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## Assessment of the durability of various cementitious materials subjected to low levels of H<sub>2</sub>S in wastewater networks

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### ► To cite this version:

Janette Ayoub, Marielle Guéguen-Minerbe, Tony Pons, Marcos Oliveira, Sabrina Guérin-Rechdaoui, et al.. Assessment of the durability of various cementitious materials subjected to low levels of H<sub>2</sub>S in wastewater networks. *Materials and structures*, 2024, 57, 10.1617/s11527-024-02346-6 . hal-04610470

**HAL Id: hal-04610470**

**<https://hal.science/hal-04610470v1>**

Submitted on 13 Jun 2024

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Journal Name	Materials and Structures	
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Schedule	Received Revised Accepted	8 Dec 2023  28 Mar 2024
Abstract	Wastewater networks are intrinsically attacked by the production of H <sub>2</sub> S, a highly reactive gas known for its extremely aggressive nature. This study employs a range of techniques, such as XRD, SEM–EDS, TGA, and Raman spectrometry, to investigate the interaction between low concentrations of H <sub>2</sub> S—averaging 1.3 ppm and various types of Portland cementitious materials (CEM I, CEM II, CEM III, and CEM V). The objective is to discern the chemical alterations contributing to structural deterioration and to provide a mineralogical characterization of the deterioration layers present on these binders.	
Keywords (separated by '-')	Biodeterioration - Cementitious materials - Low H <sub>2</sub> S concentration - Durability - SEM–EDS - μ-Raman	
Footnote Information		



## 2 Assessment of the durability of various cementitious 3 materials subjected to low levels of H<sub>2</sub>S in wastewater 4 networks

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6 Tony Pons · Marcos Oliveira ·  
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8 Received: 8 December 2023 / Accepted: 28 March 2024  
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10 **Abstract** Wastewater networks are intrinsically  
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14 SEM–EDS, TGA, and Raman spectrometry, to investi-  
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18 III, and CEM V). The objective is to discern the  
19 chemical alterations contributing to structural deterio-  
20 ration and to provide a mineralogical characterization  
21 of the deterioration layers present on these binders.

Through a comprehensive examination of the durabil- 22  
ity of these materials exposed to low concentrations 23  
of H<sub>2</sub>S in a Paris Region sewage system over nearly 24  
four years, the findings extend beyond surface-level 25  
observations. Despite the absence of visible signs of 26  
deterioration, high-precision analytical techniques 27  
reveal significant mineralogical transformations 28  
within the cementitious matrix. Expansive products 29  
such as gypsum, ettringite, and elemental sulfur are 30  
identified in mortar samples, underscoring the critical 31  
role of precise analysis in comprehending the deterio- 32  
ration process. 33

**Keywords** Biodeterioration · Cementitious 34  
materials · Low H<sub>2</sub>S concentration · Durability · 35  
SEM–EDS ·  $\mu$ -Raman 36

### 1 Introduction 37

Underneath the dynamic urban landscape lies a com- 38  
plex and often overlooked sewer system network that 39  
silently plays a crucial part in ensuring public health 40  
and environmental sustainability. Cementitious mate- 41  
rials, which form the backbone of the sewer network, 42  
are at the root of the success of these underground 43  
pipes. These materials are a key to ensuring the sewer 44  
infrastructure’s structural integrity, durability, and 45  
overall efficiency. 46

Indeed, throughout their lifespan, these pipes 47  
encounter a range of deterioration processes, which 48

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can arise from assembly defects, environmental constraints, or deterioration triggered by the presence of substances and microorganisms within the pipe. Thus, in about 40% of cases, this damage can be linked to a biogenic attack resulting from sulfuric acid production [1]. This particular mode of deterioration, encountered in concrete structures subjected to sewage environments, has the potential to substantially reduce the lifespan of these structures [2, 3]. For instance, it can diminish the 100-year expected service life to a range of 30–50 years, or even, in the most severe cases, to 10 years or less [3, 4].

The phenomenon of microbiologically induced acid deterioration in concrete has garnered significant attention since its identification. The sequence of stages that initiate and advance concrete biodeterioration in sewage environments has been delimited into several steps by various researchers [3, 5–11]. However, the most commonly agreed-upon sequences can be summarized as previously schematized by Herisson et al. [12]. This process begins with the creation of anaerobic zones at the bottom of pipes by wastewater sediments. In these specific zones, the low concentration of oxygen leads sulfate-reducing bacteria (SRB) to reduce sulfur compounds, such as sulfates, into highly volatile hydrogen sulfide ( $H_2S$ ). Subsequently, depending on the network's temperature, pH, hydrodynamics, and the concentration of oxidized sulfur compounds in the wastewater,  $H_2S$  volatilizes into the pipe atmosphere above the water flow. Gaseous  $H_2S$  condenses on the pipe surface and affects the cementitious matrix in two distinct yet interconnected ways. The first of these pathways acts directly by reducing the surface pH of cementitious materials, resulting in immediate effects. Nevertheless, it's important to note that, at this stage, the pH cannot attain an acidic value. However, the second, more complex path involves a fascinating chain of four key stages: the initial abiotic conversion of  $H_2S$  into sulfur components on the surface of the cementitious material; the subsequent bacterial oxidation of sulfur compounds into sulfuric acid; the diffusion of sulfuric acid into the cementitious matrix; and ultimately the gypsum formation.

The biodeterioration of sewage cementitious matrices has attracted considerable global research attention, with notable studies in occidental countries such as Australia, Austria, France, Germany, Denmark, and the United States among others [6–8, 10,

13]. However, among these studies, the  $H_2S$  levels investigated consistently reached high concentrations, which often exceeded 600 ppm, leaving a gap in research into low  $H_2S$  concentrations. Consequently, the ability of sewage cementitious materials to withstand low  $H_2S$  environmental conditions remains under-explored.

This study addresses this gap by investigating the performance and durability of various Portland cementitious materials (CEM I, CEM II, CEM III, and CEM V) under low  $H_2S$  concentrations exposure. Additionally, it provides a mineralogical characterization of deterioration layers found on these binders. Understanding the processes in the cementitious matrix at low  $H_2S$  concentrations is crucial for implementing effective prevention and maintenance procedures, ensuring the long-term durability and performance of vital infrastructure in wastewater networks.

Accordingly, different mortar formulations were exposed in situ for a period of nearly 4 years in a sewage system, with periodic macroscopic monitoring. Various analytical techniques found application in this study, such as X-ray diffraction (XRD), scanning electron microscopy equipped with an energy-dispersive X-ray spectrometer (SEM-EDS), and thermogravimetric analysis (TGA). Furthermore, by leveraging this wide range of practical instrument configurations, Raman spectrometry outperforms other methods with its diverse advantages [14, 15]. This technique is nowadays widely applied to characterize civil engineering materials and continuously assess their evolution throughout their life cycle, from initial anhydrous materials to hydrated and hydrating pastes, and all the way to their degraded state [16–18].

## 2 Materials and experimental approaches

### 2.1 Mortar samples

These mixtures were established to be representative of the real-world sewer network to assess their resistance to deterioration.

The mortar specimens used in this study were prepared with four different types of cement: ordinary Portland cement (CEM I), Portland-composite cement (CEM II), blast furnace cement (CEM III), and composite cement (CEM V). Three specimens

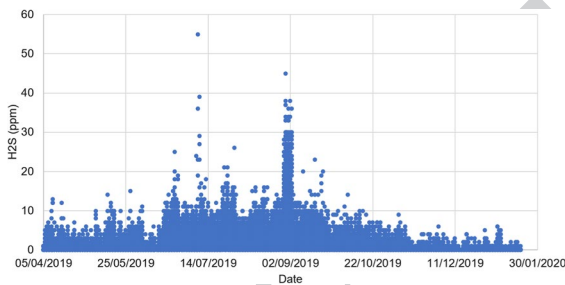


143 were prepared for each type of cement. In all mix-  
 144 tures, the water-to-cement ratio was 0.5 and the sand-  
 145 to-cement ratio was 3. The mortars were molded into  
 146 cylinders with a 6 cm diameter and a 12 cm height. A  
 147 PVC tube was also precisely inserted into the central  
 148 portion of each sample to ease their handling.

