

Key Points

- ▶ A temporary blue-green colouring is observed on concrete containing slag in the form of CEM III or CEM I cement + addition, regardless of implementation method (ready-to-use, prefabrication, structural work, etc.).
- ▶ This coloration is found in all materials containing slag (concrete, mortar, cement, pure slag).
- ▶ Colour is expressed only in the absence of oxygen (anoxic condition). Such is the case, for example, with a formwork.
- ▶ The colour of opaque materials can be studied, explained and quantified by UV-visible-near IR spectroscopy in diffuse reflectance mode.
- ▶ The greening observed is due to chemical constituents present in slag in small quantities: polysulfide ions S_2^- , S_3^{2-} et S_4^{2-} .

Greening: a temporary colouring due to polysulfide ions, having no impact on concrete usage properties



FIGURE 1 - Blue-green colouring observed on concrete containing slag (left, ready-to-use concrete; right, prefabricated concrete - © Eqiom)

INTRODUCTION

Since the late 19th century, blast furnace slag has been used in the manufacture of cements - mainly CEM III cements and later, CEM II/A and II/B as well as CEM V/A or V/B cements - giving them particular properties enabling resistance to chlorides and sulfates and limiting CO_2 emissions released during the manufacturing of clinker. It has been observed that cement-based concretes containing blast furnace slag exhibited a blue-green colour shortly after stripping. This colour, a known marker of blast furnace slag in hydraulic binders, generally disappears from the concrete's surface after some time (from a few hours to a few days; in rare instances, a few months) of exposure to the open air, although it can persist for decades inside the material's core. While concrete performance is not affected, this colouring is a temporary blight on a building's aesthetics. Furthermore, an incomplete understanding of its origins has raised issues relating to toxicity for humans, for example through the emission of volatile compounds, or to the environment, through rainwater runoff from the material.

This article collates and presents the basic data necessary to understand the conditions of the appearance of blue-green colouring on materials containing blast furnace slag cement, and necessary to characterise this colour as well as identify its origin.

STATE OF THE ART

Various hypotheses have been put forward explaining the origin of the greening observed: the presence of chromium, the formation of iron sulfides (FeS) and manganese sulfides (MnS) (1), the oxidation of iron sulfides into siderite hydrated iron sulfates ($FeSO_4 \cdot 5H_2O$) and melanterite ($FeSO_4 \cdot 7H_2O$) (2), the presence of an iron mineral in the form of green rust ($[Fe^{2+}_{(1-x)}Fe^{3+}_x(OH)_2]^{x+}[x/n A^{n-}, m H_2O]_x^-$ with $x = Fe^{3+}/Fe_{tot}$, $A = SO_4^{2-}$ or CO_3^{2-} or another anion) (3), the presence of ferrocyanide as in Prussian blue (4, 5) or the formation of an iron aluminate containing sulfide ions S^{2-} (6).

However, these are only hypotheses since the presence of these phases in slag has not been demonstrated and no spectroscopic data exists to confirm that these phases' colour is identical to that observed in slag concretes.

EXPRESSION OF COLORATION

A laboratory study of colour expression conditions shows that colour appears a few days after mixing and only if the material (pure slag paste, mortar or concrete containing CEM III) is hydrated and preserved in the absence of oxygen (anoxic conditions). This effectively simulates what happens when concrete is placed in a formwork that isolates it from the surrounding air, thus creating anoxic conditions.

If the sample is hydrated and stored in the open air, the colour does not appear. However, even the free side can be coloured under certain paving conditions, making use of a particularly meticulous slide rule finish. In this case, it is the finishing process that generates a translucent surface layer consisting of crystallographically oriented portlandite crystals (identified by X-ray diffraction) parallel to the paving plane, and isolating the rest of the concrete from the ambient atmosphere. The colouration can then take several months to disappear while carbonation acts on this fairly smooth surface. This experiment shows that temporary colouring is expressed

in concrete containing slag in the form of CEM III or CEM I cement + addition, regardless of implementation method (ready-to-use, prefabrication, structural work), but also for mortars containing slag, slag cements and ground slag mixed in pure paste.

