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Greening effect of concrete containing granulated blast-furnace slag composite cement: is there an environmental impact?

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Abstract:

The "greening effect" refers to hardened concrete containing Granulated Blast-Furnace Slag (GBFS) that displays a vivid blue-green color after removal of formwork. This temporary coloration effect, which fades within a few days to weeks, has raised concerns about its potential impact on the environment. Three types of leaching tests were conducted to assess different potential release scenarios: a sprinkling test, a static monolith tank test and a batch test on crushed samples. Slag content was linked to a higher release of sulfur anions in the leachates, in the form of sulfides, thiosulfates and sulfates. Most of these anions came from the GBFS, where sulfur is mainly in the form of sulfides with thiosulfates and sulfates as the main products of sulfide oxidation. Sulfate levels, however, were lower than threshold limit values for both inert waste and alternate materials reused in road construction. Moreover, no chromium, or other hazardous metals, were detected in the leachates.

Keywords: blast-furnace slag, greening effect, sulfide, fair faced concrete, foundation, demolition

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1 Introduction

Granulated Blast-Furnace Slag (GBFS) is a common by-product of iron and steel production. While ground GBFS has a long history of varied uses, in the late 19th century, it began being used as a supplementary cementitious material (SCM) to partially replace clinker in composite cements and strengthen durability. The blue-green coloration or "greening" effect occurs when GBFS or GGBFS are hydrated and will fade within days or weeks when exposed to air.

This greening effect is a well-documented phenomenon seen across a range of construction applications that rely on CEM III based or slag based concretes, i.e. (a) civil engineering, (b) precast concrete use in small- and large-scale construction (c) flooring and (d) masonry (Fig. 1). The issue has been addressed by several professional journals and white papers [1,2].

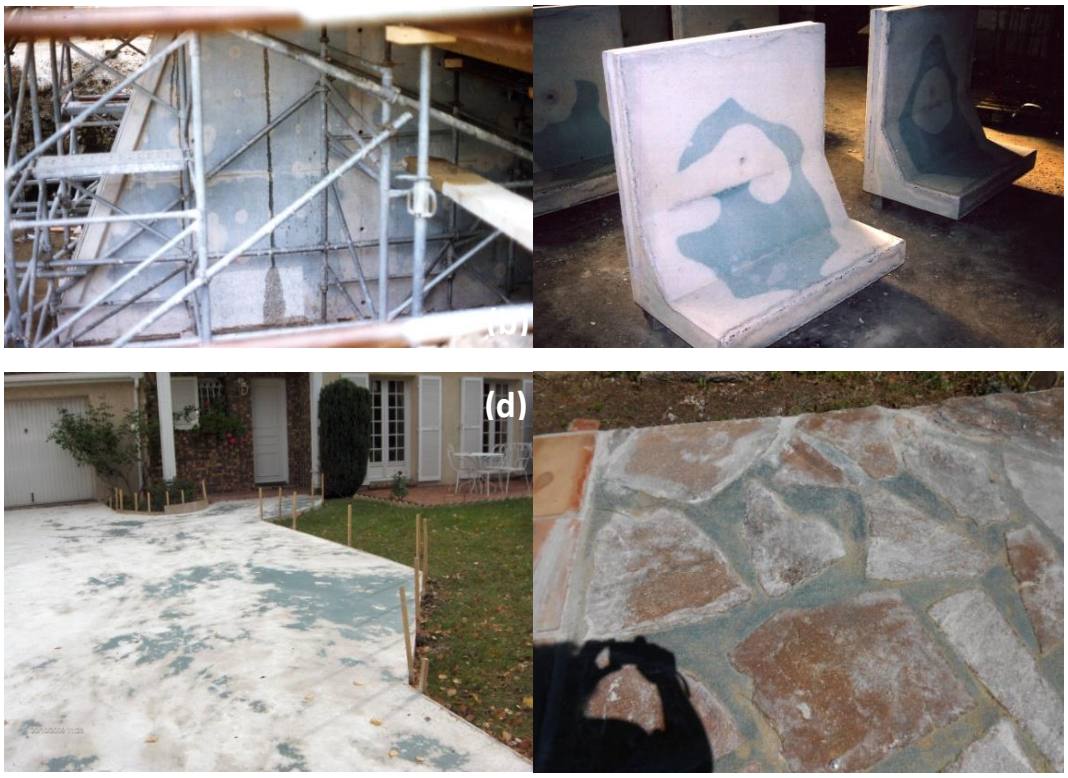


Fig. 1. Examples of the "greening effect" in various sectors of construction - *Photographs illustrating the "greening effect" in different sectors of construction: a) civil engineering, b) pre-cast industry, c) Flooring works, d) masonry works.*

In France, while CEM III cement types (cement containing from 36 to 95% GGBFS) represent roughly 10% of overall production (16.5 M metric tons in 2018), the full range of overhead applications and those using fair-faced concrete (excluding foundation work) that rely on CEM III and slag based binders (CEM I type with Slag as addition) are potentially at stake.

The origin of this coloration effect was for a long time poorly understood, but more recent investigations have pointed to the potential causal role of sulfur compounds in concrete aggregates.

One of the first studies to show how sulfides potentially contribute to coloration analyzed the cement hydrates containing the sulfide ion into hydrated mortar, and found that hexagonal aluminates hydrates contained a solid solution of sulfides and sulfates that displayed a characteristic green color [3]. More recent studies have explored the origin of this coloration in GGBFS-containing materials by using UV-Visible [4] or XANES spectroscopy [5] and concluded that radical polysulfides

anions are primarily responsible for the greening effect. In cement materials containing slag, low porosity acts to prevent important oxygen penetration, and soluble sulfides are most likely consumed by precipitation with cement hydrates rather than by an oxidative reaction [3]. Cement hydration will then likely form a protective surrounding to the chromophore species, allowing the metastable blue-green color to occur for hours, days or weeks.

To date, few studies have examined this phenomenon, despite a wide and historical use in civil engineering and the cement industry. To the best of our knowledge, no studies have focused on the potential environmental impacts whereas CEM III cement customers regularly question producers and resellers about the safety of 'blue-green concrete'. The concern is that this effect is consistently present through several key construction phases including form removal, but also during deconstruction, given that the blue-green color remains visible when a GBFS-containing concrete is demolished.

The objective of this study was to assess the environmental impact of the greening effect occurring in GBFS-rich material and CEM III based concretes. For this purpose, leaching tests were conducted on materials made with commercially available GBFS-composite cements. These tests were performed on cement Portland paste, for example, to study transport mechanisms of leached components, or long-term leaching of hazardous trace metals [6,7]. Other authors have studied the leaching characteristics of standard cement mortars during their whole life cycle, from first use to reuse or recycling purposes [8]. Van der Sloot advised situating leaching tests as closely as possible to the field conditions to be assessed. Studies that have focused on slag-based materials have emphasized the intrinsic properties of the structure and its geochemical behavior [9].

Our understanding of the potential environmental impact of this phenomenon is surprisingly limited. The fact that GBFS is widely used as a construction material merits a closer look at its geo-environmental characteristics. The leaching tests were conducted on a standardized basis (monolithic and crushed samples) in order to simulate the behavior of foundation concrete (monolithic) and during a recycling process (crushed). The impact of rainfall on fair- faced (green) concrete was assessed by means of a configuration (sprinkling test) developed by the authors for this specific purpose. In addition, H_2S emissions during demolding were determined using a second specific configuration designed the authors.

2 Materials and methods

2.1 Materials

Four industrial containing slag cements were used to formulate the concretes and cement pastes. As our primary focus was studying the greening effect and environmental implications of using cementitious materials containing various amounts of GBFS, only commercially available CEM III cements were used composed mainly of clinker and GBFS. This cement type is available in three classes differentiated by the amount of incorporated GBFS: CEM III/A (36–65% of GBFS), CEM III/B (66–80% of GBFS), and CEM III/C (81–95% of GBFS). For comparison purposes, we determined that the best reference material would be CEM I cement, which is mostly composed of clinker and minor additives, but contains no GBFS. The fineness of cements, given as Blaine specific surface area, was not modified, and ranged between 3600 and 5400 cm^2/g (Table 1). Sulfides content in cement powders was quantified accordingly to the French cement norm, by acid distillation of sulfides and recovery of gaseous H_2S in an alkaline antioxidant solution (NF EN 196-2, 2013). A notable modification of the recovery method and analytic technic was conducted. The outlet of the distillation apparatus was connected on the bubble jar which was filled with a Sulfides Antioxidant

Buffer (SAOB) solution. The SAOB solution was prepared with 80 g of NaOH, 35 g of ascorbic acid and 67 g of EDTA for one liter. This solution was then analyzed using a Silver/Sulfide ion-selective electrode. All leachates were analyzed using the same method (see section II.4.d). Major composition of cements was determined by X-Ray Fluorescence (XRF) on a Bruker S4 Explorer spectrometer using SpectraPlus software (Table 1). Samples were prepared as melted beads by mixing 1 g of cement or GBFS with 8 g of Lithium Tetraborate (LiB_4O_7) in a Pt-Au crucible (95-5 % w/w). Melting was performed on an Autofluxer Breitlander fusion bead machine. Concretes were made with siliceous alluvial (Moselle river) aggregates used for producing concrete in northeastern France. The cement paste was made solely with CEM III/C, to assess the most concentrated sample in GBFS. Throughout the rest of this article, concrete samples will be referred to by the cements used (i.e. CEM I, CEM III/A, B or C) and the cement paste sample will be referred to as "P CEM III/C".

