregate. For the first time, the method will be
126 extended to the case of reacting aggregate to explain the strength increase mechanism
127 in Hamaoka walls.

128 We start by presenting experimental data from the other three units of the Hamaoka
129 power plan. Then, from the ICP-AES data, we will compute the oxide composition of the

130 dissolved aggregate. A coupled model of moisture transport and reaction degree will be
 131 proposed to understand the reaction rate. The mechanism behind the strength increase
 132 will be discussed. We will show how the study's findings can be applied to predict
 133 strength evolution over time in plant life management.

134 2 Material and method

135 2.1 Samples

136 Concrete samples were cored from thick concrete walls of the Hamaoka nuclear power
 137 plant in the Shizuoka prefecture in Japan, which is now under decommissioning. The
 138 power plant comprises five units (H1 to H5), constructed at different times. In this study,
 139 we used samples cored from the Biological Shielding Wall (BSW), pedestal (PEDE) and
 140 Internal wall 1st floor (IW1-1F) and basement 2nd floor (IW1-B2F) of H2, internal wall
 141 (IW1) of H3 and internal wall (IW1) of H5. The coring method is the same as described
 142 in [2,29], where samples from BSW, IW1, and PEDE of H1 have been studied. The mixture
 143 design of the concrete is listed in Table 1, as well as the age of the concrete at the time
 144 when the samples were cored. Table 2 shows the mass of raw materials per unit volume
 145 of concrete. The oxide compositions of used cement are shown further in Table 4,
 146 together with experimental results to reduce the number of tables.

147

148 Table 1 Mixture proportion of concrete for the studied walls

	Age of construction at testing time (years)	Cement type ^a	Design strength (MPa)	Slump (cm)	Air content (%)	Water to cement ratio (%)	Sand volume to aggregate volume ratio (%)
H1- IW1	45	OPC	21	12	3.5	48.3	38.5
H1- BSW	45	MPC	21	12	3.5	48.0	39.7
H1-	45	MPC	21	15	3.5	49.0	42.0

PEDE							
H2	46	MPC	21	12	3.5	48.0	43.0
H3	37	MPC	21	12	3.0	52.0	45.2
H5	20	MPC	21	15	4.0	49.0	45.5

^aOPC: Ordinary Portland cement; MPC: Moderate heat Portland cement (according to the Japanese Industrial Standard JIS R 5210 [30]).

149

150 A schematic representation of the power plant building is shown in Fig. 1 of [2] for H1.
 151 The building designs were the same for the other three units in this study. Cylindrical
 152 cores were taken from one side of the walls. In the case of BSW and PEDE, the coring
 153 was started from the room side (opposite side of the reactor). The water cooling method
 154 was used when the core was intended to test strength and phase composition. The dry
 155 air-cooling method was also used during coring to test relative humidity. The diameter
 156 of the coring was 200 mm. After getting the core, several samples with defined thickness
 157 were cut for testing. These samples were noted by the distance between their center
 158 and the wall's surface. The thickness of the walls and the number of samples per core
 159 are summarized in Table 3.

160

161 Table 2 Mass of raw materials per unit volume of mixture (kg/m³)

	Cement	Water	Water reducing agent	Sand	Gravel
H1-IW1	300	145	2.3	734	1178
H1-BSW	300	144	2.3	758	1160
H1-PEDE	310	152	2.4	792	1096
H2	300	144	3.3	832	1105
H3	288	150	3.0	858	1060
H5	331	162	1.5	822	1004

162

Table 3 Details of the walls

Target wall	Wall thickness (mm)	Number of samples per core	Surface condition ^a	Temperature during operation (°C)	Temperature after operation (°C)	Duration of operation (years)
H1-IW1	1500	7	N/N	20-30	20-30	16.5
H1-BSW	2200	7	N/L	30-38/50-55	20-30	16.5
H1-PEDE	1220	5	E/E	50-55	20-30	16.5
H2-IW1-1F	1700	7	N/N	20-30	20-30	18.4
H2-IW1-B2F	1700	7	N/N	20-30	20-30	18.4
H2-BSW	2200	7	N/L	30-38/50-55	20-30	18.4
H2-PEDE	1380	5	E/P	50-55	20-30	18.4
H3-IW1	1300	5	N/N	20-30	20-30	18.4
H5-IW1	1000	5	N/N	20-30	20-30	3.1

^aN: bare surface; L: steel liner; E: epoxy resin coating; P: steel plate.

165 2.2 Experiments

166 Multiple experiments were performed to characterize the aged concrete. Here, only the
167 relevant ones are described. It is noted that, as part of the whole project, the
168 experimental methods in this study were the same as those in [2,3].

169 Compressive strength was measured on samples from wet coring. Cylindrical samples of
170 size $\varphi 200$ mm \times 100 mm were polished and measured according to the Japanese
171 Industrial Standard JIS A 1149 [31].

172 Water content was measured using samples from dry coring. Approximately 1500 g of
173 sample was roughly crushed into particles of size 10-20 mm and then dried at 105 °C
174 until a constant mass was reached while a 100 mL/min nitrogen gas flow passed through
175 during the whole heating. Water content was obtained by taking the mass loss as the
176 mass of evaporable water in the sample and normalizing it with the mass of the sample
177 after heating at 105 °C.

178 Relative humidity at the coring time was measured using samples from dry coring. The
179 samples were sealed immediately after coring and shipped to the constant temperature
180 room at 20 ± 0.2 °C, where around 10 g samples were chipped from inside the portion.
181 Then, the chipped block was sealed in an aluminum-coated polyvinyl bag, roughly
182 crushed, and put inside a water activity meter (AQUALAB 4TE, METER Group) to measure
183 the relative humidity.

184 Total porosity was measured using samples from wet coring. Samples of size $\varphi 200$ mm
185 \times 100 mm were immersed in water and vacuumed for one hour. Then, the samples
186 remained in water while the mass was measured every 24 hours. When the difference
187 between the two subsequent measurements was less than 0.1 g, the samples were
188 considered fully saturated, and saturated mass was noted. The apparent volume of the
189 sample was measured using the Archimedes method. Finally, we obtained the dry mass
190 by drying the sample at 105 °C with a 100 mL/min nitrogen gas flow. Taking the
191 difference between saturated and dry mass as the mass of water filling all the pores, we
192 obtained the total volume of the pores and normalized to the apparent volume of the
193 sample.

194 Quantitative X-ray diffraction (Q-XRD) was measured using samples from wet coring.
195 Samples were roughly crushed into sizes less than 5 mm, and visible aggregates larger
196 than 3 mm were removed. The remaining part was considered mortar and ground into
197 a fine powder of less than 90 μ m particle size. The objective was to determine the phases

198 in the cement paste; preparing such mortar by removing big aggregates was considered
199 valid. The fine powder was dried at a relative humidity of 11% for two weeks and then
200 mixed with a 10% mass of corundum as an internal reference. X-ray diffraction profiles
201 were measured between $2\theta=2-65^\circ$, using three replicates for each sample. The
202 diffraction patterns of H2-IW1-1F&B2F, H2-PEDE, H3-IW1, and H5-IW1 were measured
203 by a D8 ADVANCE (Bruker AXS) that uses a Cu-K α X-Ray source at 40 kV and 40 mA, in
204 increments of 0.02° , with a speed of $0.5^\circ/\text{min}$. For H2-BSW, the diffraction patterns were
205 measured by a PANalytical Empyrean diffractometer (Malvern PANalytical) that uses a
206 Cu-K α X-Ray source at 45 kV and 40 mA, in increments of 0.026° , with a speed of 300
207 s/step.

208 Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was measured using
209 the same mortar powder samples as Q-XRD. In the first step, around 1 g of mortar
210 powder sample was put in hydrochloride acid solution (1.65 mol/L) and stirred for 30
211 minutes. Then, the insoluble residue was filtered out while the solution was collected
212 (noted as solution 1). In the second step, the filtered insoluble residue was put in
213 potassium hydroxide solution (0.2 mol/L) and left at 70°C for 60 minutes. Again, the
214 solution was collected (noted as solution 2) while the insoluble solid was filtered out. In
215 the third step, on the one hand, the final residue was heated at 1000°C for 60 minutes
216 to obtain the mass of the insoluble part of the initial mortar sample. On the other hand,
217 analyzing solutions 1 and 2 by ICP-AES, the oxide compositions (CaO, SiO₂, Al₂O₃, Fe₂O₃,
218 MgO, SO₃, Na₂O, and K₂O) of soluble part of the mortar sample were obtained. The
219 difference, obtained by subtracting the sum of the oxides' mass and the insoluble mass
220 from the initial mass of the mortar sample, was considered as the sum of loss on ignition
221 (OH⁻ and CO₃²⁻) and of other minor elements.

222 Similar dissolution processes in solutions 1 and 2 were performed on fine aggregates,
223 yielding the oxide composition of the soluble part of the aggregate and the insoluble
224 mass.

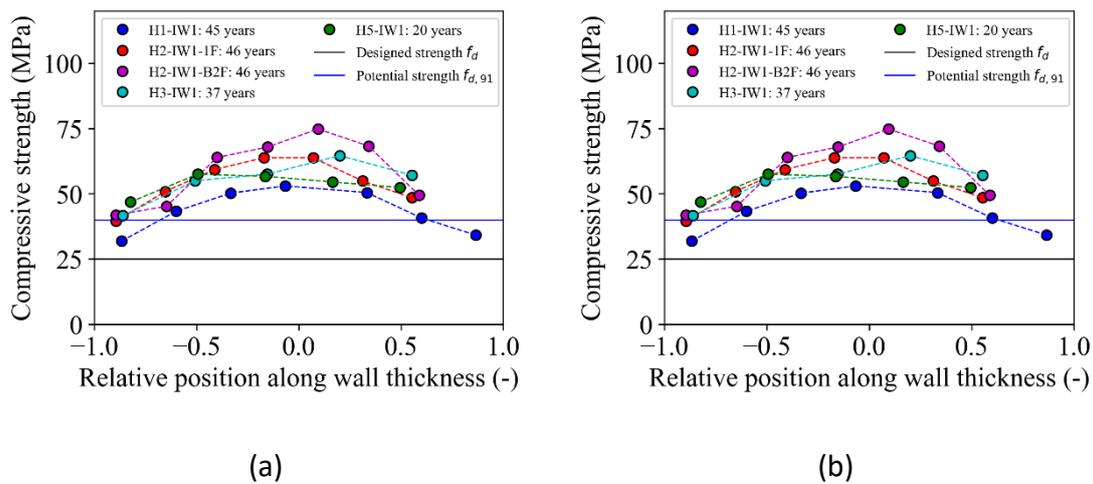
225 3 Experimental results

226 3.1 Compressive strength, water content, relative humidity, and total porosity

227 The strength of cores is displayed in Figure 1 in the function of core position, which is
228 defined as a linear transformation of the distance between the core center and wall
229 surface. In this linear transformation, the center of the core is noted as 0, and the outer
230 and inner surfaces as -1 and +1, respectively. The compressive strength is higher than
231 the designed strength of 21 MPa and even increased further in the inner parts to surpass

232 the potential strength of 40 MPa expected at 91 days. In the IW1s, which were submitted
 233 to a constant temperature of 25 °C since the construction, the profile of compressive
 234 strength along the wall thickness is a convex shape (see Figure 1a), whereas, in BSW and
 235 PEDE with high-temperature history, increase of compressive strength is more significant
 236 towards the inner part where the temperature during operation was high.

237



238 Figure 1 Compressive strength versus the core position along the wall thickness. X-axis
 239 0 represents the wall center, while ± 1 represents the two surfaces. (a) internal walls
 240 without high-temperature history; (b) BSWs and PEDEs with high-temperature history.

