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Greening effect of slag cement-based concrete: environmental and ecotoxicological impact

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Data accessibility statement

Data pertaining to this manuscript are deposited in figshare at DOI: 10.6084/m9.figshare.13049582

Highlights

- Greening effect is not associated with hazardous leachates or ecotoxic effects
- Alkaline pH (> 11) is the main issue with cement or slag-based materials
- The algae *R. subcapitata* is not affected by high pH unlike the crustacean *D. magna*
- GBFS contain sulfides up to 1 wt.% release in eluates of concretes and pastes
- Sulfides are quickly neutralized in natural environment

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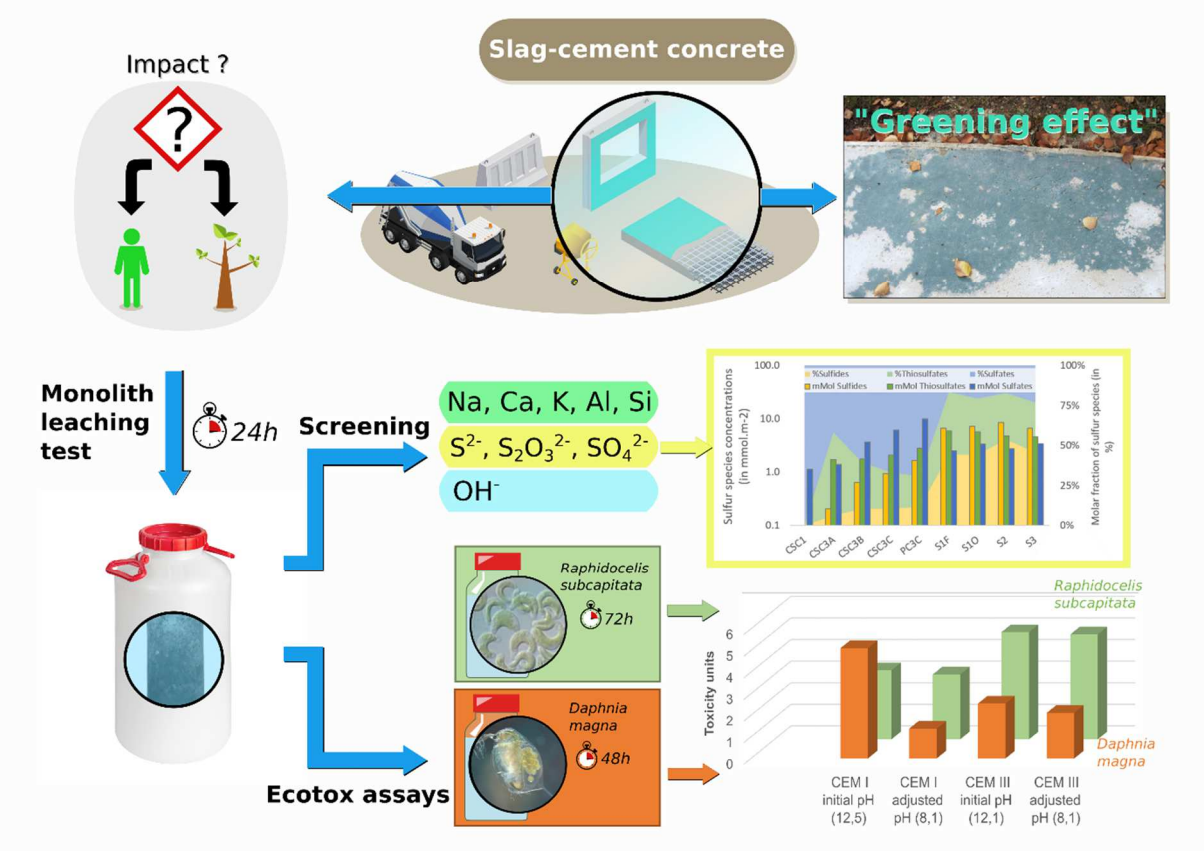
Abstract

Materials containing ground granulated blast furnace slag (GGBFS) display a transient green-blue color after demolding. This greening effect have been investigated for leaching behavior and ecotoxicological impact. Color of concretes and pure pastes containing GGBFS was assessed with a portable spectrophotometer, and samples were then submitted to a tank monolith leaching test. Ecotoxicological tests were conducted on reference sample and a green concrete sample at both natural and adjusted pH of 8.1. Main results support that the temporary greening effect of GGBFS-containing materials has no particular impact neither on the chemistry of leachates, nor ecotoxicity. Additionally, alkaline leachates are the main issue of leached cement or GGBFS based materials with pH around 11.5 – 12.5. Alkaline pH is a preponderant factor of ecotoxicity to sensitive organisms such as *Daphnia magna*, immobilization assay (48h) resulting in 5.10 Toxic Units (TU) for reference sample at pH 12.50 against 1.38 TU at pH 8.10. Furthermore, sulfides are a specific issue of GGBFS materials concentrated up to 0.94 $mmol.m^{-2}$ in leachates, having an ecotoxic impact on living organisms at all trophic levels. At pH 8.10, green concrete leachates have 4.85 TU for *Raphidocelis subcapitata* growth assay (sulfides concentration of 0.63 $mmol.m^{-2}$) against 3.0 TU for green concrete sample. However, sulfides are easily removed from natural solution by oxidation or evaporation.



Graphical abstract (color on web only): Green slag cement-based concrete releases cations and sulfur anions, including sulfides, associated to a very low ecotoxic effect.

Keywords: blast-furnace slag, greening effect, sulfides, cement, ecotoxicological assay, leaching test

1. Introduction

Granulated Blast Furnace Slag (GBFS) is generated during iron production, as a by-product, solidified by high-pressure water quenching. In 2019, about 371 Mt of blast furnace slag (BFS) have been produced worldwide (including GBFS, but also air-cooled, expanded, and pelletized), against 227 Mt in 2000 (Worldsteel Association 2020). Quenching of molten slag develops interesting properties, among which a vitreous structure allowing GBFS to be used as a Supplementary Cementitious Material (SCM) in civil engineering, combined to clinker in composite cements. GBFS is a sought-after SCM for its mechanical and durability properties in aggressive environment.

Hydrated and activated Ground GBFS (GGBFS) depicts a noticeable blue-green coloration after form removal, either with clinker or not. This transient phenomenon, called “greening effect”, disappears in days to weeks following the contact with air. Widely known from public workers, builders, or civil engineers, the greening effect has long been ignored in the research field until recently. Diverse hypothesis have been discussed in literature on the origin of the coloration, mostly involving iron compounds (Mansfeldt and Dohrmann 2001; Sioulas and Sanjayan 2001; Schwab et al. 2006), and sulfides (Vernet 1982). This latter hypothesis has been consolidated by a recent study using UV-visible-near infrared Diffuse Reflectance spectroscopy (Le Cornec et al. 2017). Le Cornec’s main findings sustain a mechanism of coloration involving optical transitions due to ionic sulfides radicals. Such chromophore species, $S^{2\cdot-}$ and $S^{3\cdot-}$, rather unusual, are well known in gemology to be responsible of the blue color of the semi-precious stone Lapis Lazulis (Steudel 2003; Chivers and Elder 2013). In the case of GGBFS-containing materials, it is most likely that these species are formed during early hydration, and trapped by solid solution of sulfides in aluminates hydrates (Vernet 1982; Le Cornec et al. 2017).

However, despite the widely known greening effect phenomenon, in tune with the use of GGBFS in local small constructions and in more important work, the transient vivid color has long been of minor concern in the research field. For operator's safety and environmental considerations, users of composite cements (CEM III type cements) have started asking questions over time to the cement industry about the environmental and health impact of colored GGBFS-containing materials. Some studies have focused on the global environmental impact of slags (Piatak et al. 2015), but none have focused on the potential effect of this transitory coloration. More generally, leaching tests have been used in the construction materials field to evaluate multiple environmental and geochemical aspects, such as diffusion and transport mechanisms or short and long-term leaching of hazardous substances (Hillier et al. 1999; Haga et al. 2005; Kamali et al. 2008; Müllauer et al. 2015; Märkl et al. 2017; Parron-Rubio et al. 2019).

Besides classical physicochemical screening of known compounds in eluates, ecotoxicity assessment allows the determination of a potential total toxicity of bioavailable substances/materials towards living organisms. However, not much researches have been conducted on classical construction materials, such as ordinary Portland cement, or GBFS (Kobetičová and Černý 2017). The green microalgae *Raphidocelis subcapitata* and the freshwater microcrustacean *Daphnia magna* are extensively used in aquatic toxicology studies (Lapa et al. 2007; Choi et al. 2013; Rodrigues et al. 2020). The bioassays performed using these species frequently follow international guidelines for chemicals. To determine the acute toxicity of a given chemical, the population growth rate of *R. subcapitata* and the mobility of *D. magna* are assessed according to the international standardized protocols ISO 8692 (2012) and ISO 6341 (2012), respectively.