Table 1. Composition of cements used for concretes and cement pastes preparation

	Blaine surface area	**GBFS**	**S^{2-}**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**MnO**	**Na_2O**	**SiO_2**	**SO_3**
	cm^2/g	wt.%	g(S)/100g					wt.%				
CEM I	4370	0	-	5.44	62.91	3.03	0.81	1.89	0.08	0.20	20.69	3.33
CEM III/A	5400	62	0.61	9.91	48.91	1.84	0.55	4.64	0.39	0.35	29.74	2.72
CEM III/B	3643	71	0.55	9.56	47.62	1.15	0.55	4.99	0.24	0.22	31.32	3.52
CEM III/C	4662	85	0.74	10.54	44.87	0.79	0.34	5.80	0.28	0.31	33.74	3.00

Description: *Composition of CEM I, CEM III/A, CEM III/B and CEM III/C cements is given in this table. Blaine surface area is given as cm^2/g, GBFS content of cement is given as wt.%, sulfides content is given as g of sulfur for 100 g of cement, and major elements are given as oxides in wt.%.*

2.2 Concrete and cement paste preparation and conditioning

Concrete and cement paste samples were prepared by mixing the required amounts of components in a concrete mixer (Controlab Perrier). Concrete was made with a water/cement (w/c) ratio of 0.5, with 420 kg/m^3 of cement, 210 kg/m^3 of water, 885 kg/m^3 of 0–5 mm sand, and 750 kg/m^3 of 4–8 mm gravel. Cement paste was made solely with water and cement with a w/c = 0.5. The mixing procedure was performed according to the NF EN 196-1 (09/2016) standard for concrete samples, and the NF EN 196-3 (09/2017) for cement pastes. Immediately after mixing, the paste was poured into cylindrical hermetically sealed HDPE bottles (12.5 cm height and 7.2 cm diameter) at 3 time intervals, each vibrated for 30 s on a vibrating table to remove air pockets within the sample. Samples were cured in the dark for 3 days in a tank at 25°C and with a relative humidity greater than 90%.

2.3 Color analysis

Coloration of the samples was examined using a portable spectrophotometer Konica Minolta CM-700d. This device allows a precise characterization of the color in each color space. We used a common color space defined in 1976 by the International Commission on Illumination known as CIE 1976 (L*a*b*) or CIELAB, according to the NF EN ISO/CIE 11664-4 (07/2019) standard. The L* parameter quantifies the brightness of the color (from darkest to lightest on a scale of 0 to 100), whereas a* and b* quantify the chromaticity. On a diagram, the color on the a* axis ranges between -60 (green) and +60 (red), and on the b* axis between -60 (blue) and +60 (yellow). All concrete and cement paste samples subjected to the different leaching tests were assessed for their color just

before the test. The bottom face, being smaller, was analyzed for at least 3 different points, whereas the larger side curved face was analyzed for at least 5 different points. Values were averaged for each sample and each face, and then averaged for different samples.

2.4 Leaching tests

In the present study, we constructed three separate scenarios to determine where the greening effect might have an impact on the surrounding environment. The rainfall leaching of a freshly unmolded facing wall made with GBFS-rich cement is the scenario that is most visible by workers and outside observers. To assess potential leaching of hazardous substances, we used a custom designed test that involved sprinkling the block surface. The second scenario considered involved leaching by immersion of freshly unmolded building foundations, largely because GBFS-rich cements are frequently used in more aggressive wet environments. In this context, we used a standard monolith leaching test. The last scenario considered rainfall leaching in deconstruction of materials containing GBFS-rich cement, which constitutes the final step of building construction. In this case, a standard batch leaching test on crushed samples was used.

2.4.1 Sprinkling leaching test

On working sites, after removal of formwork, “green” surfaces of slag cement-based concretes may be subjected to rainy weather, especially heavy rainfall. To assess the effect of rainfall events on concrete surfaces, an innovative leaching test was designed (Fig. 2). Its process consists of sprinkling deionized water on a concrete or cement paste block and collecting it in a tank connected in a close circuit to the sprinkler using a peristaltic pump.

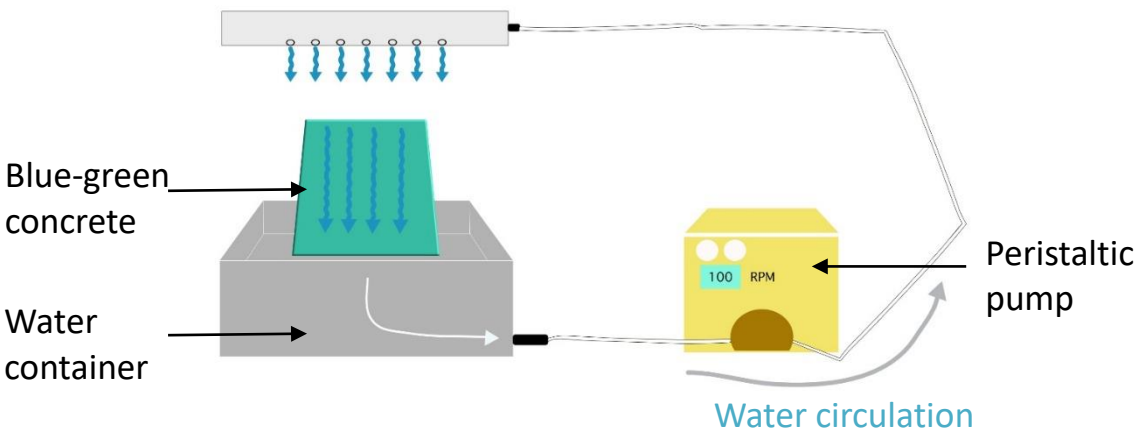


Fig. 2. Experimental device of the sprinkling leaching test - *A block of sample is fixed above a container filled with water. Water is pumped with a peristaltic pump, and sprinkled on the sample by a perforated tubing.*

After a curing time of 3 days, a block of about 21.5 x 15.2 x 3.5 cm was fixed to the device above a container filled with about 5 L of water, with a tilt angle of 40°. A peristaltic pump (Watson-Marlow 323E) at the speed of 100 RPM sprinkled the water over the surface of the block on a mean surface of 370 cm^2 through a regularly perforated PVC tubing (one hole of a rate of roughly 1 mm every 4 mm). The mean liquid/area ratio (L/A) obtained was close to 13.5 cm^3/cm^2. The water flowed on the surface of the block at a rate of about 125 mL/min, and dropped into the container, to circulate again for a total of 4 hours. Marprene tubing was used between the container and the top PVC tubing.

Before the first use, and between each use, the sprinkling device was cleaned with soap, HNO_3 0.1M, and deionized water.

2.4.2 Monolith leaching test

In civil engineering, GBFS-based cements are commonly used in building foundations. In this case, the concrete can be subjected to water flooding, or leaching by infiltrated rainwater. A tank monolith leaching test following the XP CEN/TS 15862 (10/2012) standard has been used to assess the environmental impact of GBFS-based cement applied in a flooded environment. The principle is to immerse a solidified monolith in deionized water for 24h, without water renewal. The L/A ratio for all samples was defined to 12 cm^3/cm^2 of exposed solid. Exposed samples were used directly after demolding for an average dimension of 12.5 cm height and 7.2 cm diameter. To ensure proper leaching on every faces, with a minimal 2 cm height of water above and below the sample, all samples were placed on a cut HDPE mesh at the bottom of an HDPE container of 5 L. A magnetic stirrer ensured the homogenization of the solution during the test.