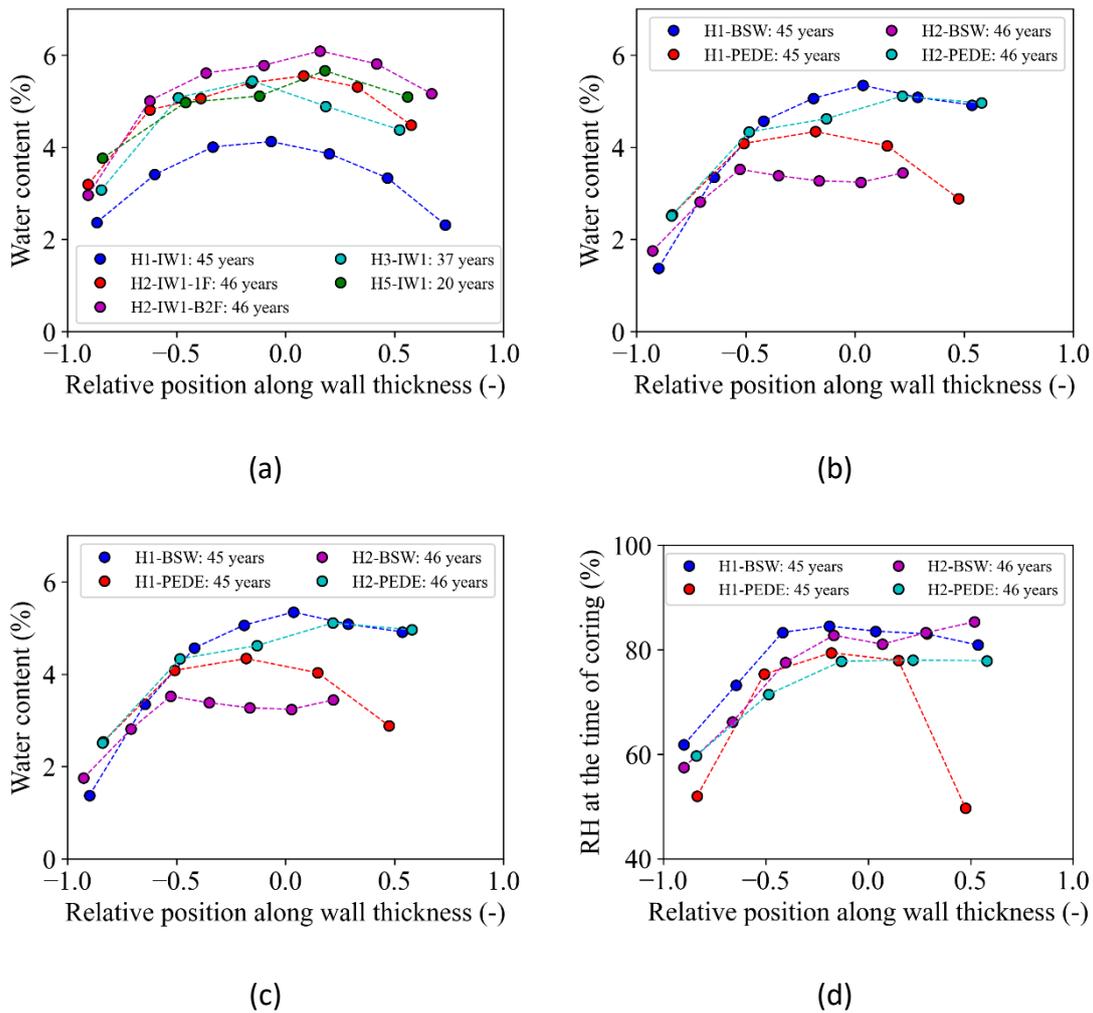
241

242 The results of water content and relative humidity measurement are shown in Figure 2.
 243 Like the strength profile, a convex shape was shown in water content and relative
 244 humidity of IW1s. The water content of H1 was significantly lower than other IW1s. At
 245 the same time, the relative humidity was similar to that of other IW1, indicating a
 246 fundamental difference between H1-IW1 and all other IW1: H1-IW1 was OPC, whereas
 247 all other walls were composed of MPC. The OPC concrete has higher water diffusivity
 248 than MPC concrete due to its higher calcium content in the main hydrate phase C-S-H,
 249 through which the water diffuses. The water content of IW1 of H2, H3, and H5 were
 250 similar despite the age difference (see Table 1).

251 Nevertheless, this similarity can be explained by the difference in thickness. Taking the
 252 half thickness of the wall as the diffusion length and considering the same diffusion
 253 coefficients, the ratio of the characteristic diffusion times in H2 and H5 would be 2.9.
 254 The 16-year age in H5-IW1 is equivalent to 46 years in H2-IW1.

255 In BSWs, water content and relative humidity were lower near the outer surface
 256 (position -1 in Figure 2b and d), which was not coated. Thanks to the metallic liner, the
 257 water content and relative humidity were kept higher towards the inner surface (position
 258 1 in Figure 2b and d). The water content profile and relative humidity PEDEs were
 259 consistent with their corresponding coating conditions.

260



261 Figure 2 Water content and relative humidity versus core position along the wall
 262 thickness. X-axis 0 represents the wall center, while ± 1 represents the two surfaces.
 263 (a)(c): IW1s without high-temperature history; (b)(d): BSWs and PEDEs with high-
 264 temperature history.

265

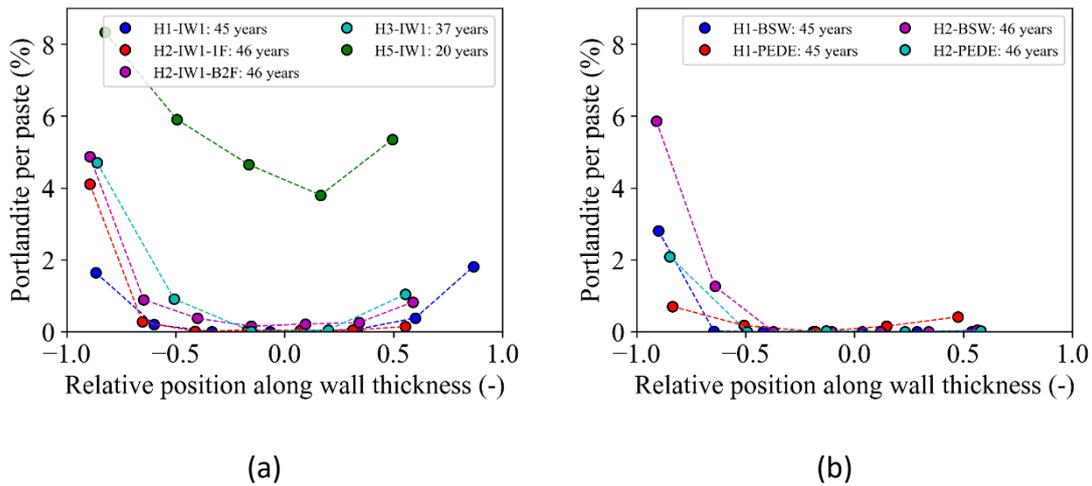
266 The results of the porosity measurement are shown in Appendix A, Figure A1. In contrast

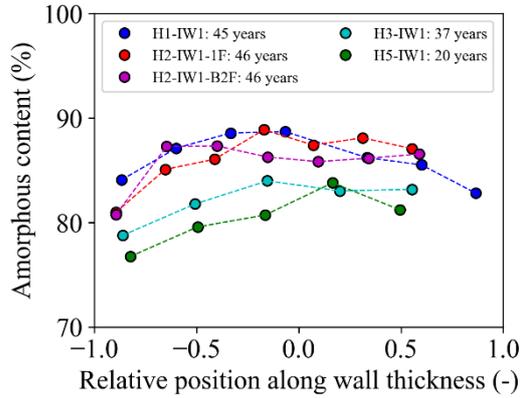
267 to water content, the porosity did not show any clear trend along the wall thickness but
268 was approximately constant. We attribute the quasi-uniform porosity to the same
269 mixture proportion and similar hydration degree along the wall thickness, which was
270 confirmed by the XRD results in the next section.

271 3.2 XRD results

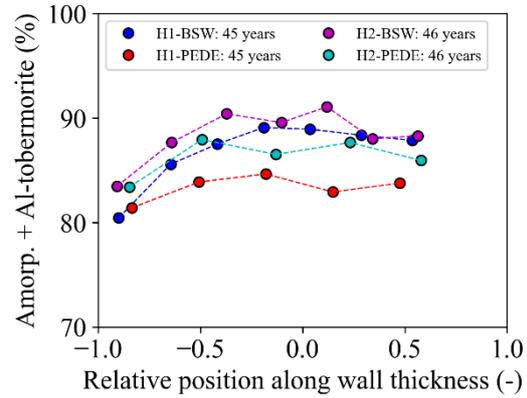
272 XRD diffraction patterns were analyzed using the Rietveld method following the protocol
273 established in [26] and using the same phases listed in [4], given the same origin of
274 aggregate. From the obtained phase compositions of each core position, aggregate
275 minerals (i.e., quartz, albite, muscovite, chlorite, illite, biotite, and microcline) were
276 excluded to obtain the phase composition of cement paste only. Similar to the findings
277 in H1 shown in [2], portlandite was absent in the inner part of the walls where water
278 content was relatively high. The crystal form of C-A-S-H, Al-tobermorite was observed in
279 H2-PEDE, in addition to H1-BSW and PEDE. The decrease in portlandite was consistent
280 with the increase of amorphous content in IW1s, as shown in Figure 3a and c. In Figure
281 3b and d of BSW and PEDE, the sum of amorphous content and Al-tobermorite was
282 inversely correlated to portlandite. Unreacted cement clinker phases were
283 approximately uniform along the depth of each wall.

284





(c)



(d)

285 Figure 3 Portlandite and the sum of amorphous phase and Al-tobermorite content in
 286 the cement paste versus core position. X-axis 0 represents the wall center while ± 1
 287 represents the two surfaces. (a)(c): IW1s without high-temperature history; (b)(d):
 288 BSWs and PEDEs with high-temperature history.

289

290 3.3 ICP-AES

291 In the ICP-AES measurement, we obtained the oxide composition $m_i^{diss,m}$ ($i = \text{CaO}$,
 292 SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , SO_3 , Na_2O , and K_2O) of soluble part, insoluble mass, and mass
 293 of ignition loss for mortar sample at each coring position for each wall, as well as for
 294 sound fine aggregate. Assuming that the insoluble part of mortar is from fine aggregate
 295 only, the dissolved oxides $m_i^{diss,a}$ from aggregate, was estimated. Subtracting $m_i^{diss,a}$
 296 from the total dissolved oxides, we obtained the oxide composition of the cement paste
 297 part: $m_i^p = m_i^{diss,m} - m_i^{diss,a}$. Significant differences between this oxide composition
 298 m_i^p and the oxide composition of the original OPC/MPC in Table 4 confirmed the
 299 dissolution of some aggregates into the paste, hence the aggregate-paste reaction.

300

301 Table 4 Oxide compositions of Ordinary Portland cement, Moderate heat Portland
 302 cement, and cement paste part from three walls for comparison.

