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1 **Optimisation of 3D printed concrete for artificial reefs: biofouling**
2 **and mechanical analysis**

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17

18 **Abstract**

19 Protection, restoration, and regeneration of aquatic habitats are an increasingly important issue and are
20 requiring intensive research. In the marine environment, artificial reefs may be deployed to help offset
21 habitat loss, increase local biodiversity and stimulate the recovery of ecosystems. This study aimed at
22 the fabrication of artificial reefs by 3D printing. In the framework of the European INTERREG
23 Atlantic Area collaborative project “3DPARE”, six printed concrete formulations with limited
24 environmental impact, based on geopolymer or cement CEM III binders and recycled sands, were
25 immersed in the Atlantic along British, French, Portuguese and Spanish coasts. The colonisation of the
26 concrete samples by micro- and macroorganisms and their durability were assessed after 1, 3 and 6
27 months of immersion. Results showed that both parameters were better with CEM III compared to
28 geopolymer-based formulations. Therefore the use of CEM III should be prioritised over these
29 geopolymer binders in 3D printed concrete for artificial reef applications.

30 *Keywords:* Artificial reef, 3D printing, Bio-receptive concrete, Geopolymer, Cement, Biofouling, Eco-
31 engineering

32 **1. Introduction**

33 Artificial reefs are man-made structures deployed on the seafloor with a history that goes as far as
34 back as the Roman Empire and Ancient Greece. Reefs were initially built for strategic military
35 purposes such as the blockade of harbours or the trapping of enemy ships [1]. Yet artificial reefs now
36 serve more specific objectives related to the restoration of fisheries and biodiversity and their
37 deployment is often aimed at mitigating the effects of resource exploitation including destructive
38 practices such as trawling [2]. Marine biodiversity provides beneficial ecosystem services such as
39 commercial fisheries and tourism, including recreational scuba diving [3], so conservation and
40 restoration is an imperative. Knowledge gained from the deployment of artificial reefs is also being
41 applied to the ecological enhancement of other coastal structures [4].

42 Evidence of artificial reef works dating from 1789 has been found in Japan [5] and in the USA during
43 the 19th century [6]. Their global deployment increased after World War II with the first national

44 programmes in Japan [7] and later to other continents [8]. In Europe, many private or public-funded
45 programmes were instigated in the Mediterranean Sea, however fewer have been deployed in the
46 Atlantic area due to high storm frequency and strong currents in the benthic zone that make it much
47 less stable and more difficult to study [9]. About 60 artificial reefs are listed in the OSPAR Maritime
48 Area, from Norway to Portugal [10], 25 of which being in Spanish territorial waters [11]. Reefs in this
49 area consist of car wrecks, shipwrecks, tyres and concrete blocks [12] [3] and geotextiles [13]. The
50 design of concrete reefs has been very simple as they were made by casting fresh concrete into
51 formwork and, in addition, the blocks were made of ordinary concrete [14]. Shapes varied from simple
52 cubes or pipes called Bonna, to more elaborated geometric structures called Typi and Babel, deployed
53 in chaotic or organised heaps, as seen on the French Atlantic coast [15]. First results of faunal
54 monitoring studies on the Aquitaine coast in France showed the major presence of benthic fishes
55 around the artificial reefs with higher taxa richness in more complex assemblies [16]. As complexity
56 of design is important [12], but difficult to attain with conventional fabrication methods, 3D printing
57 of concrete is a recent and promising technique which allows the design of very complex reefs (Fig.
58 1). In civil engineering, it consists of the upward fabrication of structures by the deposition of
59 successive layers of concrete slurry with the help of a robotic arm or gantry. Debuts of 3D concrete
60 printing for artificial reefs date from 2017 with projects in the Mediterranean Sea and in the Maldives.



61

62 **Fig.1.** 3D-printed artificial reefs submerged near Monaco coasts [17].

63 *Artificial Reef 3D Printing for Atlantic Area (3DPARE)* is a European project which gathers partners
64 from France, Portugal, Spain and the UK. It aims to design and then fabricate 3D printed artificial
65 reefs made of concrete to be deployed in the northern Atlantic area (Fig. 2). The first step was to

66 optimise and choose the concrete formulations to facilitate colonisation and provide shelter to small
67 and large species. The design aimed to be compatible with the marine environment, having less
68 negative environmental impact, and to be chemically and physically resistant to marine conditions and
69 stable on site against storms [18].



70 **Fig.2.** 3D-printed artificial reefs submerged

71 In the framework of 3DPARE project, these formulations are made from eco-friendly or recycled
72 materials including crushed seashell sand, glass sand or geopolymers as a binder. Geopolymer binder is
73 made of alumina-silicates, alkaline reagents such as sodium hydroxide NaOH or potassium hydroxide
74 KOH, and water. They release less carbon dioxide in the atmosphere upon fabrication than ordinary
75 Portland cement [19]. Other materials were also used, namely a ground granulated blast furnace slag
76 cement CEM III which has been commonly used by the Dutch for a century in marine applications
77 [20], and limestone sand.

78 While biofouling, *i.e.* the colonisation of wetted surfaces by biological microorganisms or
79 macroorganisms, is more often overlooked in the case of marine infrastructures deployment *i.e.* Dikes,
80 quay, etc – there is a large amount of literature on marine antifouling strategies. One major objective
81 of this work is to get the highest rate possible of biocolonisation and biodiversity.

