

Sustainability, transfer and containment properties of concrete subject to delayed ettringite formation (DEF)

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1	Sustainability, transfer and containment properties of concrete subject to Delayed
2	Ettringite Formation (DEF).
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4	
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7 Abstract

8 This work used numerous experimental techniques to evaluate the physicochemical and 9 mechanical modifications of concrete damaged by swelling due to internal sulfate attack. The 10 first objective was to determine property sensitive to DEF (delayed ettringite formation) and able to detect it before apparent cracking. The second objective was to quantify the evolution 11 12 of the properties that impact the containment property and the sustainability of concrete after expansion and damage. It was found that gas permeability, electrical resistivity and static 13 moduli results were the most promising techniques to detect DEF during the latency period. 14 15 The loss of containment appears for damage lower than 20%.

16 <u>Keywords:</u> Delayed Ettringite Formation (DEF); Sustainability indicators; Internal Sulfate
17 Attack (ISA); Swelling; Nuclear structure; containment property.

18 <u>1. Introduction</u>

19 Internal Sulfate Attack (ISA) can be due to the formation of delayed ettringite (DEF) in 20 cementitious material, after concrete hardening and without external sulfate supply. Many 21 engineering structures are susceptible to develop these pathologies. This reaction requires the presence of three main factors: high sulfate and aluminate contents, water, and a rise in 22 23 temperature at young age and/or later. The reaction mechanisms of DEF are complex but Brunetaud has proposed a global mechanism, described in four phases, grouping many 24 25 theories [1]. Several parameters have an influence on the development of DEF, and can be 26 divided into two groups: those related to the formulation of concrete and those related to the 27 environment. Concerning the formulation parameters, the expansion generated is strongly 28 dependent on the nature of the binder, in particular on the sulfate, aluminate and alkali 29 contents [2, 3]. The amount of added water is also influential. It modifies the porosity and therefore the ionic transfer [2, 4]. In addition, the nature and size of aggregates are important; 30 31 it has been shown that the use of small siliceous aggregates significantly increases the kinetics 32 and the swelling potential of DEF [5, 6]. As far as the environmental conditions are

concerned, DEF requires a minimum of 90% relative humidity and a rise in temperature to 33 34 above 65°C once in its history [7]. Expansion increases with the water content of concrete [8]. In terms of temperature, results from the literature show a combined influence of the maximal 35 36 temperature and the duration when the temperature is higher than about $65^{\circ}C$ [9]. The 37 evaluation of DEF damage in nuclear power plants represents an important economic and societal challenge. The main consequences of DEF are expansion and cracks. They affect the 38 39 physicochemical and mechanical properties of the concrete. Cracks lead to an increase of transfer properties and a decrease of mechanical properties and may lead to a loss of 40 41 containment, which is harmful for nuclear power plants. Massive elements can be particularly sensitive to DEF due to the risk of temperature increase at young age caused by the heat 42 production during cement hydration [10]. It therefore becomes necessary to propose a 43 44 measurement method to assess the state of degradation of the concrete generated by DEF in 45 such elements. Few data can be found in the literature on the evolution of the physicochemical and mechanical properties of concrete according to the degree of 46 47 advancement of DEF. The present study had two objectives: first, to find a very sensitive test allowing DEF to be detected before cracking can be observed visually and, second, to 48 49 evaluate the evolution of the properties that impact the containment and also the sustainability 50 of concrete affected by usual concrete pathologies such as carbonation, corrosion, etc. A test 51 protocol to accelerate DEF development was carried out and provided a good representation 52 of the reality on site [11]. A large number of samples were used to characterize the impact of 53 DEF on concrete properties at different levels of expansion. Chemical tests were performed to observe the initiation and the presence of DEF, while physical and mechanical tests evaluated 54 the impact of DEF on mechanical and transfer properties. 55

56 <u>2. Experiments</u>

57 **<u>2.1. Materials</u>**

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2.1.1. Components

In this study, two cements and two types of aggregates were used. The choice of cements focused on a CEMI and a CEMII, the main characteristics of which are summarized in Table 1. The aggregates used were based on silica or limestone according to the formulations. These two cements have been used in previous studies and show a high swelling potential in the case of DEF, in particular because of their high sulfate, alkali and aluminate contents [8, 11].

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Mass content (%)	CEM I 52.5 N	CEMII/A-LL 42.5 R
SiO ₂	19.3	19.7
CaO	63.2	63.5
Al ₂ O ₃	5.3	4.6
Fe ₂ O ₃	2.6	3.2
K ₂ O	0.94	1.36
Na ₂ O	0.08	0.11
SO ₃	3.5	2.7
Total	94.92	95,17

Table 1: Cement composition

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2.1.2. Mix designs

68 The mix designs have already been studied in other experimental works, which make it 69 possible to complete the database on the behavior of these concretes [8, 11]. The first study 70 have highlighted the risk of DEF in these concretes under variable moisture conditions; a decrease of mechanical properties and an increase of transfer properties under DEF 71 72 degradation have also been shown [8]. Moreover, the impact of accelerating tests method has 73 studied on theses concretes at scale structure, in terms of concrete expansion in [11]. 74 However, some modifications were made in the nature of aggregates used. Indeed, the 75 limestone aggregates used in [8, 11] contain a part of siliceous phase which is not qualified 76 with respect to the risk of Alkali-Silica Reaction (ASR). To avoid a possibly ASR gel 77 formation, the limestone aggregates used in this study is qualified as non-reactive for ASR 78 degradation. The proportion of aggregates was determined with respect to Dreux method in 79 order to reproduce the same aggregate skeleton. The formulations are detailed in Table 2. 80 The CEMII-Si and CEMI-Ca concretes contained siliceous and limestone aggregates, 81 respectively, to show the impact of the nature of aggregates on DEF. The choice of siliceous 82 and limestone aggregates respectively with CEMII and CEMI has been conducted to 83 reproduce mix design representative of nuclear structures. They have also been used for 84 concrete blocks, as part of a new platform test developed by the Radioprotection and Nuclear 85 Safety Institute (IRSN), to study the impact of DEF degradation at scale structure. The 86 concrete casting procedure used in this study followed the protocol of French standards [12, 13]. 87

