



Greening effect in slag cement materials



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ABSTRACT

This article presents the first spectroscopic data describing the processes responsible for the temporary blue-green coloration that forms during the hydration of various materials containing Ground Granulated Blast-furnace Slag (GGBS) under anoxic conditions. UV-visible-near infrared Diffuse Reflectance (DR) spectra demonstrate a striking similarity of the coloring center forming during the curing of a broad range of GGBS-bearing materials (pure GGBS with different compositions, mix Portland cement/GGBS (30/70), concrete and mortar). All spectra are similar to those of polysulfide complexes contained in the interlayer spacing of a synthetic green-colored hydrated calcium aluminate phase (AFm). This “greening effect” demonstrates a progressive oxidation of sulfide-based compounds initially contained in these materials during curing of GGBS bearing materials.

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1. Introduction

In order to decrease the environmental impact of concrete within an environmentally sustainable design and reduce CO₂ emissions due to its production, Ground Granulated Blast-furnace Slag (GGBS), a glassy by-product of pig iron and steel manufacturing, is commonly used to produce blast-furnace slag cements and GGBS-concrete mixtures [1]. However, concrete based on CEM III cements, or on equivalent binders of GGBS in combination with Portland cement, tends to develop, under certain circumstances, a temporary blue-green color immediately after casting [2]. This coloration, sometimes referred to as a “greening effect”, has been noticed since early uses of GGBS in the cement industry, at the end of the 19th century. Since that time, it has raised some degree of concern due to a lack of knowledge of its origin. However, there are neither indications of inferior engineering properties or adverse consequences nor evidence of impacts on occupational health or environmental consequences during demolding or aging of the concrete. In particular, it does not

affect mechanical strength or other concrete properties but it impacts the visual aspect with mediatized consequences. Such coloration is temporary: the color vanishes at the surface of these materials after a few days or weeks of exposure to air and adopts the typical light grey color of slag cement concrete, even though the inside may remain green for years. When old GGBS-based concrete is being demolished, it often shows internal evidence of greening when it is fractured or drilled. A similar coloration has been recently observed in solidified cementitious waste forms containing GGBS, which showed a deep blue fading coloration that has raised concerns about its influence on other physical properties of this solidified waste over long times [3].

In the absence of experimental or analytical data, the origin of the blue-green coloration of GGBS-based materials has only been speculated: formation of new phases during GGBS hydration, such as FeS or MnS [4], or charge transfer processes in various phases or complexes, such as green rusts [5], hydrated ferrous sulfates [2,5] or ferro/ferricyanide complexes and Prussian-blue type pigments [6]. The presence of S²⁻ in hydrated calcium aluminates with substituted Fe(III) has also been speculated as being responsible for the coloration during GGBS hydration [7]. As the sulfide anion S²⁻ does not absorb in the visible region, it cannot be a coloring agent

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by itself, by contrast to polysulfides that may form during its oxidation under controlled conditions [8]. Sulfur speciation in GGBS has been investigated using X-ray absorption near-edge structure spectroscopy (XANES) but these studies were not linked to the greening [9,10].

The purpose of this study is to understand the origin of the “greening effect” using UV-visible-near infrared Diffuse Reflectance (DR) spectroscopy, a method that provides direct information on the coloration. For the first time, this coloration has been assigned to the presence of original absorption bands in the DR spectra. The spectral parameters do not change over a broad range of GGBS-bearing materials: hydrated pastes of pure GGBS from various origins, hydrated pastes of a mix Portland cement/GGBS (30/70), CEM III based concrete and mortar. This demonstrates a striking similarity of the coloring center. A comparison with the DR spectrum of a synthetic green-colored hydrated calcium aluminate phase (AFm) with interlayer polysulfides and presenting the same absorption bands allows the identification of polysulfide anions as the coloring centers forming during curing of GGBS-based materials. The metastability of this color, which bleaches when the sulfide-based compounds initially contained in the materials are progressively oxidized, makes this “greening effect” a witness of the progressive oxidation of GGBS-bearing materials.

2. Experimental

2.1. Materials

Ground Granulated Blast-furnace Slag (GGBS) samples from Fos-sur-mer and Dunkerque (France), Seraing (Belgium) and Dillingen (Germany) were investigated. Their chemical compositions (Table 1) were obtained by X-Ray Fluorescence using a PANalytical/Zetium spectrometer. The LOI 950 °C O₂ and LOI 500 °C N₂ were determined by calcination for 60 min ± 15 min of respectively 2 g ± 0.1 g of GGBS at 950 °C ± 25 °C and 1 g ± 0.1 g of GGBS at 500 °C ± 25 °C under inert N₂ atmosphere. The content of sulfides S²⁻ was determined by potentiometric back titration with a combined Ag-ring electrode. These GGBS samples were ground at a Blaine specific surface area around 4000 cm²/g to speed up the hydration. The specific surface area was determined by the Blaine method according to the NF EN 196-6 standard of April 2012. 100 g of each of these dry powders were hydrated at room temperature

Table 1
Composition (in wt %) of the GGBS investigated.