A mixed approach involving chemical screening and ecotoxicological assessment has been recently emphasized towards construction products as more efficient to identify non-specific

effects of possible hazardous substances (Bandow et al. 2018). The ecotoxicological assessment of construction materials will be soon normalized by a coming European standard (draft standard "Construction Products - Assessment of release of dangerous substances – Determination of ecotoxicity of construction product eluates" FprCEN/TS, 2019).

The goal of the present study is to assess the environmental impact of the greening effect in GGBFS-containing materials (e.g. mortar or concrete) subjected to a leaching contact with water through a well-known standardized single-batch leaching test on solidified monolith. Two research axes are followed: i) an assessment of the physicochemical composition of leachates, followed by ii) an ecotoxicological evaluation of selected leachates with appropriate tests. *Daphnia magna* has been selected regarding its recognized sensitivity (Lapa et al. 2007; Rodrigues et al. 2020), combined with *Raphidocelis subcapitata* to assess a different trophic level. Since pH of leachates might be out of the living range of the organisms used, both ecotoxicological assays will be conducted with natural and adjusted pH (Kobetičová and Černý 2017).

2. Materials and methods

2.1. Materials of the study

Concretes and cement pastes were formulated with four industrial cements (CEM I and CEM III), and pure GGBFS pastes with three pure GGBFS of distinct origins directly obtained from producers. Cements were used to make one cement paste and concretes, with aggregates, and GGBFS were used to make pure pastes. The studied samples contained a variable amount of GGBFS, from 0% to 100%. The 0% sample was a concrete made with CEM I cement, used as a comparison reference. CEM I cement is mainly produced with clinker, gypsum and possibly some minor additions up to 5 wt.% and contains no GGBFS. Three commercially available

118 CEM III cements were used, mainly constituted from GGBFS, clinker and gypsum or
119 anhydrite, the class of which depends on the amount of GGBFS incorporated: CEM III/A
120 contains between 36 and 65% of GGBFS, CEM III/B between 66 and 80% of GGBFS, and
121 CEM III/C between 81% and 95% of GGBFS. The three pure GGBFS come from 3 different
122 blast furnaces (named "S1", "S2", and "S3"), with two S1 GGBFS used, one from a fresh
123 production (<2 months) and named "S1F", and a second from an older production in stock
124 (around 3 years) named "S1O".

125 The fineness of cements and GGBFS, given as Blaine specific surface area, was not modified
126 and ranged between 3600 and 5400 $cm^2.g^{-1}$ for the four cements, and between 4000 and 4815
127 $cm^2.g^{-1}$ for the four GGBFS. The BFS of fresh production was received as a sand 0/2 and and
128 was ground with a ring mill to about 4000 $cm^2.g^{-1}$. All data concerning the materials used in
129 the present study are gathered in Table 1.

130 **Table 1**. Composition of cements and GGBFS used as hydraulic binder for concretes and pure
131 pastes preparation.

Materials	GBFS	S^{2-}	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	SiO_2	SO_3
	wt.%	g(S)/100g					wt.%				
CEM I	0	-	5.44	62.91	3.03	0.81	1.89	0.08	0.20	20.69	3.33
CEM III/A	62	0.61	9.91	48.91	1.84	0.55	4.64	0.39	0.35	29.74	2.72
CEM III/B	71	0.55	9.56	47.62	1.15	0.55	4.99	0.24	0.22	31.32	3.52
CEM III/C	85	0.74	10.54	44.87	0.79	0.34	5.80	0.28	0.31	33.74	3.00
S1F	100	0.84	11.42	41.81	0.74	0.37	6.90	0.30	0.24	37.37	1.47
S1O	100	0.84	11.40	41.65	0.62	0.38	6.97	0.42	0.22	37.29	1.53
S2	100	0.79	11.89	41.49	0.35	0.41	7.16	0.29	0.27	37.57	0.86
S3	100	0.76	11.20	42.41	0.40	0.50	6.63	0.27	0.33	37.28	1.22

132

133 Description: Composition of CEM I, CEM III/A, CEM III/B, CEM III/C cements, and S1F
134 (fresh production of S1), S1O (stock production of S1), S2 and S3 GGBFS is given in this
135 table. GGBFS content is given as wt.%, sulfides content is given as g of sulfur for 100 g of
136 binder, and major elements are given as oxides in wt.%.

137 Concretes were formulated with cement and a siliceous alluvial aggregate (from Moselle
138 river), commonly employed for concrete preparation in the North-East of France. A cement
139 paste was formulated only with the CEM III/C cement, which have the highest GGBFS
140 content of CEM III type cements according to EN 197-1. Pure pastes of GGBFS were made
141 with a mix of several productions of a same production site, water and 5% w/w of NaOH as
142 activator of the hydraulic setting.

143 Cements and GGBFS major composition was established by X-Ray Fluorescence (XRF) with
144 a Bruker S4 Explorer spectrometer, on fused beads. Data were recovered and processed with
145 the SpectraPlus software (Table 1).

146 GGBFS has usually noticeable amounts of sulfur, usually between 0.2 and 3.5 wt.%, mostly
147 under reduced form (Glasser et al. 1988; Piatak et al. 2015). Thus, sulfides are quantified in
148 GGBFS-containing cements and pure GGBFS powders, accordingly to the French cement
149 standard (NF EN 196-2, 2013) through an acid distillation and subsequent recovery of H_2S in
150 an alkaline solution. Regarding to the standard, some modifications were made: an alkaline
151 buffer solution called Sulfides Anti-Oxidant Buffer (SAOB) was used as recovery solution,
152 allowing analysis with an ion-selective electrode. The SAOB solution was prepared with 67 g
153 of Ethylenediaminetetraacetic acid (EDTA), 35 g of ascorbic acid and 80 g of NaOH for one
154 liter. A bubble jar filled with the SAOB solution was connected to the outlet of the distillation
155 apparatus to recover the gases. At the end, the SAOB solution was analyzed with an ion-
156 selective electrode Thermo Scientific Orion Silver/Sulfide 9616BNWP plugged on an HP
157 multimeter (model 3478A). The electrode calibration was achieved with serial dilutions of a
158 sulfide stock solution. Dilutions were prepared daily from a 1000 $mg.L^{-1}$ Mettler Toledo
159 sulfide ISE standard, formerly standardized with an $AgNO_3$ solution. Silver calibration
160 solution was beforehand calibrated with a KCl solution. All calibrations were made using the
161 silver/sulfide electrode on a Tacussel TT-Processeur 2 automated titrator.

2.2. Concrete, cement and GGBFS paste preparation and conditioning

A Controlab Perrier concrete mixer was used for the preparation of concretes and of cement and GGBFS pastes. The water-to-binder ratio was kept to 0.5 for all preparations. Concretes were prepared according to the following formula: 885 $kg.m^{-3}$ of 0–5 mm sand, and 750 $kg.m^{-3}$ of 4–8 mm gravel, 210 $kg.m^{-3}$ of water and 420 $kg.m^{-3}$ of cement. Concrete samples were named "CSC1" for Concrete Sample with CEM I cement, "CSC3A" for CEM III/A based concrete, "CSC3B" for CEM III/B based concrete and "CSC3C" for CEM III/C based concrete. The cement paste was only made up with water and CEM III/C cement, to keep the water-to-binder ratio to 0.5, and is named "PC3C". The GGBFS pure pastes were made of GGBFS mixed with water with a water-to-binder ratio of 0.5, activated by NaOH with an activator-to-binder ratio of 5 wt.%. GGBFS pastes were named accordingly with previous denomination, i.e. "S1F" and "S1O" for fresh and old production of S1 GGBFS, "S2", and "S3" for the two others GGBFS used.

All compounds were mixed following the NF EN 196-3 (09/2017) standard for cement and GGBFS pastes, and the NF EN 196-1 (09/2016) standard for concrete samples. Cylindrical high density polyethylene (HDPE) bottles (7.2 cm diameter, 12.5 cm height) were used as molds. Paste is poured in 3 times with 30 s of vibration on a vibrating table between each pouring to ensure the maximum removing of air bubbles within the sample. Bottles are hermetically sealed and samples were cured for 3 days in dark tanks, at a 25°C temperature and relative humidity greater than 90%.