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(a) CEMII	Si	(b) CEMI-	Ca
Material	Content (kg/m ³)	Material	Content (kg/m ³)
CEMII/A-LL 42.5 R	350	CEM I 52.5 N	400
0/0.315	264	0/4	718
0.315/1	151	4/11.2	289
1/4	254	11.2/22.5	813
4/8	145	Effective water	185
8/12	399	Na ₂ O _{eq}	5
12/20	616		
Effective water	188		
Plasticizer	0,35		
Na ₂ O _{eq}	3,5		

91

Table 2: Mix designs of "CEMII-Si" (a) and "CEMI-Ca" (b) concrete

92 <u>2.2. Degradation process</u>

In order to allow rapid development of DEF, IFSTTAR Test Nº 66 was adopted, with some
modifications [14]. This test comprises four stages: concrete mixing, heat treatment, dry/wet
cycles, and final immersion of samples in water at 20°C. The thermal treatment at young age
corresponded to that in Al Shamaa's study [8].



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Once cast, specimens were placed in a climate chamber at controlled temperature and relative
humidity. The heat treatment was applied for 7 days and comprised four stages: a hold at
20°C, 95% RH for 2h, followed by a rise in temperature from 20°C to 80°C, 95% RH at a rate

of 2.5°C/h. Stabilization at 80°C, 95% RH for 72h and a temperature decrease from 80°C to
20°C, 95% RH at a rate of 1°C/h (Figure 1).

104 As Kchachek and Brunetaud show, the maximum temperature reached in concrete is not the 105 only factor to be taken into account and it cannot be decoupled from the holding time [1,9]. 106 The useful temperature generated by this duration of heat treatment is about 1240°C.h and 107 corresponds to the area under the curve of heat treatment for a temperature above 65°C in 108 Figure 1. The selected dry/wet cycles correspond to the accelerated protocol of IFSTTAR Method N° 66 [15]. They are composed of two 14-day cycles: drying at 38°C, HR < 30% for 109 7 days and humidification in water at 20°C for 7 days (Figure 1). These cycles allow the 110 111 initiation of micro-cracking in the concrete and thus accelerate the kinetics of DEF appearance within the concrete without increasing the amplitude of the deformations [2]. The 112 113 beginning of the degradation is considered to occur at 35 days, at the end of the heat treatment 114 and wet/dry cycles, in this case. During the first 35 days, the concrete is considered to be in a 115 state of hydration where no expansion due to DEF develops. The storage water is not 116 renewed.

117



119

Figure 2: Sample storage and measurements of dimensions

When the wet/dry cycles had been completed, the samples were stored in isothermal containers at 20°C, equipped with a pump to homogenize the temperature and the species present in the water (Figure 2). The reference specimens underwent the same elaboration process but were not subjected to the heat treatment. During the first 7 days, the reference specimens were stored in water at 20°C instead of being heated. Wet/dry cycles were also applied (Figure 1). 126 The mass and expansion monitoring was performed on three cylindrical test pieces (11 x 22 127 cm). The shrinkage plots were fixed directly on the mold and were therefore embedded in the 128 concrete. Longitudinal expansion was measured by a digital micrometer having an accuracy 129 of $\pm 1 \mu m$. The transversal expansion was measured by a micrometer having an accuracy of $\pm 5 \mu m$ (Figure 2).

131 **<u>2.3. Test protocols</u>**

The physicochemical and mechanical tests performed during the experiments are listed inTable 3.

Chemical tests	Physical tests	Mechanical tests
pH of pore solution	Electrical resistivity	Compressive strength
Portlandite content	Chloride migration	Static moduli
SEM observation	Water porosity	Dynamic moduli
Alkali content	Gas permeability	

134

Table 3: Physicochemical and mechanical tests performed during the experiments

135 In order to observe the evolution of the physicochemical and mechanical properties of 136 concrete during its degradation by DEF, chemical analyses were performed to ensure the 137 presence of pathologies in the concrete. When the pathology was initiated (expansion of 138 (0.04%), measurement of the physical properties revealed the impact of the micro-cracking 139 generated on the transfer properties. Finally, measuring the mechanical properties gave some indications on the state of damage of the concrete subjected to these pathologies. 140 141 Measurements of all the properties were made at the different degrees of expansion shown in 142 Figure 3. The expansion curve due to DEF can usually been described as a sigmoid (Fig. 3), 143 with three phases:

The latent period is characterized by the precipitation of DEF in the microstructure
(Porosity, Interface Transition Zone (ITZ), Hadley grain) [1]. Expansion is small in this
period. When the tensile strength of concrete is reached due to internal pressure, cracks were
generated.

148 - The precipitation of DEF in cracks, leads to cracks propagation and so to the acceleration of149 expansion.

- Finally, the deceleration of swelling occurs when one reactant is consumed and/or when the
cracks opening is sufficiently significant to accommodate new products without generation of
supplementary expansion [1].

153 In order to detect the presence of DEF, the first characterization was conducted after curing in 154 the initial state, at 35 days. When swelling begins, during the latent period, two 155 characterizations were performed. Two other measurements were carried out during the 156 acceleration phase and a final characterization was performed during the stabilization period.





Figure 3: The 6 levels of expansion for the measurement of properties

159

2.3.2. Chemical tests

160 Two chemical tests were performed: pH measurement and determination of portlandite161 content.

162 The pH measurement was carried out on an 11 x 22 cm cylindrical specimen. The test piece 163 was broken in compression. The pieces present in the center of the specimen were placed in a 164 press to extract the interstitial solution present in the concrete. The pH was measured by a 165 probe. The pore solution was then stabilized by acid and analyzed by Inductively Coupled 166 Plasma Mass Spectrometry (ICP-MS) to determine the elements and their amounts.

167 The portlandite content was experimentally determined by Thermo-Gravimetric Analysis 168 (TGA) on a sample taken from an 11 x 22 cm cylindrical specimen. The central part of the 169 test piece was broken into small pieces and dried in a lyophilizer for 1 day. This part was then 170 polished and metallized for Scanning Electron Microscopy (SEM) observation to check that 171 DEF was present in the concrete.