It is therefore an intrinsic characteristic of hydrated slag and not the result of slag/cement interaction.

The more finely slag is ground (small grain size), the higher the pH (basic conditions) and the higher the temperature, the faster the coloration appears. All these parameters accelerate the slag's hydration, which explains the faster appearance of coloration. Finally, for CEM II-type cements, it is often reported that coloration is only expressed for slag contents higher than 20 to 25%. This threshold value is indeed confirmed by spectroscopic measurements showing that the colour is not detectable on hydrated cements containing less than 20-25% slag.

CHARACTERISING THIS COLORATION

This colouring is too often viewed within qualitative macroscopic parameters (apple green, almond green, sea green, etc.) despite the fact that it can be quantified, thereby revealing the material's physico-chemical makeup. This article takes a look at two colour analysis methods: UV-visible near-IR diffuse reflectance spectroscopy and $L^*a^*b^*$ colorimetry.

■ UV-visible-near-IR diffuse reflectance spectroscopy

Ultraviolet (UV)-visible-near-infrared (IR) spectroscopy makes it possible to identify the sample's absorption bands, which correspond to the wavelengths absorbed by the material, as well as the transmission windows, which correspond to the wavelengths that aren't absorbed, thereby giving the material its colour. Absorption bands are characteristic of an element in a given environment geometry and therefore enable identification of the coloration-causing elements. For materials such as pure cement or pure slag paste, mortar or solid concrete, near-opaque at the macroscopic scale, measurement is performed in diffuse reflectance mode. Because the material prevents light from passing through it, it isn't possible to measure its absorption through transmission, as can traditionally be done for transparent coloured thin films or solutions. A light beam is projected onto the sample, which diffuses it in every direction. The scattered beams are collected using a white material-coated sphere containing the sample. The beams are then shone onto a detector, making it possible to identify the material's absorption bands.

Measurements are made between 5,000 and 30,000 cm^{-1} (i.e. between 2,000 and about 330 nm) in order to cover both the colour-related visible spectrum (12,500 to 25,000 cm^{-1}), but also near-UV and near-IR bands where selective absorptions (electronic transitions) can also occur. Though said bands aren't at the origin of

the colours observable by the human eye, they are part of the sample's signature and may reveal the presence of certain colouring elements which also have absorption bands outside the visible range. The spectra obtained are plotted as the remission function $f(R)$, as a function of the wave number. The remission function is a magnitude without unit used for diffuse reflectance measurements on opaque samples. It is proportional to the material's absorbency. The wave number (in cm^{-1}) is the inverse of the wavelength (in nm); it is commonly used in spectroscopy because it is proportional to energy.

The spectrum of a non-hydrated slag from Dunkirk (Dunkerque) is shown in Figure 2(a). This spectrum has a broad absorption band around 8,000 cm^{-1} characteristic of Iron(II) and an intense rise towards UV (large wave number region) characteristic of an interaction between iron and oxygen (referred to as iron-oxygen "charge transfer"). No other bands are visible.

The spectrum of the same Dunkirk slag, tempered with a water/slag ratio of 0.5 and kept away from the air (anoxic conditions), is presented in Figure 2(b). This spectrum has three absorption bands, at 15,600 cm^{-1} , 18,700 cm^{-1} and 22,900 cm^{-1} respectively. These three bands create two transmission windows, TW1 and TW2. The first sits at 17,800 cm^{-1} , corresponding to a green colouring, and the second at 20,800 cm^{-1} , corresponding to a blue colouring. The result is a material with a blue-green appearance.

The study of slags of various origins and compositions shows that this spectrum remains identical, both for the position of the absorption bands and their relative intensities (Figure 2c). The same applies when comparing the spectra, measured at 28 days, of a pure slag, a mixture [30% CEM cement I + 70% slag], a mortar containing slag and a concrete based on CEM III/A. Colouring is therefore an intrinsic characteristic of slag. It is due either to a single colouring species, with 3 absorption bands; or to several species but always in the same proportions. Indeed, the relative intensity of the bands, which depends on the concentration of colouring species, always holds constant.