82 **2. Experimental program**

83 **2.1. Materials used and sample preparation**

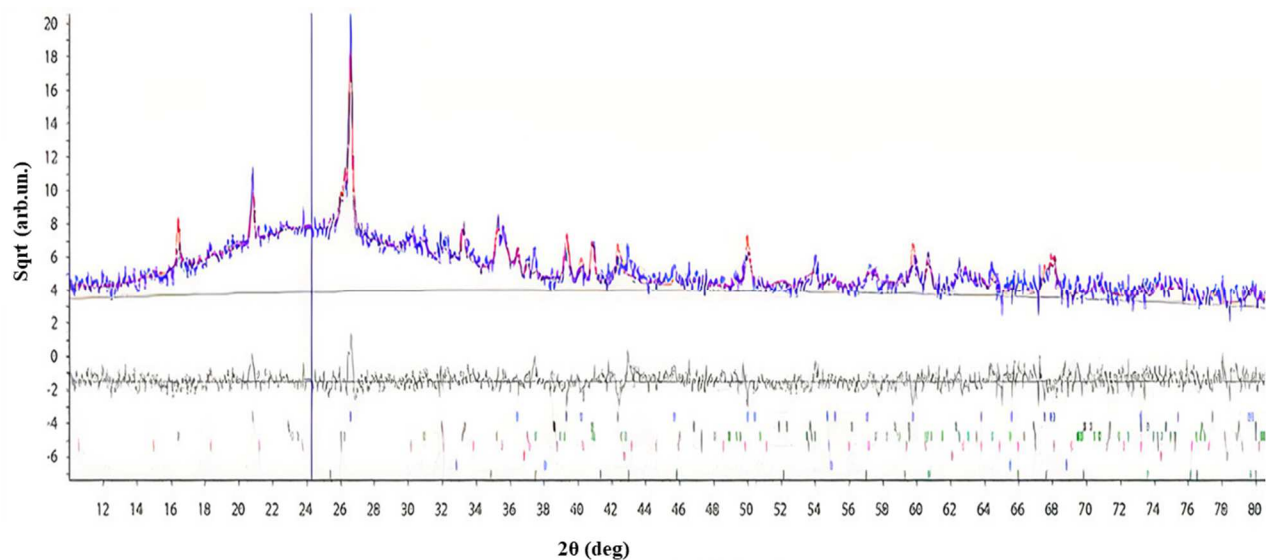
84 To manufacture artificial reefs by 3D printing, six formulations made with geopolymer and cement
85 mortars were analysed.

86 The terminology used for the identification of the formulations was the following: GL: geopolymer
87 mortar with limestone sand; GG: geopolymer mortar with 30% glass sand; GS: geopolymer mortar
88 with 50% shell sand; CL: cement mortar with limestone sand; CG: cement mortar with 50% glass
89 sand; CS: cement mortar with 50% seashell sand.

90 The geopolymer mortars (GX) were manufactured with fly ash as the main binder; sodium hydroxide
91 (NaOH), tap water, additives, and limestone sand, glass sand and seashell sand, as fine aggregates. On
92 the other hand, cement mortars (CX) were manufactured with cement CEM. III/B 32.5 N-SR, tap
93 water, superplasticiser as additive, fly ash and kaolin as additions; and the same fine aggregates used
94 for the geopolymer mortars.

95 Fly ash was characterised by X-ray diffraction (XRD). For this, the ordinary range 10-80° (2θ) with
96 the standard conditions for the diffractometer was explored working in the Bragg-Brentano
97 configuration with a copper tube with filtration of the radiation K_{β} ($\lambda = 1.5418 \text{ \AA}$). The estimate of
98 the amorphous contribution over the diffraction pattern was focused on $2\theta = 24.2^\circ$, compatible with
99 the amorphous phase of silicon oxide (SiO₂).

100 Fig. 3 shows the quantification of the possible crystalline phases, the most present being mullite
101 ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$): 44.4%; quartz ($\alpha\text{-SiO}_2$): 23.4%; maghemite ($\gamma\text{-Fe}_2\text{O}_3$): 21.2%; magnetite (Fe_3O_4):
102 8.4%; and corundum (Al_2O_3): 2.0%. Loss of weight by calcination (LWC) was 2.4%.



103

104

Fig. 3. Relative percentages over the total of crystalline phases (% in weight).

105 NaOH in industrial form with initial molar concentration 25 M was employed after dilution in tap
 106 water to be used as an activator. The solution was prepared at least one day ahead of use.

107 Cement type III/B had an ordinary content of 31% clinker and 66% steel slag (data provided by the
 108 manufacturer). The physical properties of cement used are summarized in Table 1. MetaKaolin was
 109 analysed by X-ray fluorescence spectrometry and its composition was shown in Table 2.

110 **Table 1. Physical properties of cement**

Blaine fineness (cm ² /g)	28 days compressive strength (MPa)	Setting time (min)	
		Initial setting time	Final setting time
4500	44	210	265

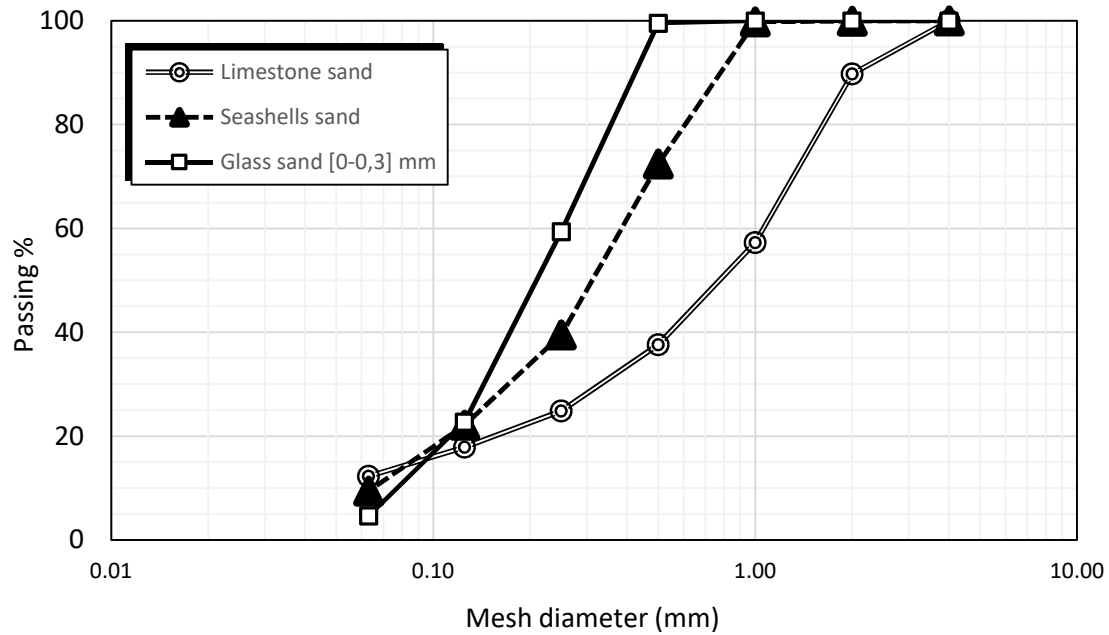
111

112 **Table 2.** Chemical composition of metakaolin (%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	LWC
48.3	35.5	1.5	0.24	0.4	0.1	1.35	0.28	12.5

113

114 Limestone sand, coming from quarry stone crushing, was provided in the fraction [0-3] mm. The
 115 crushed shells were obtained from the recycling of seashells coming from the canning industry. The
 116 glass came from smashed car windows in the fraction [0-0.3] mm. Fig. 4 represents the granulometric
 117 curves of the sands used in the mortars.