172 *2.3.2. Physical tests*

173 Four physical tests were performed: electrical resistivity, chloride migration, porosity174 measurements, and gas permeability.

The electrical resistivity and non steady state chloride migration tests were performed according to the standard, on the same three 11×5 cm cylindrical samples obtained from an 11×22 cm one [15,16]. The saturated concrete solution of the tests was replaced by a NaOH concentration of 0.1 mol/l according to a new test protocol (PerfDub).

Gas permeability and water porosity tests were performed according to the standards [17, 18]. However, the drying temperature has been adopted at 40°C for two reasons: this helps to avoid the destabilization of the delayed ettringite formed during the development of ISR and on the other hand allows limiting the additional cracking caused by drying to 105°C, proposed in the standards. In this case, the evolution of gas permeability during the expansion will mainly due to concrete DEF damage by limiting supplementary cracks due to high drying temperature.

186 2.3.1. Mechanical tests

187 Three mechanical properties were measured: the compressive strength, and the static and the 188 dynamic moduli. Linear and nonlinear acoustic methods were employed to determine the 189 dynamic moduli.

190 Compressive strength and static moduli were measured on three 11 x 22 cm cylindrical191 specimens according to the standards [19, 20].

192 Several tests in development to determine the dynamic moduli are presented in the literature. 193 These tests have already been performed in the case of DEF damage [1, 8]. In this study, the 194 dynamic moduli was determined by two measurements. Linear acoustic emission was 195 performed in transmission and reception on the same specimens. The equipment used 196 included a SOFRANEL 5077PR signal generator, a TEKTRONIX oscilloscope and 250 kHz 197 longitudinal and transversal wave transducers. To improve the signal quality, a viscous liquid 198 was needed at the concrete/transducer interface; in this test, honey was used. The dynamic 199 moduli was determined from equation 1:

200
$$E_{dyn} = \rho V_t^2 \cdot \left(\frac{3V_l^2 - 4V_t^2}{V_l^2 - V_t^2}\right)$$
(1)

with E_{dyn} the dynamic moduli (Pa), ρ the density in kg/m³, V_t the shear wave velocity (m/s), V₁ the compression wave velocity (m/s).

A nonlinear acoustic emission method was also used to evaluate the dynamic moduli. The principle is to generate a pulse at the base of the test piece using a hammer. The resonance of the specimen generates a signal collected by an accelerometer on the other side of the specimen and treatment of the signal by a Fourier transformation gives the natural frequencyof longitudinal resonance of the material. The moduli is then determined by equation 2:

208
$$f_{long} = \frac{1}{2L} \sqrt{\frac{E_{dyn}}{\rho}} \qquad (2)$$

with L the specimen length (m) and f_{long} the longitudinal natural frequency of the material (Hz).

211 <u>3. Experimental results</u>

212 <u>3.1. Expansion</u>

Figure 4a shows the evolution of expansion as a function of time for the CEMII-Si and CEMI-Ca concretes and their corresponding references CEMII-Si-ref and CEMI-Ca-ref. IFSTTAR method n^o 66 refers to a swelling limit of 0.04% in an expansion test [14]. Beyond this threshold, there is a risk of the concrete being damaged by DEF. The reference formulations did not exceed the limit threshold and showed a maximum swelling of 0.02%.



218 *Figure 4: Evolution of expansion (transversal and longitudinal) (a) and mass gain (b) versus*

219

Specimens developing DEF showed significant swelling, around 0.9%, at the end of the 220 expansion for CEMII-Si. The latent period began at around 70 days, or 35 days after curing. 221 For the CEMI-Ca design, this period started at 60 days and ended quickly. The first point of 222 223 inflection was at 80 days for the CEMI-Ca and 110 days for the CEMII-Si concrete. CEMI-Ca 224 contained large limestone aggregates that lead to a decrease of the latent period [21]. This 225 phenomenon is attributed to the higher bonding in case of limestone aggregates with the 226 cement matrix. In this case, cracks generated at the ITZ during the heat treatment due to a 227 differential dilatation coefficient between paste and aggregates, were reduced [21]. On the one 228 hand, the low cracking results in a lower volume available to accommodate the new phases 229 due to DEF without inducing cracking and expansion. On the other hand, the low cracking 230 leads to a decrease of transfers properties in concrete and thus to delay DEF expansion. These 231 two phenomena are opposed. Indeed, a decrease in transfer properties cannot explain the 232 lowest latency period observed in the case of limestone aggregates. The decrease in available volume caused by the low cracking at the ITZ therefore seems to be the cause of the decrease 233 234 in latency period. In this case, the volume of DEF necessary to generate pressure is reduced 235 and it leads to a decrease of latent period.

The final expansion of CEMI-Ca showed a swelling of around 0.6%. This lower swelling was attributed to the presence of limestone aggregates, which allowed the bond between aggregate and cement paste to be increased by the formation of calcium hydrates around the aggregates and equally due to a high mechanical interlocking behavior [5, 22, 23, 24]. The cracks generated by DEF at the ITZ were also reduced, allowing a lower final expansion [5, 23].

241 Figure 4b shows the evolution of mass as a function of time. The initial mass, m_0 , was 242 measured at 35 days. Reference samples have a mass gain of 0.4% stabilizing around 200 days. This increase was due to their storage in water at 20°C. For CEMII-Si and CEMI-Ca 243 244 concretes, the mass increase was proportional to the swelling of the concrete. In addition, the kinetics of the mass gain for these two pathological concrete was in agreement with the 245 246 kinetics of swelling, which confirms the short latent period in the CEMI-Ca specimens 247 (Figure 4a). The mass gain of CEMII-Si and CEMI-Ca concrete reached respectively 1.5 and 248 1.2% at the end of expansion.



The longitudinal and transversal expansion measurements reported in Figure 5 are proportional. The slope of proportionality is equal to 1, confirming the isotropy of the swelling already observed in stress free conditions [25]. However, the transversal swelling is slightly lower on the CEMII-Si concrete at the end of expansion.