2.3. Color analysis

The blue-green color of GGBFS-containing materials is a key parameter in this study. However, visual color determination is not objective and greatly varies between individuals. A portable spectrophotometer Konica Minolta CM-700d objectively determined the color of

formulated samples, working in the L*a*b* (or CIELAB) color space and following the NF EN ISO/CIE 11664-4 (07/2019) standard. The measure used 3 parameters to quantify a color: one for the brightness (L*), and two for axis of opposite colors (a* and b*). The L* parameter ranges from the darkest (-100) to the brightest (+100), the a* parameter ranges from green (-60) to red (+60), and the b* parameter ranges from blue (-60) to yellow (+60).

The coloration measurements were conducted for all concrete and cement/GGBFS samples just after demolding. At least 3 different points were analyzed on the face of the samples in contact with the bottom of the molds ('bottom face'), and 5 points on the larger curved side ('side face'). Values were averaged for each side of each samples.

2.4. Tank Monolith Leaching test

The common and well-known tank monolith leaching test was chosen to mimic a green fair-faced concrete washed by flowing or surrounding water, in line with the recommendations to evaluate materials close to the effective real conditions (van der Sloot 2000). This test is presumed to be quite representative of real scenario since GGBFS-rich cements are often employed in wet aggressive environments, in particular in presence of sulfates or chlorides (Osborne 1999). In these conditions, concrete can be subjected to leaching by infiltrated rain water, or by flooding with groundwater or surface water. The tank monolith test used in the present study followed the XP CEN/TS 15862 (10/2012) standard. A solid monolith has been immersed in deionized water for 24 h, in a single batch and without water renewal. The ratio of Liquid on exposed solid surface Area (L/A) was defined to 12 cm^3/cm^2 for all samples. Average dimensions were of 7.2 cm diameter for 12.5 cm height. A minimal thickness of 2 cm of the water layer around the sample has to be observed, to facilitate a proper leaching on every faces. Thus, samples were put on a HDPE mesh disposed at the bottom of a 5 L HDPE container. Homogenization of the solution was ensured with a magnetic stirrer during the test.

210 *2.5. Leachates analysis*

211 Leachates were filtrated through a 0.45 µm pore size cellulose acetate filter. Four subsamples
212 were created: the first for pH and conductivity measurement with a Knick Portavo® 907
213 Multi portable multimeter, the second subsample for anions analysis, the third subsample was
214 mixed with SAOB solution for sulfides analysis, and the fourth was acidified with 2 mL
215 HNO_3 65% analytical grade (Merck) for element analysis.

216 Chlorides and sulfur species were the analyzed anions. Sulfates SO_4^{2-}, thiosulfates $S_2O_3^{2-}$ and
217 sulfides S^{2-} have been regularly reported into GGBFS-containing materials effluents (Glasser
218 et al. 1988; Gruskovnjak et al. 2006; Lothenbach et al. 2011). This is not surprising
219 considering that sulfur is on an average concentration of 1.27 wt.% in Fe-slag (which includes
220 BFS and steel slags), ranging from 0.38 to 3.15 wt.% (Piatak et al. 2015), with sulfur being
221 predominantly under the reduced sulfide form (Glasser et al. 1988). In the alkaline and mildly
222 reductive environment at work in leachates of GGBFS-containing materials, these sulfur
223 species are in a close thermodynamically stable range (Pourbaix and Pourbaix 1992). Anions
224 analysis was performed by ion chromatography. Subsample was filtrated a second time on
225 0.22 µm Sartorius filter, before being stored at 4°C in the dark. The Metrohm 882 Compact
226 ion chromatography was equipped with a Metrosep A Supp 5 Guard/4.0 precolumn (5 x 4.0
227 mm) and a Metrosep A Supp 4 column (250 x 4.0 mm). The conductimetric detection was
228 enhanced with a chemical suppressor. A mobile phase constituted of a 1.8 mM Na_2CO_3 and
229 1.7 mM $NaHCO_3$ mix, with 2% acetone, was used at a $1 mL.min^{-1}$ flow rate with 20 µL of
230 injection volume. Calibration was made with standard solutions, prepared with commercial
231 certified Alfa Aesar multi-anions 1000 $mg.L^{-1}$ (ref 041693) solution.

232 For sulfide analysis, the third subsample was mixed with SAOB solution at a 1:1 ratio into 50
233 mL polypropylene (PP) tubes, in a way to minimize the gas headspace. A modified USEPA

234 method 9215 (12/1996) was used to carry out sulfides analysis. Analyses were conducted in
235 the same way that solution coming from the acid distillation of solid samples to analyze
236 sulfides content (cf. section II.1).

237 The fourth acidified subsample was used for major and minor element analyses (Si, Al, Fe,
238 Mn, Mg, Ca, Na, K, Cr) by ICP-OES (Thermo Scientific iCAP 6500) and Atomic Absorption
239 Spectroscopy (Varian AA240FS).

240 *2.6. Ecotoxicological assessment*

241 *2.6.1. Microalgae: growth inhibition assay*

242 The green microalgal species used for the test was *Raphidocelis subcapitata* (SAG 61.81).
243 Briefly, six different replicates were conducted for each concentration, using a 96-well
244 microplate according to ISO 8692 (2012) guideline. Wells are completely filled with solution
245 and covered hermetically. Zinc (prepared from $ZnSO_4$) was used as positive control. The algal
246 culture in the exponential growth phase was diluted in ISO medium for freshwater algae (pH
247 8.1 ± 0.2) to obtain an inoculum for the test with a cell density of 20,000 cells.mL^{-1} and the
248 recommended dose of nutriments in exposure medium. As initial pH of leachates was very
249 high, pH has been considered as potential confounding factor. Thus ecotoxicity assessment
250 was led at initial pH and at adjusted value of pH 8.10. The test plates were incubated in a
251 room with continuous illumination of 100 µmol.m^{-2}.s^{-1} (cool-white fluorescent lamps) at 23 ±
252 2ºC. After 72 h of incubation at 23 ± 2°C, the fluorescence variation was measured at
253 wavelength of 485 nm for excitation and 640 nm for emission with VICTOR Nivo multimode
254 plate reader (PerkinElmer). EC50 were determined by using Regtox macro and results were
255 presented in TU (Toxic Unit = 100/EC50).

256 *2.6.2. Microcrustacea: immobilization assay*

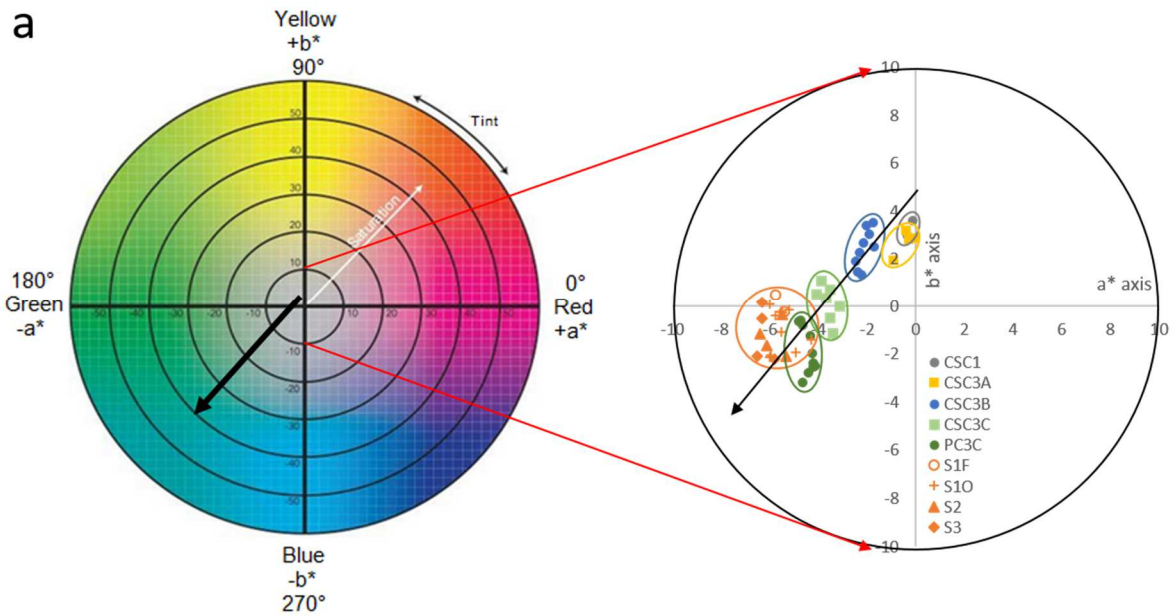
257 The microcrustacean immobilization assay was performed according to ISO 6341 (2012).
258 Three different experiments (with four replicates/tubes for each one) were performed. An
259 assay tube with 10 mL of culture medium (pH 7.8 ± 0.5, aerated overnight) plus the
260 appropriate concentration of leachate was prepared for each replicate. Tubes are completely
261 filled with solution and covered hermetically. Leachates were tested at initial pH and at
262 adjusted value of pH 8.10. Five young *D. magna* (up to 24 hours of life) were then added to
263 each tube. Potassium dichromate was used as positive control. The test tubes were covered
264 with aluminum foil to keep light out and were kept in an incubator at 20 ± 2ºC. Inhibition of
265 the mobility of the individual *D. magna* was determined visually after 48 h of exposure. EC50
266 were determined by using Regtox macro and results were presented in TU (Toxic Unit =
267 100/EC50).