2.4.3 Leaching test on crushed samples

The greening effect is often still visible when a building is demolished. Even after several decades, a concrete's interior can display a vivid blue-green color when exposed. This indicates that the demolition debris might be subjected to water leaching, either by rainfall or manual sprinkling. In this case scenario, a simple batch of crushed leaching was tested following the NF EN 12457-4 (12/2002) standard to assess the environmental impact of GBFS-based cement after deconstruction. The monolith was crushed with a jaw crusher to ensure 95% w/w of passing to 10 mm sieve. Once crushed, the sample was weighted for about 90g (dry weight) and poured into a HDPE bottle with the leaching water to ensure a L/S ratio of 10 L/kg. Preliminary tests allowed the determination of a mean water content, considering that the leaching test has to be carried out immediately after demolding and could not allow the proper case-by-case determination of the water content of each sample. After 3 days of curing, the tested concretes showed a mean water content of about 6.5%, and the CEM III/C cement paste showed roughly 25% water content. Real water content was determined for each sample to evaluate the deviation to the mean value used and adjust the L/S and L/A ratio. When water and the sample were mixed, the bottle was deoxygenated with N_2 for about 8 min to limit the oxidation of solubilized sulfides. The bottles were then agitated on a turnaround shaker at 7 RPM for 24 hours.

2.4.4 Leachates analysis

Immediately after each test, leachates were vacuum filtrated on a 0.45 µm Sartorius cellulose acetate filter. The filtrates were analyzed for pH and conductivity on a portable multimeter (Knick Portavo® 907 Multi), and divided into 3 subsamples: one subsample without other treatment for the anion analysis, one acidified with 2 mL HNO_3 65% analytical grade (Merck) for elemental analysis, and one mixed at a 1:1 ratio with SAOB for sulfides analysis. We focused on anion analysis of the leachates on the sulfur compounds, since the presence of several sulfur anions, i.e. S^{2-}, $S_2O_3^{2-}$ and SO_4^{2-}, has been regularly reported in leachates of hydrated GBFS and cements containing GBFS [10–12]. These species have been shown to be thermodynamically stable considering the alkaline and mildly reductive environment occurring in the leachates [13]. Sulfides analysis was carried out accordingly to a modified USEPA method 9215 (12/1996). The SAOB solution was prepared with 80 g NaOH, 35 g of ascorbic acid and 67 g of EDTA for one liter. An alkaline solution (pH > 10) favored the trapping of sulfides under the S^{2-} form, protected from oxygen oxidation by a reducing agent as the ascorbic acid and by trapping of metals with EDTA. Sulfides were then analyzed with an ion-selective electrode Thermo Scientific Orion Silver/Sulfide 9616BNWP, plugged on an HP multimeter (model

3478A). An electrode was calibrated with a serial dilution of a stock solution of Na_2S. The stock solution was sulfide ISE standard of 1000 mg/L bought at Mettler-Toledo and prepared daily with Roth analytical grade Na_2S in 0.4M NaOH. The stock solution was standardized with an $AgNO_3$ solution, calibrated beforehand with a KCl solution, using a Tacussel TT-Processeur 2 automated titrator equipped with the ion-selective silver/sulfide electrode. The subsamples for anion analysis (SO_4^{2-}, $S_2O_3^{2-}$, Cl^-) were filtrated on 0.22 µm Sartorius filter and stored in the dark at 4°C. The analysis was conducted on an ion chromatography instrument (Metrohm 882 Compact IC) with a chemical suppressor and conductimetric detection, equipped with a Metrosep A Supp 4 column (250 x 4.0 mm) and a Metrosep A Supp 5 Guard/4.0 precolumn (5 x 4.0 mm). A mix Na_2CO_3 1.8 mM / $NaHCO_3$ 1.7 mM / 2% acetone was used as a mobile phase with a 1 mL/min flow rate and an injection volume of 20 µL. Standard solutions for calibration were prepared in the laboratory from a certified Alfa Aesar multi-anions commercial solution (ref. 041693) at 1000 µg/mL. Concentrations were determined from peak areas. Major element analyses (Si, Al, Fe, Mn, Mg, Ca, Na, K, Cr) were carried out by ICP-OES (Thermo Scientific iCAP 6500) on acidified subsamples.

2.5 H_2S assessment

A custom designed device was used to assess the potential release of H_2S during the demolding of concretes containing GBFS (Fig. 3). This instrument is composed of a cell with a cylindrical section with transparent PMMA (approx. 10.1 cm diameter and 25.4 cm height), and top and bottom sections made of PTFE with an O-ring to ensure water and air tightness. Openings are situated on the lower section and underneath to allow for inlet and outlet of fluids. The bottom cap is pierced and a cable gland is inserted to allow for vertical movements of a metal rod equipped with a PTFE bucket. Concrete is poured into the bucket, with a metal hook fixed at the top cap that dips into the concrete. After 3 days, once the concrete has hardened, the hook becomes firmly secure and pulling the metal rod allows the concrete cylindrical faces to be exposed. During the demolding process, a constant argon flow is injected by the inlet valve at the bottom of the cell, and a pipe is connected to a washing bottle filled with 200 mL of SAOB solution to trap H_2S gas. The sulfide analysis of the SAOB solution was performed with the silver/sulfide ion-selective electrode following the protocol described previously (section II.4.d.).