255 3.2. Microstructure evolution

256 The presence of delayed ettringite was observed by SEM for each degree of expansion.

257

259 Figure 6 shows the presence of delayed ettringite in massive and compressed form for different degrees of swelling. In the CEMII-Si formulation, siliceous aggregates were used. 260 The SEM images show that the initiation of swelling was induced by the formation of delayed 261 262 ettringite in Hadley grains (Figure 6a) and at the ITZ (Figure 6b). The swelling measured at 263 this degree was 0.05%. As expansion continued, delayed ettringite continued to develop in 264 these areas and in the porosity (Figure 6c and 6d). Then there was a separation from the 265 cement paste all around the aggregates (Figure 6d). At the time corresponding to 0.25% of swelling, the cracks propagated from this interface to the porosity, causing an acceleration of 266 267 swelling. When expansion continued, the presence of delayed ettringite became increasingly 268 significant, both in the cement paste (Figure 6e) and in the porosity (Figure 6f).

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270 271

Figure 7: SEM images of the CEMI-Ca concrete

272 The SEM observations on the CEMI-Ca were consistent with those observed on the CEMII-Si concrete as ettringite developed primarily at the ITZ, in the Hadley grains and in the porosity 273 274 (Figures 7a and 7b). As expansion continued, delayed ettringite continued to propagate in 275 these areas (Figures 7c and 7d). When these preferential zones began to be completely filled 276 by ettringite, the cracking propagated between them (Figures 7e and 7f) and the ettringite gradually began to fill the generated cracking. This step marked the acceleration of the 277 278 degradation. However, cracking generated at the ITZ in the case of limestone aggregates did 279 not propagate all around the aggregate, thus confirming the observations of Yang et al. [23].

(a) 0.92%; 320d

(b) 0.92%; 320d

280

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Figure 8: CEMII-Si SEM images (a) initial image and (b) sulfur image (mapping)

282 These results show that, for each formulation, the presence of delayed ettringite is found first 283 at the ITZ in the Hadley grains and in the porosity. Ettringite then propagates in and between 284 these preferential zones, generating more and more cracking. This cracking marks the 285 acceleration of the expansion. As mentioned above, the cracking generated at the ITZ depends 286 on the nature of the aggregates [23]. In the case of siliceous aggregates, cracking is generated 287 all around the aggregate but it only partially surrounds limestone aggregates. Ettringite then 288 spreads in existing fissures. Figure 8b shows the presence of sulfur in the sample (yellow in 289 Figure 8b), proving the presence of delayed ettringite in concrete cracks. These observations 290 confirm that the cracks caused by the pathology are filled with ettringite during the expansion. Recently, Brunetaud [1] had proposed a global swelling theory to explain the DEF 291 292 propagation. This theory is based on a homogeneous swelling of concrete. Delayed ettringite 293 would initially form in Hadley grains and porosity. The pressure generated by the DEF in the 294 cement matrix would lead to the presence of cracks at the ITZ (rigid inclusion) and the 295 development of delayed ettringite in this area. The crystallization pressure generated by the 296 formation of ettringite in these areas would lead to cracks propagation and thus accelerate the 297 degradation. These results are in agreement with this theory: delayed ettringite was first 298 observed in the Hadley grain, in the porosity and at the ITZ. Then delayed ettringite was 299 observed in the cracks.

300 3.3. Detection criterion

The first aim of this experimental work was to find a very sensitive test allowing DEF detection. DEF can be detected if the evolution of one of the properties measured in this work is significant (sufficiently higher than the scatter on results) and only due to DEF expansion (not to concrete hydration). In this aim, a DEF detection criterion for physicomechanical properties was developed, taking the effect of hydration and experimental scatter into account(equation 3).

307
$$X_{i \, threshold}(t) = X_0 \left(1 + \frac{X_{i \, ref}(t) - X_0 \, ref}{X_0 \, ref} \right) \pm 2\overline{\sigma_{ref}}$$
(3)

with X_i threshold(t) the threshold value of detection of the property measured in time, X₀ the initial value of the pathological concrete, X₀ ref the initial value of the reference concrete, X_i $r_{ef}(t)$ the value of the property of the reference concrete in time and $\overline{\sigma_{ref}}$ the average of the standard deviations obtained on the reference specimens.

For the measurement of the chemical properties, the high dispersion of results did not allowthis criterion to be used.

314 3.4. Chemical properties

315 3.4.1 pH measurement and portlandite content

The pH analysis of the interstitial solution was performed for different degrees of expansion. 316 317 Figure 9a shows the evolution of the pH for the CEMII-Si and CEMI-Ca concretes and Table 318 4a summarizes the pH results obtained on the reference concretes. No significant change in 319 the pH was observed on the reference specimens or on those developing the pathology (Table 320 4a and Figure 9a). The pH of the interstitial solution of CEMII-Si concrete remained stable at 321 a value of approximately 13.3 and that of the CEMI-Ca was also stable during the expansion, 322 at around 13.4. The associated reference specimens showed the same trends, with pH around 13.4 for CEMII-Si-ref and around 13.5 for CEMI-Ca-ref. 323

(a)	35d	90d	180d	(b)	(wt.%)	35d	90d	180d
CEMII-Si-ref	13.5	13.3	13.4	CEN	/III-Si-ref	13.4	11.9	11.4
CEMI-Ca-ref	-	13.7	13.3	CEN	II-Ca-ref	15.7	15.9	17.3
				-				

324 *Table 4: pH (a) and portlandite (b) evolution over time for reference concretes*

The leaching of alkalis should have lowered the pH to about 12.6 over time, due to portlandite pH buffering [26]. The test protocol may have been partly responsible for these stable, high pH values. Chappex and Scrivener observed an increase in alkali concentrations in accordance with the pressure applied up to 800 MPa [27]. During the present test, the pressure was about 900 MPa. It is possible that the alkalis adsorbed physically on the surface of the hydrates were released into the solution, leading to a pH buffering.

The evaluation of portlandite content performed by ATG on concrete samples (Figure 9b) shows that it remained stable during the degradation, at between 11 and 17% for all concretes. The oscillation of the values was a consequence of the sample used. This test is usually performed on cement paste.

X-Ray Diffraction (XRD) analyses were conducted on the same samples. During the degradation, no new formed phase was observed. The delayed ettringite being poorly crystallized, its presence was not detected. In addition, the large peaks of calcite or silica, depending on the nature of the aggregates used, masked the hydrated phases, thus making the analysis complex.