268 # 3. Results and discussion

269 *3.1. Color evaluation of GGBFS-containing materials*

270 The color was evaluated immediately after demolding. The first result emerging from these
271 measurements is the overall green-blue color borne by all samples, with a clear evolution
272 towards the green-blue quadrant of the circle, as showed by the black arrow (Fig. 1a). The a*
273 parameter has a maximum of -0.24 for CSC1 and a minimum of -6.24 for the S3 GGBFS
274 (Fig. 1b). This parameter evolves quite linearly with the GGBFS content (R^2 = 0.876), with a*
275 decreasing while GGBFS content heightened, meaning color is moving towards the green side
276 of the axis. For concrete materials, CSC1 and CSC3A samples have a close value of a* (-0.24
277 and -0.40 respectively), despite CSC1 has no GGBFS content, and CSC3A having 11.5 wt.%
278 GGBFS in the total material. However, a slight increment of GGBFS in the total material

leads to a noticeable raise of the a* parameter. CSC3B sample has 1.7 wt.% more of GGBFS than CSC3A (for a total of 13.2 wt.%), with a* decreasing to -2.09, and CSC3C sample has 4.3 wt.% more of GGBFS than CSC3A (total of 15.8 wt.%) with a* decreasing to -3.61. Comparatively, the high increase of GGBFS content for PC3C to 56.7 wt.% doesn't go along with a steep decrease of a*, lessening to -4.43. For the four GGBFS pure paste samples, a* oscillates between -5.47 and -6.24. The freshness of the GGBFS production does not seem to influence much the a* parameter, by comparing a* value of S1F and S1O.



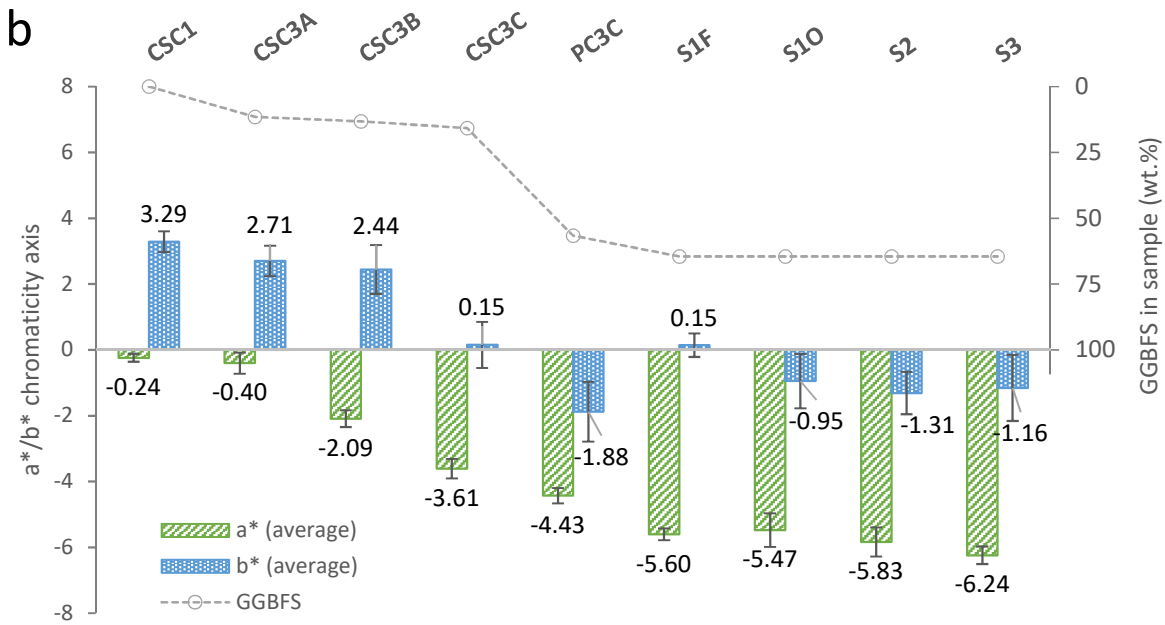


Figure 1 (color on web only). Dispersion of samples on a* and b* axis depicted on the chromatic circle representing the L*a*b* CIE 1976 color space, modified from www.colorimax.com (a), and average values for a* and b* parameters and wt.% proportion of GGBFS in concrete, cement and GGBFS paste samples, with error bars standing for standard deviation (SD) (b).

The b* parameter has a maximum of +3.29 for CSC1 sample and a minimum of -1.88 for PC3C sample. Its evolution is less linear, PC3C having the smallest value while having not the highest GGBFS content (56.7 wt.% against 64.5 wt.% into GGBFS pure paste). However, the coefficient of correlation between b* parameter and GGBFS content being $R^2 = 0.774$ still indicates a positive and noticeable correlation between those two parameters, b* decreasing while GGBFS content raises, meaning that color of the samples is moving towards the blue side of the axis. Similarly than for a*, the addition of GGBFS from CSC1 to CSC3A comes with a slight decrease of b*, from 3.29 to 2.71. However, a discrepancy is observed not between CSC3B sample and CSC3C sample (b* decreasing from 2.71 to 2.44), but between

CSC3B and CSC3C, b* falling to 0.15, for a +2.6 wt.% increase of GGBFS content. The evolution of samples from concretes to pure paste goes along with a decrease of b* from 0.15 for CSC3C concrete to -1.88 for the PC3C. Then, for the four GGBFS pastes, the b* value oscillates between 0.15 and -1.31.

Nevertheless, this is noticeable that the color of samples is much more spread on the b* axis than the a* axis (Fig. 1a). Most of the samples are more scattered vertically on the blue-yellow axis. It seems that the color characterization of GGBFS-containing materials might be more reliable on the a* component in the L*a*b* color space, and more uncertain on the b* component.

The color investigation of GGBFS samples is generally consistent with the common visual observation made during civil engineering works involving GGBFS-containing concretes. Samples color is tending towards the green-blue color after casting of formwork, color which usually fade away in days. The color of GGBFS pure paste with GGBFS originated from different cast iron production sites seems to have some slight differences, a* ranging from -5.47 for S1O to -6.24 for S3, and b* from 0.15 for S1F to -1.31 for S2. Despite these differences, it is difficult to attribute these variations to the different origins of GGBFS, because of the relatively important standard deviation SD, particularly for b* parameter (SD of b* ranging from 0.36 to 1.00).

3.2. Leachates chemistry of tank monolith leaching test

A tank monolith leaching test was performed over 24 h for all samples and leachates were characterized immediately after. Concentrations in eluates as $mg.L^{-1}$ (and $mmol.L^{-1}$) are normalized with the L/A ($L.m^{-2}$) ratio as $mg.m^{-2}$ (and $mmol.m^{-2}$).

3.2.1. Metals measurement

The results are given in Table 2. Minor elements Fe, Mn and Cr were monitored because of their hypothetical -but never demonstrated- role in the greening effect. The Fe^{2+} and Cr^{3+} ions give the green color in silicates minerals like olivine or diopside. In addition, chromium was also monitored due to its well-known presence in cements and its hazardous behavior when under chromate form (Cr^{6+}) towards environment and human health. In the present study no chromium was found in the leachates, as well as no iron nor manganese, except iron in CSC1 leachates to an amount of 0.06 $mmol.m^{-2}$ close to the limit of detection (Table 2). The absence of chromium in leachates is consistent with the usual utilization of cement (either with GGBFS or not) for the treatment by stabilization/solidification of hazardous wastes contaminated with trace metals such as chromium (Paria and Yuet 2006). Considering the overall highly alkaline conditions at work in concretes and pastes samples, iron and manganese were not expected to be leached in detectable amounts.