149 Once formed, the specimens were exposed to a  
 150 100% relative humidity atmosphere over 24 h, then  
 151 unmolded and stored in sealed plastic bags for a cur-  
 152 ing period of 28 days. Then, they were placed inside  
 153 a 60×40×30 cm<sup>3</sup> compartment that was afterward  
 154 installed inside the sewer network and exposed to the  
 155 specific sewer gas flow. Figures 1 and 2 in Herisson  
 156 et al.'s [12] study provide a clear understanding of the  
 157 appearance and placement of the specimens on site.

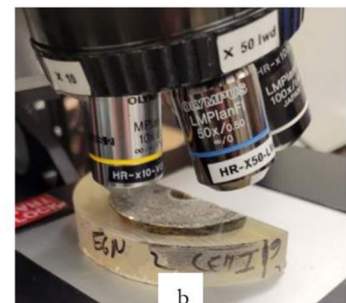
158 2.2 Exposure site of mortar samples

159 The northern part of the greater Paris Sanitation  
 160 Authority (SIAAP in French), has been selected as a  
 161 suitable exposure site for the 44 months study period.  
 162 In addition to stormwater and industrial wastewater,  
 163 SIAAP carries and purifies the wastewater of nine  
 164 million residents within and around Paris, enhancing  
 165 the dynamic natural environments of the Seine and



**Fig. 1** H<sub>2</sub>S concentration versus Time over 9 months at the SIAAP facility

**Fig. 2** LabRam HR800 (a) and CEM I sample before 2D mapping (b)



166 Marne rivers. The selected site has been chosen based  
 167 on precise previous results showing that the area  
 168 exhibited relatively low H<sub>2</sub>S concentrations.

169 OdaLog® safety sensors were inserted alongside  
 170 the samples in the compartment in order to track the  
 171 concentration of H<sub>2</sub>S and temperature throughout the  
 172 study period. Figure 3 and Table 1 present a 9-month  
 173 example of the results obtained from these sensors  
 174 used to assess the environmental conditions. During  
 175 this period, the site recorded an average H<sub>2</sub>S concen-  
 176 tration of 1.3 ppm, which categorizes it as a mod-  
 177 erately chemically aggressive environment accord-  
 178 ing to the NF EN 206/CN [19], designated as XA2.

Cement	T0	21 months	29 months	44 months
CEM I				
CEM II				
CEM III				
CEM V				

**Fig. 3** In-situ visual evolution of mortar samples exposed over 44 months at a low H<sub>2</sub>S concentration



**Table 1** Overview of H<sub>2</sub>S concentration (ppm) data over 9 months of the study period

Mean	Standard deviation	1st quartile	3rd quartile	Minimum	Maximum
1.3	2.7	0.0	1.0	0.0	55.0

179 Moreover, as detailed in Table 1, the data shows that  
 180 the first quartile stands at 0.0 ppm, representing the  
 181 lower 25% of the measured concentrations, while  
 182 the third quartile is at 1.0 ppm, signifying the value  
 183 below which 75% of the data falls. The computed  
 184 values presented in Table 1 provide a comprehensive  
 185 view of the distribution of H<sub>2</sub>S concentrations, which,  
 186 in turn, reveals that the specimens were not exposed  
 187 to a severe H<sub>2</sub>S environment with respect to this gas.

## 188 2.3 Testing procedure

### 189 2.3.1 *In-situ evolution monitoring*

190 At each sampling time step (21, 29, and 44 months  
 191 after exposure), in situ photographs of the specimens  
 192 were captured to document the macroscopic degra-  
 193 dation of the specimens over time. Additionally, the  
 194 weights of the mortars (measured with a scale accu-  
 195 rate to 0.1 g), surface pH (determined using pH paper  
 196 with a precision of 0.2), and diameters (measured  
 197 with a caliper) were recorded to monitor changes in  
 198 the properties over time.

199 After a 44-month exposure period in the sewage  
 200 network, the mortars were carefully collected from  
 201 their cases and accurately processed to secure consist-  
 202 ent test conditions and results. The specimens were  
 203 then entirely covered with epoxy resin (EpoFix, Stru-  
 204 ers) under vacuum conditions to preserve the deterio-  
 205 ration condition. This precaution was taken to ensure  
 206 the sample's structural integrity for further testing.

207 Before all the analysis, the mortars exposed in-situ  
 208 for 44 months underwent a meticulous diamond pol-  
 209 ishing process with ethanol that yielded homogene-  
 210 ous and plane test surfaces.

### 211 2.3.2 *Scanning electron microscopy with energy 212 dispersive x-ray spectrometer (SEM–EDS)*

213 Analyses were carried out using a Scanning elec-  
 214 tron Microscope (Quanta 400 FEI) equipped with

an Energy Dispersive X-ray Spectrometer (EDS, 215  
 Xplore30, Oxford), operating at an acceleration volt- 216  
 age of 20 kV. After carbon metallization of the pol- 217  
 ished surface, a panorama was acquired using back- 218  
 scattered electrons in order to identify deteriorated 219  
 areas. Maps were acquired using the intensity of the 220  
 K $\alpha$  rays for the relevant chemical elements (Si, Ca, 221  
 Mg, K), modifications being expected after the attack 222  
 for these specific ones. 223

### 224 2.3.3 *X-ray diffraction (XRD) analyses*

225 In order to detect and identify the crystalline phases 226  
 present and their possible in-core degree of penetra- 227  
 tion, three holes were drilled at three successive dis- 228  
 tances, from the sample's edge to its center, using 229  
 3 mm diameter drills, as shown in Fig. 8 of Appen- 230  
 dix 1. Subsequently, the resulting cement powder 231  
 was gathered for qualitative analysis by X-ray dif- 232  
 fraction (XRD). The XRD measurements were per- 233  
 formed using a PANalytical Empyrean diffractom- 234  
 eter equipped with Co K $\alpha$  radiation and a PIXcel<sup>3D</sup> 235  
 detector. Current and voltage on the X-ray tube were 236  
 30 mA and 40 kV, respectively. The diffractograms 237  
 were acquired in the range of 2 $\theta$  from 4° to 76° with 238  
 a step size of 0.013° 2 $\theta$ /s. Mineral identification was 239  
 carried out using the HighScore Plus software with 240  
 the crystallography open database (COD) [20–27].

### 241 2.3.4 *Thermogravimetric analysis (TGA–DTA) 242 coupled with a mass spectrometer*

243 Using the resulting cement powder gathered from 244  
 the drilling process described in the subSect. 2.3.3., 245  
 the thermogravimetric (TGA) and differential ther- 246  
 mal (DTA) analysis for the identification of the dif- 247  
 ferent phases, progressing from the edge of the sam- 248  
 ple towards its center, was carried out in a dry argon 249  
 atmosphere using a NETZSCH STA 409E simulta- 250  
 neous thermal analyzer, performing both TGA and 251  
 DTA simultaneously. The selected temperature ramp 252  
 was 30–1250 °C, with an argon flow rate of 40 ml/ 253  
 min and a heating rate of 10 °C/min. All through the 254  
 heating process, weight changes are generated by the 255  
 loss of H<sub>2</sub>O and CO<sub>2</sub> as the temperature increases. 256  
 Emitted gas, H<sub>2</sub>O, and CO<sub>2</sub> were monitored over time 257  
 using a mass spectrometer, with 18.09 g/mol, and 258  
 44.09 g/mol respectively used as molar masses.