■ $L^*a^*b^*$ colorimetry

It is also possible to quantify colour by calculating parameters called colour coordinates. Several quantification models have been defined by the International Commission on Illumination (CIE) (7). Among them, the $L^*a^*b^*$ model has the advantage of being isometric, i.e. two displacements of equal distance in this space correspond to equal differences in colour perception. L^* represents brightness, varying from 0 (black) to 100 (white). The a^* axis varies from green (negative values) to red (positive values) and the b^* axis from blue (negative values) to yellow (positive values).

$L^*a^*b^*$ coordinates are calculated from previous diffuse reflectance spectra by considering the response of a model human eye looking at this material in midday sunlight in Western Europe.

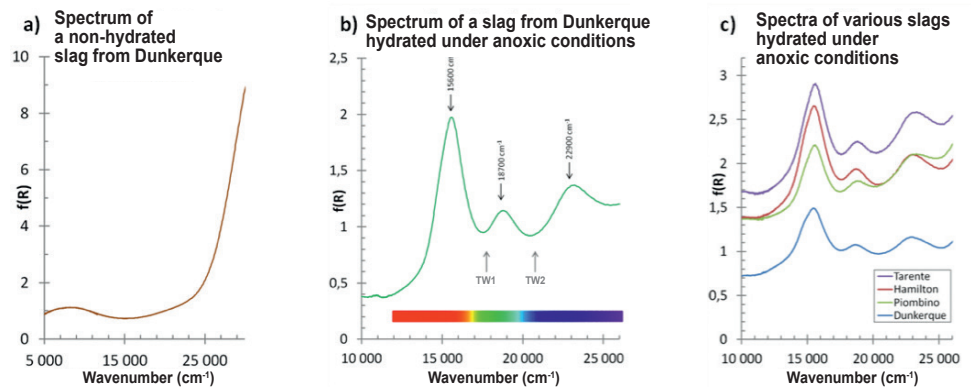


FIGURE 2 - (a) UV-visible near-IR spectrum, measured in diffuse reflectance, of a non-hydrated Dunkirk (Dunkerque) slag. (b) UV-visible near-IR spectrum, measured in diffuse reflectance, of a Dunkirk slag hydrated in pure paste under anoxic conditions. (c) UV-visible near-IR spectra, measured in diffuse reflectance, of slags of different origins, hydrated in pure pastes, under anoxic conditions.

These colorimetric characteristics can also be measured very easily, using a portable spectro-colourimeter for example.

Monitoring the $L^*a^*b^*$ coordinates of a slag during hydration makes it possible to analyse the progressive appearance of colour. This can be tracked with particular efficacy through the a^* parameter whose value decreases as the material turns green (see Figure 3).

PINPOINTING THE CAUSES OF GREENING

■ Synthesis of an AFm phase (calcium aluminate hydrate) with sulfur

When slag is hydrated, a hydrated calcium aluminate phase called AFm, is formed. This AFm phase has a lamellar double hydroxide (LDH) structure with calcium aluminate $[Ca_2Al(OH)_6]^+$ sheets separated by water molecules and anions. LDHs are known for their strong ability to trap and exchange anions.

Various authors have suggested that the presence of S^{2-} , sulfide ions, in particular in an AFm phase, could be the reason for slag cements' colouring, though this claim is unproven (1, 6). To verify this hypothesis, an AFm phase was synthesized from calcium sulfides (CaS) and aluminium sulfides (Al_2S_3). This synthesis was carried out under nitrogen flow, i.e. in the absence of oxygen, and under basic conditions (pH = 13) in order to stabilise the S^{2-} sulfides. The powder obtained, noted as AFm-S in reference to the presence of sulfur, is light green in colour (8).