118

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Fig. 4. Granulometric curves of the sands used in the mortars.

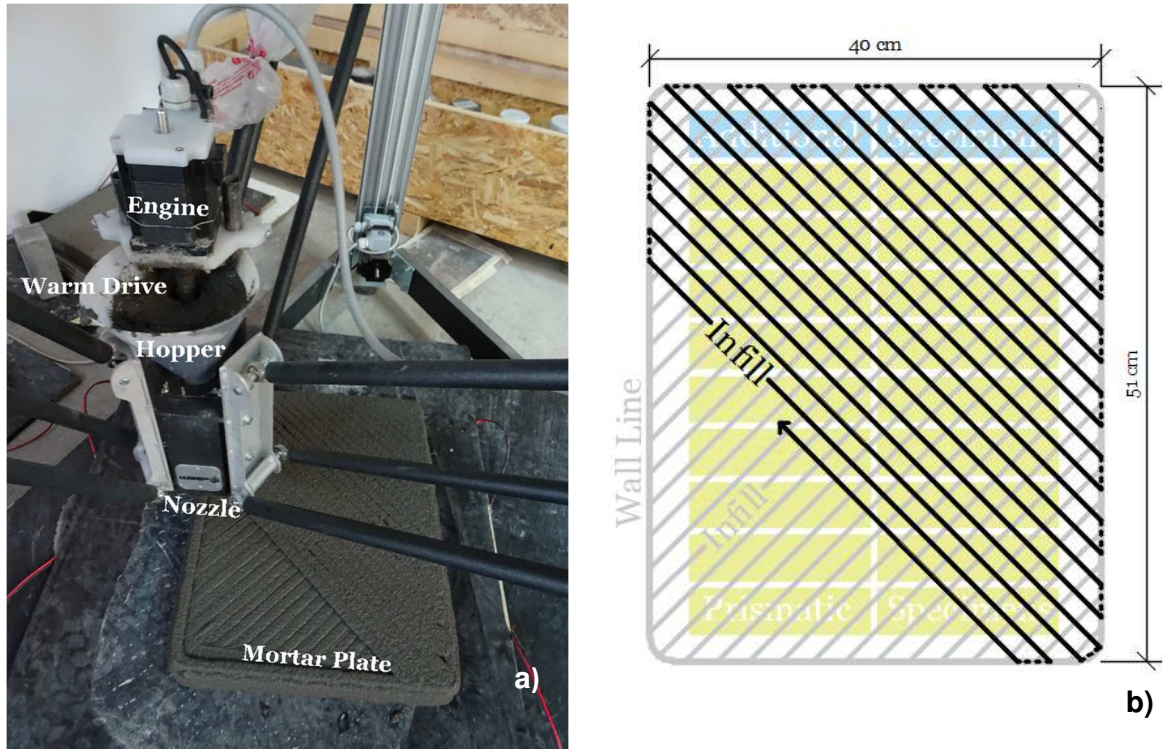
120

To carry out the experimental programme, $4 \times 4 \times 16$ cm prismatic specimens were fabricated with a 3D printer type Delta of deposition per layer, whose maximal printing volume is 1 m diameter and 1 m height. The printer has a head which is composed of a hopper and a 3D worm drive inside, which, by spinning thanks to an electrical motor, drags the material to print towards the nozzle (Fig. 5a).

124

To obtain the prismatic specimens, mortar plates were printed with the 6 formulations under study, whose measurements were $40 \times 51 \times 6.4$ cm. The plate perimeter was printed with a wall line, while the area was filled with lines at 45° (with respect to the perimeter) which alternated layer after layer (Fig. 5b). From each plate, 20 prismatic specimens were obtained, including two more than necessary in case any were damaged or there was any problem during sawing.

128



129 **Fig. 5.** a) 3D printer head details. b) Mortar plate printing and cutting scheme.

130 The distribution prismatic specimens was as follows: 4 partners (France, Spain, Portugal and United
 131 Kingdom); 6 different formulations; 5 immersion periods and one extra (1, 3, 6, 12, 24 months, extra);
 132 3 replicates per formulation. This led to a total of $432 + 108 = 540$ prismatic specimens.

133 The plates were printed with a nozzle of 20 mm diameter. A variable forward speed of the head of the
 134 printer was used, covering from 100 to 300 mm/s. The rotation speed of the worm drive to extrude the
 135 mortars was variable as well, going from 100 to 300 rpm.

136 From each plate, the required number of prismatic specimens by formulation was obtained for each
 137 partner. So, 6 mortar plates were fabricated per day, one plate for each formulation. In this way, the
 138 specimens corresponding to each partner were the same age.

139 After 7-14 days, the prismatic specimens were cut from plates with a circular saw. The cutting process
 140 was carried out carefully so as not to mix the different mortars nor losing the printing orientation.
 141 Once the cutting was completed, the upper printing face of the prismatic specimens were identified.

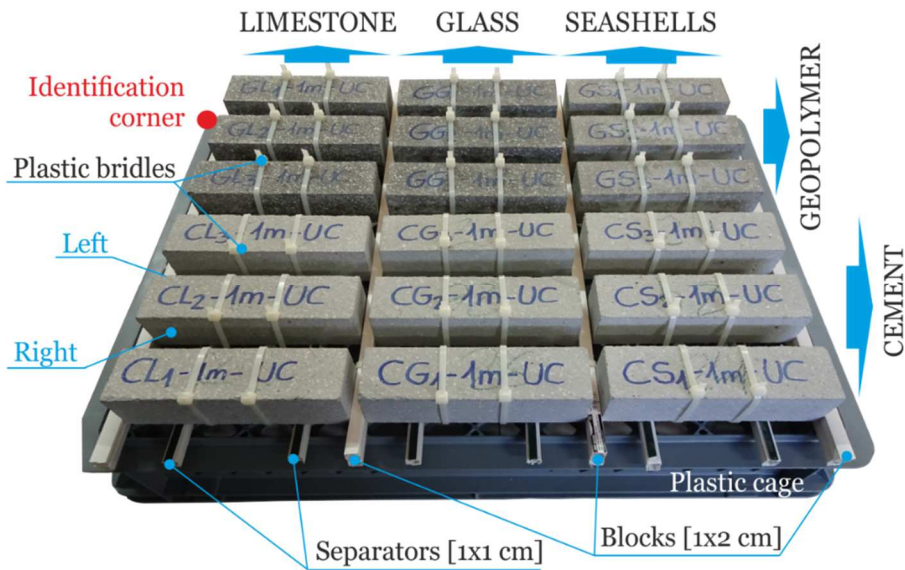
142 All mortars, both at the plate stage and also as prismatic specimens, were cured in air in a lab
143 environment.