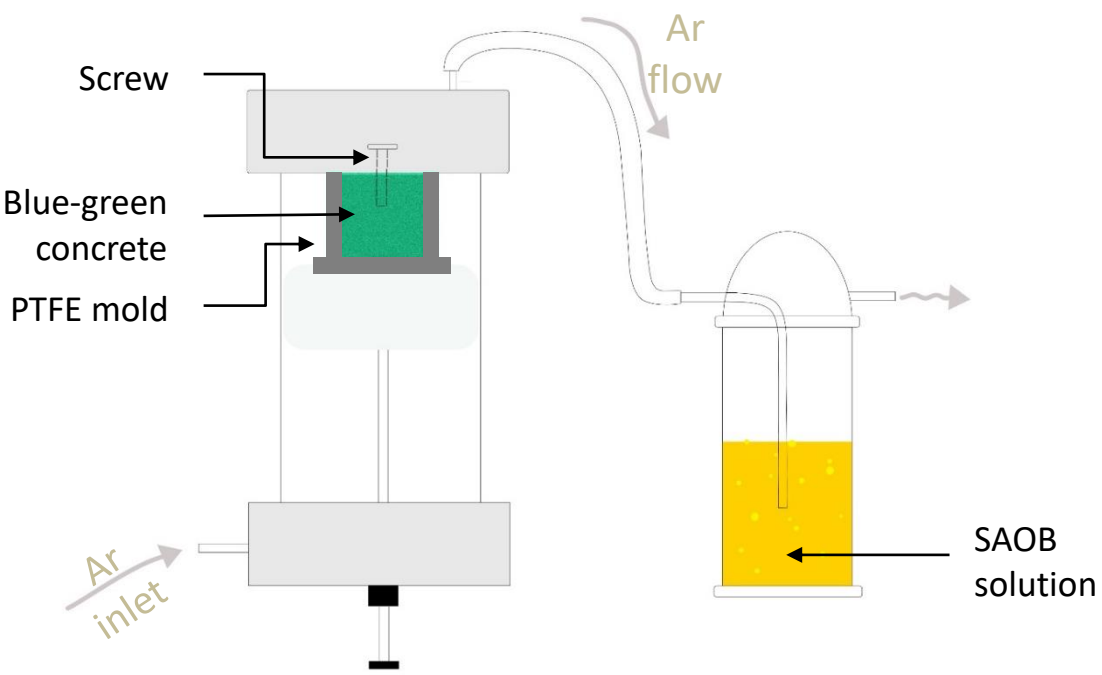


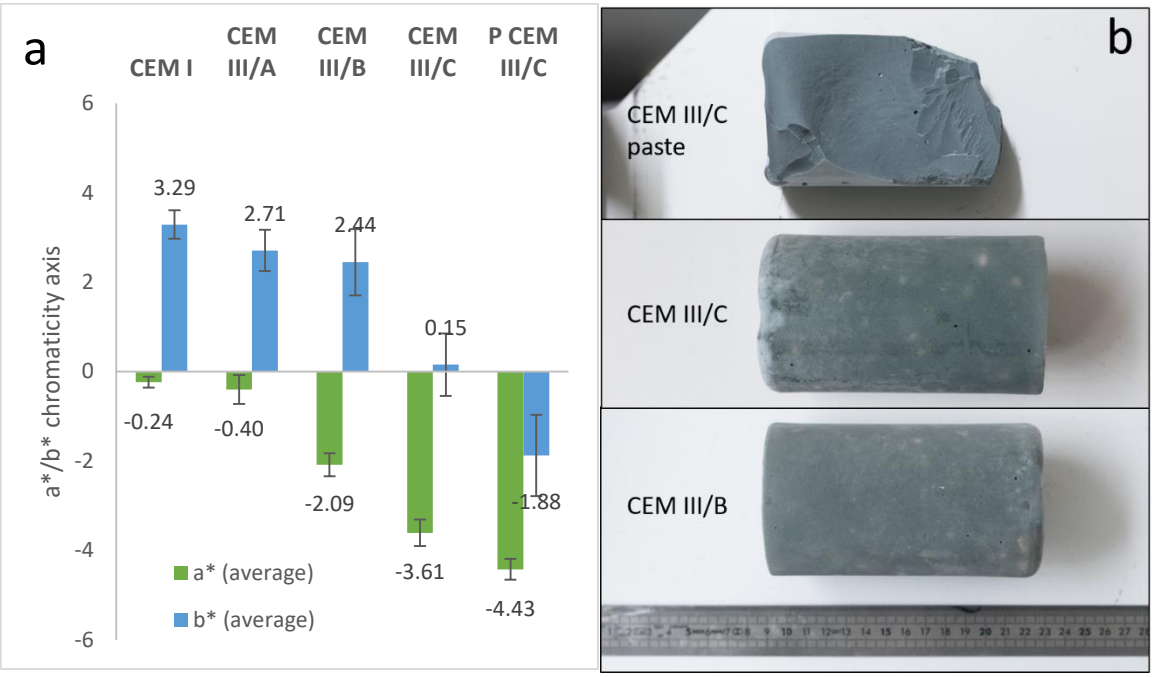
Fig. 3. Experimental device for H_2S emission assessment - *A closed chamber contained a concrete sample in a mold, maintained by a screw to the cap of the device. A metal rod can move vertically in the bottom of the device to remove the mold and expose the sample to an Ar flux bubbling in an alkaline protective solution to trap H_2S.*

3 Results

The greening effect of GBFS-containing concrete has gained increasing attention as a public health concern, in part due to its visibility. From the demolding stage through to building deconstruction, a number of known environmental events can cause deleterious interactions with green materials and release potentially harmful compounds into the environment that could pose a risk to human health.

3.1 Analysis of the greening effect

The color of GBFS-containing materials was evaluated just prior to setting-up the leaching tests. The effect of the GBFS concentration in the different samples was highlighted by the shifting of the color to the green-blue side of the color space. Ranging from -0.24 for CEM I to -4.43 for the cement paste of CEM III/C, a* decreased while the GBFS content increased in the mixture (Fig. 4a). This indicates that the color turning more green corresponded with increased levels of GBFS (see Fig. 4b for example). For the blue-yellow axis b*, the overall trend showed a decrease from 3.29 for CEM I to -1.88 for the cement paste of CEM III/C. The color then shifted toward blue with increased GBFS content. However, in this case, standard deviation between samples was considerably higher than for a*, and ranged between 0.32 for CEM I sample and 0.9 for the cement paste of CEM III/C (for a* it was contained in a 0.12–0.32 range). On an a*–b* plot, the samples are more scattered along the b* axis than the a* axis (Fig. 4c). Samples with the same mixture appear gathered in clusters, and those clusters are fairly widely spaced vertically.



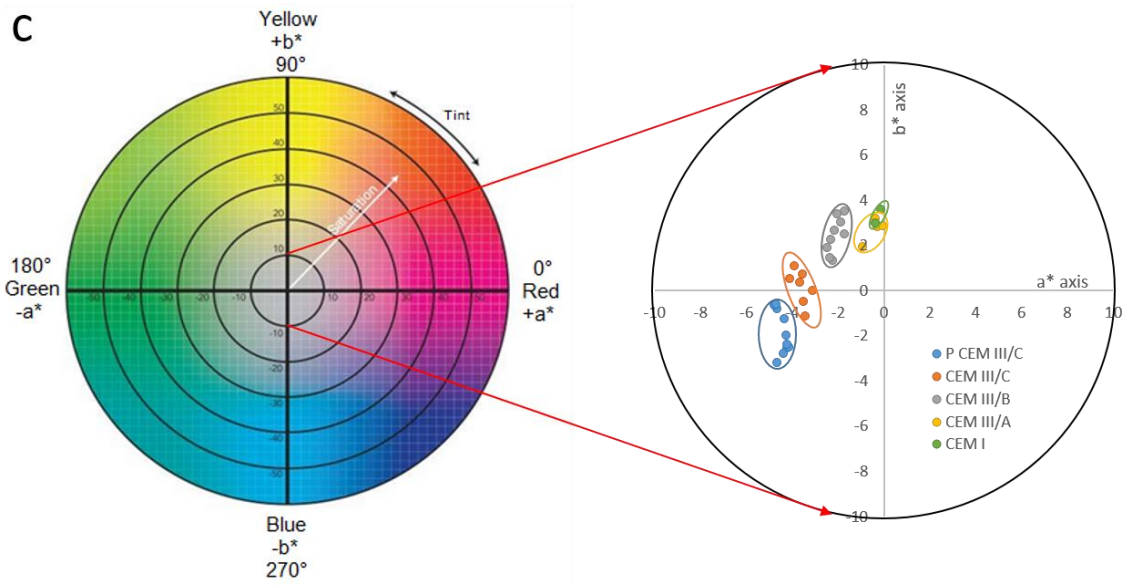


Fig. 4. Color analysis of concrete and cement paste samples - *Average values for a* and b* parameters of concrete and cement paste samples (a), pictures of concretes and cement paste (b), and dispersion of samples on a* and b* axis depicted on the chromatic circle representing the L*a*b* CIE 1976 color space, modified from www.colorimax.com (c).*

Results for L* are not shown, as variation of the brightness for the different samples is close in range (between 47.5 and 58.3 with SD from 2.65 to 7.77), without any identifiable trend.

3.2 Rainfall leaching of building faces: sprinkling test

The first leaching event on a freshly unmolded wall normally comes from rainfall. Given that classical leaching tests for assessing environmental impact are less practical for gauging rainfall leaching on horizontal concrete surfaces, we relied on our own test designed specifically for this purpose, as described previously (cf. section II.4.a and Fig.2).

Concrete and cement pastes are alkaline mineral materials, as shown in our pH analysis following leaching (Fig. 5). Concretes made with CEM III/A and CEM III/B are the most alkaline when subjected to a surface dynamic leaching, with a pH value of about 11.3. For concrete with CEM III/C and cement paste of CEM III/C, the pH is lower, around 10.9. Conductivity of the samples decreased from 0.36 mS/cm for CEM III/A concrete to about 0.18 mS/cm for CEM III/C concrete and cement paste. Conductivity in this case appeared to increase with the Portland clinker content.

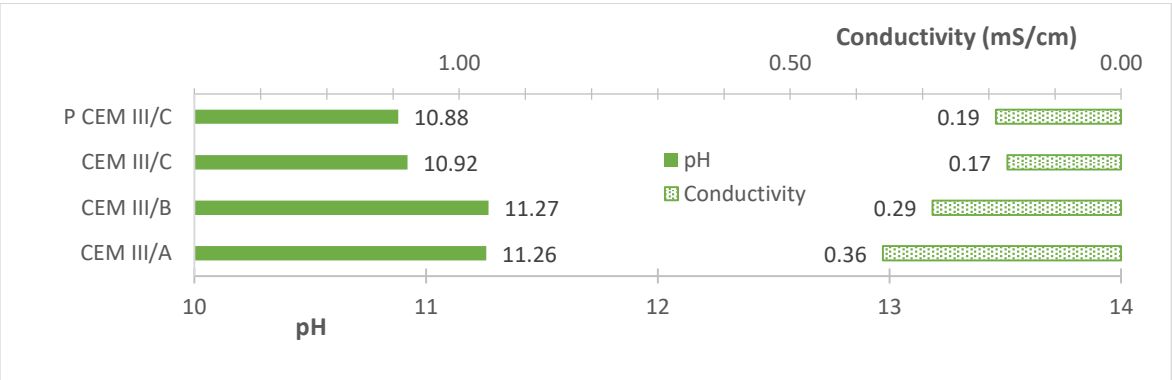


Fig. 5. pH and conductivity in leachates of the sprinkling test from concretes and cement pastes - *pH in leachates (green plain bars) ranges from 10.88 for P CEM III/C sample to 11.27 for CEM III/B sample. Conductivity (green dotted bars) ranges from 0.17 mS/cm for CEM III/C sample to 0.36 mS/cm for CEM III/A sample.*

For leaching tests based on a leached surface, concentrations in eluates as mg/L are normalized with the L/A (L/m^2) ratio as mg/m^2. Concentrations of sulfur anions into the leachates increased when the GBFS ratio in concretes/paste also increased (Fig. 6). Sulfides were observed to be the least released anions and varied from 10.6 mg/m² for CEM III/A, the least concentrated with GBFS, to 25.8 mg/m² for the CEM III/C cement paste. On the other hand, sulfates were the measured anion that showed the highest release levels and followed the same pattern, from 524 mg/m² for CEM III/A concrete to 918 mg/m² for the CEM III/C cement paste. Thiosulfates were released at roughly the same concentration for all samples, between 180 and 230 mg/m². Overall, sulfur was predominantly under its higher oxidation degree in leachates, with more than 70% as sulfates, and 15 to 25% in thiosulfates form.