### 259 2.3.5 $\mu$ -Raman spectroscopy

260 As shortly mentioned in the introduction, Raman  
261 spectroscopy is now implemented in the characteriza-  
262 tion of civil engineering materials, and in the continu-  
263 ous monitoring of some of their evolution. In addition  
264 to all the advantages that Raman spectroscopy offers,  
265 such as being a non-destructive and rapid technique,  
266 it has been found to successfully detect the sulfate  
267 attack product in cementitious materials [28, 29].

268 Precise punctual measurements were conducted  
269 along a radial line over a section of the samples (cf.  
270 Figure 9 of Appendix 1 ) to enhance the investigation  
271 of the mineralogical characterizations of the mortar  
272 samples. The analyses were performed using two dif-  
273 ferent instruments.

274 The first one was a BWTek iRaman spectrom-  
275 eter operating with a 532 nm laser wavelength  
276 and delivering nearly 50 mW power output. The  
277 2048-pixel CCD detector provided spectra over the  
278 150–4000  $\text{cm}^{-1}$  spectral range with a resolution of  
279 4  $\text{cm}^{-1}$ . It was paired to a BAC151C microscope, and  
280 spectral measurements were made through an  $\times 50$   
281 objective lens from Olympus. Both BWTek instru-  
282 ments are managed by BWSpec 4.11\_1 software.

283 The second spectrometer was a LabRAM HR800  
284 spectrometer operating with a 514 nm laser wave-  
285 length and delivering nearly 1 mW power output.  
286 The instrument is optically coupled to a BX-model  
287 microscope from Olympus, with a  $\times 50$  (NA 0.75)  
288 MPlanN objective. The diffraction-limited spot size is  
289 then about 1  $\mu\text{m}$ . The detector provided spectra over  
290 the 50–4000  $\text{cm}^{-1}$  spectral range with a resolution of  
291 1  $\text{cm}^{-1}$ . An XY-motorized stage allowed to taking of  
292 in-line profiles and 2D mappings with a displacement  
293 step as low as 1  $\mu\text{m}$ . All devices are controlled by  
294 LabSpec 6 software.

## 295 3 Results

### 296 3.1 In situ visual evolution monitoring

297 Photographs taken at each time scale provided an  
298 overview of a qualitative visual evolution of the  
299 cementitious materials, as shown in Fig. 3. Since  
300 the very first sampling period (21 months), the dete-  
301 rioration of all the specimens has been observed and  
302 has evolved over the years. Indeed, according to the

literature with samples exposed to average  $\text{H}_2\text{S}$  con- 303  
centrations of 5 and 100 ppm respectively [30, 31], 304  
samples were expected to show much more notice- 305  
able visual deterioration after 44 months of exposure. 306  
Therefore, it can be noticed that the mortars are mod- 307  
erately well preserved and that this limitation of deg- 308  
radation can be strongly linked to their exposure to a 309  
very low concentration of  $\text{H}_2\text{S}$ . 310

311 Based on the visual characteristics only, through-  
312 out the study period, the changes in all samples were  
313 characterized by the presence of white crystals and  
314 brownish deposits. At the end of the 44 months, the  
315 specimens had somewhat darkened and showed some  
316 deterioration marks, notably the growth of expansive  
317 products.

318 Alongside a visual inspection of the degradation,  
319 sample weights were measured during the *in-situ*  
320 exposure period. All the examined mortars exhibited  
321 identical behavior, as illustrated in Fig. 4. Over the  
322 first 21 months, a weight gain is recorded, which can  
323 be linked to the accumulation of water in the pores  
324 of the mortar specimens and the formation of sulfide  
325 reaction products, followed by a slight weight loss.  
326 It is crucial to highlight that all the types of cement  
327 used in the study showed a similar variation in weight  
328 percentage.

329 The examination of pH values throughout the  
330 study period revealed a significant drop in the sur-  
331 face pH, from its initial alkaline value to an acidic  
332 value after 21 months, followed by stabilization in the  
333 4–6 range over the subsequent months. This pattern  
334 reflects the results documented in existing literature  
335 [30–32].

336 Furthermore, the investigation of the diameter  
337 evolution over the 44 months did not reveal any

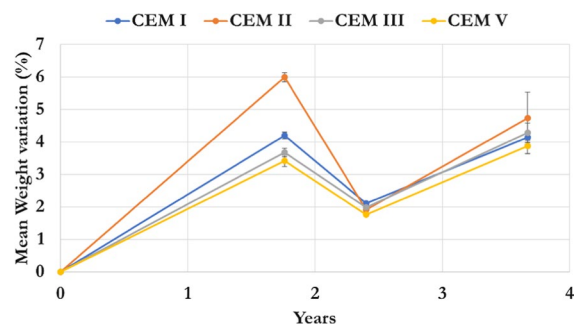


Fig. 4 Mean weight variation of mortar samples exposed for 44 months at a low  $\text{H}_2\text{S}$  concentration





338 significant change for all the specimens. The percent  
339 change in diameter ranged from 0 to 0.7% of expansion  
340 over the study period, which is consisted with  
341 the visual observations that did not reveal any notice-  
342 able expansion of the mortars.

### 343 3.2 Chemical profile maps determination

344 SEM observations and elemental map investiga-  
345 tions facilitated the identification of diverse elemen-  
346 tal chemical distributions and sample zonation. Fig-  
347 ures 10–13 in the Appendix illustrate the multimodal  
348 analysis of the mortar specimens, presenting visualiza-  
349 tions of cross-sections obtained using KEYENCE,  
350 SEM imaging of half the section and the selected sec-  
351 tion to be analyzed with EDS. The interpretation of  
352 chemical variations relied on the distribution of ele-  
353 ments compounds determined through EDS analysis.  
354 The identification of various microstructural zones  
355 in all examined deteriorated mortar samples closely  
356 aligns with previous findings [32–35]. Furthermore, a  
357 consistent behavior was observed across all samples,  
358 attributed to their shared composition of Portland  
359 cement. This emphasizes the reliability of the results  
360 and underscores a uniform response to selected envi-  
361 ronmental factors.

362 Four distinct zones have been distinguished in  
363 these samples through meticulous analysis, as illus-  
364 trated in Figs. 5 and 6. Each zone reveals unique fea-  
365 tures indicating specific compositional, mineralogical,  
366 and microstructural characteristics.

367 The first zone, prominently visible in the SEM  
368 images, consisted of a strongly altered area. This  
369 near-surface zone is locally enriched in sulfur and  
370 calcium (cf. zone 1 in Fig. 5), precipitating mainly  
371 along long reticulated crack systems.

372 Moving on to a second zone, its composition dif-  
373 fered notably from the first, with a porous structure  
374 characterized by the presence of Si and the depletion  
375 of the S and Ca elements, creating a distinctive void  
376 in the elemental composition. Additionally, this zone  
377 is characterized by the absence of anhydrous phases  
378 (such as C2S, C3S, etc.). In the backscatter images,  
379 anhydrous phases typically appear as white elements;  
380 however, they are absent in this specific zone of the  
381 section. This particular zone can be most precisely  
382 described as an outer transition zone, representing a  
383 boundary between the strongly deteriorated external  
384 zone and the slightly deteriorated internal zone.