144 **2.2. Protocol of 3D printed samples immersion**

145 The specimens were printed in Spain and were consequently delivered to the other partners before they
146 were 28 days. For the delivery, the specimens were fully wrapped in bubble wrap and laid in plastic
147 boxes, to avoid damage. Upon arrival at destination, the bubble wrap was removed and the specimens
148 were left in air in a lab environment. The immersion was carried out when the specimens were around
149 70 days.

150 At each location, the 18 specimens (3 replicates of 6 formulations) were fixed to plastic platforms and
151 deployed in the sea. One platform was used for each age of immersion (in addition to an extra one set
152 in case there was a problem). This paper indicates the results of the specimens with immersion periods
153 of 1, 3 and 6 months, while those with periods of 12, 24 and extra are still immersed.

154 The platforms consisted of plastic boxes of 590 mm length, 365 mm width, 80 mm height and mesh
155 opening 20×20 mm. The boxes were inverted sideways to lay the specimens. Initially, plastic
156 separators with 1×1 cm of section were inserted between the box and the specimens; the specimens
157 were placed according to the order and distances shown in Fig.6. Specimens were set between blocks
158 (1×2 cm of section) to ensure that they could not move. Once the specimens were in place, they were
159 fixed to the boxes with plastic cable-ties of 4 mm width. The fastening of the samples was done in a
160 way that allowed the free circulation of seawater all around the samples.



161

162

Fig. 6. Arrangement of specimens on the platform.

163

The platforms with the specimens were immersed in the sea, separated by at least 1 m from the seabed and 1 m from the sea surface. Platforms were deployed in relatively sheltered locations to ensure that they did not swing in waves. All samples were immersed in the North-east Atlantic Ocean, off the coast of England (Poole Bay), France (Saint-Malo Bay), Portugal (Matosinhos Bay) and Spain (Santander Bay). Cages were removed at 1, 3 and 6 months of submersion.

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2.3. Monitoring protocol for the characterisation survey and post deployment of pilot reefs surveys

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The main objective of artificial reefs is to enhance the biodiversity of the deployment site. For this, they first have to attract microorganisms which will colonise the material and become one of the first links in the food chain. Attractiveness of the samples to marine life was measured by two means: first, the visual assessment of the biocolonisation of the samples by image processing, and second, the amount of biomass of the micro- and macroorganisms attached to the samples. The first method gives clues about the surface area that is colonised by organisms, whereas the second indicates the intensity of this colonisation. They thus provide complementary data on the bioreceptivity of the materials.

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2.3.1. Visual assessment of biocolonisation by image processing

178 After the recovery of the samples at each time step, each of their sides (up, down, right, left) was
179 immediately scanned on arrival at the laboratory on a Canon Lide 300 office scanner (Canon, Japan)
180 with a 2400 × 4800 dpi resolution until the point at which they were colonised by macroorganisms. A
181 scanner was preferred to photographs as it ensured the same image quality for all partners in terms of
182 resolution, focal length or brightness. Scanned images were then processed on ImageJ (NIH, MD,
183 USA) open source software.

184 The protocol for the scanned images processing was as follows: 1) definition of the region of interest
185 (i.e. the samples boundaries) for each side; 2) 8-bit transformation of the raw image, assigning only
186 grey values to each pixel, from 0 (black pixel) to 255 (white pixel); 3) thresholding: this allows to
187 make the distinction between zones of interest (white colonised vs. black uncolonised); 4) computation
188 of the percentage of covering: this value was defined considering the mean grey values (Eq. 1) of the
189 samples following Eq. 2.

$$190 \text{ mean grey value} = \text{sum of each side's grey values} / \text{number of pixels} \quad (1)$$

$$191 \text{ covering percentage (\%)} = (\text{mean grey value} / 255) \times 100 \quad (2)$$

192 2.3.2. *Biomass of collected micro- and macroorganisms*

193 When scanning was performed, the entire surface of the samples was scrubbed manually with a brush
194 under distilled water in order to scrape off and collect all micro- and macroorganisms attached to the
195 samples. The water containing the biomass was then filtered on 25- μ m filter papers which were
196 weighed after having being dried at 105 °C.

197 **2.4. Mechanical tests**

198 Mechanical tests were performed on the printed prismatic samples after the assessment of
199 biocolonisation procedure. For this, flexural strength, compressive strength and Young's modulus
200 were determined according to European standard EN 196-1, using an IGM 250 kN press (IGM,
201 France), at 28 days of curing (reference properties), and at 1, 3 and 6 months after immersion. Briefly,
202 a load of 0.05 kN/s was applied for the flexion test on the upper side of the whole prismatic sample

203 according to the printing direction, until failure. The obtained halves of each sample then underwent
204 the compression test on the same direction with a load of 2.4 kN/s. The Young's modulus was
205 obtained measuring the slope of the compression curve between 30 and 80% of the compressive
206 strength where the curve is the most linear.