Oxide	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	Sum
OPC	65.37	22.13	5.25	3.23	1.62	1.72	0.28	0.40	100

MPC	64.51	23.68	3.84	3.93	1.10	2.27	0.26	0.40	100
H2- BSW- 690	51.94	35.59	5.00	4.05	1.14	1.37	0.64	0.27	100
H3- IW1- 550	53.73	33.27	5.20	3.59	1.58	1.80	0.50	0.33	100
H5- IW1- 252.5	58.67	29.94	4.43	3.60	1.15	1.81	0.25	0.15	100

303

304 We assumed that all the calcium oxide in the cement paste part m_i^p originated from
305 the original OPC/MPC. Comparing the mass fraction m_{CaO}^p of calcium oxide in the
306 cement paste part with m_{CaO}^{OPC} or m_{CaO}^{MPC} in the OPC/MPC, the mass fraction φ_a of
307 oxides originating from the dissolved aggregate was estimated. Then, the reaction
308 degree of aggregate ζ , i.e., the mass ratio of the reacted aggregate over the initial
309 aggregate, was calculated by:

310

$$\zeta = \frac{\varphi_a}{a/c} = \frac{m_{CaO}^{MPC} - m_{CaO}^p}{m_{CaO}^p} \frac{1}{a/c'} \quad (1)$$

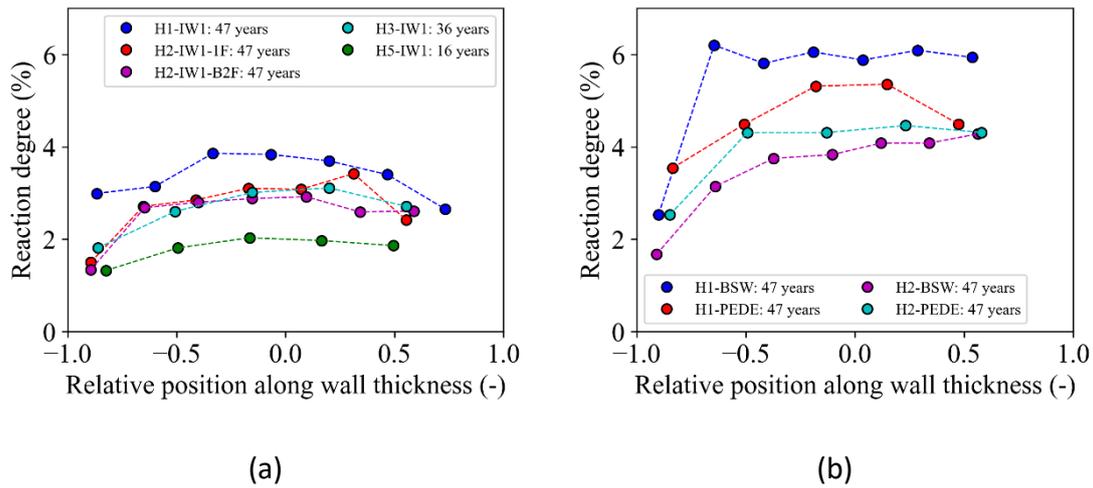
311

312 with a/c as the aggregate-to-cement mass ratio from the initial mixture proportion.

313 The obtained reaction degree of aggregates is displayed in Figure 4 as a function of the
314 relative position of the cores along the wall thickness. The results show that the reaction
315 degree of aggregate evolves with time, showing a higher reaction degree in H1 and H2,
316 whose construction ages were ~46 years, than in the other units, H3 and H5. For each
317 wall, the reaction degree is higher in the inner part than in the parts near the surface,
318 indicating that water content and relative humidity are necessary conditions for the
319 aggregate reaction. In H1 and H2, the walls that experienced high temperatures during
320 the power plant's operation (i.e., BSW and IW1) showed higher reaction degrees, which
321 the thermal activation of the reaction can explain. The lower reaction degree in H2-BSW,

322 when compared with that in H1-BSW, is likely attributed to the longer high temperature
 323 in H2. Due to the longer duration of higher temperatures, drying could be accelerated,
 324 resulting in less water and a lower reaction degree in H2-BSW.

325



326 Figure 4 Reaction degree of aggregate versus core position. X-axis 0 represents the wall
 327 center, while ± 1 represents the two surfaces. (a): IW1s without high-temperature
 328 history; (b): BSWs and PEDEs with high-temperature history.

329

330 For example, the reaction degree of 3.1% in the center of H2-IW1-1F indicates that 26
 331 kg aggregates dissolved and reacted in 1 m³ of concrete, increasing 39 MPa of
 332 compressive strength compared to the designed strength of 25 MPa. It is even more
 333 significant for walls with a high-temperature history. For instance, the reaction degree
 334 of 6.2% in H1-BSW implies a reaction of 47 kg aggregates per m³ of concrete and an
 335 increase of compressive strength by 47 MPa. Therefore, the aggregate-paste reaction
 336 and its contribution to the strength increase are significant. Clarifying reaction kinetics
 337 and strength increase mechanisms are helpful for the aging management of thick
 338 concrete walls.

339

340 4 Analysis of the aggregate-paste reaction

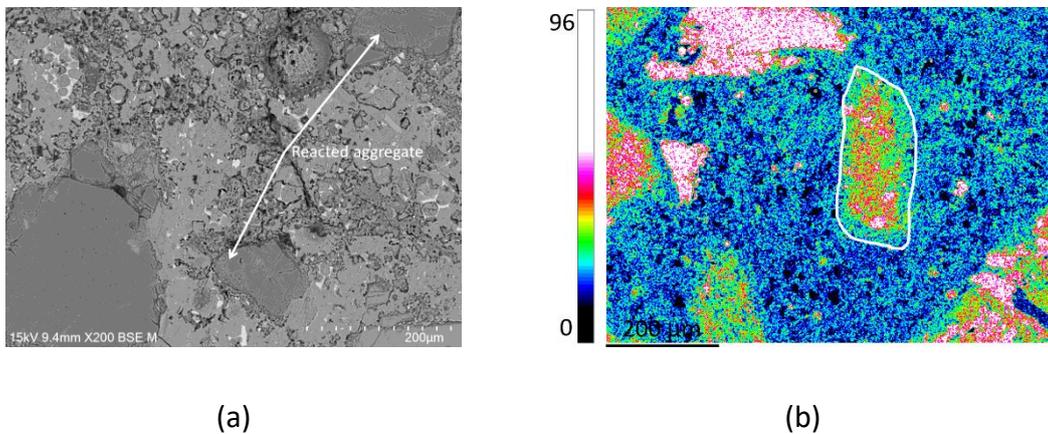
341 The reaction between aggregate and cement hydrates happened in all the walls and
 342 showed time-dependent characteristics, as shown in section 3.3. Even though those
 343 walls were constructed in different decades, aggregates from the same origin were used.

344 Therefore, we believe that the reaction in these walls is a universal phenomenon and
345 that the reaction scheme and kinetics are worth investigating and can be extrapolated
346 to broader applications. In the first part of this section, the oxide composition of
347 dissolved aggregate will be deduced from ICP-AES results to infer the reacting minerals
348 of the aggregate. In the second part, we aim to understand the time evolution of the
349 aggregate-paste reaction, considering given temperature and moisture conditions.

350 4.1 Composition of dissolved-reacted aggregate

351 Reacted aggregates were identifiable from the texture in backscattered electron (BSE)
352 images in previous studies, such as Figure 5a, measured in [2]. Moreover, the EDS maps
353 measured in [4] showed silica released from sandstone aggregates (see Si-Map in Figure
354 5b). On the other hand, the mineral composition of the aggregates has been studied
355 extensively in [3,32], whose results are summarized in Table 5. To clarify which of these
356 rock-forming minerals dissolved and reacted, the oxide composition of the dissolved part
357 needs to be analyzed quantitatively first.

358



359 Figure 5 Identifiable reacted aggregates: (a) BSE image retrieved from [2]; (b) Si map
360 from EDS measurement retrieved from [4].

361

362 For oxide i (where $i = \text{SiO}_2, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{MgO}, \text{SO}_3, \text{Na}_2\text{O},$ and K_2O), using the ratio
363 $m_{\text{CaO}}^p / m_{\text{CaO}}^{\text{MPC}}$ of the calcium oxide in the cement paste to that in the original MPC (same
364 procedure for OPC system), the mass originating from the initial MPC was estimated.
365 Then, subtracting this mass from the total mass m_i^p of the oxide i in the cement paste,
366 the mass w_i^{agg} from the dissolved aggregate is computed:

367

$$w_i^{agg} = m_i^p - m_i^{MPC} \frac{m_{CaO}^p}{m_{CaO}^{MPC}} \quad (2)$$

368

369 Neglecting the oxides whose mass is less than 1% and normalizing to 100%, the oxide
370 compositions of dissolved aggregate were obtained for each core sample. The results of
371 dissolved aggregate composition for each core are listed in Table B1 of Appendix B.
372 Figure 6a shows the compositions of dissolved aggregate per wall, including the three
373 walls from H1. The compositions of dissolved aggregate are not the same in all walls but
374 can be categorized into three main types:

375 - General case excluding H1-IW1 and H1-BSW, composed approximately from ~85%
376 of SiO₂, ~9% of Al₂O₃, ~3% of Fe₂O₃ and of minor amount of MgO and Na₂O.

377 - Case of OPC system for H1-IW1: compared with the general case, does not contain
378 MgO.

379 - Case of H1-BSW: compared with the general case, does not contain MgO but K₂O.

380

381 Table 5 Mineral composition of aggregates (retrieved from [3,32])

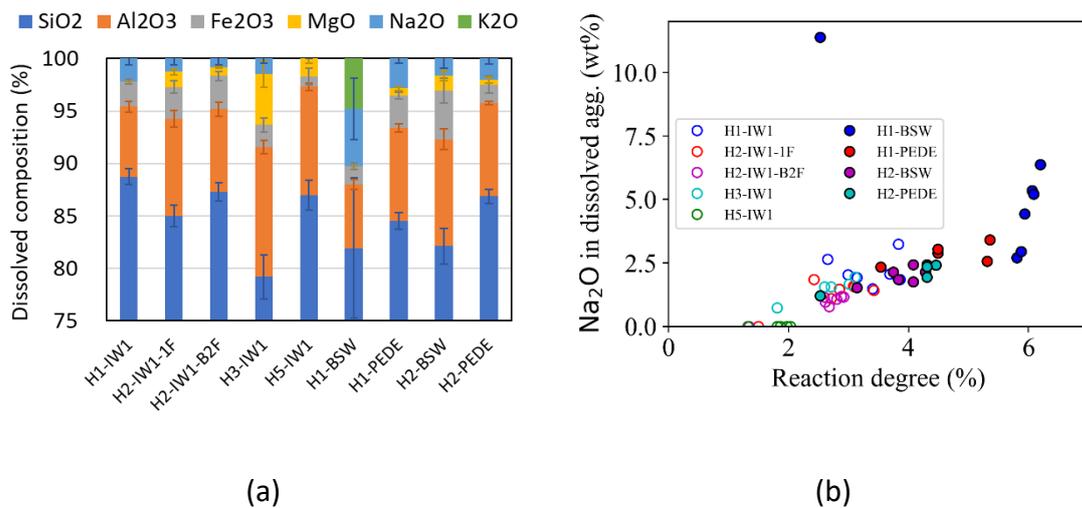
Mineral name	Chemical formula
Quartz	SiO ₂
Albite	NaAlSi ₃ O ₈
Microcline	KAlSi ₃ O ₈
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(F,OH) ₂
Chlorite	(Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·(Mg,Fe) ₃ (OH) ₆
Illite	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ,(H ₂ O)]
Biotite	K(Mg,Fe) ₃ (AlSi ₃ O ₁₀)(F,OH) ₂

382

383 Since SiO₂ is the dominant oxide in all cases, it can be inferred that quartz is the main

384 dissolving mineral. The presence of Na indicates that albite dissolved in all the walls;
 385 meanwhile, from the same feldspar group, microcline and muscovite dissolved only in
 386 H1-BSW. From Fe and Mg content, it is deduced that chlorite was also dissolving in all
 387 the walls. It is also possible that the incongruent dissolution of feldspar minerals resulted
 388 in high silica content in the dissolved oxides.

389



390 Figure 6 (a) Composition of dissolved aggregate averaged per wall. Error bar is the
 391 standard deviation of all the samples of the same wall; (b) Na₂O fraction in dissolved
 392 aggregate versus reaction degree.

393

394 The variation of dissolved aggregate composition over time can be inferred by comparing
 395 the oxide composition at different reaction degrees. The percentages of SiO₂, Al₂O₃, and
 396 Fe₂O₃ in dissolved components did not show any trend with the reaction degree of
 397 aggregate. As shown in Figure 6b, Na₂O increased with the increase of reaction degree,
 398 suggesting that albite may have dissolved more at later stages.