The third zone can be most accurately described 385  
as an inner transition zone, marked by the accumu- 386  
lation of K and Mg elements, followed by the suc- 387  
cessive incorporation of S and Ca. Furthermore, 388  
this zone can be subdivided into two distinct inter- 389  
zones, labeled 3a and 3b. These sub-zones are 390  
clearly differentiated by the absence of anhydrous 391  
phases in zone 3a and their presence in zone 3b, 392  
with an additional layer of complexity to the min- 393  
eralogical composition in this transitional region. 394  
This zone further contributes to the comprehensive 395  
understanding of the sample's heterogeneity. 396

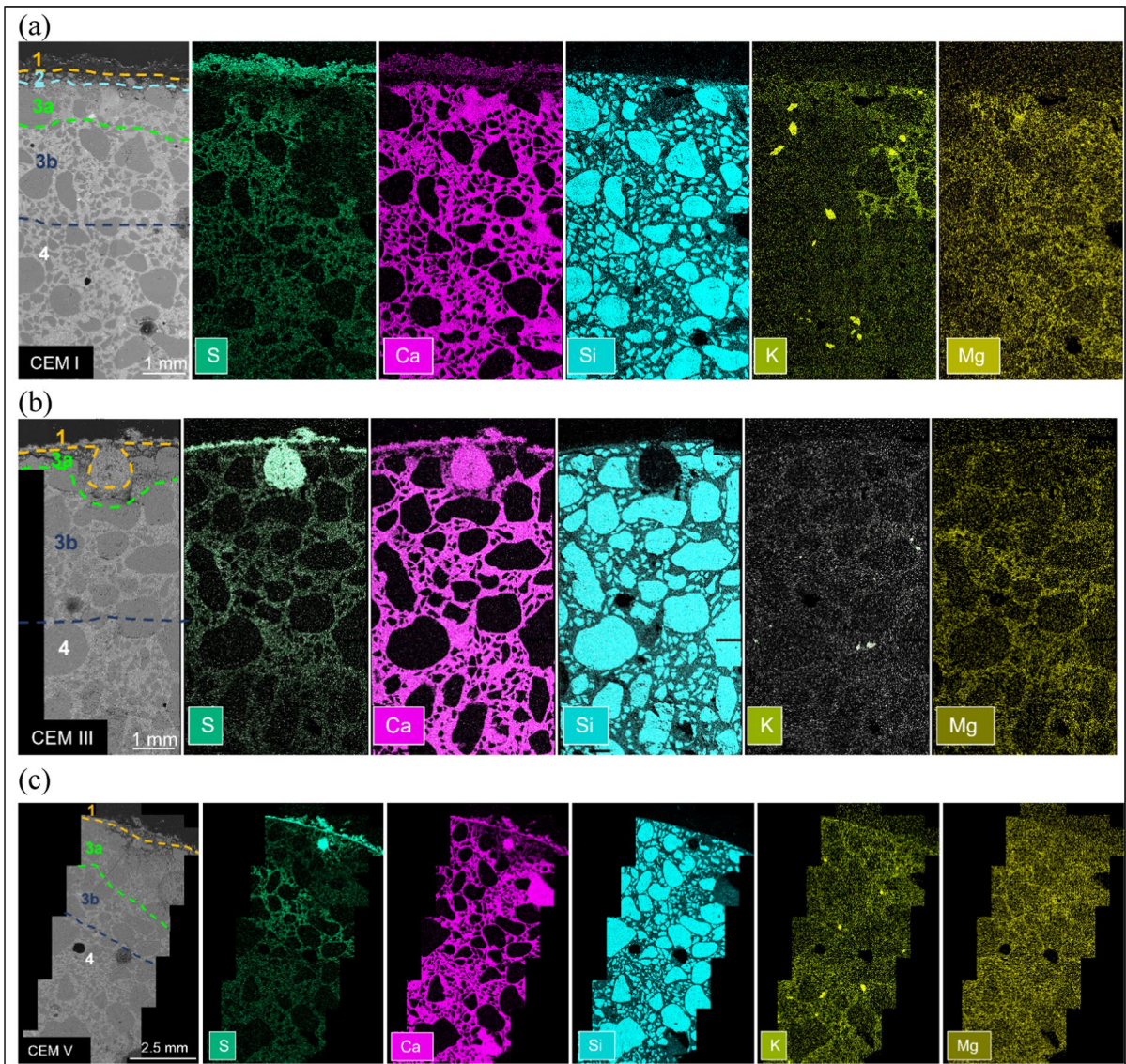
397 These deteriorated layers probably consist of  
398 newly formed calcium sulfates. These layers are  
399 identified by regions where calcium and sulfur have  
400 accumulated. Additionally, they are less defined  
401 layers containing silicon. However, in cases where  
402 only sulfur was detected in the elemental distribu-  
403 tion images, the presence of elemental sulfur was  
404 probable.

405 Lastly, a fourth zone, which can be described as  
406 the pristine zone, indicates that its mineralogical  
407 composition has remained relatively unchanged.  
408 This zone features an abundance of anhydrous  
409 phases (such as C2S, C3S, slag, ...) identifiable  
410 on BSE images. The presence of anhydrous phases  
411 indicates a chemical reaction of the water with the  
412 initial cement, potentially contributing to the zone's  
413 resistance to the deleterious effects of H<sub>2</sub>S. Indeed,  
414 the distinction between all the zones can be effec-  
415 tively discerned through the variations in texture  
416 from one zone to its neighbors.

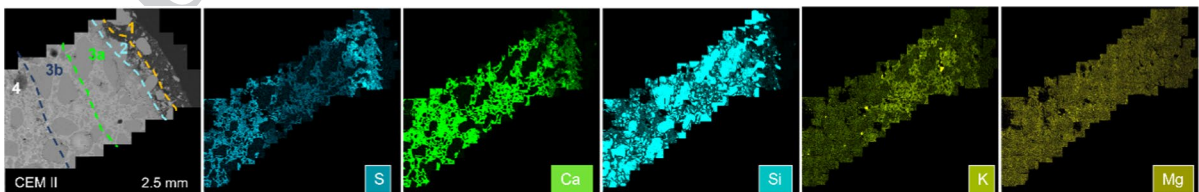
417 From the results illustrated in Fig. 5, the CEM I  
418 sample features all four of the identified zones. On  
419 the other hand, the CEM III and CEM V samples  
420 exhibit similar zonation, whereby the second zone  
421 is notably lacking. Conversely, the CEM II sample  
422 presents a marked change in element distribution,  
423 as illustrated in Fig. 6. Particularly in its third zone,  
424 where the element sulfur is notably absent.

425 With these findings and ImageJ software [36],  
426 measurements of minimum and maximum values  
427 were taken for each zone of the samples for com-  
428 parative analysis, as shown in Table 1. The results  
429 reveal that all the samples present deteriorated lay-  
430 ers in varying degrees of proximity. Remarkably, **AQ4**  
431 the CEM II sample was found to be the most deter-  
432 iorated of all the Portland cement samples studied  
433 (Table 2).





**Fig. 5** High resolution and elemental distribution images of S, Ca, Si, K, and Mg of cross-sections in **a** CEM I, **b** CEM III, and **c** CEM V samples, revealing the varied zones from the exterior deteriorated zone to the interior pristine zone



**Fig. 6** High resolution and elemental distribution images of S, Ca, Si, K, and Mg of cross-sections in the CEM II sample, revealing the varied zones from the exterior deteriorated zone to the interior pristine zone



**Table 2** Alteration zone thickness variations for various cement types in mm (min–max)

	Zone 1	Zone 2	Zone 3a	Zone 3b
CEM I	0.2–0.5	0.2–0.3	0.9–1.1	1.9–2.3
CEM II	0.8–1.4	0.6–0.7	1.7–2.1	1.7–2.4
CEM III	0.3–0.9	NA	0.2–0.3	2.623.2
CEM V	0.2–0.7	NA	1.9–2.1	1.9–2.1

### 3.3 Mineralogical characterization

XRD (X-ray Diffraction) and TGA (Thermogravimetric Analysis), analyses were carried out for the mineralogical characterization of the cementitious samples into the depth of the materials constituting the samples. Nevertheless, considering the information presented in Sect. 3.2 and the fact that the holes in the samples were obtained using 3 mm drills, it can be asserted that the first hole falls within the three pre-defined zones. Consequently, differentiation of results based on specific zones, according to XRD and TGA, is not feasible. However, it can be considered that the first hole occurred in the deteriorated part of the sample (zones 1, 2, 3a, and 3b previously described in Sect. 3.2 and shown in Figs. 5 and 6), while the other two occurred in the intact zone (zone 4 previously described in Sect. 3.2.).