349 3.4.2 Alkali concentrations

351 352

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<u>storage water (b) versus time</u>

353 Figures 10a and 10b represent the evolution of the equivalent alkali content, expressed in 354 mmol/l, contained in the interstitial solution and in the storage water, respectively, for each 355 concrete. Figure 10b shows the strong leaching of alkali during the first 35 days. In fact, the 356 initial Na₂O_{eq} concentration of the storage water was 0.6 mmol/l. At 35 days, this water contained a concentration of 25 mmol/l. This significant leaching came, in particular, from the 357 358 fact that micro-cracking was generated during the wet/dry cycles. Underwater storage, 359 resulting in alkali leaching, continued over time. However, the leaching of specimens 360 developing the pathology seems to be greater than that of the reference concretes. At 200 361 days, the storage water of concretes developing DEF was found to have a concentration of 50 362 mmol/l, against about 40 mmol/l for reference concretes. This supplement of leaching can be 363 attributed to micro-cracking in the material, generated by the swelling of DEF.

364 Figure 10a confirms these results. The alkali leaching of interstitial water is greater for the pathological concretes. In addition, the concentration of Na₂O_{eq} of the reference concretes 365 366 seems to stabilize after 100 days. This stabilization could be attributed to the filling of the 367 pores at the periphery of the test piece with calcite. This phenomenon has also been observed 368 and discussed by Thibaut [28]. However, although the initial amount of alkali in the CEMI-Ca 369 and CEMI-Ca-ref concretes was higher, the leaching generated during the first 35 days 370 significantly decreased their concentration. The Na₂O_{eq} concentration of the CEMI-Ca and 371 CEMII-Si concretes was found to be close respectively 308 and 261 mmol/l at 35 days despite 372 the difference of alkali content in the initial state.

The measurement of the portlandite content and the pH of the interstitial solution showed noevolution during the degradation. The significant leaching of alkali over time was mainly due

to the storage. These chemical properties do not make it possible to detect DEF during thedegradation.

377 **3.5.** Physical properties

378 3.5.1. Chloride migration

Non steady state chloride migration tests and electrical resistivity measurements were performed on the same test specimens. Figure 11 shows the evolution of the chloride migration coefficient as a function of the expansion generated by the pathology. The CEMII-Si-ref and CEMI-Ca-ref references had a migration coefficient that hardly varied over time (by $13x10^{-12}$ and $11x10^{-12}$ m² respectively (Table 5)).

	35u	90d	1800
CEMII-Si-ref	12.6 ±0.2	12.8 ±0.3	14.9 ±1.8
CEMI-Ca-ref	10.3 ± 0.4	11.2 ± 0.3	10.2 ±1.1
	CEMII-Si-ref CEMI-Ca-ref	CEMII-Si-ref 12.6 ±0.2 CEMI-Ca-ref 10.3 ±0.4	CEMII-Si-ref 12.6 ±0.2 12.8 ±0.3 CEMI-Ca-ref 10.3 ±0.4 11.2 ±0.3

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392

<u>reference concretes</u>

Concretes developing pathology had a higher migration coefficient, around 30x10⁻¹² m², before DEF expansion. There are several reasons to believe that this increase in comparison with the reference concrete was due to the heat treatment effect. The heat treatment may have generated a modification of the composition of the cement paste and the hydrates formed [29]. In addition, the thermal expansion effects may have damaged the cement paste and the ITZ [21, 30].

For the concretes developing the pathology, no significant increase in the migration coefficient was observed. This phenomenon can be explained by the fact that the chloride ions diffused uniformly in the cement paste through the porosity and micro-cracking due to DEF after expansion. When measurements were taken, this generated a linear penetration front despite the presence of macro-cracking. The wide scatter of the results did not allow the detection of DEF.

401 *3.5.2. Electrical resistivity*

402 The electric resistivity tests (Figure 12) showed greater sensitivity. Reference concretes 403 CEMII-Si-ref and CEMI-Ca-ref had a resistivity of 45 Ω .m at 35 days (Table 6). The 404 concretes developing the pathology had a lower resistivity, around 35 Ω .m, at the same time, 405 the heat treatment having caused additional damage.

(Ω.m)	35d	90d	180d
CEMII-Si-ref	45.0 ±2.2	55.0 ±3.8	58.0 ±4.9
CEMI-Ca-ref	45.0 ±1.0	51.0 ±1.7	55.0 ±4.0

<u>Table 6: Evolution of the electrical resistivity over time for reference concretes</u>

In Figure 12, a gradual decrease in the resistivity is observed during the degradation for each pathological concrete. A threshold of around 25 Ω .m is reached at 0.3% expansion. This threshold of resistivity could be due to the cracking caused by the pathology being gradually filled by ettringite. In contrast, for the reference concretes, the electrical resistivity increased significantly between 35 and 90 days. A resistivity gain of 25% was observed from day 35 to day 180, due to the continuation of the hydration reactions causing a densification of the concrete.

414

406

415

417 Figure 12: Evolution of the coefficient of the electrical resistivity according to the expansion 418 for concretes damaged by DEF

With the chosen criterion (Eq. 3), the detection of DEF took place between 0.05 and 0.1% of
expansion, during the latent period. Between these two expansion levels, the decrease of
resistivity was sufficient to point out significant damage.

422 *3.5.3. Water porosity*

Figure 13 shows the evolution of the water-accessible porosity as a function of the expansion
caused by DEF. The reference concretes CEMII-Si-ref and CEMI-Ca-ref show no evolution
over time despite the continuation of hydration reactions (Table 7).

_	(%)	35d	90d	180d
	CEMII-Si-ref	11.2 ±0.7	11.4 ±0.2	11.9 ±0.3
	CEMI-Ca-ref	12.8 ±0.3	13.4 ± 0.4	13.7 ±0.3

426

416

Table 7: Evolution of water porosity over time for reference concretes

427 The porosity measured on the CEMII-Si concrete remains lower than that measured on the 428 CEMI-Ca concrete. The use of limestone aggregates of higher porosity for CEMI-Ca 429 concretes could explain this difference, the water absorption coefficient of these aggregates being greater: 2.6% against 0.6%. When the concrete is damaged by delayed ettringite 430 431 formation, porosity tends to increase, this being attributed to the formation of a crack 432 network, filled by water. The increase in porosity is rapid at the beginning of the expansion 433 and then stabilizes at the end of the expansion period. This stabilization can be explained by a 434 competition between crack opening and crack filling with delayed ettringite.