207 **3. Results and discussion**

208 **3.1. Biocolonisation**

209 Biocolonisation and biomass results are summarised in Fig. 7 and 8, and Tables 3 to 5.

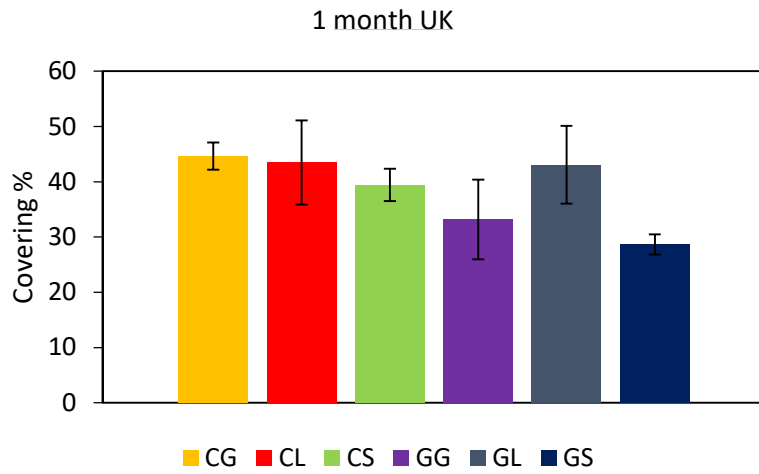
210 *3.1.1. Image processing*

211 Fig. 9 shows an example of raw scan image of one sample and the corresponding 8-bit and thresholded
212 equivalent. It should be noted that no scanning was performed for 3 and 6 months samples from
213 England and Portugal because of the presence of macroorganisms, as specified in the protocol
214 mentioned in Paragraph 2.3.1 (Fig. 10). A general observation was that all samples were colonised as
215 indicated by a noticeable change of colour (from grey and dark grey to brownish or greenish)
216 However, biofouling was different according to the immersion location. In fact, colonisation was
217 much higher in the southern part of the Atlantic (Portuguese and Spanish northern coasts) compared to
218 its northern part (British and French coasts). Results may appear mitigated, for samples – especially
219 the French ones – for which the colonisation was visually difficult to assess. For these, results were
220 highly dependent on the eye and discrimination capacity of the experimenter; however this bias was
221 reduced by ensuring that all image analyses were carried out by the same person. On the contrary,
222 highly colonised samples – like Portuguese and Spanish ones – were unequivocal.

223 UK 1 month results (Fig. 7a) showed that the best colonisation rates were observed for CG and CL
224 with a covering percentage of 44.6% and 43.8% respectively. CL is closely followed by GL with
225 43.1% of the surface covered. A quite different rank was found for Portuguese 1 month samples (Fig.
226 7b), dominated by CS (92.1%) followed by GS (87.4%) and CG (87.3%) on the last step. Here again,
227 the second and third best results are similar. With the French and the Spanish results at 1 month of
228 immersion (Fig. 8), it appears that generally, the best colonisation behaviour is observed for CX

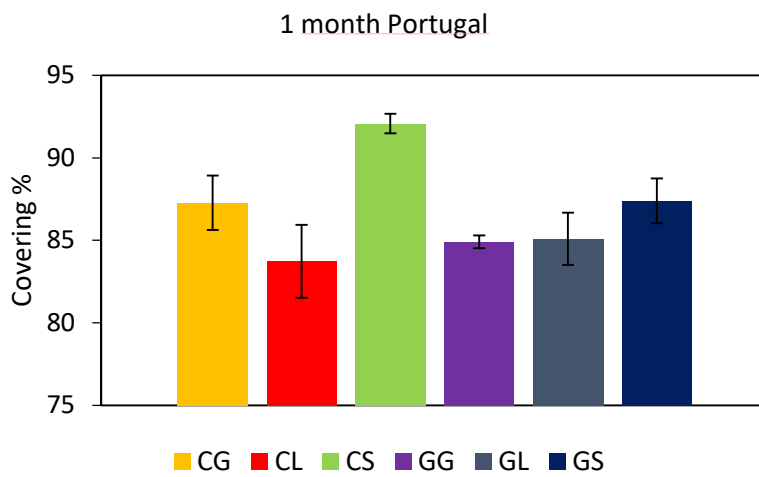
229 samples whereas it is less good with GX samples, though this is less true for Spanish 3 months results.
230 The hypothesis is that geopolymers leach high amounts of OH^- which affect the pH of the local habitat
231 (between 7.4 and 7.6 for seawater according to [21] and [22]), making it more alkaline. This release
232 can lead for some cases to a soaring pH of deionised water in a logarithmic trend from up to more than
233 10 in tens of minutes at 90 °C [23]. Yet a modification of pH to extremes – either basic or acid – is
234 known to be adverse to marine organisms. Indeed, pH can be used by potential basibionts (*i. e.* living
235 organisms as substrates) in their immediate vicinity as a chemical deterrent against epibionts (*i. e.*
236 organisms living on the surface of another living organism) in an antifouling defence strategy [24].
237 However, [25] showed that the pH decreases slowly, from 11.3 to 10.2 on average up in 60 mL of
238 distilled water over 28 days. We can assume that the decrease of pH is more important in the large
239 quantity of water represented by the sea, and that dilution compensated the early “toxicity” of
240 geopolymer towards microorganisms later on. Portland blast furnace slag cement also leads to an
241 increase of pH but the variation appears much less important than with geopolymers, about 0.2 after 7
242 days in artificial seawater [26].

243 Despite those differences, we can see with the French and Spanish samples (Fig. 8) that all samples
244 follow the same trend, namely the tendency of the biofilm to cover the whole surface of the samples,
245 and we can assume that this is the same for the British and the Portuguese samples. In some way, it
246 supports the notion that all materials will be colonised to some extent, even if it were toxic on its
247 surface or by leaching, as claimed in the literature [27] [28]. Nevertheless, as they were tied to
248 platforms with cable ties which hide a small part of the available surface to colonisation accounting
249 for uncolonised zones, biofouling will never reach 100%.



250

a)



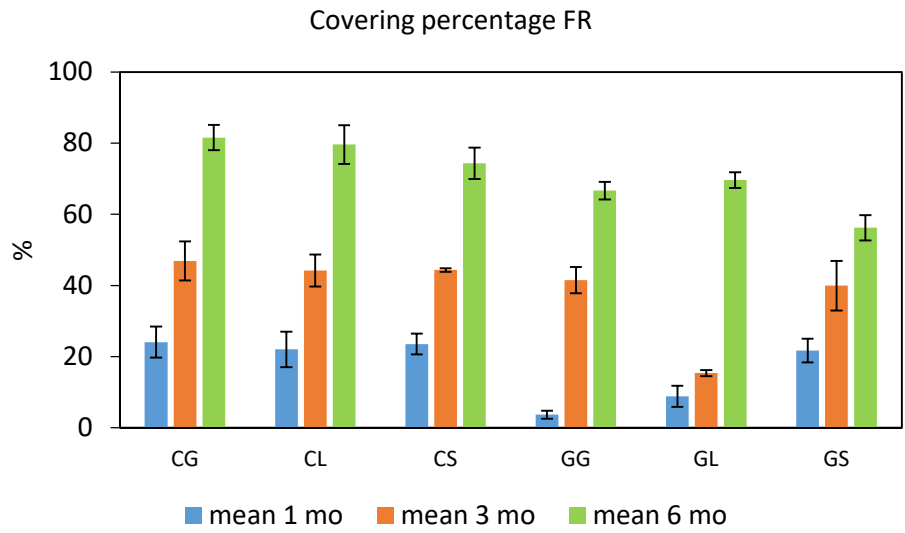
251

b)