Qualitative XRD analyses of the resulting cement powder showed the quartz (peak at 3.34 Å) contained in the sand to be the main crystallized phase for all the holes of the four cement types.

For the Ordinary Portland cement sample CEM I, XRD results revealed the presence of the semi-hydrated phase of gypsum ‘bassanite’ ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , peak at 3.00 Å) and calcite ( $\text{CaCO}_3$ , peak at 3.04 Å), in the altered layer of the sample indicating the local variation in the mineralogical composition of the sample due to the biogenic  $\text{H}_2\text{S}$  attack. Furthermore, portlandite (peak at 2.63 Å) was detected throughout the core of the sample. Figure 14 of Appendix 1 shows the diagrams of the three holes of the CEM I specimen.

For the CEM II and CEM III samples, XRD analyses confirmed the predominance of quartz, but other phases such as calcite and portlandite were also identified throughout the radial line of the samples. Moreover, vaterite (peak at 3.29 Å) was also detected in the CEM III sample.

Nevertheless, for the CEM V sample, no other phases apart from quartz were detected in the intact zone of the sample. However, in the deteriorated zone, gypsum (peaks at 7.62 and 4.27 Å) and calcite were identified.

On the other side, the TGA-MS results for all the samples revealed the presence of four distinctive stages of weight loss over the entire temperature range, spanning from 30 to 1250 °C.

The initial weight loss, occurring between room temperature and 220 °C, was attributed to the evaporation of all free water and of water from the C–S–H and ettringite components. The following weight loss, between 380 and 500 °C, is mainly due to the liberation of water during the dehydration process of portlandite. This percentage weight loss can be effectively used to estimate the portlandite content of samples. With the third stage of weight loss, which takes place between 700 and 800 °C,  $\text{CO}_2$  is released, making it possible to estimate the  $\text{CaCO}_3$  content in the mortar samples. The final weight loss observed above 1000 °C is attributed to the release of  $\text{SO}_3$ , which originates from the sulfates contained in the gypsum and ettringite due to the  $\text{H}_2\text{S}$  attack in the mortar samples [9].

Taking all the findings together, it is confirmed that the samples have undergone an alteration with a mineralogical modification. However, it should be noted that this change was not as severe as that previously recorded for samples heavily exposed to  $\text{H}_2\text{S}$  [8–10, 37]. The mineral phases identified in the samples of this study suggest alteration, but to a lesser degree, underlining the importance of environmental conditions in the mineral alteration process.

Moreover, these results demonstrate that after 44 months of in-situ exposure in a sewer environment, all Portland cement-based mortars contain portlandite all over the different zones of the samples. This finding can be justified by the low concentration of  $\text{H}_2\text{S}$  in the exposition zone, as the reduced presence of hydrogen sulfide leads to a less aggressive chemical environment.

### 3.4 Mineralogical characterization by micro-Raman spectroscopy

Among the different methods assessed, the Raman spectroscopy analysis consistently identified the presence of gypsum in the deteriorated layers of all



519 the specimens under investigation. Notably, gyp-  
520 sum formation is characteristic of the sulfate attack  
521 of a cementitious material. This material has a spe-  
522 cific peak at  $1003\text{ cm}^{-1}$ , as indicated in the literature  
523 [38]. A photograph of an altered zone of a polished  
524 section of the exposed CEM V sample is shown in  
525 Fig. 7a. Additionally, Fig. 7b presents its spectral  
526 analysis over two spectral ranges (laser at 514 nm,  
527 25-s acquisition time, and averaged over 4 spectra),  
528 with an emphasis on the intensification characteristic  
529 of the gypsum spectrum. It is crucial to outline that  
530 the observed vibrational modes closely align with the  
531 literature data [29, 37, 39, 40].

532 Starting with the CEM I specimen exposed to the  
533  $\text{H}_2\text{S}$ -enriched environment, alongside gypsum, the  
534 analysis revealed the presence of ettringite and two  
535 calcium carbonate polymorphs (calcite and vaterite,  
536 with a main intense peak respectively at  $1085\text{ cm}^{-1}$   
537 and  $1077\text{--}1090\text{ cm}^{-1}$ ) [29, 41–43]. Ettringite and  
538 gypsum were detected in the altered zone, and  
539 according to the literature, they have been identified  
540 as the main reason for the sulfate attack damage [29,  
541 44]. However, calcium carbonate was detected along  
542 the radial line of the sample.

543 Moving on to the CEM II specimen, calcite was  
544 identified in all the measurements taken, indicating its  
545 consistent presence. The existence of this supplemen-  
546 tary phase within the alteration layer suggests that the  
547 formation of gypsum might have arisen either from  
548 calcium ions present in the constituent phases of the  
549 cementitious matrix (portlandite and C–S–H) or from  
550 calcite. Moreover, it is worth noting that calcite is  
551 consistently observed in all the samples and at greater  
552 depths within the mortars. The presence of  $\text{CaCO}_3$  in

the samples' sections could also be attributed to an  
unavailable carbonation occurring once the inner part  
of the samples had been exposed to the atmosphere  
and during the polishing process, despite cautious  
storage conditions.

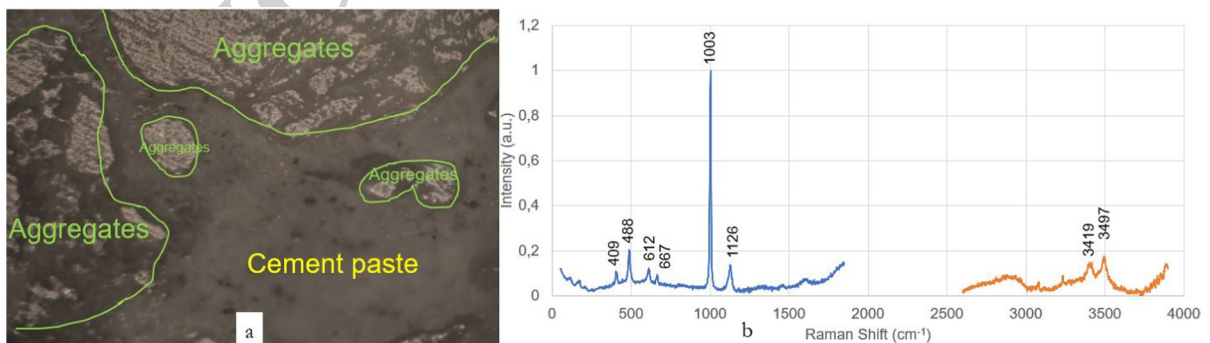
For the CEM III sample, the sulfite mineral hanne-  
bachite was also detected at the surface of the mortar  
sample [45]. As per prior studies, Pons et al. [37] also  
identified hannebachite in a previous CEM III mortar  
sample.

Lastly, in the case of the CEM V specimen, ettrin-  
gite and calcite were also detected in addition to  
gypsum.

All these findings reinforce the spectroscopic tech-  
nique's importance for assessing the cementitious  
matrix's bio-alteration, but also about its spatial reso-  
lution with respect to TGA and XRD.