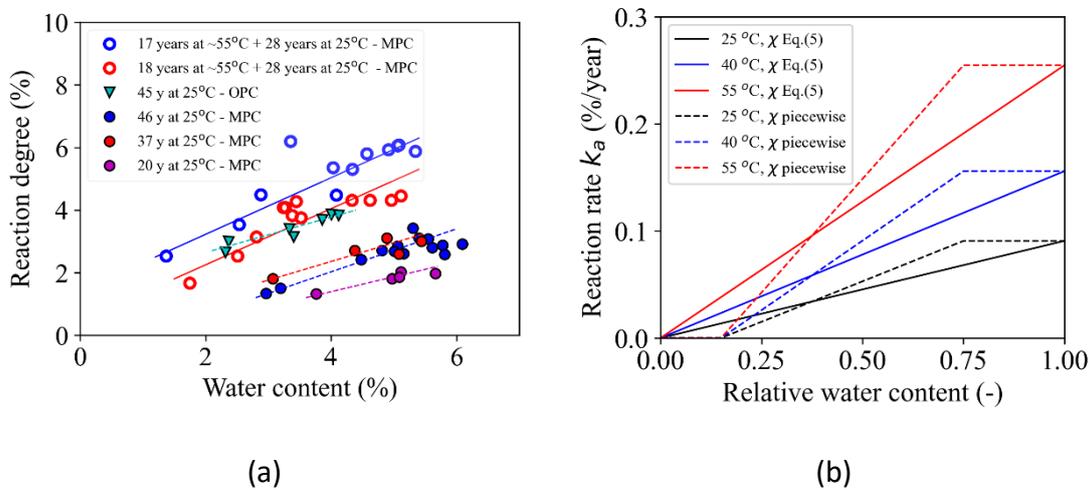
399

400 4.2 Time evolution of reaction degree

401 Given the reaction degree in walls of different ages in Figure 4, this section proposes a
 402 model for the time evolution of the aggregate-paste reaction. Since the reaction was
 403 confirmed to be a dissolution-precipitation process in [4], the main factors influencing
 404 the reaction rate would be evaporable content, temperature, and pH values. The

405 measured reaction degrees are plotted in function of water content for different
 406 temperature histories in Figure 7a, showing the role of water content and temperature
 407 respectively: i) Higher water content corresponds to a higher reaction degree; ii) In walls
 408 without high-temperature history, the reaction degree reached only 3.4%, whereas for
 409 walls with high-temperature history, the majority of the cores showed a higher reaction
 410 degree than 3.4%. Due to a lack of measurement and estimation methods, the impact
 411 of the pH will not be considered in the following.

412



413 Figure 7 (a) Measured reaction degree versus age of walls, water content, and
 414 temperature history. (b) Proposed model for reaction rate depending on relative water
 415 content and temperature.

416

417 Hence, it is necessary to know water content $w(t)$ to predict the time evolution of
 418 reaction degree $\zeta(t)$. Water content changes are controlled by two phenomena:
 419 moisture transport and water consumption by aggregate-paste reaction. Reduction in
 420 water content slows down the aggregate-paste reaction, whereas the progress of the
 421 reaction makes the moisture transport more difficult by densifying the microstructure.
 422 These couplings between water transport and aggregate-paste reaction are shown in
 423 Figure 9. The model is written as two coupled equations:

424

425

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} D(w) \frac{\partial w}{\partial x} - \theta \frac{d\zeta}{dt}, \quad (3)$$

$$\zeta = \int_0^t k_a(T, w) dt. \quad (4)$$

426

427 with D , θ , k_a diffusion coefficient (m^2/s), the ratio of reacted aggregate and
 428 consumed water, and the dissolution rate of aggregate, respectively. Coupled solution of
 429 Eqs. (3) and (4) will result in time-evolution of water content and reaction degree. The
 430 input parameters of the model are explained below.

431 Eq.(3) is based on a developed version of the Akita model [33,34], which related $D(w)$
 432 to water content-dependent permeability $K(w)$ ($m^2/s \cdot g/m^3 \cdot (J/g)^{-1}$) via

433

$$D(w, T) = \alpha K(w) \frac{p_{sat}(T)}{p_{sat}(T_0)} \frac{\partial \mu}{\partial w} = \alpha \frac{K_{60}}{5 - 9.1\chi + 4.15\chi^2} \frac{p_{sat}(T)}{p_{sat}(T_0)} \frac{\partial \mu}{\partial w}. \quad (5)$$

434

435 In Eq.(5), K_{60} is the reference permeability at a water content of 60%, obtained from
 436 the empirical relation in the same reference [33], and equal to $4.25 \times 10^{-7} m^2/s$. The term
 437 $\partial \mu / \partial w$ represents the change of water chemical potential μ (J/g) with respect to the
 438 change of water content, and its value has been fitted to be 0.0026 J/g for the cement
 439 paste of water-to-cement ratio 0.55 of MPC system in Table 2 of [34]. Term
 440 $p_{sat}(T)/p_{sat}(T_0)$ accounts for the impact of temperature on moisture transport
 441 kinetics, with $p_{sat}(T)$ representing the saturated vapor pressure of water at
 442 temperature T . In contrast to a constant value in [33,34], α is supposed to depend on
 443 the reaction degree to take into account the impact of the reaction on water transport,

444

$$\alpha = \alpha(\zeta) = \alpha_0 10^{-\beta \zeta}, \quad (6)$$

445

446 with α_0 reference value for the concrete without aggregate-paste reaction, β
 447 reduction factor due to aggregate-paste reaction.

448 Regarding aggregate-paste reaction, the dissolution rate of aggregate k_a depends on

449 temperature T and water content w as seen in Figure 7a, thus can be written as
450 $k_a(T, w) = k(T)\chi(w)$, with $k(T)$ and $\chi(w)$ are the functions to account for the
451 impact of temperature and water content, respectively. The term $k(T)$ accounting
452 temperature impact is considered similar to the Arrhenius equation, i.e.:

453

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right), \quad (7)$$

454

455 where A is a constant (%/year), E_a is the activation energy (J/mol), and R is the
456 universal gas constant (8.314 J/mol/K).

457 About the function $\chi(w)$ role of water content, the straightforward choice with the
458 least parameters is the relative water content:

459

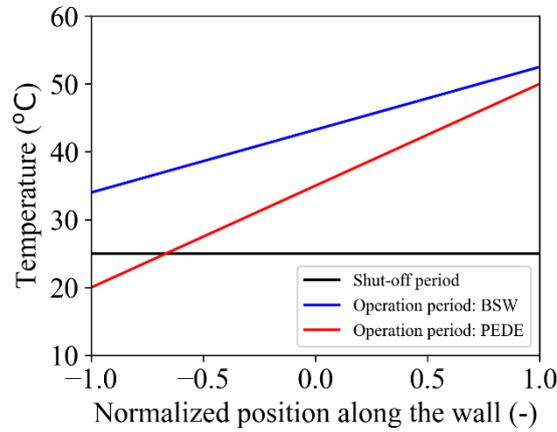
$$\chi(w) = \frac{w}{w_{sat}}, \quad (8)$$

460

461 with w_{sat} the saturated water content, which is estimated from the measured total
462 porosity. The reaction rate k_a obtained by a combination of Eqs.(7) and (8) is shown in
463 Figure 7b for three different temperatures. It should be noted that the horizontal axis in
464 Figure 7a is the water content at the end of the reaction, whereas it is the actual water
465 content during reaction time. Similarly, the vertical axis is the reaction degree and rate,
466 respectively, in Figure 7a and Figure 7b.

467 Both water transport and aggregate-paste reaction depend on the temperature. The
468 temperature history $T(t)$ can be estimated according to Table 3 from the power plants'
469 operation time: for IW1 in all four units, the temperature was constant at 25 °C. For BSWs
470 and PEDEs, during the period of operation, the temperature was considered linearly
471 distributed along the thickness of the wall and constant over time, as shown in Figure 8.
472 For the following period, during which the power plants were shut off, the temperature
473 was considered equal to 25 °C. Note that the temperatures listed in Table 3 were based
474 on measurement, but the details of measurement and results were not revealed to the
475 authors for confidentiality reasons.

476



477

478 Figure 8 History of temperature distribution in BSW and PEDE of H1 and H2.

479

480 Input parameters of the FDM simulations include: i) initial conditions (i.e., initial water
481 content) were based on measurement results in Figure 2; ii) boundary conditions were
482 chosen to be Neuman boundary conditions, with the value of derivate depending on the
483 surface coating conditions of the wall, as listed in Table 6. iii) reference permeability
484 $K_{60} = 4.25 \times 10^{-7} \text{ m}^2/\text{s}$; iv) five other fitting parameters: $\alpha_0, \beta, \theta, E_a,$ and A . By varying
485 these five parameters, it is possible to obtain multiple combinations that give the best
486 fit of the experimental results of water content and reaction degree. Nevertheless, such
487 combinations lack physical meaning and applicability. Instead, the following strategy was
488 adopted to retrieve meaningful conclusions.

489

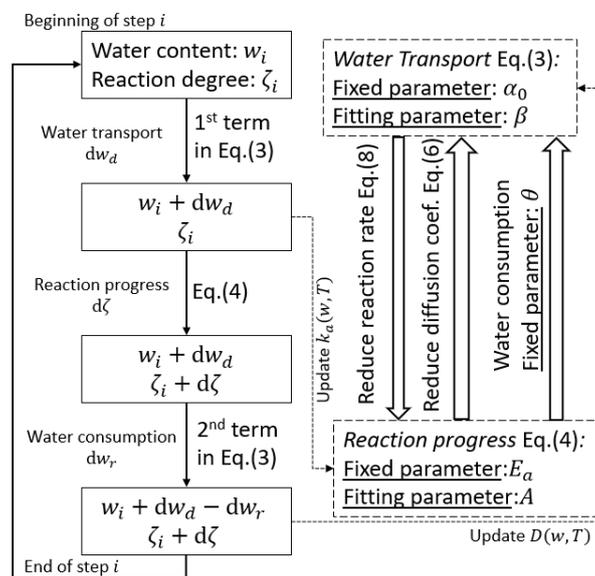
490 Table 6 Boundary condition in the FDM simulations

Surface condition	Derivative [m^{-1}]
No coating	0.12
Epoxy	0.09
Metallic liner	0.02
Steel plate	0.02

491

492 Firstly, since the concrete mixture compositions and total porosity of the walls are similar,
 493 the value of α_0 is fixed to be 0.1 for all walls. Secondly, the value of θ is set to be 0.1
 494 based on a preliminary study by many simulations. Thirdly, various combinations of E_a
 495 and A may give the same results; hence, it was decided to fix the value of E_a to 28
 496 kJ/mol to be consistent with the previous work [2]. Consequently, only β and A are
 497 changed to obtain the profile of water content and the profile of reaction degree that
 498 best fits the measured results. The flow chart of the combined FDM solution of Eqs.(3)
 499 and (4) is shown in Figure 9, with a recapitulation of the model's fixed and fitting
 500 parameters.

501



502

503 Figure 9 Interaction between moisture transport and reaction; flow chart of FDM
 504 solution of the model

505

506 The values of fitting parameters are summarized in Table 7, while the simulation results
 507 are compared with experimental results in Figure 10.

508

509 Table 7 Summary of fitting results of moisture transport and reaction degree model.

Without high-temperature history	With high-temperature history
----------------------------------	-------------------------------

Walls	β	$k(20^\circ\text{C})^a$	Walls	β	$k(20^\circ\text{C})$
	(-)	(%/year)		(-)	(%/year)
$\alpha_0=0.1, \theta=0.1, E_a=28 \text{ kJ/mol}$					
H1-IW1	10	0.086	H1-BSW	20	0.094
H2-IW1	100	0.056	H1-PEDE	20	0.108
H3-IW1	100	0.079	H2-BSW	20	0.064
H5-IW1	100	0.108	H2-PEDE	50	0.075

^aFor ease of understanding physical meaning, reaction rate $k(20^\circ\text{C})$ is given instead of A . The relation between A and $k(20^\circ\text{C})$ is shown in Eq.(7).