Table 2. Concentrations of major and minor elements elements in the leachates of the tank monolith leaching test

	Na	Ca	K	Al	Si	Fe*	Mn**	Cr***	Ca/Si	Al/Si
				mmol.m^{-2}					-	-
CSC1	80.76	524.19	82.43	1.63	5.48	0.06[a]	n.d.	n.d.	95.61	0.30
CSC3A	118.24	178.79	45.89	4.92	9.89	n.d.	n.d.	n.d.	18.08	0.50
CSC3B	57.34	172.92	42.80	4.24	11.89	n.d.	n.d.	n.d.	14.55	0.36
CSC3C	35.68	105.37	13.49	5.23	12.90	n.d.	n.d.	n.d.	8.17	0.41
PC3C	38.78	154.48	27.00	8.39	19.61	n.d.	n.d.	n.d.	7.88	0.43
S1F	1861.59	53.23	14.99	15.33	26.81	n.d.	n.d.	n.d.	1.99	0.57
S1O	1893.76	40.26	14.98	13.53	20.83	n.d.	n.d.	n.d.	1.93	0.65
S2	2224.62	36.78	12.51	15.15	25.33	n.d.	n.d.	n.d.	1.45	0.60
S3	1522.16	26.82	9.12	12.43	18.90	n.d.	n.d.	n.d.	1.42	0.66

n.d.: not determined. Result is lower than the limit of detection, which prevents from calculating concentrations as $mmol.m^{-2}$

[a] Fe concentration in leachate = 2.9×10^{-2} $mg.L^{-1}$

* LD(Fe) = 1.0×10^{-2} $mg.L^{-1}$

** LD(Mn) = 1.0×10^{-3} $mg.L^{-1}$

*** LD(Cr) = 2.0×10^{-1} $mg.L^{-1}$

Description: Concentrations of major elements (Na, Ca, K, Al, Si) and minor elements (Fe, Mn, Cr) in leachates of the tank monolith leaching test are given as $mmol.m^{-2}$. Ca/Si and Al/Si ratio are also displayed.

Major elements

Na, Ca, K, Al and Si were the major elements released in leachates (Table 2). For alkaline metals, potassium is released in samples leachates between 9.12 and 82.43 $mmol.m^{-2}$. The global trend is a reduction in leachates with the increase of GGBFS. Potassium releases are roughly correlated with the initial potassium content as K_2O ($R^2 = 0.797$) (Table 1), probably also controlled as a very soluble element by diffusion in matrix which porosity decreased with the increased amounts of GGBFS. Sodium is a highly soluble cation quantified in cement-made samples leachates at concentrations between 35.7 and 118.2 $mmol.m^{-2}$. Sodium concentrations are ten to twenty times higher in GGBFS pure pastes leachates, until 2224 $mmol.m^{-2}$ for S2 paste leachates. Such discrepancy is explained by the addition of 5 wt.% NaOH to the initial mix of GGBFS pure pastes to accelerate the setting kinetic.

Calcium is the most released element, with exception of sodium in GGBFS pure pastes. Calcium concentrations range between 26.82 $mmol.m^{-2}$ for S3 GGBFS paste and 524.19 $mmol.m^{-2}$ for CSC1 concrete, and calcium leaching correlates well with the total concentration as CaO in cement and GGBFS ($R^2 = 0.982$). Aluminum and silicon leaching are also quite correlated to their total oxide contents with respective correlation coefficient of 0.637 and 0.766. In leachates, aluminum is analyzed to concentrations between 1.63 $mmol.m^{-2}$ for CSC1 concrete and 15.33 $mmol.m^{-2}$ for S1F paste, and silicon between 5.48 $mmol.m^{-2}$ for CSC1 concrete and 26.81 $mmol.m^{-2}$ for S1F paste.

The correlation between major elements leaching and their oxide content is linked to the similar raw composition of cement and BFS, mainly composed of CaO, SiO_2 and Al_2O_3.

However, one of the main differences between both is the respective proportion of the oxides. From Table 1 and compared to the four GGBFS, CEM I cement (mainly made of Portland and minor secondary constituents) is richer in CaO (62.91 versus 41.49 – 42.41 wt.%), and depleted in Al_2O_3 (5.44 versus 11.40 – 11.89 wt.%) and SiO_2 (20.69 versus 37.28 – 37.57 wt.%). In composite cements, CEM III/A, CEM III/B and CEM III/C, the partial complement of Portland cement by GGBFS from 62 to 85 wt.% modifies the mass proportion of main oxides in the mix. In fact, increasing the GGBFS content heightens the SiO_2 and Al_2O_3 content and decreases the CaO content, which is reverberated on the further available elements for the formation of cement hydrates after hydration. Experimentally, the minerals observed in hydrated cement-slag systems are portlandite, C–(A)–S–H, ettringite, Afm and an hydrotalcite-type phase (Lothenbach et al. 2011). In GGBFS high-substituted mix, the lack of available calcium leads to the consumption of portlandite hydrates to supply the precipitation of C–S–H (Kolani et al. 2012). Furthermore, enrichment in Al_2O_3 leads to the greater incorporation of aluminum into C–S–H to form C–A–S–H, as well as increasing other aluminates hydrates (Lothenbach et al. 2011).

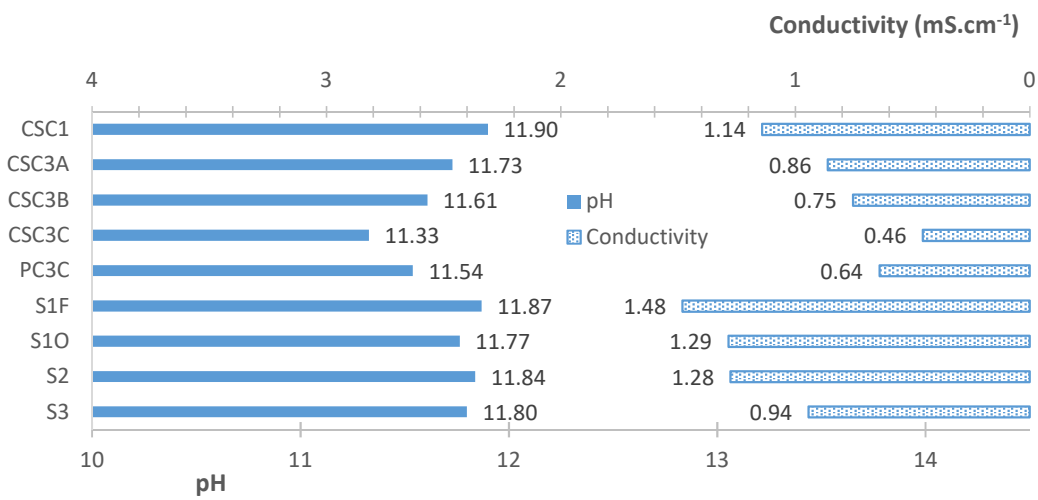
Ca/Si and Al/Si ratios

Discrepancies in the quantities and composition of hydrates formed during hydration then influence the chemistry of leachates, which is noticeable in the evolution of Ca/Si and Al/Si ratios between all systems (Table 2). Increasing the proportion of GGBFS in the mix leads to a net decrease of the Ca/Si ratio, from 95.61 for CSC1 to 8.17 for CSC3C. For GGBFS pure pastes, Ca/Si ratio oscillates between 1.42 and 1.99. Calcium is less eluted in leachates of GGBFS-containing pastes and concretes mostly because of two alongside mechanisms. Firstly, calcium is less available to leaching solution due to the portlandite consumption by C–S–H. Analyses of CEM I and CEM III/A cement pastes by TGA showed that GGBFS-containing paste contained less than half the portlandite content of CEM I paste (Kamali et al.

2008). In addition to ions in interstitial solutions, portlandite is the main source of calcium leaching in cement-based materials, while silicon mainly comes from the incongruent dissolution of C–S–H (Faucon et al. 1996; Müllauer et al. 2015), although depending on the leaching solution C–S–H may also contribute to calcium leaching (Kamali et al. 2008). Secondly, one of the main structural effect of GGBFS addition in cement mix is the reduction of porosity, combined to a more important resistance to ions movement increasing with the decrease of Ca/Si ratio of C–S–H (Luan et al. 2012). In cement-based materials, the transport is controlled by diffusion mechanisms, depending on the porosity (Haga et al. 2005). This porosity effect is particularly seen on sodium leaching. Although CSC3C concrete has a higher Na_2O content with 0.31 wt.% than CSC3B (0.22 wt.%) or CSC1 (0.20 wt.%), only 35.68 $mmol.m^{-2}$ are leached, versus 57.34 $mmol.m^{-2}$ for CSC3B and 80.76 $mmol.m^{-2}$ for CSC1, consistently with literature (Müllauer et al. 2015). The Al/Si ratio is heightened with the increase of GGBFS from 0.30 for CSC1 to 0.41 for CSC3C with a higher than expected value of 0.50 for CSC3A. Both aluminates and silicates evolve in the same way with the substitution of Portland cement with GGBFS. In GGBFS pure pastes, Al/Si ratio oscillates in a narrow range between 0.57 and 0.66. Despite GGBFS have a very similar composition regarding main oxides, i.e. Al_2O_3, CaO and SiO_2, it seems that other factors influence the composition of leachates. For example, S1F and S1O leached 53.23 and 40.26 $mmol.m^{-2}$ of Ca respectively, or 26.81 and 20.83 $mmol.m^{-2}$ of Si. Fresh production seems to be more easily "leachable". Further investigations should be conducted to evaluate factors that lead to the different leaching behavior observed. In particular, mineralogical investigations should focus on the identification of hydrates formed and their relative proportions. Finally, alkalis Na and K are quickly and easily eluted because of their weak bonding with C–S–H gels (Müllauer et al. 2015).