436 *Figure 13: Evolution of water porosity as a function of expansion for concretes damaged by* 437 <u>DEF</u>

438 Depending on the criterion chosen, the detection takes place between 0.15 and 0.25% of439 expansion, at the beginning of the acceleration phase.

440 *3.5.4. Gas permeability*

435

Figure 14 shows the evolution of the apparent air permeability coefficient according to the
expansion generated by DEF. The reference concretes CEMII-Si-ref and CEMI-Ca-ref show
no change in their coefficients of permeability over time of 110x10⁻¹⁸ m² (Table 8).

(x10 ⁻¹⁸ m ²)	35d	90d	180d
CEMII-Si-ref	110 ±23	106 ±12	101 ±27
CEMI-Ca-ref	101 ±38	111 ±13	120 ±10

444 <u>*Table 8: Evolution of apparent gas permeability coefficient over time for reference concretes*</u>

445 The CEMII-Si and CEMI-Ca concretes developing the pathology have apparent gas permeability coefficients that are similar, respectively equal to $125 \times 10^{-18} \text{ m}^2$ and $60 \times 10^{-18} \text{ m}^2$ 446 447 before expansion. During expansion, the CEMII-Si concrete shows a strong increase in the 448 coefficient of permeability at the beginning of expansion (permeability at 0.05% is double 449 that before expansion). The CEMI-Ca also shows an increase but it occurs later and is 450 smaller. This difference could be due to the mineralogical nature of the aggregates used. The 451 ITZ of concretes containing limestone aggregates seems to be improved [5, 22, 23]. As mentioned above, cracks due to DEF passing through this interface are reduced in the case of 452 453 limestone aggregates [23]. There may be fewer preferential paths in the CEMI-Ca concrete, 454 causing a smaller increase in the coefficient of permeability at early expansion. When the 455 acceleration phase of the pathology is reached, at around 0.2% of swelling, the permeability is 456 significantly impacted. This drastic increase can be attributed to the formation of more and 457 more percolating paths within the material, generating a large increase of gas flow during the 458 test. These results are therefore in agreement with those of Al Shamaa et al. [31].

460 *Figure 14: Evolution of apparent gas permeability coefficient according to the expansion for* 461 *concretes damaged by DEF*

462 Depending on the criterion chosen, the detection takes place during the latent period before
463 0.05% expansion for CEMII-Si concrete and at the beginning of the acceleration phase,
464 between 0.17 and 0.29%, for CEMI-Ca concrete.

465 **3.6. Mechanical properties**

466 *3.6.1 Compressive strength*

The compressive strength measurements also show the impact of the heat treatment on the
mechanical properties. The reference concretes CEMII-Si-ref and CEMI-Ca-ref have
compressive strengths of 34 MPa and 44 MPa, respectively, at 35 days (Table 9).

(MPa)	35d	90d	180d
CEMII-Si-ref	34.0 ± 2.0	34.1 ±1.3	38.3 ±0.5
CEMI-Ca-ref	43.5 ±1.5	48.2 ±1,4	49.0 ±0.3

470

Table 9: Evolution of the compressive strength over time for reference concretes

The compressive strengths of CEMII-Si and CEMI-Ca are lower, at 23 MPa and 29 MPa, respectively. The reduction of the compressive strength by the heat treatment can be explained as previously by the occurrence of damage in the cement paste and the ITZ and by

the modification of the composition of hydrates [21, 29, 30]. The compressive strength of 474 475 CEMI-Ca and CEMI-Ca-ref concretes remains higher than those of other concretes and 476 increases with time following the hydration process. This difference is explained by the fact 477 that these concretes contain a larger amount of cement and a lower W/C ratio, and also 478 because the presence of limestone aggregates in the formulation improves the ITZ. The 479 CEMII-Si and CEMI-Ca pathological concretes show compressive strength that remains 480 stable during the initiation of the pathology. However, during the acceleration phase, the strength decreases spontaneously and then stabilizes at the end of the acceleration period. 481 482 These results are in accordance with those of Bouzabata et al. [25]. The compressive strength 483 drop is 30% and 20% for the CEMII-Si and CEMI-Ca concretes, respectively, at the middle 484 of expansion.

486 487

485

488 Depending on the criterion chosen, the detection takes place between 0.17 and 0.25% of 489 expansion, at the beginning of the acceleration phase.

490 *3.6.2 Static moduli*

- 491 The static moduli of CEMII-Si-ref and CEMI-Ca-ref reference concretes shows small changes
- 492 between 35 and 190 days (Table 10). The moduli is still higher for CEMII-Si-ref concrete
- 493 (equal to 40 GPa) than for CEMI-Ca-ref concrete (31 GPa) at 35 days.

(GPa)	35d	90d	180d
CEMII-Si-ref	40.4 ±2.5	39.4 ± 0.4	43.3 ±1.0
CEMI-Ca-ref	31.9 ±0.01	32.1 ±0.5	33.0 ±0.5

⁴⁹⁴

Table 10: Evolution of the static moduli as a function of time for reference concretes

However, the CEMII-Si and CEMI-Ca pathological concretes reveal that the moduli decreases progressively during the expansion. A significant decrease in the moduli is observed for swelling of around 0.2% during the acceleration phase of the pathology (Figure 16). At this time, the moduli decreases by 40% and 50% for the CEMII-Ca and CEMII-Ca-ref concretes, respectively. The loss of static moduli seems to be proportional to the expansion rate caused by the pathology. These results are not in agreement with those of Al Shamaa et al., who show no decrease of static moduli during the latent period [10].

502

503 Figure 16: Evolution of the static moduli according to the expansion for concretes damaged
 504 by DEF

505 Depending on the criterion chosen, the detection takes place between 0.05 and 0.1% of 506 expansion, during the latent period.