510

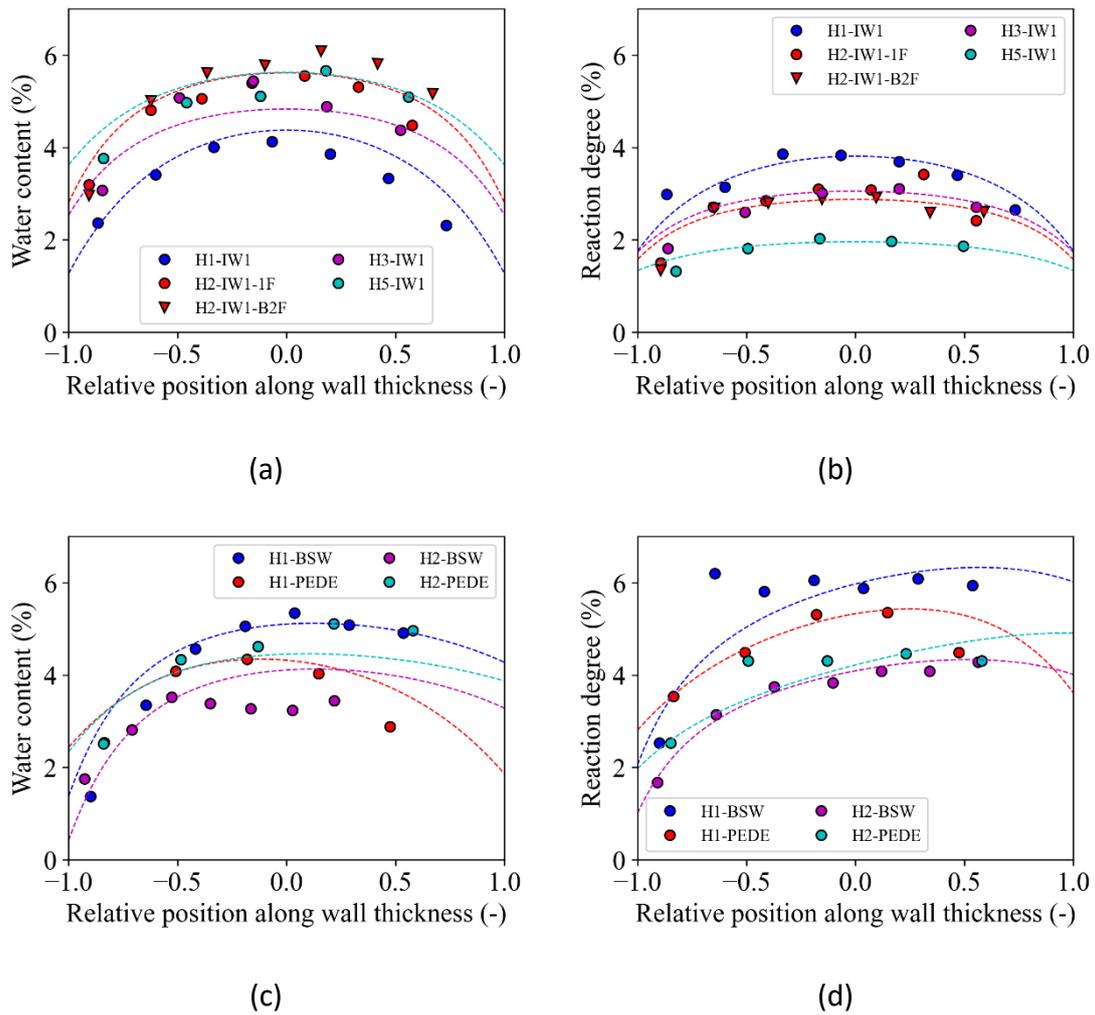
511 The reduction factor β was equal to 100 for all IW1s made with MPC (i.e., H2, H3, and
512 H5). In walls with high-temperature history, β was equal to 50 for three walls except
513 from H2-PEDE. Hence, we infer that the aggregate-paste reaction similarly reduced the
514 water diffusion coefficient in all MPC systems and that such reduction impact is less
515 significant at higher temperatures. In the OPC system of H1-IW1, the reduction seems
516 even less severe.

517 The reaction rate $k(20^\circ\text{C})$ of aggregates was not equal for all walls but higher for
518 younger walls than older ones. One of the reasons for faster kinetics in younger walls
519 might be the choice of $\chi = w/w_{sat}$, which implies that the reaction rate decreases
520 linearly proportional to the decrease of water content. It is plausible that below a certain
521 water content, $w_{cr,l}$, aggregate minerals cannot dissolve any more, and the reaction
522 ceases. Similarly, for water content above a certain level of $w_{cr,u}$, the water content may
523 not impact the dissolution rate. From Figure 7a, we may deduce that $w_{cr,l}=1\%$,
524 $w_{cr,u}=5\%$ for IW1s, and $w_{cr,l}=0, w_{cr,u}=4\%$ for BSWs and PEDEs. By choosing a piecewise
525 function for χ (1 for $w > w_{cr,l}$, 0 for $w < w_{cr,u}$ and linear function in between,
526 shown in dashed lines in Figure 7b), we have solved Eqs.(4) and (3). The shape of the
527 obtained reaction degree profile does not match the measured results. Adjusting values
528 of $w_{cr,l}$ and $w_{cr,u}$, and choosing another function shape rather than linear, we might
529 get better fitting, but it would let the model look like curve-fitting.

530 Another possible reason for the difference in reaction rate between walls could be the

531 change in pH. Though no pH data is available in this study, it is known that the dissolution
 532 of SiO₂ and alkali oxides reduces the pH value of the pore solution. The disappearance
 533 of portlandite also supports the decrease in pH. As shown in [8], decreasing pH from 13
 534 to 12 reduced the release rates of SiO₂ from quartz and albite by almost half. Thus, it is
 535 reasonable to assume that the reaction becomes slower with the progress of the
 536 reaction.

537



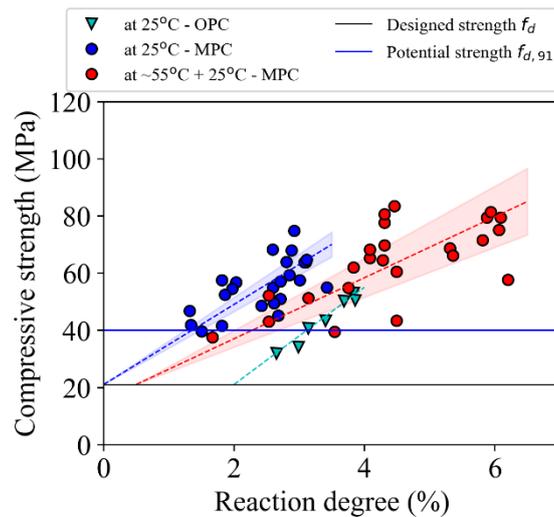
538 Figure 10 Results of simulation compared with measurement, (a)(c) water content and
 539 (b)(d) reaction degree. Points are experimental results; dashed lines are simulation
 540 results. The color of the dashed lines represents the simulated wall.

541

542 5 Mechanism of strength increase

543 Since the measured porosity (see Figure A1 in the appendix) is approximately constant
544 and does not show any clear trend with regard to the core position, the increase of
545 compressive strength in the center cannot be explained simply by porosity. Instead, the
546 compressive strength is correlated with the reaction degree, as shown in Figure 11.
547 Despite the difference in the age of construction between different walls, compressive
548 strength and reaction degree show a single relationship for all walls without high-
549 temperature history, i.e., IW1s. Another single relation is also seen for walls with high-
550 temperature exposure (i.e., BSW and PEDE), in which a higher reaction degree
551 corresponds to the same compressive strength in IW1s. Therefore, the reaction degree
552 and temperature history can be considered the main factors explaining the increase of
553 compressive strength in these walls.

554



555

556 Figure 11 Correlation between compressive strength and reaction degree. The shaded
557 areas represent prediction using a 95% confidence interval for the slope of best fit,
558 blue for walls without high temperature, and red for walls with high-temperature
559 history.

560

561 For the mechanism of strength increase due to aggregate-paste reaction, we assume
562 that the reaction increased the gel-space ratio. By filling the space more efficiently with
563 the reaction product, an increase in reaction degree resulted in a higher strength.

564 Concerning the temperature, the impact of high temperature is twofold: on the one
565 hand, higher temperature increases reaction degree by accelerating aggregate
566 dissolution. On the other hand, an increase in temperature might have caused: i)
567 coarsening of amorphous C-A-S-H agglomeration; ii) different thermal strains in
568 aggregate and cement paste resulting in volume mismatch and hence cracks [35–45].
569 These two phenomena also explain the lower reduction factor β for BSWs and PEDEs
570 in Table 7. The reduction effect of these two phenomena explains why the $f_c \sim \zeta$ line for
571 walls with high-temperature history lies below that for walls without high-temperature
572 history in Figure 11.

573 The following part of the section is dedicated to supporting the hypothesis on the role
574 of aggregate-paste reaction by evaluating the gel-space ratio of the samples. Two
575 methods are applied.

576 The first method was based on the XRD-Rietveld analysis, from which the mass of
577 cement hydrates and amorphous phases were known. The volume V_g of the reaction
578 product (i.e., all hydrates) was computed as the sum of cement hydrate minerals and
579 amorphous phase volumes. The density of cement hydrate minerals and amorphous
580 phase is listed in Table 8. Considering the theoretical ignited mass of minerals and
581 amorphous phase equal to the sum of the mass of reacted cement clinker and reacted
582 aggregate, we obtained the sum of the mass of reacted aggregate and reacted clinker.
583 Then, combined with the reaction degree, we obtained the mass of the reacted
584 aggregate and reacted clinker, respectively. The sum of the volume of these two and of
585 water was computed as the volume V_s of initial space. Then, the gel-space ratio g/s
586 was obtained from:

587

$$\frac{g}{s} = \frac{V_g}{V_s}. \quad (9)$$

588

589 Regarding the second method, the aggregate-paste reaction was first simulated using
590 the software GEMS[46,47] (<https://gems.web.psi.ch>), which is widely used for the
591 thermodynamic simulation of chemical reactions in cementitious materials. The input
592 reactants were MPC, water, and dissolved aggregate composition based on ICP-AES
593 results. The CSHQ model from database Cemdata18 [21] was used in the simulation,
594 noting that no C-S-H model in the database of GEMS includes Al-tobermorite. Then, the

595 volume V_g was computed as the sum of solid reaction products, whereas the space
 596 volume V_s was estimated using the density data in Table 8. Finally, inserting V_g and V_s
 597 into Eq.(9), the gel-space ratio is computed.

598

599 Table 8 shows the Density of cement hydrates, cement clinker, and aggregate used to
 600 estimate the gel-space ratio from XRD results, in g/cm³.

Amor phou s	Al- Tober morit e	Portl andit e	Ettrin gite	Hydr ogar net	Mon osulp hate	Mon ocarb onat e	Hemi carbo nalumina te	Calcit e	Clink er	aggre gate
2.3	2.45	2.24	2.38	2.52	2.4	2.4	2.4	2.7	3.15	2.65

601

602 The reaction products obtained in GEMS simulations differ slightly from the XRD
 603 measurement. For instance, in H1-IW1, portlandite was still present in the inner part of
 604 the wall, whereas XRD measurements show no portlandite remained. Another
 605 difference is that, with respect to the total volume of reaction products, the amorphous
 606 phase in XRD results accounts for more fraction than the CSHQ phase in GEMS results.
 607 One of the probable explanations could be that the reaction products in real structures
 608 were in an unsteady state and had not yet reached thermodynamic equilibrium and
 609 hence contained more amorphous. In contrast, the GEMS simulates a thermodynamic
 610 equilibrium state.