■ Characterisation of this phase

AFm-S light green powder was characterised by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) with Rietveld refinement. These analyses confirmed that the compound formed was indeed part of the AFm family. They also showed that the anions present in the interlayer were not only S^{2-} and that the structure was compatible with the presence

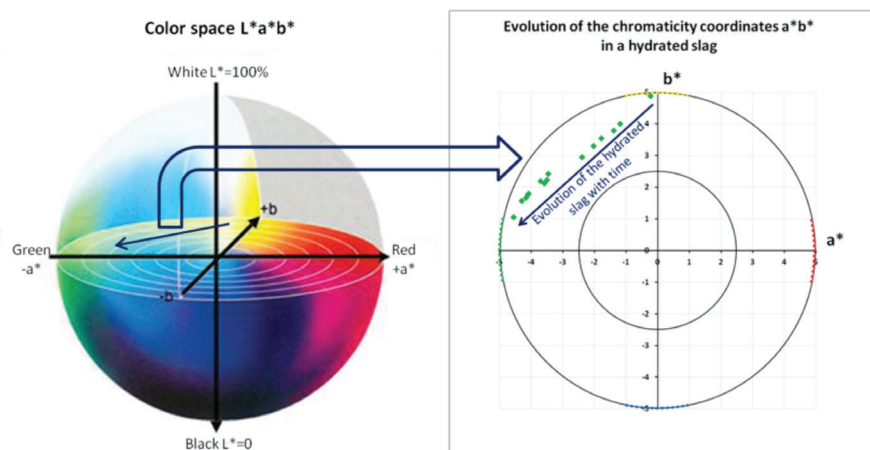


FIGURE 3 - Evolution over time of a hydrated slag's a^*b^* chromatic coordinates. The decrease in parameters a^* and b^* during hydration makes it possible to quantify the appearance of the blue-green coloration.

READING COMMITTEE:

- Anne DENOYELLE
- Jean-Philippe GANDY
- Xavier GUILLOT
- Dominique GUINOT
- Gilbert NOWORYTA
- Manuela TANCOCNE-DEJEAN

ATILH
7, place de la Défense
92974 Paris-la-Défense
Tél. : 01 55 23 01 30

Contact : contact@atilh.fr
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Anne Bernard-Gely
Managing editor:
Laurent Izoret

of polysulfide radical ions such as S_2^- (i.e. S-S \cdot^- , not to be confused with the sulfide ion S^{2-} which corresponds to S^{2-}), S_3^- and S_4^- (8). The UV-visible near-IR spectrum of the synthesized AFm-S, measured in diffuse reflectance, has 3 absorption bands, at 15,600, 18,700 and 22,600 cm^{-1} respectively (Figure 4). The position of these bands, as well as their respective intensities and widths at mid-height, are similar to those observed on the spectrum of a hydrated slag under anoxic conditions with a characteristic blue-green colouring. However, the overall spectrum intensity is much lower than for hydrated slag. In terms of chromatic coordinates, this results in similar a^* and b^* but a much higher L^* , meaning a similar but much lighter colour. This difference in colour intensity may be due to a lower concentration of colouring elements, or simply because the AFm-S powder is finely divided and therefore diffuses more light than solid coloured slag.

■ Origin of greening: polysulfide ions

The similarity between the spectrum of AFm-S and that of coloured slag, suggests that the colour of these materials is due to sulfur-derived ions. At the same time, it rules out all colouring hypotheses based on the presence of iron or CN $^-$ cyanide ions. Similarly, chromium, either in Cr(III) or Cr(VI) forms, cannot be responsible for the colouring. Indeed, Cr(VI), which gives cements a "canary" yellow colour, absorbs only in UV and has no absorption band in the visible range, as tested here (9). Cr(III), on the other hand, only has two absorption bands, around 15,000 cm^{-1} and 22,000 cm^{-1} , and not three (10). These bands are close to the first and third slag spectrum absorption bands and the slag may contain some chromium. However, any Cr(III) contained in slag is already present before hydration, so its bands should already appear on the spectrum of non-hydrated slag (Figure 2a), which is not the case. The colouring is therefore not due to chromium.