#### 4 Discussion

This study highlights the significant synergies arising  
from the utilization of diverse analytical techniques.  
While each method provided valuable data inde-  
pendently, the true strength of the results emerged  
when considering the correlations and relationships  
revealed through their collective examination. The  
interconnections observed among XRD, SEM–EDS,  
TGA–MS,  $\mu$ -Raman spectroscopy, and in situ moni-  
toring collectively present a comprehensive portrayal  
of the impact of low  $\text{H}_2\text{S}$  concentrations on cemen-  
tious materials in sewage systems. These techniques,  
when integrated, offer a holistic view, uncovering  
mineralogical modifications and chemical alterations



**Fig. 7** **a** Photograph in reflected light of a CEM V altered zone, and **b** a normalized Raman spectrum (obtained with the LabRAM HR800 spectrometer) after 44 months of exposure in a sewage system



584 within the cementitious matrix. This multifaceted  
585 approach proves crucial, as it goes beyond the limita-  
586 tions of any single analytical method.

587 The intricate nuances of material degradation in  
588 cement samples exposed to an H<sub>2</sub>S-enriched atmos-  
589 phere in wastewater networks are brought to light  
590 through meticulous scanning electron microscopy  
591 observations. The SEM reveals a fascinating diversity  
592 within the deteriorated portions of the sample, where  
593 different zones, each characterized by distinct chemi-  
594 cal features and sizes, emerge even in the thinnest  
595 sections. This microscale analysis, with its capacity  
596 to discern minute variations, surpasses the capabili-  
597 ties of traditional tools such as TGA and XRD. The  
598 revelation of specific characteristics within each zone,  
599 despite their thinness, underscores the non-uniform  
600 nature of the degradation process. It becomes evi-  
601 dent that a comprehensive understanding of this com-  
602 plex interaction necessitates a diversified analytical  
603 approach. This exploration not only highlights the  
604 limitations of singular analytical tools but emphasizes  
605 the imperative role of complementary techniques.

606 In this context, SEM, with its precision at the  
607 microscale, and Raman spectroscopy stand out as piv-  
608 otal contributors. Their integration facilitates a more  
609 holistic analysis, providing unparalleled insights into  
610 the intricate interplay between cement samples and  
611 H<sub>2</sub>S. This synergy between SEM and Raman spec-  
612 troscopy transcends the individual constraints of each  
613 technique, offering a comprehensive understanding  
614 of the material deterioration process. In essence, this  
615 approach broadens the horizons of material science,  
616 demonstrating the indispensability of diverse analyti-  
617 cal tools in unraveling the complexities of biodegra-  
618 dation in cement exposed to environmental stressors.

619 In this research, the analysis of element distri-  
620 bution in deteriorated concrete layers revealed a  
621 dynamic system influenced by pH and diffusion of  
622 elements into the cement matrix. It revealed a clear  
623 sequence of element accumulation closely linked to  
624 pH levels, the dissolution and precipitation of solids,  
625 some variations in chemical compositions of cementi-  
626 tious binders, and the spatial distribution of bacteria  
627 present in the wastewater.

628 The strongly deteriorated surface layer (zone  
629 1) extending from 0.2 to 1.4 cm featured a com-  
630 position comprising filamentous structures  
631 composed of S and Ca. These structures repre-  
632 sented the precipitation of secondary sulfate

salts, including gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), ettrin- 633  
gite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O), anhydrite 634  
(CaSO<sub>4</sub>), hannebachite (CaSO<sub>3</sub>·H<sub>2</sub>O), and bassanite 635  
(CaSO<sub>4</sub>·0.5H<sub>2</sub>O). The formation of hannebachite and 636  
bassanite can be explained by cycles of humidifica- 637  
tion and drying, leading to fluctuating SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>O 638  
activities in the mortar's interstitial solutions. Si-rich 639  
layers, on the other hand, consisted of amorphous 640  
silica. 641

The transition zone, segmented into three distinct 642  
inter zones (Zones 2, 3a, and 3b) between strongly 643  
deteriorated and intact concrete, was bounded within 644  
a range of 3–5 mm. This led to dynamic dissolution 645  
and precipitation of individual phases, as shown by 646  
the concentrations of individual elements in Figs. 5 647  
and 6. The interface between Zones 2 and 3 in the 648  
transition zone was characterized by a reduction in Ca 649  
concentration following acid penetration. Meanwhile, 650  
a simultaneous process of sulfate incorporation along 651  
the grain boundaries was observed, suggesting that 652  
this could be associated with the interfacial transition 653  
zone and its higher portlandite content (Ca(OH)<sub>2</sub>) 654  
[46]. This resulted in the microstructural deteriora- 655  
tion of the cement matrix through the formation of 656  
expansive sulfate phases [47]. From the very initial 657  
edge of zone 3, Mg accumulation occurred as a result 658  
of the precipitation of Mg hydroxides, such as brucite 659  
(Mg(OH)<sub>2</sub>). In this process, hydroxide (OH<sup>-</sup>) diffused 660  
from alkaline areas in the intact mortar, while diffu- 661  
sion of Mg ions was induced by Mg precipitation and 662  
the associated concentration gradient. Given that the 663  
stability of Mg-containing precipitates is limited to 664  
strongly alkaline conditions, the cessation of Mg pre- 665  
cipitation marks the end of zone 3. Mg thickness and 666  
concentrations in the accumulation zone have been 667  
found to correlate directly with the dominant pH gra- 668  
dient, making them indicative of the rate of deteriora- 669  
tion [33, 48]. Furthermore, in this transition zone, a 670  
noticeable accumulation of potassium (K) occurs in 671  
the elemental distribution (Figs. 5 and 6). Analysis 672  
of the compositional data suggests that these addi- 673  
tional precipitates could be identified as (K-alum) 674  
(KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O), syngenite (K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O), 675  
or alunite (KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> that is also affected by 676  
the alkaline leaching rate [33, 49]. 677

The intact pristine zone (zone 4), identified as 678  
the inferior zone, features a matrix mainly made 679  
up of calcium- and silicon-rich phases, including 680  
portlandite and hydrated calcium silicates (C–S–H 681



682 phases) as well as anhydrous grains. This matrix  
683 envelops silica and carbonate aggregates. In addition,  
684 various calcium carbonate polymorphs, such as  
685 calcite and vaterite, have been detected in this zone.

## 686 5 Conclusion

687 This research has illuminated the significant impact of  
688 low  $H_2S$  concentrations on cementitious materials in  
689 sewage systems. This impact, although often overlooked,  
690 plays a fundamental role in the degradation process of  
691 the cementitious materials that constitute these systems.  
692 Previous research has focused primarily on high  $H_2S$   
693 concentrations, yet this study unveiled the subtle but  
694 consequential effects of low  $H_2S$  levels. By combining  
695 a full range of analytical techniques, including XRD,  
696 SEM-EDS, TGA-DTA, and Raman spectroscopy, in  
697 conjunction with continuous weight measurements and  
698 visual observations, several significant breakthroughs  
699 were achieved.

700 On the visual side, samples subjected to low  $H_2S$   
701 concentrations showed no dramatic indications of  
702 deterioration compared to those exposed to more  
703 harsh environmental conditions. However, the  
704 real significance of these results lies beneath the  
705 surface, since the cementitious materials underwent  
706 considerable mineralogical alterations.

707 Most notably, these analyses highlighted the presence  
708 of several minerals in the mortar samples, underscoring  
709 the extent of the changes observed. In particular,  
710 bassanite and hannebachite, which are precursors  
711 to gypsum and have not been identified in materials  
712 subjected to higher levels of  $H_2S$ , were discovered.  
713 Moreover, gypsum, ettringite, elemental sulfur,  
714 and various polymorphs of calcium carbonate were  
715 identified along a radial line from the edge to the core  
716 of the samples. These mineralogical transformations  
717 emphasize the complex interplay between low  $H_2S$   
718 concentrations and the composition of cementitious  
719 materials, which, although less visible on the surface,  
720 have a considerable impact on their long-term durability.

721 Furthermore, magnesium and potassium were  
722 detected in the altered layers following the chemical  
723 reactions of the Portland cement-based mortars at  
724 low  $H_2S$  levels. The unexpected existence of these  
725 components underlines both the complexity and the  
726 subtlety of biogenic sulfuric attacks on cementitious  
727 materials.