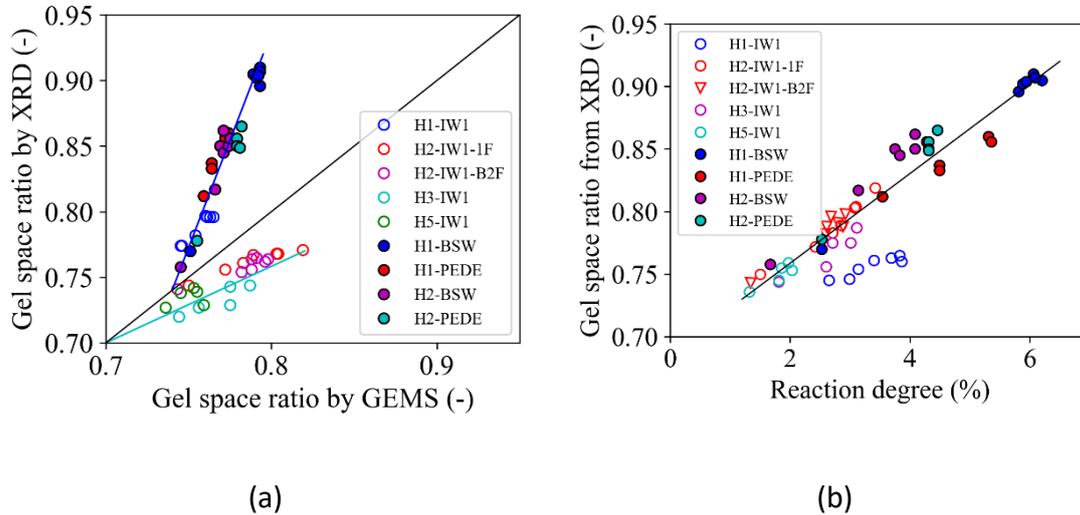
611 The gel-space ratios obtained from the two methods are compared in Figure 12a. For
 612 IW1s made with MPC, the gel-space ratio obtained from GEMS is higher than that
 613 obtained from XRD. On the contrary, for BSW, PEDEs, and H1-IW1, GEMS simulations
 614 result in a lower gel-space ratio than that from XRD results. Such a difference might be
 615 correlated to the temperature hist

616 ory. The gel-space ratios from XRD-Rietveld analysis are affected by the real temperature
 617 history under which aggregate-paste reaction progressed gradually over decades. In
 618 contrast, in the GEMS simulation, the reaction temperature was set to 20 °C, and the
 619 reaction happened as an instantaneous process.

620 Nevertheless, despite such differences in reaction conditions, both XRD results and

621 GEMS simulations show an increasing trend in the gel-space ratio with the progress of
622 the reaction.

623



624 Figure 12 (a) Comparison of gel-space ratio calculated from XRD results and GEMS
625 simulations. (b) Gel-space ratio versus Reaction degree.

626

627 The estimated gel-space ratios from XRD results are shown as a function of reaction
628 degree in Figure 12b. For all the walls made with MPC, the gel-space ratio g/s is almost
629 linearly correlated with the reaction degree. In the case of the OPC system, the gel-space
630 ratios of H1-IW1 are located below the correlation line, indicating a lesser increase in the
631 gel-space ratio than that of the MPC system. Increasing the gel-space ratio with the
632 increase of reaction degree supports the assumption that the compressive strength
633 increased due to the increase of the gel-space ratio. The space is more efficiently and
634 homogenously filled/ occupied by low-density material. It is worth mentioning that
635 relating compressive strength to the gel-space ratio in concretes with reacting aggregate
636 is new, especially with the support of long-term field data. Evaluating the gel-space ratio
637 in this case comprises many challenging points, such as considering aggregate-paste
638 reaction, which differs from thermodynamic equilibrium calculations. The analysis
639 methods used in this section remain useful despite the scarcity of data at higher
640 temperatures.

641 6 Implication for Plant Life Management

642 Coring data like in this study are essential for the safety assessment of nuclear power
643 plant buildings in the long term. Within the frame of a single project, the coring samples
644 in this study were obtained from multiple buildings of different construction ages.
645 Chemical composition and mechanical properties were examined for each core via
646 comprehensive experimental methods. The results enabled us to assess the time-
647 dependent evolution of strength and chemical composition. Recordings of
648 environmental conditions during building usage and consistent experimental conditions
649 during sampling and testing made the results even more valuable for long-term plant life
650 management.

651 The model proposed based on core data analysis can help predict material behavior over
652 extended periods. This knowledge is also beneficial for constructing next-generation
653 reactors using similar materials, ensuring reliable performance and safety. Moreover, the
654 coring strategy and experimental program developed in this project can be easily applied
655 to multiple plants for cross-comparison, offering additional benefits such as identifying
656 common trends, optimizing maintenance schedules, and improving overall plant
657 efficiency.

658 It is crucial to verify the conditions under which these insights hold true to apply them
659 to other plants. Future analysis should account for differences in design, materials, and
660 environmental factors. Since observed reactions cannot be permanent, ongoing
661 research is necessary to investigate achievable reaction degrees, long-term material
662 stability, and possible degradation mechanisms.

663 In the following, we propose a procedure, by extrapolating the findings of the study, to
664 estimate strength distribution and time evolution to support the long-term operation of
665 nuclear power plants constructed using aggregates of similar composition.

666 The key point is to relate compressive strength to the reaction degree. As the increase
667 of strength is a consequence of the increase of gel-space ratio caused by the aggregate-
668 paste reaction, an empirical relationship can be established between the increase of
669 strength Δf and an additional reaction degree $\Delta \zeta$:

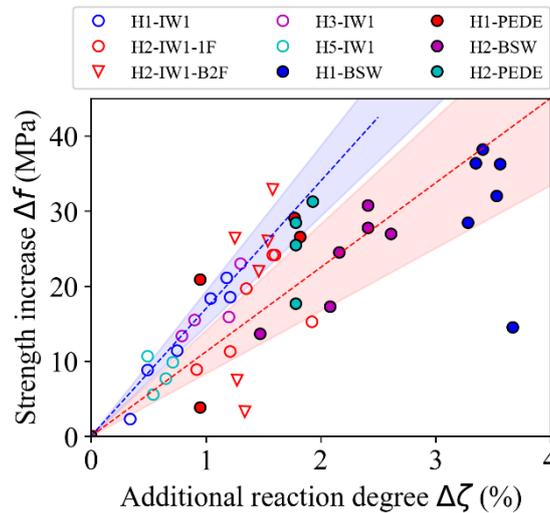
670

$$\Delta f = f - f_0 = B \Delta \zeta = B(\zeta - \zeta_0). \quad (11)$$

671

672 There are several options for both Δf and $\Delta\zeta$ based on the availability of in-situ
673 measurement in practical applications. If coring is possible near the surface, Δf can be
674 chosen as the increased strength with respect to the strength of cores near the surface,
675 such as 100 mm from the surface, $f_0 = f_{100}$. Similarly, $\Delta\zeta$ can be the additional
676 reaction degree with respect to the reaction degree of the core near the surface, $\zeta_0 =$
677 ζ_{100} . In case of no coring data, Δf can be evaluated as the increased strength with
678 respect to the design strength $f_0 = f_d$, or the potential strength $f_0 = f_{d,90}$. In the latter
679 case, the reference reaction degree can be chosen as $\zeta_0 \approx 1.6\%$ for walls without high-
680 temperature history and $\zeta_0 \approx 2.1\%$ for walls with high-temperature history similar to
681 BSWs and PEDEs, according to the data in Figure 11.

682



683

684 Figure 13 Relation between increase in strength and reaction degree of aggregate.

685

686 The coefficient B depends on the choice of reference strength and reaction degree and
687 the temperature history of the walls. Figure 13 displays the correlation between strength
688 increase Δf and additional reaction degree $\Delta\zeta$, with the strength and reaction degree
689 of the core near the surface used as the reference values. The coefficient B was 14.7
690 MPa for walls without high-temperature history and 11.3 MPa for walls with high-
691 temperature history.

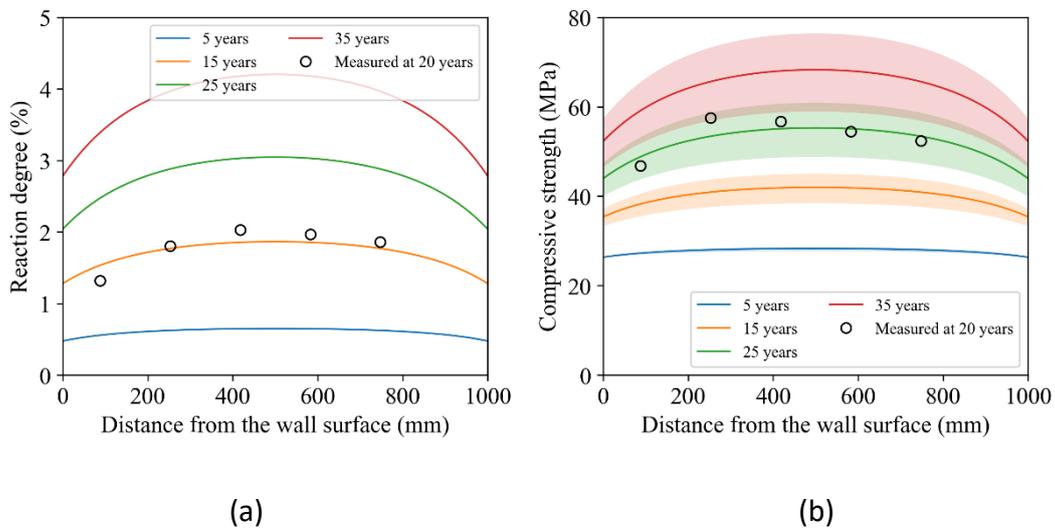
692 In the following, we propose a methodology for applying the findings of the study to
693 estimate concrete strength with a view to safety assessment for the aging management

694 of concrete structures.

695 Step 1: Estimate the time evolution of water content and reaction degree. Initial water
696 content and appropriate boundary conditions are to be known. Then, five input
697 parameters $\alpha_0, \theta, E_a, A, \beta$ of the moisture transport and reaction degree model of
698 section 4.2 are to be decided. (4)(3)The time evolution of the reaction degree is obtained
699 by solving Eqs. (4) and (3). Taking H5-IW1 as an example, using values for $\alpha_0, \theta, E_a, A, \beta$
700 from Table 7, we estimated the reaction degree evolution and showed in Figure 14a.

701 Step 2: Estimate strength as a function of reaction degree. The estimated time evolution
702 of reaction degree is to be inserted into Eq.(11) to predict strength values over time. In
703 the example of H5-IW1, we took $B = 14.7\%$. The estimated strength evolution is shown
704 in Figure 14b. Considering deviations of experimental data from Eq.(11), prediction
705 bands were also indicated, which correspond to the shaded area in Figure 11.

706



707 Figure 14 Reaction degree (a) and strength (b) evolution over time for H5-IW1,
708 estimated by coupled simulation of moisture-reaction combined with Eq.(11).

709

710 7 Conclusions

711 Cored samples were obtained from the thick concrete walls of nuclear power plants
712 during decommissioning. These walls were aged ~50 years and constructed in different
713 decades using aggregates from the same origin. The temperature and humidity
714 conditions of these walls were controlled during the operation of power plants. We

715 found that aggregate dissolved and reacted with cement hydrates. From the time
716 evolution of the reaction and its correlation to the compressive strength measured on
717 cored samples, we identified that the reaction contributed to strength development. The
718 experimental data measured on cored samples from real structures cannot be obtained
719 in conventional laboratory experiments; they are unique in the literature and serve as
720 an important basis to support the long-term operation of nuclear power plants.