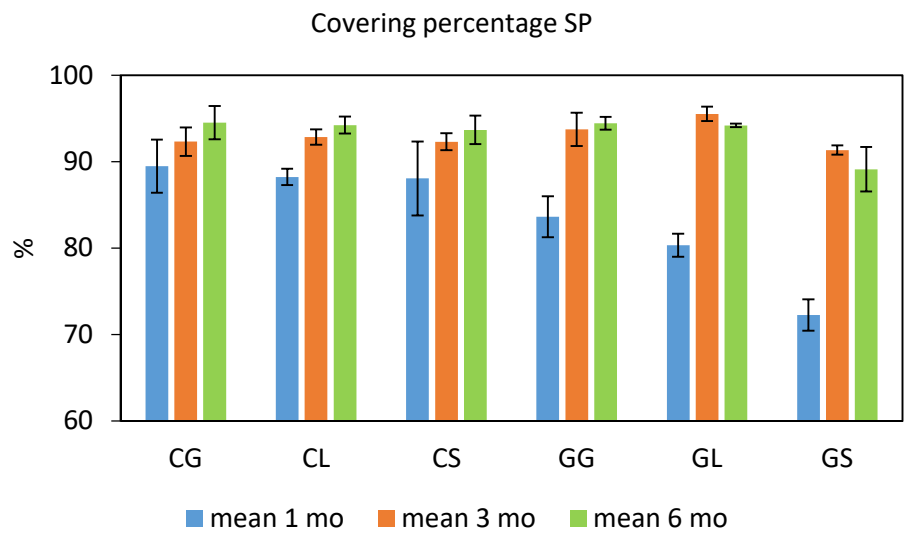
252 **Fig. 7.** Mean biocolonisation coverage per material tested at 1 month, obtained from scanned images

253

for a) the UK, b) Portugal.

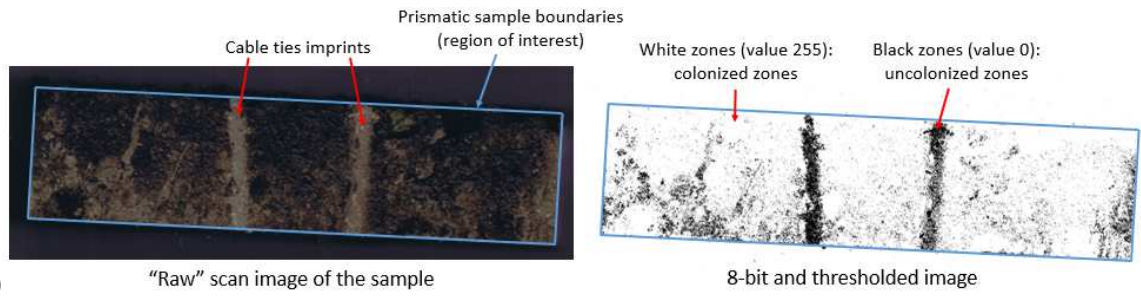


254 a)



255 b)

256 **Fig. 8.** Mean biocolonisation coverage per material tested at 1, 3 and 6 months, obtained from scanned
 257 images for a) France, b) Spain.



258 **a)** "Raw" scan image of the sample **b)** 8-bit and thresholded image

259 **Fig. 9.** Image processing: a) "Before" unprocessed scan image; b) "After" 8-bit and thresholded black
 260 and white image.



261
 262 **Fig. 10.** Example of sample partially covered with macroorganisms (mussels, ascidians). Samples with
 263 macroorganisms attached were not scanned, only biomass was measured.

264

265 **3.1.2. Biomass**

266 Slightly higher values are observed on average with GX bricks compared to CX for 1 and 3 months
 267 (means of 1.74 g vs. 1.87 g and 8.1 g vs. 9.65 g respectively, Tables 3 and 4), but the association is
 268 reversed at 6 months of immersion (mean of 8.03 g for CX vs. 6.03 g for GX, Table 5). These
 269 differences vary from 0.13 g at 1 month to 2 g at 6 months. These values contrast with visual

270 biocolonisation results for which CX were generally superior ; it might indicate that the biofouling is
 271 more important and more localised for GX samples, while for CX samples the layer of biofouling is
 272 thinner but larger in surface area. Finally, we noted that, as for coverage, the collected biomass
 273 increased over time for all samples. This is due to the extended spreading of biofouling on the surface
 274 but also to the increase in thickness of the biological layer. This observation confirms the fact that
 275 once the first microorganisms are established, they can develop to their maximum stage of maturation.
 276 It is therefore promising for the attraction of macro species and the enhancement of the local habitat
 277 with more species and more individuals. Regional variation in biofouling coverage and biomass could
 278 be due to multiple abiotic factors, notably seawater temperature, turbidity and levels of nutrients
 279 including nitrates and phosphates. There is also the possibility of biological interactions such as the
 280 abundance of local grazers and predators.

281 **Table 3.** First month biomass dry weight data for materials tested in France (FR), the UK, Spain (SP)
 282 and Portugal (PT) and overall average.

1 month	FR [g]	UK [g]	SP [g]	PT [g]	AVERAGE [g]
CL	1.07	0.49	2.65	1.11	1.33
CS	0.67	0.34	2.57	1.07	1.16
CG	0.03	0.57	9.19	1.09	2.72
GL	0.02	0.72	5.06	1.24	1.76
GS	0.04	0.37	2.31	1.61	1.08
GG	0.79	0.37	8.48	1.41	2.76

283
 284 **Table 4.** Three months biomass dry weight data for materials tested in France (FR), the UK, Spain
 285 (SP) and Portugal (PT) and overall average.