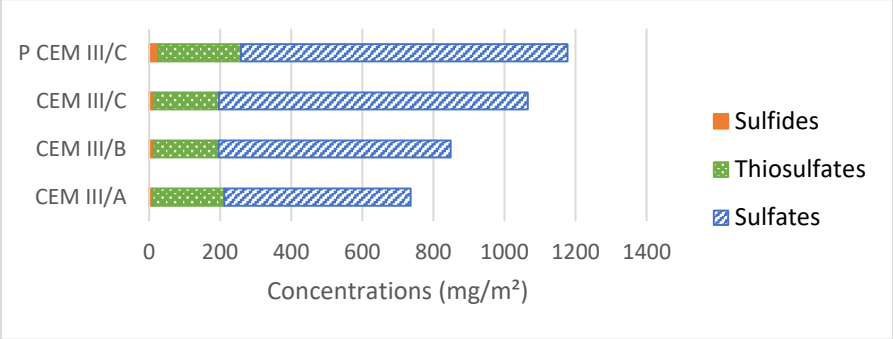


Fig. 6. Concentration of sulfides S^{2-}, thiosulfates $S_2O_3^{2-}$, and sulfates SO_4^{2-} (as mg/m²) in leachates of the sprinkling test from concretes and cement pastes - *Sulfates (blue diagonal up bars) are the most released anions with concentrations ranging from 524 mg/m² for CEM III/A to 918 mg/m² for P CEM III/C. Thiosulfates (green dotted bars) releases are close between the four samples, with concentrations between 180 and 230 mg/m². Sulfides (orange plain bars) releases are very low, from 10.6 mg/m² for CEM III/A to 25.8 mg/m² for P CEM III/C.*

3.3 Building foundations flooded by water: tank monolith leaching test

One of the primary uses of cement blended with GBFS is in building foundations. In this case, the concrete is most likely to be subjected to immersion by groundwater infiltration, as well as leaching by water percolating from the surface. We conducted a tank monolith leaching test to assess this specific situation.

Alkalinity of leachate solutions showed to be higher in this test (Fig. 7). The pH ranged from 11.33 for CEM III/C, to 11.9 for CEM I, and evolved in the same way as observed previously for the sprinkling test. The global increase may be explained by the longer test duration (24 hr. versus 4 hr. for the sprinkling test). The CEM III/C cement paste was more alkaline than the concrete, due to the higher concentration of binder in the absence of the concrete's aggregate skeleton. Conductivity followed the same scheme, showing ranges from 0.46 mS/cm for CEM III/C concrete to 1.14 mS/cm for CEM I concrete. Conductivity was also higher for the CEM III/C cement paste than for the concrete, with 0.64 mS/cm.

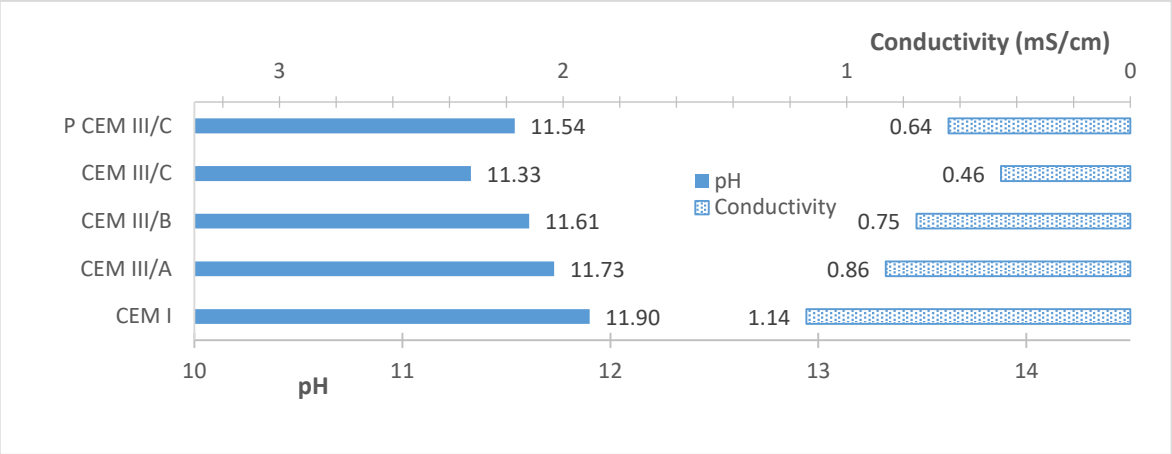


Fig. 7. pH and conductivity in leachates of the tank monolith leaching test from concretes and cement pastes - *pH in leachates (blue plain bars) ranges from 11.33 for CEM III/C sample to 11.90 for CEM I reference sample. Conductivity (blue dotted bars) ranges from 0.46 mS/cm for CEM III/C sample to 1.14 mS/cm for CEM I reference sample.*

Sulfur speciation leaching between all samples was significantly more pronounced under these leaching conditions (Fig. 8). The concrete made with CEM I only exhibited release of sulfates, for 108 mg/m². Increasing amounts of sulfates were released in samples that positively correlated with higher GBFS content, as observed previously in the sprinkling test, from 132 mg/m² for CEM III/A concrete to 960 mg/m² for the CEM III/C cement paste. The proportion of thiosulfates released was roughly 20–30% of the total amount of sulfur anions, except for CEM III/A concrete, and ranged from 192 mg/m² for CEM III/A concrete to 312 mg/m² for CEM III/C cement paste. Furthermore, sulfides were also detected and quantified in leachates and, similarly, corresponded with the GBFS content, up to 52.7 mg/m² for the CEM III/C cement paste.

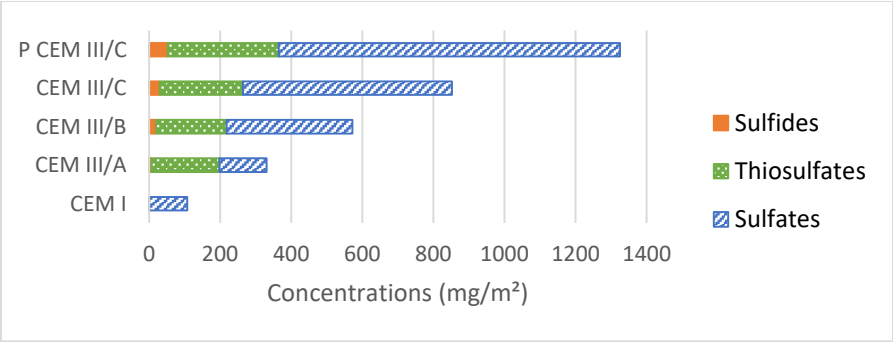


Fig. 8. Concentration of sulfides S^{2-}, thiosulfates $S_2O_3^{2-}$, and sulfates SO_4^{2-} (as mg/m²) in leachates of the tank monolith leaching test from concretes and cement pastes - *Sulfates (blue diagonal up bars) are released with concentrations ranging from 108 mg/m² for CEM I reference sample to 960 mg/m² for P CEM III/C sample. Thiosulfates (green dotted bars) releases range from 192 mg/m² for CEM III/A sample to 312 mg/m² for P CEM III/C. Sulfides (orange plain bars) releases are low, between 6.58 mg/m² for CEM III/A sample to 52.67 mg/m² for P CEM III/C sample. Thiosulfates and sulfides were not detected in CEM I leachates.*

3.4 Deconstruction products leaching by rainfalls: leaching test on crushed samples

Deconstruction is the other aspect to take into account when it comes to common uses of slag-containing cements. A leaching test on crushed samples was used to assess the potential release from deconstruction debris subjected to both natural rainfalls and artificial sprinkling.