3.2.2. pH and conductivity

Overall, the pH measured in leachates of samples is greatly alkaline, with values ranging from 11.33 to 11.90 (Fig. 2). Two trends are identifiable, depending on the materials assessed, concrete or pure paste. For leachates of concrete samples, pH values are ranging from 11.33 for CSC3C concrete to 11.90 for CSC1 concrete, almost linearly diminishing with the increased concentration of GGBFS. In leachates of PC3C sample, pH is higher than for CSC3C with 11.54 units despite GGBFS content increase (56.7 wt.% of the total sample). However, in concretes the hydraulic binder only represents 18.5 wt.% of the total sample mass against 66.7 wt.% in cement paste. The pH raise can be linked in this case to the greater proportion of binder accounting for the total mass of the sample. A second trend is related to the GGBFS pure paste, pH of which is oscillating between 11.77 and 11.87 units. Compared to the group of concrete samples, GGBFS pure pastes produce leachates with higher pH, most probably attributed to the 5 wt.% NaOH addition used for the hydraulic latent setting of GGBFS. Therefore, GGBFS of different origins conduct to minor pH differences.



435 **Figure 2 (color on web only).** pH in leachates (blue plain bars) and conductivity (blue dotted
436 bars) of leachates from concretes, cement paste and GGBFS pure pastes after having been
437 subjected to the tank monolith leaching test

438 Conductivity of the leachates ranges from 0.46 $mS.cm^{-1}$ to 1.48 $mS.cm^{-1}$ (Fig. 2). As well as
439 for pH results, a trend is clearly visible for leachates of concrete samples, with a sharp drop
440 from 1.14 $mS.cm^{-1}$ for CSC1 to 0.46 $mS.cm^{-1}$ for CSC3C. Thus, conductivity decrease is well
441 correlated to the increase of GGBFS content in the four concrete samples ($R^2 = 0.849$).
442 Conductivity for leachate of cement paste PC3C is higher than for CSC3C concrete (0.64
443 versus 0.46 $mS.cm^{-1}$), most probably because of the lack of aggregates and the simultaneous
444 augmentation of the relative fraction of binder. However, unlike pH results, conductivity of
445 leachates of GGBFS pure paste shows some discrepancies. In particular, despite the very
446 close chemical composition of the four pastes (Table 1), conductivity ranges from 0.94
447 $mS.cm^{-1}$ for S3 sample to 1.48 $mS.cm^{-1}$ for S1F sample (Fig. 2). For the four GGBFS, XRF
448 results show that Al_2O_3 ranges between 11.20 and 11.89 wt.%, CaO between 41.49 and 42.41
449 wt.% and SiO_2 between 37.28 and 37.57 wt.%, for the main components of GGBFS employed
450 to make pure pastes (Table 1).

451 **Relation with cement hydrates**

452 In cement-based materials, portlandite dissolution is responsible for the alkaline pH available
453 in interstitial water. The replacement of Portland cement by GGBFS, and the global increase
454 of GGBFS in a cement mix, induces a reduction in the CaO total content. Thereby, such
455 hydrated systems are deficient regarding to portlandite, leading to a lower pH in interstitial
456 water. In addition to the lesser portlandite precipitated, pH is reduced concomitantly in
457 GGBFS highly substituted systems by the competition of soluble sulfur species negatively
458 charged in pore water with dissolved hydroxides ions to conserve electro-neutrality of the
459 solution (Gruskovnjak et al. 2006; Lothenbach et al. 2011). In leachates, pH is lower for

460 highly substituted systems, as well as calcium leaching compared to a CSC1 concrete (Table
461 2). Concomitantly to the availability of soluble species and elements such as $Ca(OH)_2$,
462 porosity and potential resistance to ions movement created by the morphological differences
463 of precipitated hydrates (in particular C–S–H becoming 2D-shaped when Ca/Si ratio
464 decreases) may also affect pH and conductivity in the same way it affects leaching of
465 elements by reducing the potential mobility in a diffusion-controlled system (Table 2). Then,
466 the lower permeability of GGBFS high-substituted systems will lessen the release of major
467 elements (Na, Ca, K) as well as hydroxide ions, except in GGBFS pure pastes where Na is
468 highly concentrated due to the use of NaOH as activator and leached in important quantities
469 (1800 – 2200 $mmol.m^{-2}$), leading to higher than expected conductivities.

470 *3.2.3. Sulfur chemistry*

471 Sulfur anions (sulfides, thiosulfates, sulfates) have been quantified into the leachates of
472 samples subjected to the tank monolith leaching test (Fig. 3). Sulfates are leached by all
473 samples, between 108 $mg.m^{-2}$ for CSC1 sample and 960 $mg.m^{-2}$ for PC3C (Fig. 3a).
474 Thiosulfates are released by all samples, except for CSC1, between 192 and 660 $mg.m^{-2}$, as
475 well as sulfides which are released between 6.6 and 275 $mg.m^{-2}$. Sulfates ions represent 17.1
476 to 100.0% of the molar fraction of the three analyzed sulfur anions (Fig. 3b). Sulfates ions are
477 the major ion released in CSC1 (100.0%), CSC3B (60.6%), CSC3C (66.9%) and PC3C
478 (69.3%) leachates, whereas thiosulfates represent 52.0% in CSC3A leachates versus 41.7%
479 for sulfates. For GGBFS pure pastes, sulfides are the major ion released, representing from
480 44.2 to 53.5% of the total molar fraction of sulfur anions. Then, thiosulfates account for 29.4
481 to 39.1%, with sulfates being the minor ion.