3 months	FR [g]	UK [g]	SP [g]	PT [g]	AVERAGE [g]
CL	0.65	7.06	19.06	8.38	8.79
CS	0.63	5.95	14.09	10.28	7.74
CG	0.74	4.41	16.07	9.87	7.77
GL	0.99	4.62	22.63	9.77	9.50
GS	1.37	5.96	23.13	6.55	9.25
GG	1.08	5.86	19.32	14.53	10.20

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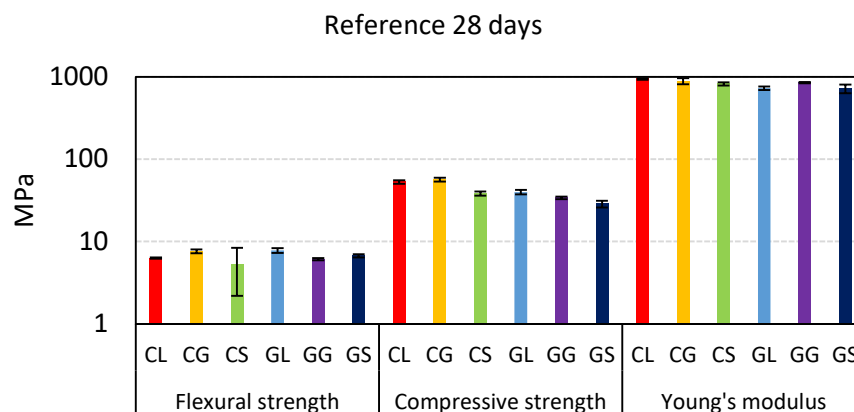
287 **Table 5.** Six months biomass dry weight data for materials tested in for France (FR), the UK, Spain
 288 (SP) and Portugal (PT) and overall average.

6 months	FR [g]	UK [g]	SP [g]	PT [g]	AVERAGE [g]
CL	1.78	5.91	8.20	17.89	8.44
CS	2.14	7.16	7.88	17.84	8.75
CG	1.91	5.94	9.93	9.80	6.89
GL	1.12	4.16	8.09	11.38	6.19
GS	1.90	4.23	8.85	9.73	6.18
GG	1.86	4.36	6.91	9.74	5.72

289

290 3.2. Mechanical results

291 Reference mechanical tests results obtained at 28 days of curing are presented in Fig. 11.

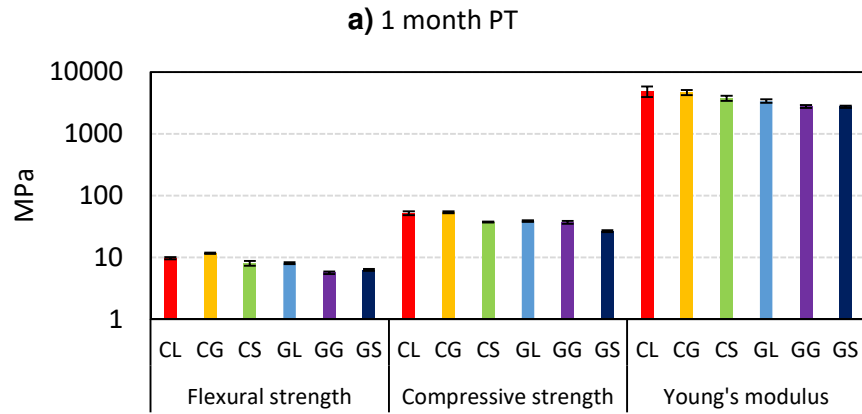


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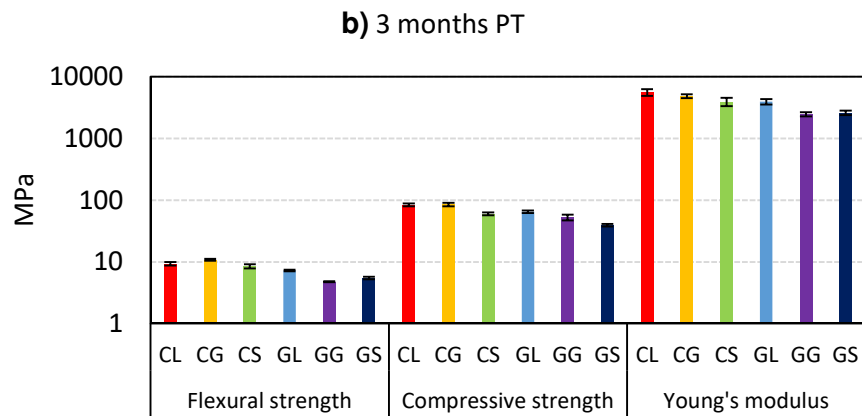
293 **Fig. 11.** Reference mechanical properties for tested materials at 28 days.

294 Mechanical tests results show the same trend over time, across all regions. Although different values
 295 were obtained from each region, the trend is similar for all three studied mechanical properties
 296 (flexural strength, compressive strength, Young's modulus). An example of what was observed for all
 297 regions is shown in Fig. 12. For each region and at each due time, even at 28 days, we observed better
 298 mechanical behaviour with CX samples than with GX except for GL which is comparable to CS.