Leachates from the crushed leaching tests showed to be the most alkaline of the three tests (Fig. 9). Regardless of the type of cement used, all leachates exceeded 12 pH units, and ranged from 12.10 for CEM III/C concrete to 12.49 for CEM I concrete. Conductivity was also higher, with 1.92 mS/cm for the CEM III/C concrete to 7.36 mS/cm for the CEM I concrete.

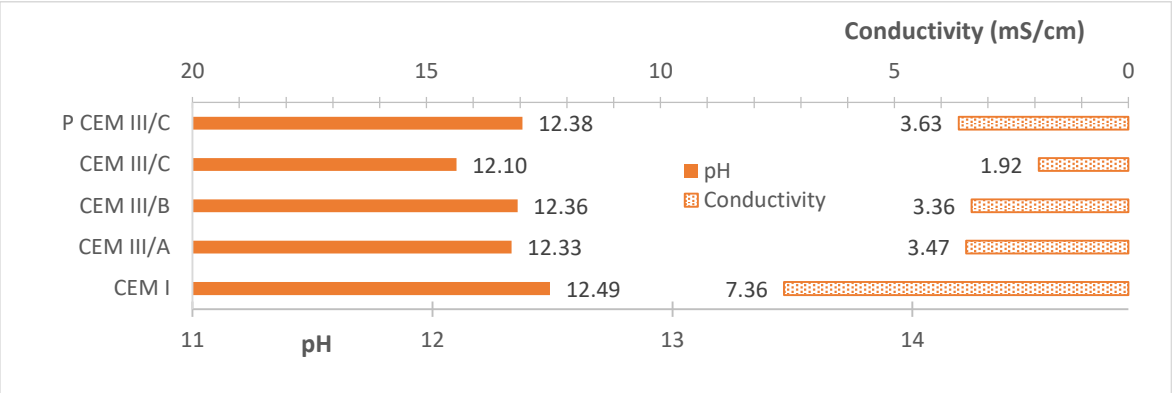


Fig. 9. pH and conductivity in leachates of the crushed leaching test from concretes and cement pastes - *pH in leachates (orange plain bars) ranges from 12.10 for CEM III/C sample to 11.49 for CEM I reference sample. Conductivity (orange dotted bars) ranges from 1.92 mS/cm for CEM III/C to 7.36 mS/cm for CEM I reference sample.*

For leaching tests dependent on the mass of the assessed materials, units in mg/L were normalized with the L/S (L/kg of dry weight material) ratio as mg/kg dry weight (DW). High releases of sulfur anions were observed in the crushed leaching test (Fig. 10). The CEM I concrete released a negligible amount of thiosulfates, about 11 mg/kg DW, but no sulfates were found in the leachates. As such, thiosulfates represented from one to two thirds of the total sulfur anions found in other concretes and cement paste, ranging from 58 to 154 mg/kg DW. The other form of sulfur was sulfates, with 31 and 25 mg/kg DW respectively for CEM III/A and B concretes leachates, and increased to 204 mg/kg DW for CEM III/C concrete, and 112 mg/kg DW for CEM III/C cement paste. Sulfur content was noticeably well divided between the 3 forms analyzed for the CEM III/C cement paste, given that close to 165 mg/kg DW of sulfides was recovered in the leachates.

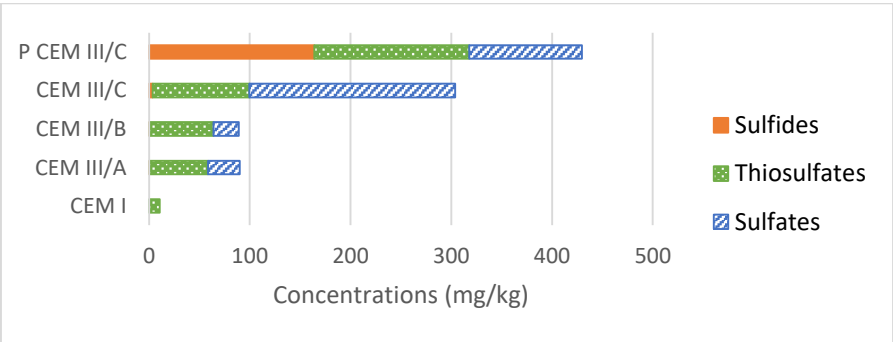


Fig. 10. Concentration of anions sulfides S^{2-}, thiosulfates $S_2O_3^{2-}$, and sulfates SO_4^{2-} (in mg/kg dry weight) in leachates of the crushed leaching test from concretes and cement pastes - *Sulfates (blue diagonal up bars) are released with concentrations ranging from 25 mg/kg DW for CEM III/B sample to 204 mg/kg DW for CEM III/C sample. Thiosulfates (green dotted bars) releases range from 11 mg/kg DW for CEM I reference sample to 154 mg/kg DW for P CEM III/C. Sulfides (orange plain bars) releases range between 6.58 mg/m² for CEM III/A sample to 52.67 mg/m² for P CEM III/C sample. Thiosulfates and sulfides were not detected in CEM I leachates.*

3.5 H_2S assessment

A typical phenomenon during formwork removal blue-green concrete is the presence of a characteristic odor resembling the distinct smell commonly associated with hydrogen sulfide. The main issue with use of this particular compound is one of safety; its high toxicity may increase health and environmental risks. According to WHO guidelines, the recommended safe exposure limit is 0.15 mg/m^3 over a 24 hour period [14].

The purpose of our customized instrument was to detect and quantify the potential emission of H_2S during the unmolding process. Argon was set to flow for 30 minutes after demolding, and bubbled in 200mL SAOB solution to trap emitted H_2S. No sulfides were recovered with this method. The limit of detection of the ISE silver/sulfide electrode is about 3.10^{-3} mg/L. Under the experimental conditions, this equated a minimum of 6.10^{-4} mg emitted by the concrete that could be quantified in the final solution.

4 Discussion

4.1 Trace and major elements releases in the different scenarios

In this study, three scenarios involving the potential impact of the greening effect of GBFS-rich cement were considered. Trace and major elements were analyzed and quantified in the leachates. Despite relatively recent investigations pointing to the potentially important role of sulfur compounds in the greening effect process, notably under the sulfide form, it was previously thought that other compounds might also be involved. This was the case for iron and manganese compounds [15–17], and even chromium salts such as $CrCl_3.6H_2O$. Accordingly, we included these elements for analysis in the leachates, and paid particularly close attention to chromium content for the known health hazards associated with its exposure. In the three cases, no Cr element was found in the leachates (detection limit was 0.06 mg/L), and Fe and Mn elements were under the detection limit, or showed statistical uncertainty near the detection limit (respectively 0.01 mg/L and 0.001 mg/L). This is consistent with the literature on the use of cement (either with or without GBFS) in cementitious solidification/stabilization (S/S) treatment processes of hazardous wastes, including those contaminated with chromium [18]. Moreover, Fe and Mn were not expected to be leached considering their significantly low solubility in the alkaline conditions of cementitious materials [19].

We observed Na, K, Ca, Al, and Si among the major elements released by cement and GBFS leaching, although their release through rainfall leaching or solubilization and diffusion into groundwater does not typically represent an environmental hazard. While cement and blast furnace slag have similar raw composition, mainly composed of CaO, SiO_2 and Al_2O_3, proportions of oxides varied. Compared with Portland cement, GBFS is richer in SiO_2 and Al_2O_3, and depleted in CaO [19]. In fact, CEM I is composed of nearly 62.9% of CaO, 5.4% of Al_2O_3, and 20.7% of SiO_2 (Table 1). In CEM III/C, where 85% of clinker was replaced by GBFS, CaO was reduced to 44.9%, with almost twice of Al_2O_3 (10.5%) and 33.7% of SiO_2. The global trend of both CEM I to CEM III/C was decreased levels of CaO, and

Table 2 Concentrations of major elements and sulfur anions in the leachates of the three leaching tests