Remarkably, this study showed no real difference 728  
in the durability of the various cement-based paste 729  
samples used. The absence of any significant dif- 730  
ferentiation in resistance to low  $H_2S$  concentrations 731  
suggests that there is no distinct hierarchy in the clas- 732  
sification of pastes according to their degree of resist- 733  
ance. It is noteworthy, however, that the CEM II sam- 734  
ple revealed a slightly thicker deteriorated layer than 735  
the others, pointing to a nuanced aspect in the perfor- 736  
mance of these cement pastes. 737

To conclude, the outcomes of this study are very 738  
consistent with the existing literature on studies at 739  
high concentrations of  $H_2S$ , highlighting the crucial 740  
importance of considering low  $H_2S$  levels when 741  
assessing the durability of cementitious matrices in 742  
wastewater systems. Moreover, this study highlights the 743  
importance of using very precise analytical techniques, 744  
such as micro-Raman and SEM-EDS, to thoroughly 745  
assess all the layers arising during the biodeterioration 746  
process. 747

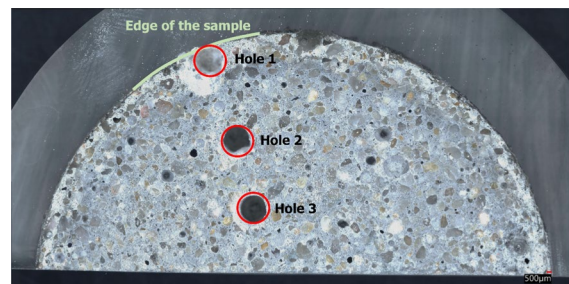
**Acknowledgements** "This project has received funding from 748  
the European Union's Horizon 2020 research and innovation pro- 749  
gramme under the Marie Skłodowska-Curie COFUND grant 750  
agreement No 101034248." The authors gratefully acknowledge 751  
Gwénaél GOUADEC for his invaluable assistance in conducting 752  
several critical Raman measurements, Béatrice Desrues for her 753  
invaluable assistance in conducting the SEM-EDS acquisition, and 754  
Céline Briand for her technical assistance at SIAAP. 755

**Funding** HORIZON EUROPE Marie Skłodowska-Curie 756  
Actions, 101034248, Janette Ayoub 757

**Data availability** Data will be provided on request. 758

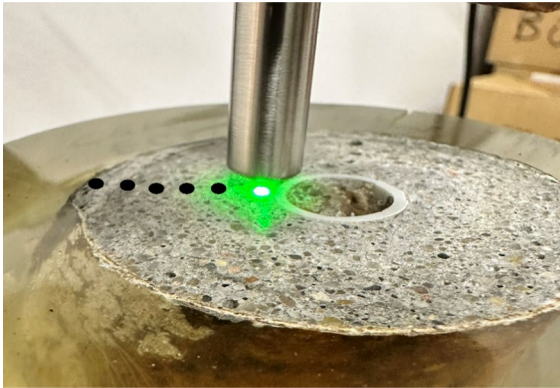
## Appendix 1 759

See Figs. 8, 9, 10, 11, 12, 13 and 14 760



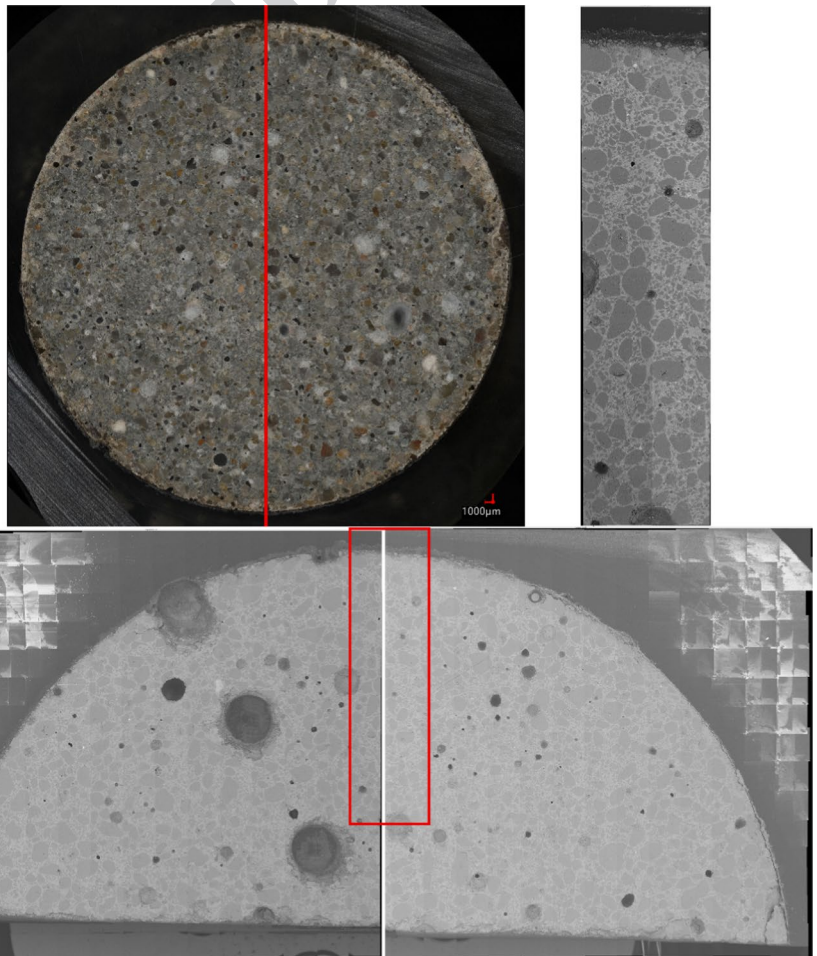
**Fig. 8** A Keyence figure of a CEM V sample showing holes drilled at successive distances from the edge

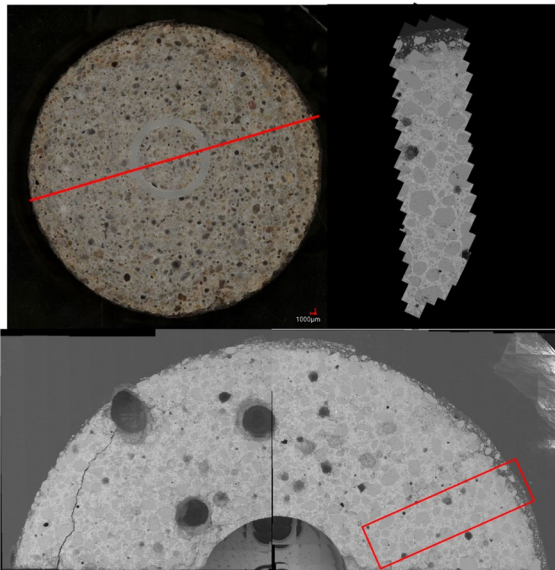




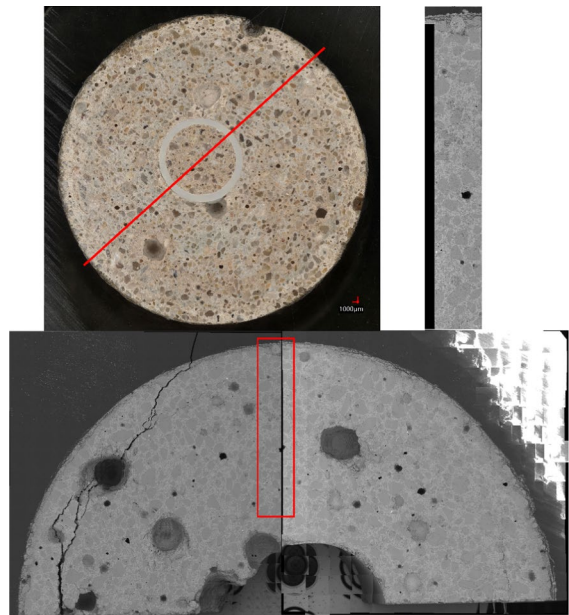
**Fig. 9** Example of punctual measurements sequencing in  $\mu$ -Raman spectroscopy. The green dot signifies the initial laser acquisition point, while the multiple black dots illustrate the subsequent acquisitions