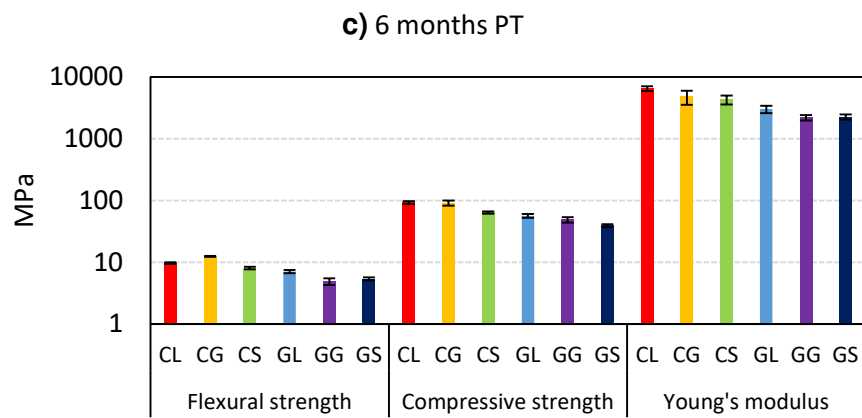
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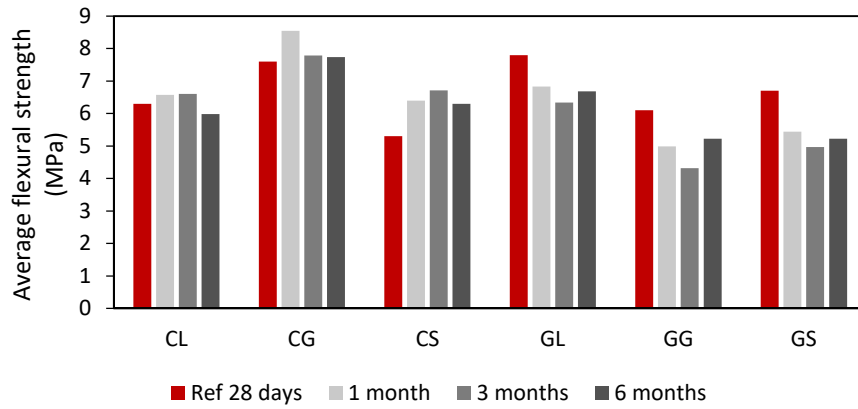
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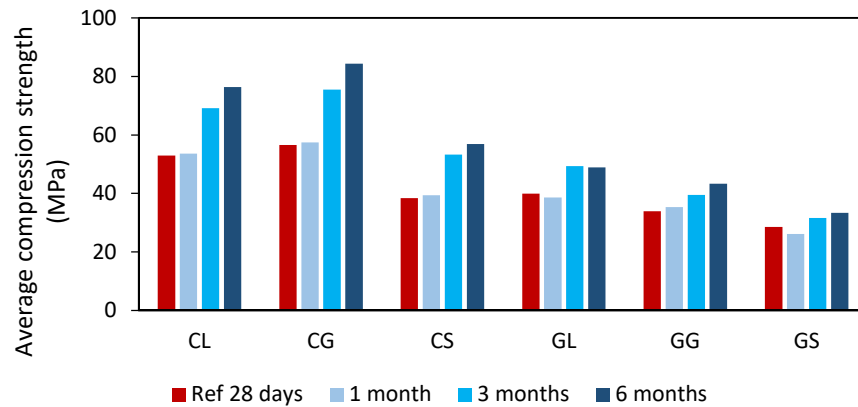
302 **Fig. 12.** Example of mechanical properties over time obtained for Portuguese samples at a) 1 month,
 303 b) 3 months, c) 6 months of submersion.

304 While averaging the mechanical properties values from all regions (Fig. 13), this association is even
 305 more clear , especially for the compressive strength and the Young's modulus with differences up to
 306 50 MPa and 2 GPa respectively (CG vs. GS at 6 months). The flexural strengths are more alike and do
 307 not vary much over time compared to the other two mechanical properties. A major observation is the
 308 increase in compressive strength for both CX and GX, with a higher variation for CX. These results

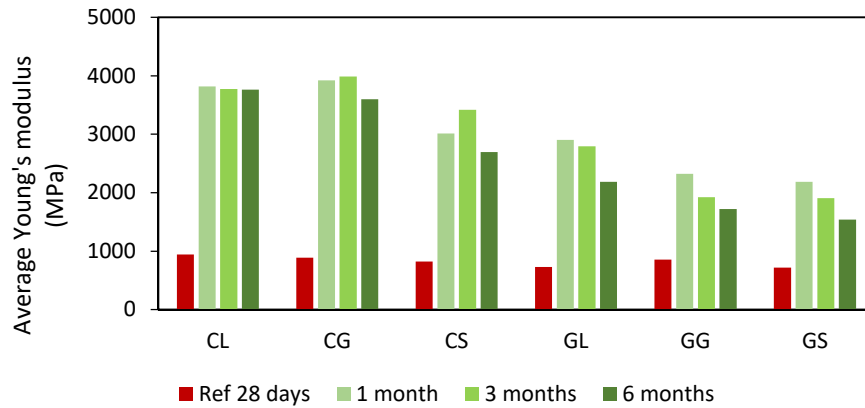
309 are consistent with the literature, as long term studies show that geopolymers can achieve 70% of their
 310 one-year compressive strength at 3 days, indicating a still-going geopolymerisation process [29]. This
 311 increase is slow [30] compared to CEM III the slow hydration process of which continues on the long
 312 term and highly contributes to the enhancement of ground granulated blast furnace slag cement
 313 performance. In fact, CEM III can achieve 128% of its 28-day strength at 180 days [31].



314 a)



315 b)



316 c)

317 **Fig. 13.** Overall average of mechanical properties of tested materials with submersion time: a) flexural
 318 strength, b) compressive strength, c) Young's modulus. Standard deviation is not represented as the
 319 values could differ a lot between regions . For one regions , it was small, like in Fig. 12.

320 Contrary to what is commonly accepted, the flexural strength may decrease as well as the elastic
 321 modulus, against the behaviour in compression, as seen here. This case has already been documented
 322 in [30] on geopolymers in seawater and can be encountered depending on the material characteristics
 323 (density, homogeneity, etc.). The same phenomenon might happen for cement in seawater. However, a
 324 low Young's modulus can be beneficial to slow down the propagation of cracks [30]. In addition, this
 325 behaviour was not strictly characteristic of all samples for one given region taken individually.
 326 Gererally the medium-term durability of all formulations was demonstrated here, with an advantage
 327 for CX. The biocolonisation might also have been an asset to protect the materials as it can be the case
 328 for other applications [32] [33].

329 4. Conclusion

330 The aim of this work was to assess the behaviour of 3D printable mortar formulations towards marine
 331 fauna and flora and their durability in seawater at medium term (1, 3 and 6 months). Both are major
 332 parameters to consider when designing artificial reefs. Yet further analysis should be undertaken and
 333 reported for the longer term deployments.

334

335 Mortar formulations with limited environmental impact composed of either geopolymers or cement
336 CEM III as binders and three kinds of sand were studied. Results showed that:

- 337 - Initial biocolonisation was better with CEM III compared to geopolymer-based formulations.
338 However, both tend to reach the maximum colonisation rate.
- 339 - On average, mechanical properties were better with CEM III-based formulations over time.
- 340 - The trend was similar across regions.

341 Regarding biocolonisation and mechanical properties, initial results indicate that CEM III-based
342 formulations should thus be prioritised over geopolymer-based formulations for the 3D-printing of
343 full-scale artificial reefs. To date, the 12 and 24 months samples are still immersed and the monitoring
344 of their biocolonisation and durability continues.

345

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350

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