	Fos-sur-mer	Dunkerque	Seraing	Dillingen
LOI 950 °C O ₂	-0.15	-0.74	1.3	-1.19
LOI 500 °C N ₂	0.78	0.54	1.07	0.49
LOI 950 °C O ₂ corrected	1.47	0.88	2.8	0.85
SiO ₂	36.08	35.84	35.46	36.5
Al ₂ O ₃	10.86	11.64	10.19	11.18
Fe ₂ O ₃	0.48	0.36	0.6	0.61
CaO	42.35	41.66	40.08	41.87
MgO	6.95	7.51	9.38	6.83
K ₂ O	0.36	0.39	0.37	0.47
Na ₂ O	0.24	0.33	0.25	0.3
SO ₃	1.73	1.7	1.24	1.99
TiO ₂	0.47	0.81	0.38	0.53
Mn ₂ O ₃	0.33	0.27	0.22	0.46
P ₂ O ₅	0.01	0.01	0.01	0.01
Cr ₂ O ₃	0	0.01	0	0
SrO	0.06	0.07	0.07	0.07
Total	99.78	99.86	99.55	99.63
S ²⁻	0.81	0.81	0.75	1.02

LOI: Loss On Ignition.

LOI 950 °C O₂ corrected = (LOI 950 °C O₂) + 1.996*S²⁻ [11].

with a water/GGBS mass ratio of 0.5 in 60 mL polypropylene containers. After casting, tap water was carefully poured on the top of the fresh pastes up to the top of the containers to minimize contact with air and to ensure anoxic conditions during curing. The containers were properly closed with their respective plastic leads to minimize contact with air. The sealed containers were left to cure at room temperature for a month and then the DR spectra of the colored GGBS were measured without opening the polypropylene containers.

A sample of a mix of industrial Portland cement (30 wt %) and GGBS (70 wt %) of usual fineness, 3800 and 3400 cm²/g respectively, was prepared by mechanical mixing in a “turbula” mixing device for 3 h. The obtained dry powder was hydrated with a water/binder mass ratio of 0.5 and then cast with the procedure used for GGBS hydration described above. A sample of C35-45 hardened concrete and another of hardened injection mortar, both of them based on slag cement and presenting a similar blue-green coloration, were also analyzed. The mortar was made from a slag-cement, with a Blaine specific surface about 12 000 cm²/g, containing 82% of GGBS and siliceous sand (58.5 vol %) with a water/binder ratio of 1.5. The concrete was made from a CEM III/A 52.5 L CE PM-ES-CP1 NF cement, with a Blaine specific surface of 4175 cm²/g, which contained 64% of GGBS. The water/binder ratio was 0.44. Granite aggregates were used and each cubic meter of concrete contained 400 kg of cement. This sample was kept under water for a month and then its DR spectrum was measured.

An AFm phase was synthesized from CaS (99% pure, Alfa Aesar) and Al₂S₃ (98% pure, Acros Organics), with a molar ratio [Ca²⁺]/[Al³⁺] = 2 in the appropriate volume of a NaOH solution at pH = 13 (0.1 mol/L) in order to obtain a total concentration [Ca²⁺] + [Al³⁺] = 0.025 mol/L. The iron content of the solution was below 0.02%. pH was kept to 13 by adding a NaOH solution at a pH of 13.5, using an automatic titrator ‘Titroprocessor 670’ (Metrohm AG). When pH was stabilized at 13, the solution was stirred for about 15 h. The synthesis was performed under a flow of nitrogen to prevent oxidation and carbonation. The hydration of sulfide that can lead to the formation of toxic H₂S should be avoided in such basic conditions. Nevertheless, the synthesis station was put in a fume hood controlled by a H₂S detector. The green powder was then separated from the mother solution by settling. The precipitate was washed twice with ethanol and dried at room temperature under dynamic vacuum. This method is commonly used to stop hydration of hydraulic binders as it removes the aqueous solution without interfering with the hydrates and prevents carbonation. The dry product was a pale-green powder whose color remained stable. The purity of this phase, hereafter referred to as AFm-S, was checked by X-ray diffraction and FTIR. The FTIR spectrum, not presented here, was used to confirm that this technique prevents the oxidation of the sulfur anions into sulfate, which occurs when the sample is dried in open air without previous washing.

2.2. Characterization methods

UV-visible-near infrared Diffuse Reflectance (DR) spectra of powdered samples were obtained from 5000 to 33 000 cm⁻¹ using a computerized PerkinElmer® Lambda 1050 spectrophotometer fitted with a Harrick® “Praying Mantis” attachment coated with halon®. BaSO₄ powder was used as white reference. For the solid samples, a large integrating sphere from PerkinElmer® was used, with solid halon® as white reference. The samples were investigated within their containers to prevent oxidation. The spectra of the empty containers were recorded to identify their spectral contributions. The Kubelka-Munk formalism was used to model the diffuse reflectance *R* (no unit) in the form of the remission function *f*(*R*) (no unit), which is a good approximation of the actual

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