		Na	Ca	K	Al	Si	S^{2-}	SO_4^{2-}	$S_2O_3^{2-}$	Ca/Si	∑cations/∑anions
Sprinkling *(mmol/m²)*	CEM III/A	65.43	91.52	32.39	6.25	9.11	0.33	5.46	1.80	10.05	26.98
	CEM III/B	35.95	67.42	21.52	4.61	11.70	0.40	6.80	1.63	5.76	15.99
	CEM III/C	52.12	73.57	9.73	4.88	10.15	0.39	9.05	1.64	7.25	13.57
	P CEM III/C	68.38	44.86	19.64	5.28	12.00	0.80	9.56	2.08	3.74	12.07
Monolith *(mmol/m²)*	CEM I	80.76	524.19	82.43	1.63	5.48	< L.D.	1.12	< L.D.	95.61	617.58
	CEM III/A	118.24	178.79	45.89	4.92	9.89	0.21	1.37	1.71	18.08	108.68
	CEM III/B	57.34	172.92	42.80	4.24	11.89	0.63	3.69	1.77	14.55	47.53
	CEM III/C	35.68	105.37	13.49	5.23	12.90	0.94	6.12	2.09	8.17	18.88
	P CEM III/C	38.78	154.48	27.00	8.39	19.61	1.64	9.99	2.78	7.88	17.22
Crushed *(mmol/kg DW)*	CEM I	17.93	135.73	23.84	0.28	0.20	< L.D.	< L.D.	0.10	681.77	1859.41
	CEM III/A	17.11	96.39	13.48	0.84	0.65	0.01	0.33	0.52	148.18	149.76
	CEM III/B	6.95	71.42	10.23	0.74	0.56	0.02	0.26	0.56	127.95	106.36
	CEM III/C	5.40	41.88	5.93	0.84	1.90	0.11	2.13	0.86	22.09	18.08
	P CEM III/C	14.63	66.03	25.29	0.98	0.53	5.12	1.17	1.37	123.56	14.04

< L.D.: result is lower than the limit of detection

Description: *Concentrations of major elements (Na, Ca, K, Al, Si) and sulfur anions (S^{2-}, SO_4^{2-} and $S_2O_3^{2-}$) are given as mmol/m² for the sprinkling leaching test, mmol/m² for the monolith tank leaching test and mmol/kg DW for the crushed leaching test. Ca/Si ratio is displayed, as well as the calculation of a ratio between the sum of the 5 major elements (Na, Ca, K, Al, Si) over the sum of the three sulfur anions (S^{2-}, $S_2O_3^{2-}$ and SO_4^{2-}), indicated as ∑cations/∑anions ratio for simplification.*

increased levels of Al_2O_3 and SiO_2. The lack of available Ca in GBFS high substituted systems leads to the consumption of Portlandite hydrates to allow precipitation of C–S–H, and the enrichment in Al_2O_3 of C–S–H to form C–A–S–H [20,21]. This behavior can be observed in the leachates chemistry and matches our own results of the Ca/Si ratio of leachates (Table 2). We observed an overarching trend in Ca and Si releases of a decreased Ca/Si ratio that appeared to correlate with increased GBFS content, presumably due to the fact that the Calcium is consumed by C–S–H incorporated into GBFS containing pastes. This was particularly the case for the crushed test and the monolith tank test, where CEM I concrete showed a Ca/Si ratio 5 to 30 times higher than the other concretes and cement paste. Consequently, Ca/Si decreased in the following order: CEM III/A > CEM III/B > CEM III/C. Calcium leaching mostly comes from the dissolution of Portlandite and interstitial solutions, whereas Si comes from the incongruent dissolution of C–S–H [9]. In the crushed test, the cement paste had a higher ratio than CEM III/C, given that the overall concentration was not diluted by aggregates. This was not observed for the other tests specific to surface leaching, unlike the crushed test.

The second effect of portlandite dissolution is that the alkalinity of the leachates increases. Cement containing more GBFS contains less clinker and consequently lowers CaO levels. If less portlandite forms when the concrete or cement paste is leached, less portlandite is dissolved which induces a lower pH. The pH ranges obtained for each test differed: the sprinkling test showed a pH range of 10.88–11.26, the monolith tank test showed a pH range of 11.33–11.90, and the crushed test pH range was observed a 12.10–12.49 (Fig. 5, 7 and 9). These differences depend, to a certain degree, on the testing method itself. The sprinkling test is carried out over a relatively short time duration and only leaches the surface of the block, often a very thin superficial layer. In the monolith tank test, the block was immersed for 24 hours, wherein water could penetrate the first millimeters of the surface, allowing a deeper leaching by diffusion. Finally, the crushed leaching test involved a highly specific surface due to block crushing, which allowed a high dissolution of hydrates and access to inner portions of the block.

Examining electrical conductivity of leachates is a particularly reliable way to assess the behavior of concrete and cement blocks subjected to various leaching test conditions. Conductivity ranges for the sprinkling test were between 0.17 and 0.36 mS/cm, for the monolith test between 0.46 and 1.14 mS/cm, and for the crushed test between 1.92 and 7.36 mS/cm (Fig. 5, 7 and 9). The crushed test proved by far to be the most “extractive” method, followed by the monolith tank test, and then the sprinkling test. Moreover, the same observations were made for a similar leaching test which showed a decrease of conductivity in leachates when GBFS content increased. In addition to the availability of the more soluble species (i.e. $Ca(OH)_2$ in particular), the porosity might also affect the dissolution, diffusion, and subsequent leaching of the more soluble species. In a solidified cement paste, and by extension in concrete, the mass transport is controled by the diffusion mechanism, and depends on the matrix’ porosity [7]. Importantly, GBFS impacts porosity, and effectively will lower the overall porosity of concretes and cement paste [22]. Thus, blocks with a high level of GBFS not only have less Portlandite, but are also less likely to diffuse and release elements and ions due to lower permeability. The amounts of the major elements (Na, Ca, and K) released in leachates decrease when GBFS increases (Table 2). Compared to those elements, the trend of Al is different. Between CEM III/A, B, and C concretes, Al slightly varies in a close range, 4.31–6.25 mmol/m² for sprinkling test, 4.24–5.23 mmol/m² for monolith tank test, and 0.74–0.84 for crushed test, with CEM III/B being lower than for CEM III/A and CEM III/C. This is consistent with the cement composition, as CEM III/B has a lower Al_2O_3 content than the two others with 9.56% versus 9.91 and 10.54% respectively for CEM III/A and CEM III/C (Table 1). Furthermore, despite the higher content of Al_2O_3 in GBFS-rich

concretes, Al leaching is most likely limited by the solubility of the incorporated hydrates, or Al dissolution may be controlled by precipitation of secondary Al-oxyhydroxides phases [23].

The leaching tests used in this study were designed to represent selected scenarios where a blue-green material is subjected to bad weather or environmental situations leading to surface or mass leaching. The choice of the monolith tank test and the crushed leaching test was made to follow as close as possible the related standard (i.e. NF EN 14957-4 12/2002 and XP CEN/TS 15862, 10/2012). For future environmental assessment of construction materials, these initial conditions could be improved. One European standard currently in development aims specifically to normalize the ecotoxicological assessment of construction materials and suggests reducing the L/S or L/A to concentrate the released compounds (draft standard "Construction Products - Assessment of release of dangerous substances – Determination of ecotoxicity of construction product eluates" FprCEN/TS, 2019). This could be specifically pertinent when applied to the monolith test, which by design concentrates on gauging minimal quantities of leaching solution required to surround the sample. Regarding the released concentrations in the crushed test, a L/S of 10 might be sufficient. This particular test, however, is possibly the most distant approximation of a real-life scenario, more so than the other two, in that it simulates a more aggressive environment than what would typically be associated with construction debris. It is highly unlikely than such debris would remain immersed in a large amount of water. It is more likely to be sporadically sprinkled with water by workers or rainfall. In this case, an innovative test could be developped, such as test that might account for column leaching but with a transient water regime, including dry phases, similar to those used in other fields as for marine sediments [24]. In the same way, the sprinkling leaching test was designed to fill a gap, since no surface dynamic test was found in literature. Even if the water regime is continuous, this test is probably the most realistic in terms of releases, although the L/A is the highest with about 13.5 cm^3/cm^2. This L/A is calculated as the ratio of the total volume of leaching solution (5000 cm^3) by the leached area of the block (about 370 cm^2, representing the top surface and one of the small sides). In this case, the L/S might be reduced, by decreasing the volume of leaching solution. Moreover, this test accounts for a virtual L/A, by taking into account the total volume of 30 liters sprinkled, because the pump is set to a speed of 125 mL/min, and the test duration is 4 hrs. On a mean surface of 370 cm^2 during the duration of the test, a mean L/A of 79 cm^3/cm^2 is obtained. This is effectively close to an annual rainfall of about 800 mm, which is equal to 80 cm^3/cm^2.

4.2 Sulfur speciation in leachates

Unlike major elements, sulfur anions tend to increase in leachates when GBFS concentrations are higher in concretes and cement paste (Table 2). However, major elements and sulfur anions are not released in the same proportions. The sum of the 3 sulfur anions (S^{2-}, $S_2O_3^{2-}$ and SO_4^{2-}) is always at least 10 times lower than the sum of the 5 major elements released (Na, K, Ca, Si, Al). For the sprinkling test, the ∑cations/∑anions ratio increased from 12 for the CEM III/C cement paste to 27 for CEM III/A concrete. For the monolith tank test, this ratio expanded from 17.2 for P CEM III/C to 108.7 for CEM III/A concrete, and even 617.6 for CEM I concrete. Finally, for the crushed leaching test, the ratio went from 14.0 for P CEM III/C to 149.8 for CEM III/A, and 1859.4 for CEM I.