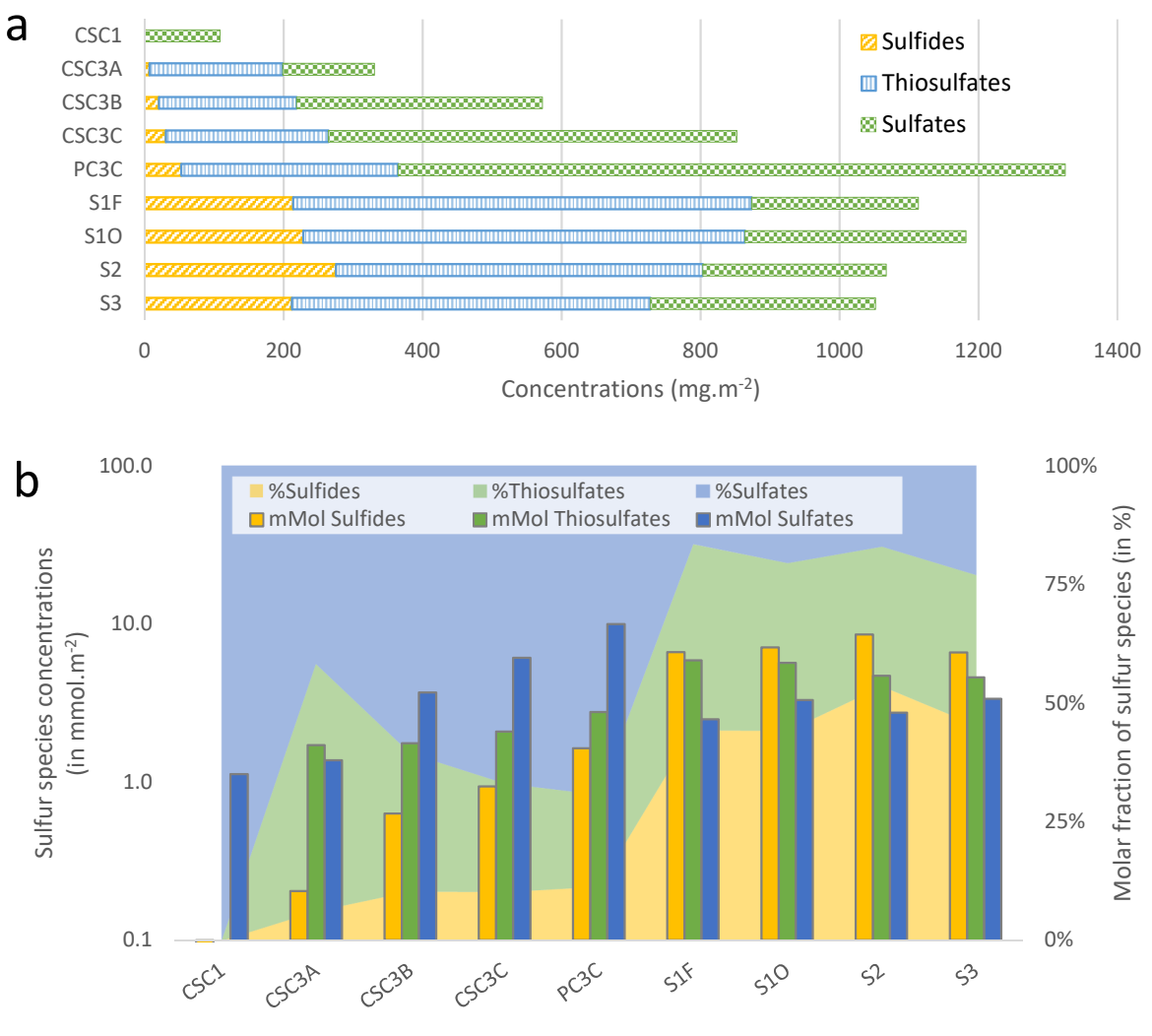


Figure 3 (color on web only). Mass concentration of anions sulfides S^{2-}, thiosulfates $S_2O_3^{2-}$, and sulfates SO_4^{2-} (as $mg.m^{-2}$) (a), molar concentration and respective molar proportions of each anions as a percent of total sulfur anions analyzed (b) in leachates of concretes, cement paste, and GGBFS pure pastes subjected to the tank monolith leaching test.

Concretes and CEM III/C cement paste

In absolute value, the three sulfur anions are increasingly released when GGBFS substitution increase in the leachates of the four concretes. More generally, evolution of sulfur anions releases between the four concretes and the cement paste follows a similar pattern for sulfides and sulfates, substantial enrichment between CSC3A and CSC3B (almost triple), and then +50 to +75% between CSC3B and CSC3C, and CSC3C and PC3C respectively. On the

contrary, thiosulfates releases are almost stable around 200 $mg.m^{-2}$ at the same time (Fig. 3a). Sulfides, missing for CSC1, appear in CSC3A leachates with 6.6 $mg.m^{-2}$, and increase to 20.3 $mg.m^{-2}$ for CSC3B, and 30.1 mg/m^2 for CSC3C. For PC3C, sulfides and sulfates concentrations are almost doubled, but not thiosulfates.

Sulfates as a major release in leachates of concretes and cement paste is not surprising, since cements include setting time regulators e.g. gypsum or anhydrite which readily precipitate with aluminates to form ettringite (Aft) and monosulfoaluminate (Afm). Still, sulfides are released in concrete leachates in far from negligible amounts, accounting for 6 to 10% of the molar fraction in concretes leachates, that is to say from 6.6 to 30.1 $mg.m^{-2}$ in term of mass (Fig 3a, 3b). This result can be expected, considering that GGBFS included into CEM III cements bring sulfides ions, for a total between 0.55 and 0.74 wt.% in the three CEM III cements.

Origin of reduced sulfur anions

GGBFS is actually a rather reducing material than Portland cement, and redox potential in cement mix with high proportion of GGBFS is able to reach -250 to -350 mV (versus Calomel) (Angus and Glasser 1985; Macphee et al. 1988). Such reducing environment leads to reduced form of sulfur, mostly as amorphous sulfides (Glasser et al. 1988; Roy 2009). Although most of the sulfides ions solubilized in pore water are precipitated with hydrates in early hours after mixing, these species are then gradually released in interstitial solutions (Vernet 1982). The early precipitation of sulfides with first hydrates created when GGBFS is hydrated is probably at the origin of the greening effect (Vernet 1982; Le Cornec et al. 2017). In pore solution, sulfides are oxidized with available dissolved molecular oxygen, leading to main oxidation products, thiosulfates and sulfates (Glasser et al. 1988; Gruskovnjak et al. 2006; Lothenbach et al. 2011). However, narrow porosity of cement-based materials limit the oxygen diffusion, hence sulfides ions are partly preserved from oxidation. When samples are

519 submitted to leaching, sulfur anions are released in the leachates from interstitial solution.
520 Sulfides, being the most sensitive to oxidation by molecular oxygen, might be oxidized during
521 the leaching process, depending on the oxygen diffusion in leaching solution.

522 In concretes leachates, the difference between sulfates and sulfides releases is noticeable.
523 Considering molar concentrations, the ratio between sulfates and sulfides releases is overall
524 constant in concretes leachates (except CSC1), and roughly oscillates around 6. Although
525 sulfates are released at lower concentration in CSC1 leachates, it is difficult to conclude on
526 the effective impact of GGBFS on sulfate leaching because of the variable additions of
527 gypsum or anhydrite in cement mix. Whether gypsum or anhydrite, sulfates in cement mix
528 precipitate with aluminates to form Afm and Aft hydrates, further remobilized by leaching
529 solution through surface dissolution, explaining sulfates releases for cement-based samples
530 (Müllauer et al. 2015). A good agreement can be found between quantities of secondary
531 constituents added to cement clinker, and sulfates releases, with 1.12 and 1.37 $mmol.m^{-2}$ in
532 CSC1 and CSC3A, and 3.69 and 6.12 $mmol.m^{-2}$ in CSC3B and CSC3C (Fig. 3b).

533 On the contrary, thiosulfates presence cannot be explained by the dissolution of a pre-existent
534 mineral specie. Consequently, thiosulfates have only two way of production: either by
535 oxidation of sulfides included in GGBFS, or by reduction of sulfates. However, sulfate
536 reduction is highly unlikely to happen in aerated environment without a microbial mediation
537 (Pourbaix and Pourbaix 1992; Miao et al. 2012). On the other hand, sulfides are very sensitive
538 to oxidation in aerated water, in particular in alkaline solution with pH higher than 11.5 (Kuhn
539 et al. 1983). In concretes leachates, thiosulfates releases are almost in the same order of
540 magnitude than sulfides in terms of molar concentrations (Fig. 3b). The thiosulfates to
541 sulfides molar ratio is about 8.3 in CSC3A leachates, and quickly decrease to 2.8 in CSC3B,
542 2.2 in CSC3C, and 1.7 in PC3C. Else, if the oxidation of sulfides to sulfates is
543 thermodynamically favored, it has been kinetically observed that the oxidation of sulfides by

544 molecular oxygen leads to thiosulfates as the main products, when pH is alkaline, i.e. pH >
545 8.5 (O'Brien and Birkner 1977; Kleinjan et al. 2005). In such pH–Eh conditions, thiosulfates
546 are stable for weeks, and tend to accumulate, with low oxidation to the final product, sulfates.
547 Therefore, only a minor part of the sulfates production in leachates is likely to come from
548 sulfides oxidation.

549 **GGBFS pure pastes**

550 In GGBFS pure pastes, sulfides releases are much more important than in the PC3C cement
551 paste, with values between 211 and 275 $mg.m^{-2}$. Sulfates are in the same order of magnitude,
552 being released in leachates with values between 240 and 324 $mg.m^{-2}$. Thiosulfates amounts
553 are much more important in GGBFS pastes leachates, ranging from 516 to 660 $mg.m^{-2}$. In
554 GGBFS pastes, no source of sulfates are added, and all sulfur species recovered in leachates
555 come from the slag itself. Considering the molar ratio, the sulfates to sulfides ratio is about
556 0.3 – 0.5, the thiosulfates to sulfides ratio is about 0.5 – 0.9, and the thiosulfates to sulfates
557 ratio is about 1.4 – 2.4. Then, it can be firstly concluded that the amounts of sulfides observed
558 into leachates are in good agreement with both sulfates and thiosulfates releases, and secondly
559 that as stated in literature, thiosulfates represent the main oxidation products in alkaline
560 solutions, but not the only one (O'Brien and Birkner 1977; Kleinjan et al. 2005).

561 ### *3.3. Ecotoxicological assessment of leachates*

562 A positive control solution containing increasing concentrations of zinc (Zn^{2+}) was tested for
563 both ecotoxicity assays. In these cases, an appropriate concentration-response curve was
564 observed and the EC_{50} was determined as 0.017 ± 0.004 $mg.L^{-1}$ for algae, and 1.96 ± 0.18
565 $mg.L^{-1}$ for daphnids. These values were according to validity criteria of ISO standards of the
566 both ecotoxicity tests.