721 To clarify the underlying mechanisms of strength increase, we discussed the dissolved
722 rock-forming minerals based on the chemical composition of the reacted aggregate from
723 ICP-AES and XRD-Rietveld analysis. The main dissolved aggregate minerals were quartz,
724 albite, and chlorite. Albite dissolved more in later stages. The Kinetics of the reaction
725 was studied in combination with moisture transport in concrete walls.

726 To promote the findings for a broader range of engineering applications, we estimated
727 universal parameters for reaction kinetics, moisture transport, and strength increase. A
728 protocol is proposed for the estimation of strength evolution over time in structures
729 constructed with aggregates of similar composition. The coring methodology and
730 experimental program, as well as the model developed in this project, can be applied to
731 next-generation power plants constructed using similar materials to monitor
732 performance and safety.

733 As a prospective improvement, accounting for the impact of pH on the aggregate-paste
734 reaction will improve the model. At the moment, in-situ variation of pH in concrete walls
735 is not yet accessible either by experimental technique or theoretical analysis. Another
736 point is understanding the non-equilibrium reaction between aggregate and cement
737 hydrates, which is currently approximated by thermodynamic equilibrium simulation
738 using GEMS.

739 Acknowledgment

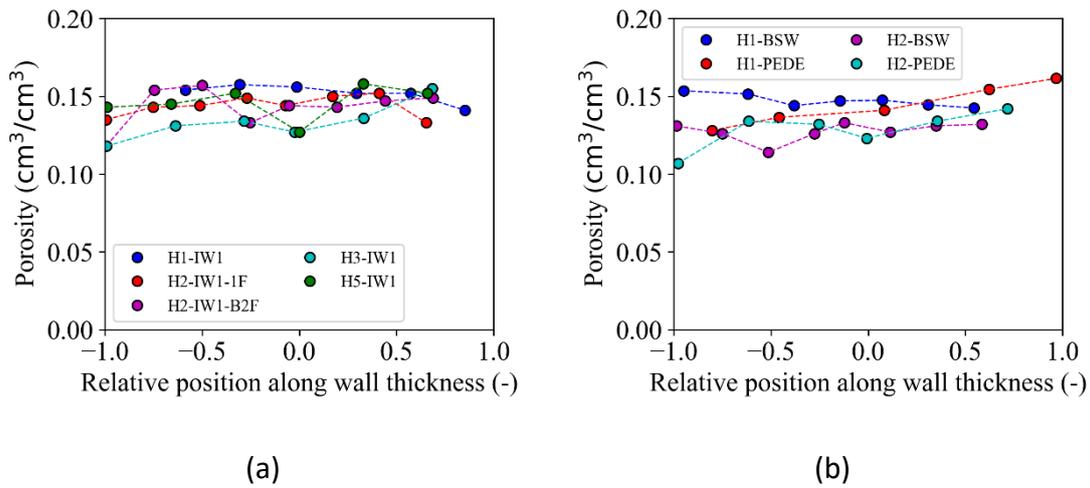
740 This project was based on a research project collaboration between the University of
741 Tokyo, Nagoya University, and Chubu Electric Power Co. Inc. and was partially supported
742 by the "R&D of the Safety Improvement of Nuclear Facilities" project by the Ministry of
743 Economy, Trade and Industry of Japan. The authors thank Kajima Corporation for
744 providing the cored samples.

745 Appendix

746 A. Porosity of the cored samples

747 This section presents the results of porosity measurement. The porosity is shown in
 748 Figure A1a for walls without a high-temperature history, while Figure A1b shows the
 749 results for walls with high-temperature history. As discussed in section 3.1, the porosity
 750 is approximately constant and does not show any clear trend with regard to the core
 751 position.

752



753 Figure A1: Porosity versus position of the core along the wall thickness. X-axis 0
 754 represents the wall center, while ± 1 represents the two surfaces. (a): IW1s without high
 755 temperature history; (b): BSWs and PEDEs with high temperature history

756

757 B. Oxide composition of dissolved aggregates

758 This section presents the composition of dissolved aggregates for each core, obtained
 759 from Eq.(2), by comparing the oxide composition of the cement paste in cores with that
 760 of the original cement. The results are listed in Table B1.

761

762 Table B1. Oxide composition of dissolved aggregates for each core

Wall	Core position	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O
H1-IW1	S-100	89.33	6.39	2.24	0.00	2.03	0.00

	S-300	89.22	6.47	2.39	0.00	1.92	0.00
	S-500	88.17	7.30	2.69	0.00	1.85	0.00
	N-700	87.40	6.80	2.55	0.00	3.24	0.00
	N-500	88.50	6.92	2.52	0.00	2.06	0.00
	N-300	89.08	6.90	2.54	0.00	1.48	0.00
	N-100	89.53	5.80	2.03	0.00	2.64	0.00
	W-110	68.66	5.40	2.34	0.00	11.38	12.22
	W-390	78.26	6.97	1.92	0.00	6.36	6.49
	W-640	88.12	6.06	1.46	0.00	2.70	1.66
H1-BSW	W-890	83.26	5.88	1.46	0.00	5.34	4.06
	W-1140	87.01	6.11	1.85	0.00	2.94	2.09
	W-1415	83.23	6.09	1.54	0.00	5.20	3.94
	W-1690	85.07	6.01	1.52	0.00	4.42	2.98
	E-100	83.81	9.34	3.54	0.98	2.33	0.00
	E-300	85.44	8.36	2.76	0.56	2.89	0.00
H1-PEDE	E-500	85.39	8.53	2.98	0.54	2.56	0.00
	E-700	84.18	8.86	2.97	0.59	3.41	0.00
	E-900	83.79	9.13	3.30	0.73	3.04	0.00
	S-90	85.31	8.67	4.21	1.87	0.00	0.00
	S-295	85.01	9.19	3.32	1.38	1.10	0.00
H2-IW1-1F	S-500	85.36	9.13	2.92	1.13	1.46	0.00
	S-705	85.86	8.47	2.57	1.54	1.56	0.00
	S-910	85.89	8.68	2.35	1.49	1.59	0.00

	S-1115	84.59	9.81	2.97	1.20	1.42	0.00
	S-1320	82.90	10.80	3.02	1.42	1.85	0.00
	N-90	89.04	6.53	3.95	0.91	0.00	0.00
	N-300	87.35	7.79	3.40	0.70	0.77	0.00
	N-510	87.24	8.07	2.73	0.89	1.07	0.00
H2-IW1- B2F	N-720	87.16	7.90	2.96	0.81	1.18	0.00
	N-930	86.97	7.92	3.13	0.82	1.15	0.00
	N-1140	86.36	8.86	2.85	0.78	1.15	0.00
	N-1350	86.81	8.17	3.17	0.89	0.96	0.00
	N-100	78.26	12.39	7.29	2.49	-0.43	0.00
	N-395	82.88	9.85	4.38	1.36	1.53	0.00
	N-690	82.63	9.53	4.43	1.27	2.14	0.00
H2-BSW	N-985	82.39	10.20	4.37	1.20	1.84	0.00
	N-1230	82.91	9.33	4.07	1.27	2.42	0.00
	N-1475	83.06	9.94	4.04	1.20	1.76	0.00
	N-1720	82.76	9.99	3.96	1.15	2.14	0.00
	W-105	85.78	9.05	3.10	0.86	1.20	0.00
	W-350	86.59	8.88	2.10	0.49	1.94	0.00
H2- PEDE	W-600	87.19	8.68	1.39	0.31	2.43	0.00
	W-850	87.45	8.71	1.26	0.18	2.41	0.00
	W-1090	87.30	8.97	1.14	0.24	2.35	0.00
	W-90	75.52	13.42	3.32	7.01	0.73	0.00
H3-IW1	W-320	79.45	12.46	1.87	4.67	1.55	0.00

	W-550	80.62	11.91	1.86	3.95	1.66	0.00
	W-780	80.44	11.85	1.67	4.10	1.94	0.00
	W-1010	79.98	12.17	1.84	4.45	1.55	0.00
	E-87.5	84.66	10.49	2.29	2.55	0.00	0.00
	E-252.5	88.33	9.86	0.30	1.51	0.00	0.00
H5-IW1	E-417.5	86.60	10.79	1.02	1.59	0.00	0.00
	E-582.5	87.45	10.30	0.67	1.58	0.00	0.00
	E-747.5	87.78	10.32	0.50	1.41	0.00	0.00

763

764 References

- 765 [1] Global Cement and Concrete Association,
766 <https://gccassociation.org/concretefuture/getting-to-net-zero/>, (2024).
- 767 [2] I. Maruyama, J. Rymeš, A. Aili, S. Sawada, O. Kontani, S. Ueda, R. Shimamoto,
768 Long-term use of modern Portland cement concrete: The impact of Al-
769 tobermorite formation, *Mater Des* 198 (2021).
770 <https://doi.org/10.1016/j.matdes.2020.109297>.
- 771 [3] J. Rymeš, I. Maruyama, R. Shimamoto, A. Tachibana, Y. Tanaka, S. Sawada,
772 Y. Ichikawa, O. Kontani, Long-term material properties of a thick concrete
773 wall exposed to ordinary environmental conditions in a nuclear reactor
774 building: The contribution of cement hydrates and feldspar interaction,
775 *Journal of Advanced Concrete Technology* 17 (2019) 195–215.
776 <https://doi.org/10.3151/jact.17.5.195>.
- 777 [4] A. Aili, I. Maruyama, G. Geng, S. Umeki, K. Sumitani, S. Sawada, S. Ueda, Y.
778 Umeki, Micro X-ray diffraction and elemental study on Al-tobermorite
779 formation in aged modern concrete, *Journal of the American Ceramic*
780 *Society* 105 (2022) 6924–6937. <https://doi.org/10.1111/jace.18624>.
- 781 [5] A. Leemann, M. Bagheri, B. Lothenbach, K. Scrivener, S. Barbotin, E. Boehm-
782 courjault, G. Geng, R. Dähn, Z. Shi, M. Shakoorioskooie, M. Griffa, R. Zboray,
783 P. Lura, E. Gallyamov, R. Rezakhani, J.F. Molinari, Alkali-silica reaction – a

- 784 multidisciplinary approach, RILEM Technical Letters 6 (2021) 169–187.
785 <https://doi.org/10.21809/RILEMTECHLETT.2021.151>.
- 786 [6] A.C. Lasaga, CHEMICAL KINETICS OF WATER-ROCK INTERACTIONS., in: J
787 Geophys Res, 1984: pp. 4009–4025.
788 <https://doi.org/10.1029/jb089ib06p04009>.
- 789 [7] M. Heřmanská, M.J. Voigt, C. Marieni, J. Declercq, E.H. Oelkers, A
790 comprehensive and consistent mineral dissolution rate database: Part II:
791 Secondary silicate minerals, Chem Geol 636 (2023).
792 <https://doi.org/10.1016/j.chemgeo.2023.121632>.
- 793 [8] M. Bagheri, B. Lothenbach, M. Shakoorioskooie, K. Scrivener, Effect of
794 different ions on dissolution rates of silica and feldspars at high pH, Cem
795 Concr Res 152 (2022). <https://doi.org/10.1016/j.cemconres.2021.106644>.
- 796 [9] Dove - 1994 - The Dissolution Kinetics of Quartz in Sodium Chloride
797 Solutions at 25 Degrees to 300 Degrees C, (n.d.).
- 798 [10] P.M. Dove, N. Han, A.F. Wallace, J.J. De Yoreo, Kinetics of amorphous silica
799 dissolution and the paradox of the silica polymorphs, Proceedings of the
800 National Academy of Sciences 105 (2008) 9903–9908.
801 <https://doi.org/10.1073/pnas.080379810>.
- 802 [11] L. Chou, R. Wollast, Study of the weathering of albite at room temperature
803 and pressure with a fluidized bed reactor, Geochim Cosmochim Acta 48
804 (1984) 2205–2217.
- 805 [12] R.T. Lowson, M.C.J. Comarmond, G. Rajaratnam, P.L. Brown, The kinetics of
806 the dissolution of chlorite as a function of pH and at 25°C, Geochim
807 Cosmochim Acta 69 (2005) 1687–1699.
808 <https://doi.org/10.1016/j.gca.2004.09.028>.
- 809 [13] C.A. Rochelle, K. Bateman, R. MacGregor, J.M. Pearce, D. Savage, P.D.
810 Wetton, Experimental determination of chlorite dissolution rates, in:
811 Materials Research Society Symposium - Proceedings, Materials Research
812 Society, 1995: pp. 149–156. <https://doi.org/10.1557/proc-353-149>.
- 813 [14] M.M. Smith, Z. Dai, S.A. Carroll, Illite dissolution kinetics from 100 to 280 °C
814 and pH 3 to 9, Geochim Cosmochim Acta 209 (2017) 9–23.
815 <https://doi.org/10.1016/j.gca.2017.04.005>.