- 507 *3.6.3 Dynamic moduli*
- 508 Figure 17a shows the evolution of the dynamic linear acoustic moduli according to expansion.
- 509 The reference concretes CEMII-Si-ref and CEMI-Ca-ref show no moduli evolution over time
- 510 (moduli of about 45GPa and 41GPa, respectively, by linear acoustics Table 11a).

	(GPa)	35d	90d	180d
	CEMII-Si-ref	44.5 ±1.5	48.4 ±0.8	43.3 ±0.9
(a)	CEMI-Ca-ref	40.9 ± 0.6	41.6 ±0.5	41.9 ±0.2
(b)	CEMII-Si-ref	-	-	-
	CEMI-Ca-ref	33.5 ± 0.5	34.6 ±0.4	35.1 ±0.7

511 *Table 11: Evolution of the dynamic moduli in linear (a) and nonlinear (b) acoustics over time*

512

for reference concretes

The CEMII-Si and CEMII-Ca pathological concretes have dynamic moduli of 36 GPa and 39 513 514 GPa, respectively, and only the dynamic moduli of the CEMII-Si concrete seems to be impacted by the heat treatment. This difference can be explained by the difference of ITZ 515 between these aggregates [21, 30]. For the pathological concretes, no evolution of the 516 517 dynamic moduli measured by linear acoustics is observed during the expansion. When the damage becomes too great, during the acceleration phase, the received signal becomes too 518 519 disturbed. It follows that a very weak signal is detected by the sensor in reception, making the 520 measurements unusable (linear acoustics).

521

522 Figure 17: Evolution of the dynamic moduli in linear (a) and nonlinear (b) acoustics 523 according to the expansion for concretes damaged by DEF

524 Dynamic moduli measurements in nonlinear acoustics (Figure 17b) show the same trend. The 525 dynamic moduli remains stable around 35 GPa over time for the reference concrete (Table 526 11b). The dynamic moduli of the pathological concrete CEMI-Ca remains slightly lower than 527 that of the reference concrete, 30 GPa at 35 days. However, it decreases rapidly around 0.2% 528 of expansion during the acceleration phase of the pathology. The loss of moduli associated 529 with the development of the DEF is of the order of 30% at 0.45% of expansion. These results 530 are in agreement with those found in the literature [10, 31, 32, 33].

531 Depending on the criterion chosen, detection by nonlinear dynamic moduli takes place
532 between 0.17 and 0.29% of expansion, at the beginning of the acceleration phase. The linear
533 dynamic moduli does not allow DEF to be detected.

- 534
- 535
- 536

537 4. Discussion

4.1. Detection of DEF 538

539 The results obtained on the evolution of the concrete properties according to expansion show that only some particular tests make it possible to detect DEF at the beginning of the 540 expansion, during the latent phase. Table 12 summarizes all the expansion values at the time 541 542 of detection of pathologies presented in the experimental results.

	Expansion at	DEF nhase		
-	CEMII-Si	CEMI-Ca		
pH of pore solution	-	-	-	
Portlandite content	-	-	-	
Chloride migration	-	-	-	
Electrical resistivity	0.05-0.11	0.05-0.11	Latent phase	
Water porosity	0.11-0.25	0.17-0.29	Acceleration phase	
Gas permeability	0.05	0.17-0.29	Latent phase	
Dynamic moduli AL	-	-	-	
Dynamic moduli NA	-	0.17-0.29	Acceleration phase	
Static moduli	0.05 / 0.11	0.05-0.11	Latent phase	
Compressive strength	0.11 / 0.25	0.17-0.29	Acceleration phase	

543

Table 12: Summary of the evolution of the properties at detection for the CEMII-Si and

544

CEMI-Ca concretes

545 Microscopic observations showed the evolution of ettringite formation during expansion in the material. However, measurements of pH and portlandite content showed no evolution 546 547 during the expansion. The potential modification of portlandite when the pathology develops 548 in the concrete cannot be identified by the technique used in this study. Some physical 549 measurements related to the transfer properties allowed DEF to be detected during the latent phase and measurements of the gas permeability and electrical resistivity appear to provide a 550 551 good sustainability indicator for the detection of DEF. The doubling of the apparent gas 552 permeability coefficient at 0.12% of expansion for the CEMII-Si concrete reveals that the loss 553 of containment occurs at a low degree of expansion for unreinforced concrete. However, the 554 CEMI-Ca concrete showed a later increase in permeability coefficient, during the acceleration 555 phase. The improvement of ITZ in the case of limestone aggregates seems to reduce the 556 cracks generated at this interface during DEF damage [23]. Thus allowing the cracks in the 557 concrete to be less percolating.

558 The electrical resistivity tests also showed significant sensitivity, the detection being effective 559 from the latent phase. The electrical resistivity decreased by 16% and 10% for the CEMII-Si 560 and CEMI-Ca concretes, respectively, for expansions of 0.12% and 0.19%. Since the electrical resistivity of the reference concretes increased substantially from 35 days to 180 days, the decrease in the resistivity associated with the development of the pathology seems to be significant. However, this parameter was very sensitive to the degree of saturation of concrete [34]. In case of existing structure, electrical resistivity is commonly used to assess the degree of saturation of concrete. So in case of DEF damage structure, it could be difficult to use the electrical resistivity to determine both the degree of saturation and the occurrence of DEF.

568 The water porosity measurements did not show any great sensitivity. The increase in porosity 569 associated with micro-cracks in the matrix was small compared to the initial pore volume, 570 making detection difficult. A relative increase of the porosity of 19% compared to the initial 571 porosity for a swelling of 0.25% was observed on the CEMII-Si concrete. At this degree of 572 expansion, cracking was already visible on the faces of the concrete specimens. Dynamic 573 moduli measurements in linear acoustics did not detect the presence of DEF in concrete but 574 tests in nonlinear acoustics showed a decrease in dynamic moduli when it was no longer 575 measurable by the previous method. A decrease of 22% for an expansion of 0.29% was 576 observed for the CEMI-Ca concrete at the middle phase of acceleration. Static moduli 577 measurements had greater sensitivity than the two previous methods and allowed detection 578 during the latent phase. A continuous decrease was observed throughout the development of 579 the pathology. A 15% loss of moduli associated with a swelling of 0.11% was observed for 580 each concrete. The compressive strength of the CEMII-Si and CEMI-Ca concretes damaged 581 by DEF decreased by 26% and 14% respectively for expansions of 0.25% and 0.29%. This 582 loss of compressive strength in the middle phase of acceleration delayed the detection of the 583 pathology. Three sustainability indicators made it possible to detect DEF earlier, during the 584 latent phase for laboratory specimens. These were the gas permeability, the electrical 585 resistivity and the static moduli.