567 The results obtained by performing *R. subcapitata* growth rate and *D. magna* mobility tests
568 are displayed in Table 3: in a general way, leachates induced very low ecotoxic effects on
569 aquatic organisms, as the maximum value did not exceed 5 TU (toxic units). There was no
570 statistical difference (ANOVA followed by Tukey test) between data obtained with CEM I
571 cement, used as a comparison reference, and CEM III/B cement, mainly constituted from
572 GGBFS (71% cf. Table 1) and clinker. Nevertheless, for daphnia, it is noteworthy that
573 ecotoxic effects were more important when pH was high (pH = 12.5), compared with adjusted
574 pH of 8.1. In the Toxicity Classification System, a compound with TU between 1.0 and 10.0
575 is classified in Class III, meaning potentially low acute toxicity (Persoone et al. 2003). Both
576 CSC1 and green CSC3B leaching samples, for both adjusted and natural pH, are classified as
577 Class III towards D. magna and R. subcapitata.

578 **Table 3**. Ecotoxicological results for CSC1 and green CSC3B concretes leachates

Materials	pH	*Raphidocelis subcapitata* (24h)		*Daphnia magna* (24h)		*Daphnia Magna* (48h)	
		EC50	TU	EC50	TU	EC50	TU
	-	% of leachate	-	% of leachate	-	% of leachate	-
CSC1	8.10	33.35	3.00	84.06	1.19	72.30	1.38
CSC1	12.50	31.30	3.19	21.91	4.56	19.60	5.10
CSC3B	8.10	20.62	4.85	64.82	1.54	47.31	2.11
CSC3B	12.10	20.16	4.96	41.85	2.39	39.95	2.50

579 EC_{50} = half maximal effective concentration; TU = Toxic Units

580 Description: Eluates of Tank monolith leaching test of CSC1 (reference, CEM I cement) and
581 green CSC3B concretes samples are subjected to growth inhibition assay (*Raphidocelis*
582 *subcapitata*) to assess chronic toxicity, and immobilization assay (*Daphnia magna*) to assess
583 acute toxicity. Results are given as EC50 (in % of leachate in the solution) and Toxic Units
584 (TU).

585 From a general point of view, not much data are available on the ecotoxicity of usual
586 construction materials (Kobetičová and Černý 2017). Considering the physicochemical
587 characteristics of Ordinary Portland Cement (OPC) concretes, there is no objective reason to
588 consider it as ecotoxic, since OPC does not release detectable concentrations of toxic trace
589 metals (Hillier et al. 1999). Incidentally, leaching of OPC pastes does not show phytotoxicity
590 (Märkl et al. 2017). When OPC concrete is used as recycled aggregates, TU are up to 6.8 at
591 48h to *D. magna*, close to our result for CSC1 of 5.10 TU at 48h (Rodrigues et al. 2020).

592 **Impact of pH on ecotoxicity**

593 When GGBFS is added, ecotoxicity is lowered towards *D. magna* test at initial pHs (12.50 for
594 CSC1 against 12.10 for CSC3B), but slightly increased at adjusted pH of 8.10. In fact, pH is a
595 factor that can explain a potential acute toxicity, in particular for sensitive living organisms
596 such as *D. magna*. And the addition of GGBFS usually decreases pH. Either at 24h or 48h, the
597 increase of pH also heightens the acute toxicity: for CSC1, with pH increasing from 8.10 to
598 12.50 (natural pH of leachates), TU increased from 1.19 to 4.56 in 24h and from 1.38 to 5.10
599 in 48h (Table 3). For CSC3B, pH increasing from 8.10 to 12.10 (natural pH of leachates)
600 induced an increase in TU from 1.54 to 2.39 in 24h, and from 2.11 to 2.50 in 48h. Results
601 show the very low sensibility of *R. subcapitata* to pH effect, with a negligible increase of
602 +0.19 for CSC1 and +0.11 for CSC3B. Other studies show that at alkaline pH of 12 produced
603 by cement system such as OPC, daphnia can be entirely immobilized (Choi et al. 2013). The
604 addition of GGBFS can induce a higher ecotoxicity, up to 17.67 TU, but with pH lowered to
605 8-9, this ecotoxicity is reduced to about 2. Effect of pH on D. magna is also observed after
606 48h on sewage sludge combustion ashes, with TU ranging from < 1.1 to 10.0 for pH between
607 8.0 and 11.3 (Lapa et al. 2007).

608 **Impact of sulfides on ecotoxicity**

609 Apart from pH, cations and anions are likely to represent a harm to living organisms, but only
610 if they are bioavailable. Bioavailability highly depends on physical and chemical parameters,
611 and in the case of the leaching of a solid material, it mainly depends on particle size
612 distribution, porosity, wet/drying cycles, storage conditions, hydrophobicity (Kobetičová and
613 Černý 2017). In the case of leaching of GGBFS cement-based materials, the only potentially
614 harmful analyte detected is sulfide ion. From the adjusted pH of 8.1 to the natural pH of
615 eluates, sulfides are highly available as they are under HS^- or S^{2-} soluble form (Pourbaix and
616 Pourbaix 1992). Since *R. subcapitata* is little sensitive to pH, sulfides could explain the
617 slightly higher ecotoxicity observed with both pH, and in the same way the slightly higher
618 ecotoxicity for *D. magna* assay at adjusted pH (Table 3). In the case of natural pH, *D. magna*
619 being highly sensitive to pH, in particular in such extreme conditions, the higher ecotoxicity
620 observed for CSC1 may rather be attributed to the higher pH. In fact, *D. magna* has been
621 proven as a highly sensitive organism towards sulfides, as well as many freshwater and
622 marine invertebrates (Wang and Chapman 1999; Küster et al. 2005). For lower trophic levels,
623 sulfides impact is variable. Marine bacteria are diversely affected, with growth rate modified
624 or interrupted (Mirzoyan and Schreier 2014), or microalgae's photosynthesis disrupted and
625 viability lowered (González-Camejo et al. 2017). Although, sulfide ion may play a more
626 subtle role in natural water and environment since it has been recognized to reduce the
627 toxicity caused by available metal by binding with them and reducing their bioavailability to
628 organisms such as *D. magna* (Bianchini et al. 2002).

629 More generally, and in another field, blast-furnace and steel-making slags have also been
630 evaluated as potentially suitable for an environmental amendment use (with dilution to limit
631 alkaline pH effects), showing low ecotoxicity of their leaching assessed by microalgae
632 *Chlorella sp*., cladocerans *Ceriodaphnia dubia*, and bacteria *Vibrio fischeri* (Wendling et al.
633 2013). Analysis of the composition of GGBFS concretes leachates has led to the conclusion

634 that they are very similar to those of OPC leachates, and are thereby safe environmentally
635 (Parron-Rubio et al. 2019). All these results should lead to the conclusion that the use of
636 GGBFS, whether as construction material in civil engineering or other fields, does not
637 represent a threat to the environment, including the greening effect whatever it is originated
638 from. Two major points have been highlighted, the alkaline pH and the release of sulfides
639 ions. For alkaline pH, GGBFS lowers the pH in concretes compared to OPC, which can only
640 be an improvement towards the receiving environments. Regarding the sulfides release, they
641 can be a minor ecotoxic threat to living organisms. However, sulfides are very sensitive to
642 oxidation by molecular oxygen, especially around natural pH of 7.0–8.0. Under pH 8, sulfides
643 equilibrium is displaced towards H_2S which is a low soluble specie in water, and hydrogen
644 sulfide evaporates being then diluted and oxidized in ambient air. Further investigations
645 should be conducted on the aging of cement-based materials containing GGBFS, including
646 the assessment of the ecotoxicological impact.

647 4. Conclusions

648 - The temporary greening effect of GGBFS-containing materials has no particular
649 impact neither on the chemistry of leachates, nor ecotoxicity.
650 - The alkaline pH, usually around 11–12.5, is the main issue with cement-based
651 materials in general, but in real conditions eluates are usually quickly buffered by
652 carbonation or diluted in the soil or running water.
653 - High pH may impact the most sensitive organisms, such as the crustacean *Daphnia*
654 *magna* much more sensitive to extreme pH than the algae *Raphidocelis subcapitata.*
655 - GGBFS contains noticeable amounts of sulfides easily released when GGBFS-
656 concretes are leached. Very slight ecotoxic effects attributed to sulfides are observed

for *D. magna* and *R. subcapitata* (0.7 to 1.85 TU of differences between reference and green concrete samples).

- Sulfides being highly sensitive to oxidation by molecular oxygen, sulfides released in solution will quickly be neutralized in environment by oxidation, or by evaporation with pH lowering.

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