- 816 [15] G. Yuan, Y. Cao, H.M. Schulz, F. Hao, J. Gluyas, K. Liu, T. Yang, Y. Wang, K. Xi,
817 F. Li, A review of feldspar alteration and its geological significance in
818 sedimentary basins: From shallow aquifers to deep hydrocarbon reservoirs,
819 *Earth Sci Rev* 191 (2019) 114–140.
820 <https://doi.org/10.1016/j.earscirev.2019.02.004>.
- 821 [16] V.A. Alekseyev, L.S. Medvedeva, N.I. Prisyagina, S.S. Meshalkin, A.I. Balabin,
822 Change in the dissolution rates of alkali feldspars as a result of secondary
823 mineral precipitation and approach to equilibrium, *Geochim Cosmochim*
824 *Acta* 61 (1997) 1125–142.
- 825 [17] S. Poyet, Water transport properties of virtual fractal porous media:
826 Implications for the unsaturated transport properties of cement-based
827 materials, *Cem Concr Res* 150 (2021).
828 <https://doi.org/10.1016/j.cemconres.2021.106613>.
- 829 [18] H. Akita, T. Fujiwara, Y. Ozaka, Akita - 1994 - An analytical method of
830 moisture transfer within concrete due to drying, *JSCCE Journal Proceedings*
831 23 (1994) 101–110.
- 832 [19] G. Plusquellec, M.R. Geiker, J. Lindgård, J. Duchesne, B. Fournier, K. De
833 Weerd, Determination of the pH and the free alkali metal content in the
834 pore solution of concrete: Review and experimental comparison, *Cem*
835 *Concr Res* 96 (2017) 13–26.
836 <https://doi.org/10.1016/j.cemconres.2017.03.002>.
- 837 [20] B. Lothenbach, T. Matschei, G. Möschner, F.P. Glasser, Thermodynamic
838 modelling of the effect of temperature on the hydration and porosity of
839 Portland cement, *Cem Concr Res* 38 (2008) 1–18.
840 <https://doi.org/10.1016/j.cemconres.2007.08.017>.
- 841 [21] B. Lothenbach, D.A. Kulik, T. Matschei, M. Balonis, L. Baquerizo, B. Dilnesa,
842 G.D. Miron, R.J. Myers, Cemdata18: A chemical thermodynamic database
843 for hydrated Portland cements and alkali-activated materials, *Cem Concr*
844 *Res* 115 (2019) 472–506.
845 <https://doi.org/10.1016/j.cemconres.2018.04.018>.
- 846 [22] T.C. Powers, T.L. Brownyard, Studies of the Hardened Paste by Means of
847 Specific-Volume Measurements, *Portland Cement Association Bulletin*
848 (1947) 669–712.

- 849 [23] T.C. POWERS, Structure and Physical Properties of Hardened Portland
850 Cement Paste, *Journal of the American Ceramic Society* 41 (1958) 1–6.
851 <https://doi.org/10.1111/j.1151-2916.1958.tb13494.x>.
- 852 [24] A. Schöler, B. Lothenbach, F. Winnefeld, M. Zajac, Hydration of quaternary
853 Portland cement blends containing blast-furnace slag, siliceous fly ash and
854 limestone powder, *Cem Concr Compos* 55 (2015) 374–382.
855 <https://doi.org/10.1016/j.cemconcomp.2014.10.001>.
- 856 [25] B. Pichler, C. Hellmich, J. Eberhardsteiner, J. Wasserbauer, P. Termkhajornkit,
857 R. Barbarulo, G. Chanvillard, Effect of gel-space ratio and microstructure on
858 strength of hydrating cementitious materials: An engineering
859 micromechanics approach, *Cem Concr Res* 45 (2013) 55–68.
860 <https://doi.org/10.1016/j.cemconres.2012.10.019>.
- 861 [26] I. Maruyama, G. Igarashi, Cement Reaction and Resultant Physical
862 Properties of Cement Paste, *Journal of Advanced Concrete Technology* 12
863 (2014) 200–213. <https://doi.org/10.3151/jact.12.200>.
- 864 [27] P. Termkhajornkit, Q.H. Vu, R. Barbarulo, S. Daronnat, G. Chanvillard,
865 Dependence of compressive strength on phase assemblage in cement
866 pastes: Beyond gel-space ratio - Experimental evidence and
867 micromechanical modeling, *Cem Concr Res* 56 (2014) 1–11.
868 <https://doi.org/10.1016/j.cemconres.2013.10.007>.
- 869 [28] B. Lothenbach, M. Zajac, Application of thermodynamic modelling to
870 hydrated cements, *Cem Concr Res* 123 (2019).
871 <https://doi.org/10.1016/j.cemconres.2019.105779>.
- 872 [29] Y. Ichikawa, I. Maruyama, H. Wada, K. Yokokura, S. Ishikawa, G. Saito,
873 Soundness evaluation method for concrete structures based on the data
874 obtained from decommissioning Hamaoka nuclear power plant, Part 3:
875 Investigation on core sampling method, *Proceeding of Annual Conf.of AIJ*
876 *Structure* (2017) 1259–1260.
- 877 [30] JSA, Portland cement (JIS R5210), Tokyo, Japanese Standards Association
878 (1973).
- 879 [31] JSA, Method of test for static modulus of elasticity of concrete (JIS A 1149),
880 Tokyo: Japanese Standards Association (2017).

- 881 [32] A. Meawad, K. Murakami, T. Ohkubo, O. Kontani, J. Etoh, M. Do Thi, C.
882 Aparicio, C.M. Silva, I. Maruyama, Evaluation of radiation-induced
883 amorphization of α -quartz in concrete aggregates using Raman
884 spectroscopy, *Journal of Nuclear Materials* 604 (2025) 155523.
885 <https://doi.org/10.1016/j.jnucmat.2024.155523>.
- 886 [33] I. Maruyama, G. Igarashi, N. Kishi, Fundamental study on water transfer in
887 portland cement paste, *Journal of Structural and Construction Engineering*
888 76 (2011) 1737–1744. <https://doi.org/10.3130/aajs.76.1737>.
- 889 [34] H. Sasano, I. Maruyama, A. Nakamura, Y. Yamamoto, M. Teshigawara,
890 Impact of drying on structural performance of reinforced concrete shear
891 walls, *Journal of Advanced Concrete Technology* 16 (2018) 210–232.
892 <https://doi.org/10.3151/jact.16.210>.
- 893 [35] H. Sasano, I. Maruyama, Mechanism of drying-induced change in the
894 physical properties of concrete: A mesoscale simulation study, *Cem Concr*
895 *Res* 143 (2021) 106401.
896 <https://doi.org/10.1016/j.cemconres.2021.106401>.
- 897 [36] H. Sasano, I. Maruyama, Investigation into the changes in the splitting
898 tensile strength of concrete subjected to long-term drying using a three-
899 phase mesoscale RBSM, *Cem Concr Compos* 148 (2024) 105462.
900 <https://doi.org/10.1016/j.cemconcomp.2024.105462>.
- 901 [37] F. Soleilhet, F. Benboudjema, X. Jourdain, F. Gatuingt, Effect of transient
902 drying on mechanical properties of concrete specimens, *European Journal*
903 *of Environmental and Civil Engineering* 26 (2022) 6650–6669.
904 <https://doi.org/10.1080/19648189.2021.1952488>.
- 905 [38] M. Lin, M. Itoh, I. Maruyama, Mechanism of Change in Splitting Tensile
906 Strength of Concrete during Heating or Drying up to 90°C, *Journal of*
907 *Advanced Concrete Technology* 13 (2015) 94–102.
908 <https://doi.org/10.3151/jact.13.94>.
- 909 [39] I. Maruyama, H. Sasano, Y. Nishioka, G. Igarashi, Strength and Young's
910 modulus change in concrete due to long-term drying and heating up to
911 90°C, *Cem Concr Res* 66 (2014) 48–63.
912 <https://doi.org/10.1016/j.cemconres.2014.07.016>.

- 913 [40] J. Glucklich, U. Korin, Effect of Moisture Content on Strength and Strain
914 Energy Release Rate of Cement Mortar, *Journal of the American Ceramic*
915 *Society* 58 (1975) 517–521. [https://doi.org/10.1111/j.1151-](https://doi.org/10.1111/j.1151-2916.1975.tb18772.x)
916 [2916.1975.tb18772.x](https://doi.org/10.1111/j.1151-2916.1975.tb18772.x).
- 917 [41] A. Idiart, J. Bisschop, A. Caballero, P. Lura, A numerical and experimental
918 study of aggregate-induced shrinkage cracking in cementitious composites,
919 *Cem Concr Res* 42 (2012) 272–281.
920 <https://doi.org/10.1016/j.cemconres.2011.09.013>.
- 921 [42] I. Yurtdas, H. Peng, N. Burlion, F. Skoczylas, Influences of water by cement
922 ratio on mechanical properties of mortars submitted to drying, *Cem Concr*
923 *Res* 36 (2006) 1286–1293.
924 <https://doi.org/10.1016/j.cemconres.2005.12.015>.
- 925 [43] N. Burlion, F. Bourgeois, J.-F. Shao, Effects of desiccation on mechanical
926 behaviour of concrete, *Cem Concr Compos* 27 (2005) 367–379.
927 <https://doi.org/10.1016/j.cemconcomp.2004.05.004>.
- 928 [44] I. Yurtdas, N. Burlion, F. Skoczylas, Experimental characterisation of the
929 drying effect on uniaxial mechanical behaviour of mortar, *Mater Struct* 37
930 (2004) 170–176. <https://doi.org/10.1007/BF02481616>.
- 931 [45] S.E. Pihlajavaara, A review of some of the main results of a research on the
932 aging phenomena of concrete: Effect of moisture conditions on strength,
933 shrinkage and creep of mature concrete, *Cem Concr Res* 4 (1974) 761–771.
934 [https://doi.org/10.1016/0008-8846\(74\)90048-9](https://doi.org/10.1016/0008-8846(74)90048-9).
- 935 [46] D.A. Kulik, T. Wagner, S. V. Dmytrieva, G. Kosakowski, F.F. Hingerl, K. V.
936 Chudnenko, U.R. Berner, GEM-Selektor geochemical modeling package:
937 revised algorithm and GEMS3K numerical kernel for coupled simulation
938 codes, *Comput Geosci* (2012). [https://doi.org/10.1007/s10596-012-9310-](https://doi.org/10.1007/s10596-012-9310-6)
939 [6](https://doi.org/10.1007/s10596-012-9310-6).
- 940 [47] T. Wagner, D.A. Kulik, F.F. Hingerl, S. V. Dmytrieva, GEM-SELEKTOR
941 GEOCHEMICAL MODELING PACKAGE: TSoIMod LIBRARY AND DATA
942 INTERFACE FOR MULTICOMPONENT PHASE MODELS, *The Canadian*
943 *Mineralogist* 50 (2012) 1173–1195.
944 <https://doi.org/10.3749/canmin.50.5.1173>.

945

946