586 4.2. Sustainability of concretes damaged by DEF

Figure 18 shows the evolution of the damage as a function of the expansion for the two
concretes undergoing DEF. In this study, the damage was proportional to the expansion due to
DEF. The damage was calculated from the static moduli according to Equation 4:

590
$$D = 1 - \frac{E_i}{E_0}$$
 (4)

A study by Martin et al. on coupled AAR and DEF expansion on concrete shows an almost
linear trend. The loss of damage according to the expansion is in accordance with these results
[35].

596 597

Figure 19: Evolution of the apparent permeability rate as a function of damage

598 The evolution of the apparent gas permeability rate presented in Figure 19 shows that the 599 increase in the permeability seems to be an exponential function of the damage. However, the 600 percolating paths in CEMI-Ca concrete specimens would appear at around 20% of damage, at 601 the beginning of the acceleration phase of the pathology. For the CEMI-Si concrete, the 602 percolating paths appear for slight damage, around 7%, causing a considerable increase of the 603 air flow through the material. The greater bonding at the ITZ in the case of limestone 604 aggregates seems to allow the containment properties to be maintained during the beginning 605 of the DEF damage, when it is lower than 20%.

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607

Potential Sustainability							
Sustainability indicators	Concretes	Initial state	Latent phase	Acceleration phase	Stabilization phase		
Expansion $(\%)$ -	CEMII-Si	0	0.02-0.15	0.15-0.7	0.8		
	CEMI-Ca	0	0.02-0.1	0.1-0.45	0.55		
Electrical resistivity	CEMII-Si	Very low	Very low	Very low	Very low		
	CEMI-Ca	Very low	Very low	Very low	Very low		
Gas permeability (40°C)	CEMII-Si	Medium	Low	Very low	Very low		
	CEMI-Ca	High	High	Medium	Low		
Water porosity (40°C)	CEMII-Si	High	Medium	Low	Low		
	CEMI-Ca	Medium	Medium	Low	Low		

608 <u>Table 13: Classification of concrete damaged by DEF relative to limit values for the potential</u> 609 sustainability and properties of concrete [36]

610 Table 13 shows the evolution of the potential durability of concretes during the development 611 of the pathology. The "low" classification at the initial state of concretes is mainly due to the 612 effects of heat treatment and wet/dry cycles as mentioned previously [21, 29, 30]. 613 Sustainability indicators show lower potential sustainability as early as the latent period for 614 CEMII-Si concrete and this trend continues throughout the degradation. The presence of 615 limestone aggregates in CEMI-Ca concrete seems to maintain the same sustainability during 616 this phase. During the acceleration phase of the pathology, the potential sustainability of 617 concretes becomes greatly affected. This could accelerate the kinetics of appearance of other 618 pathologies such as AAR, carbonation and corrosion, causing premature aging of the 619 structures.

620 <u>5. Conclusion</u>

621 A large experimental program has been proposed in order to obtain a sensitive measurement of DEF, allowing its detection before it can be observed visually. The second objective was to 622 623 evaluate the evolution of the properties that have an impact on the containment and on the 624 sustainability of concrete where other pathologies are also present. Numerous 625 physicochemical and mechanical properties were measured by the use of a large quantity of 626 samples. These tests were performed on two concretes showing a high swelling potential 627 when DEF occurs and containing aggregates of different mineralogical natures. First, it 628 confirms the results of the scarce studies reported in the literature:

• DEF expansion is isotropic in stress-free conditions [25].

- Microscopic observations have shown DEF development in accordance with the theory of swelling proposed by Brunetaud [1].
- 632 Second, original results have been obtained on the durability indicators for concrete damaged633 by DEF:
- The measurements of pH and portlandite content do not show any evolution during the
 pathology in spite of strong leaching of alkalis.
- The measurement of physical properties shows that electrical resistivity and gas permeability are sensitive to the expansion generated by DEF, the detection being effective from the latent period for laboratory specimens. However, the electrical resistivity could be difficult to use for damaged structures due to its sensitivity to other parameters [34]. Water-accessible porosity and chloride migration tests are not suitable for the detection of the pathology, their sensitivity being too low with respect to the presence of cracks through the cementitious matrix.
- For a given expansion, the permeability increase of concrete damaged by DEF is
 greater for concrete containing silica aggregate than for concrete with limestone
 aggregate.
- The mechanical tests show that, despite the filling of the ettringite cracking at the end
 of expansion, no improvement is observed in the measured properties. Only the
 measurement of the static moduli allows detection of the pathology during the latent
 period and shows that the loss of moduli seems to be proportional to the expansion
 measured in stress free conditions.
- Three sustainability indicators seem to allow the detection of pathology in the short term during the latent period: gas permeability, electrical resistivity, and static moduli.
- The loss of containment in case of nuclear power plants related to the presence of DEF
 depends of the nature of the aggregates and occurs for less than 20% of damage.
- At the acceleration phase, the potential sustainability of concretes is greatly altered and could lead to the premature appearance of other pathologies.
- The presence of limestone aggregates seems to improve the sustainability of concrete
 subject to DEF.

29

659 This study was performed on a large quantity of laboratory specimens in stress free swelling 660 and fully saturated conditions. It is necessary to pursue the study to evaluate the influence of a larger volume of concrete, the presence of reinforcement and the presence of a water content 661 662 gradient in order to detect DEF on existing structures. In the case of nuclear power plants, it is 663 also necessary to develop nondestructive methods related to the properties sensitive to DEF 664 proposed in this study in order to maintain the containment property of concrete. In this 665 context, a test platform for the measurement of DEF sustainability indicators on concrete at structure scale is being developed in the ODOBA (Observatoire de la Durabilité des Ouvrages 666 667 en Béton Armé) project.

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