The increase of sulfur anions in the leachates of GBFS-rich materials is not surprising, given that GBFS includes noticeable quantities of reduced sulfur compounds which promptly react when GBFS is hydrated. This mechanism is probably at the origin of the blue-green color. Unlike clinker, essentially all sulfur in GBFS is present in sulfide form due to the reducing conditions in the blast furnace [12,25]. Cement containing up to 90% GBFS can reach a redox potential of -250 to 350 mV (versus calomel electrode) [26,27]. Thus, sulfur speciation might take different forms in interstitial water, from sulfides (oxidation degree of –II) to sulfates (+VI) [10,11]. When GBFS-rich material is subjected to

leaching, those sulfur species can be easily leached, and most oxidizable species, i.e. sulfides, might be readily oxidized when leached, depending on the oxygen diffusion during the leaching test. The three tests performed in this study showed not only the presence of sulfates in leachates, but also thiosulfates and sulfides. Up to 0.80 mmol/m² (0.19 mg/L measured in the solution) of sulfides were quantified in the sprinkling test for the CEM III/C cement paste. Sulfides concentration reached 1.64 mmol/m² (0.44 mg/L in the solution) for the same material in the monolith tank test, and 5.12 mmol /kg DW (16.55 mg/L) in the crushed leaching test. In the same way, thiosulfates in the CEM III/C cement paste was quantified to 2.08 mmol/m², 2.78 mmol/m² and 1.37 mmol/kg DW respectively in the sprinkling test, monolith test, and the crushed leaching test. Thermodynamically, sulfides are oxidized in sulfates. However, it has been shown than the main products of sulfides' oxidation by molecular oxygen at pH > 8.5 are thiosulfates, and oxidation to the most stable product can take weeks [28–30]. From the three leaching tests used in this study, the sprinkling test was estimated to favor oxygen diffusion by creating a thin moving water slide upon a large area, unlike the monolith tank test for example. Yet, despite the bottles in the crushed test being purged with N_2, it is likely that oxygen concentrations were lowered, but not removed, as a function of the short duration time of the bubbling. Thus, even with reduced oxygen content, the crushed leaching test is more likely highly oxidative for released sulfides because of the 24 hours of turnaround shaking. Our results show a relatively low recovery of sulfides, for example for CEM III/B concrete, in the crushed samples test compared to the monolith test (0.02 mmol/kg DW versus 0.63 mmol/m², or 0.06 mg/L versus 0.17 mg/L in the leachates solutions) (Table 2). Moreover, CEM I only released about 1.12 mmol/m² of sulfates in the monolith test, or 0.10 mmol/kg DW of thiosulfates for the crushed test, meaning that for other samples, the majority of sulfur anions leached comes from the sulfides leaching and oxidation originated from GBFS. Finally, it is not surprising not to find gaseous H_2S during the unmolding process. With a pK_{a1} = 7.04 and a pK_{a2} = 11.96, and considering the strong alkaline pH, it seems unlikely that sulfides turn into H_2S.

The most striking aspect of the sulfur chemistry occurring in GBFS-rich materials is the origin of the blue-green color. In fact, the intensity of the color effect is basically a slag conditional mechanism and is related to sulfides content. In particular, the association of the three chromophorous radical ions $S_4^{\cdot-}$, $S_3^{\cdot-}$, $S_2^{\cdot-}$ is responsible for the blue-green color of the hydrated slag [2]. In Lapis Lazulis, the mix of chromophores $S_2^{\cdot-}$ (yellow) and $S_3^{\cdot-}$ (blue) in zeolithe-type structures explains the ultramarine colors ranging from deep blue to green [31]. For cement, the appearance of the greening color depends more highly on the replacement ratio of clinker by GBFS (Fig. 4). From almost 100% of clinker (for CEM I) to 85% replacement by GBFS (CEM III/C), the color shifts to green, toward –a*, and blue, toward –b*. Vernet proposed that the color is concentrated in a fraction containing a solid solution of sulfides and sulfates in an aluminate hydrate [3]. The precise chemistry governing the appearance and disappearance of the blue-green color has not yet been determined. However, the disappearance of the color probably involves an oxidation of the sulfides by molecular oxygen penetrating in the superficial surface. Preliminary experiments showed that the color took some weeks to disappear. Below 20 cm of water, the color does not visually change for months.

Finally, concerning the human health impact of such leachates, we detected no hazardous substances, except dissolved sulfides. Regarding these dissolved sulfides, there is no threshold value in any recommendation from Word Health Organization.

Gas emission from use of hydrogen sulfides is unlikely to occur, but depending on the GBFS content, sulfides might be released during leaching by rainfall or groundwater. As chemical oxidation of sulfides to sulfates by molecular oxygen is a slow process, sulfides might be spilled into groundwater [32]. However, two processes will quickly prevent any accumulation or damages to the environment.

Firstly, even if the chemical oxidation is slow, some ionic species act as catalysts for this reaction, such as Mn^{2+}, Fe^{2+} or Cu^{2+}, and reduce the meta-stability of sulfides from one or two orders of magnitude [33,34]. Biotic oxidation with sulfo-oxidant bacteria is also highly effective for sulfides oxidation [32]. Additionally, precipitation with trace metals is another means of removing sulfides from the leaching solution, since metals such as Zn (pKs = 23 for Sphalerite), Cu (pKs = 47.6 for Cu2S) or Pb (pKs = 27 for PbS) form insoluble sulfides [35]. Incidentally, no threshold was determined for soluble sulfides by WHO [14]. Concerning the environmental impact, sulfate is the only compound which can be potentially problematic. For comparison purposes, the values obtained in this study can be compared to French legislation, concerning the admission of inert wastes into classified installation [36]. Concrete is included in the category of recognized inert wastes. For this purpose, the waste is submitted for leach testing and needs to comply with threshold values for 18 parameters. Sulfates are one of the parameters, with a threshold value of 6000 mg/kg DW for L/S = 10 ml/g DW. Also, a more severe threshold is observed for the reuse of slags in road construction, with a threshold value for sulfates of 1300 mg/kg DW for type 3 use [37]. The highest value obtained in this study was 204 mg/kg DW for CEM III/C concrete, almost 20 times lower than the legislation threshold (Fig. 10).

For a more thorough environmental study of construction materials, additional aspects might well be considered. In particular, beyond the chemical leaching behavior, it could be useful to assess the ecotoxicological aspects [38].

5 Conclusions

Greening effect occurs either during removal of formwork of blast furnace cement (CEM III) based concrete, or demolishing CEM III based old concrete, and has raised question about its environmental and health safety. Three scenarios were studied, with a specific leaching test for each:

- Freshly demolded fair faced blue-green concrete subjected to leaching by rainfall was assessed with an innovative leaching test designed to sprinkle water on the surface of a concrete block;
- CEM III based concrete of building foundations immersed in groundwater was assessed with a standard monolith leaching test;
- Demolition debris of old concrete blocks containing GBFS, sprinkled with water by workers or by rainfall was assessed with a standard batch leaching test on crushed samples.

Three cements with GBFS were selected (CEM III/A, CEM III/B and CEM III/C) to form concrete blocks and one cement paste (with CEM III/C cement), and one reference (CEM I, clinker only) as concrete. The greening effect was observed to correlate with concentrations of GBFS, wherein the color shifted to green and blue with the increase of GBFS content. Slag content in concretes and cement paste was also linked to a higher release of sulfur anions in the leachates, in the form of sulfides, thiosulfates and sulfates. Compared to the very low releases of sulfur anions in CEM I leachates, 108 mg/m^2 of sulfates in tank monolith test and 11 mg/kg of Dry Weight (DW) of thiosulfates in a crushed leaching test, it appears that most of these anions came from GBFS, where sulfur is mainly under sulfides form. As such, thiosulfates and sulfates are the main oxidation products of sulfides included in GBFS. For example, sulfates release in the monolith tank test for CEM III/C concrete is 588 mg/m^2, with 30.1 mg/m^2 of sulfides and 234 mg/m^2 of thiosulfates. Nevertheless, sulfates levels reported here are lower than thresholds for inert wastes or for reuse of alternate materials in road construction. Moreover, no chromium, or other hazardous metals, were detected in leachates. The major elements released were Na, K and Ca.

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