**Fig. 10** Analysis of CEM I Mortar: **a** Cross section visualization with Keyence, **b** Back scatter image, and **c** EDS elemental analysis selection





**Fig. 11** Analysis of CEM II mortar: cross section visualization with Keyence, SEM imaging, and EDS elemental analysis selection



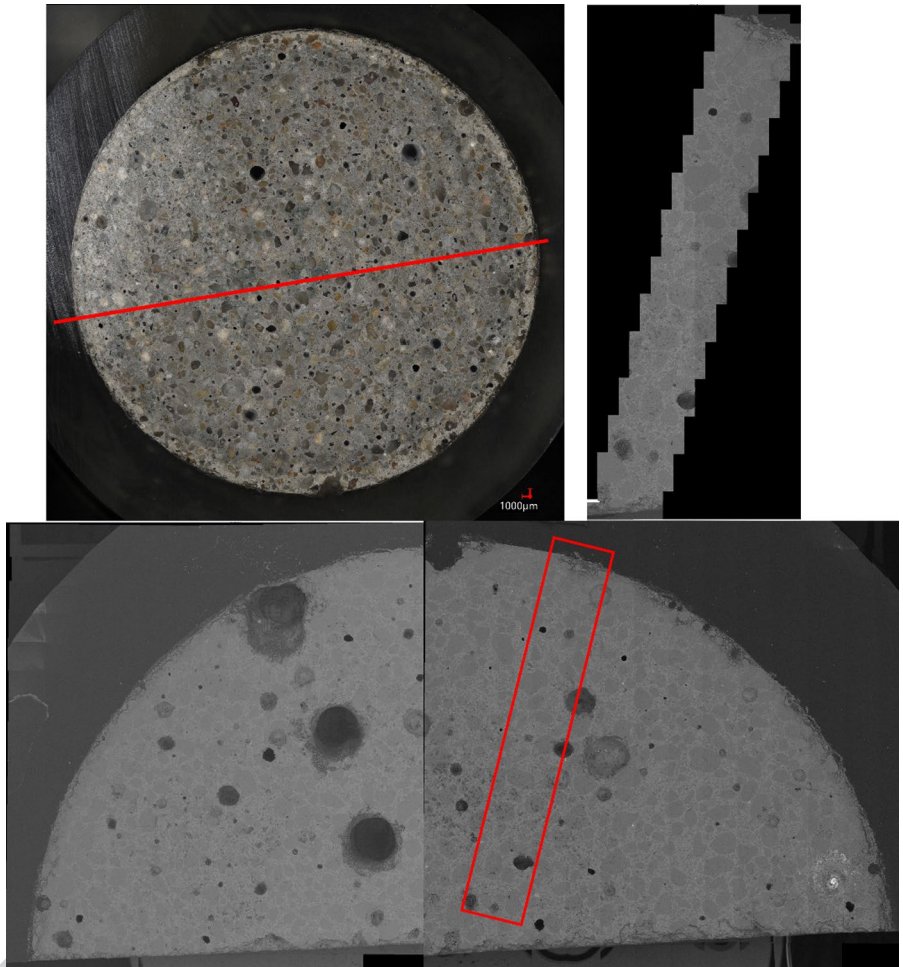
**Fig. 12** Analysis of CEM III mortar: Cross section visualization with Keyence, SEM imaging, and EDS elemental analysis selection

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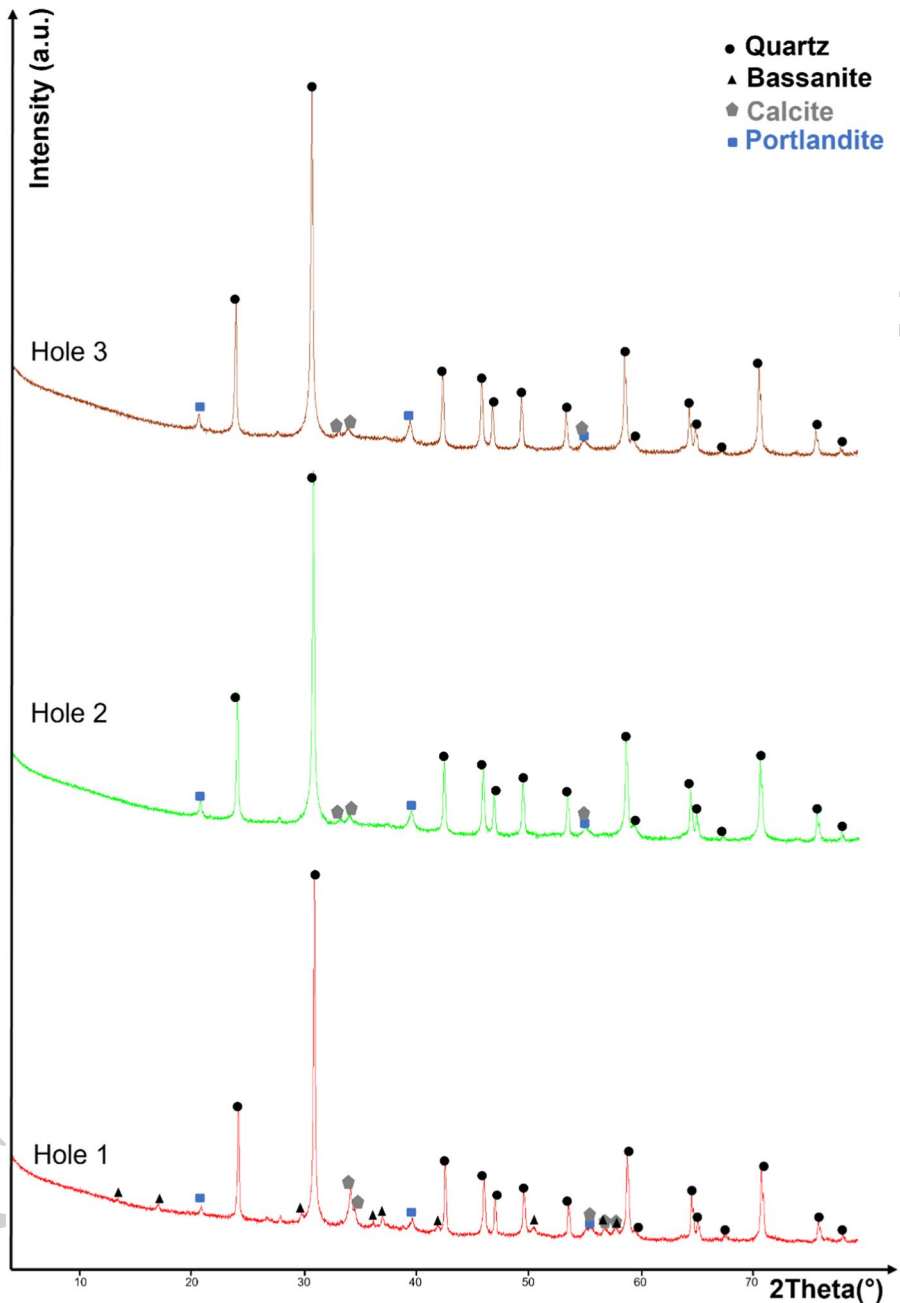
**Fig. 13** Analysis of CEM V mortar: Cross section visualization with Keyence, SEM imaging, and EDS elemental analysis selection



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**Fig. 14** RDX diagram of the three holes in the CEM I specimen



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