The sulfide ion S^{2-} present in slags, is formed under reducing conditions in blast furnaces. However, this ion is not a dye and therefore cannot be at the origin of the greening observed. Polysulfide ions such as S_2^- (i.e. S-S \cdot^-), S_3^- and S_4^- which can be formed by controlled oxidation of the sulfide ions S^{2-} (S^{2-}) are colouring elements which have been extensively studied in pigments such as ultramarine (11, 12). According to literature, the spectrum's three bands can be assigned as follows:

- The first band, at 15,600 cm^{-1} , corresponds to the trisulfide radical ion S_3^- (13, 15)
- The second band, at 18,700 cm^{-1} , corresponds to the radical ion S_4^- (or the neutral form S_4) (12, 13)
- The third band, at 22,900 cm^{-1} , corresponds

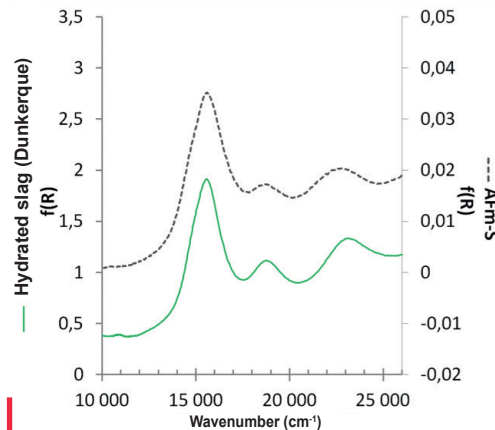


FIGURE 4 - Comparison of UV-visible near-IR spectra in diffuse reflectance of the synthesized AFm-S compound and a hydrated slag under anoxic conditions.

to the radical ion S_2^- (12, 14).

The greening observed is therefore due solely to the presence of these three polysulfide radicals. The latter are always found in very similar proportions, regardless of the slag's origin. The same three-band spectrum can also be observed in cases where polysulfides are associated with very different matrices, such as in a lamellar double hydroxide (LDH) composed of magnesium and aluminium (16) or with kaolinite in a pulp mill (17). This shows that there is a balance between these three polysulfides or that they are associated with each other.

Polysulfides are stable in the absence of oxidising elements such as oxygen in the air, which is why the blue-green colour of slag is stable and remains permanent as long as it is protected from the air (anoxic conditions). When in solution, polysulfide ions oxidise rapidly when in contact with atmospheric oxygen (11). However, when trapped in certain crystal structures (such as in ultramarine pigments containing two of the three polysulfides), they remain stable even in the open air. In the case of hydrated slag, polysulfide ions are destabilised when in contact with atmospheric oxygen. Discoloration is slower than in solution due to the more complex local polysulfide environment. The colour is visible for a few hours or days but gradually disappears from the air-exposed surface. The core of the material has little contact with the oxygen in the air. This is why the colour can remain present at the core. It is thus possible to observe concrete whose core is still coloured decades later.

HEALTH AND ENVIRONMENTAL IMPACT

In the almost 100 years since this phenomenon was discovered, the blue-green colouring discussed in this article has neither been linked to any pathology affecting construction site operators, nor with proven environmental pollution. On this basis, we believe that such temporary colouring has no environmental or health impact. However, as the chemical origin of the colouration has now been demonstrated, ATILH will undertake a specific study of these potential impacts, due to repeated questions on these issues.

CONCLUSIONS

Studies of the blue-green colouring resulting from hydration of cement materials containing blast furnace slag (concrete or mortar based on CEM III or CEM I + addition, cements containing slag, pure slag, etc.) show that this colouring only appears in the absence of oxy-

gen (anoxic conditions). Its characterisation by UV-visible near-IR spectroscopy reveals this to be due to the presence of three polysulfide radicals, S_2^- , S_3^- and S_4^- derived from sulfur present in the slag, which are always found in the same proportions regardless of a slag's origin. These are the only elements responsible for colouring, with iron or chromium probably having no effect, at least as first-order parameters. The colour is permanent in the absence of oxygen but gradually disappears in contact with air.

Authors

Laurent IZORET
ATILH

Domitille LE CORNEC
ATILH and Sorbonne University, IMPMC laboratory

Brian STACY
English version

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Conclusion

- ▶ Blue-green colouring is therefore a temporary effect and a marker of the presence of blast furnace slag, with no impact on the usage properties of slag-containing concretes and mortars.
- ▶ In the absence of any declared pathology and/or ascertained pollution, this colouring may be considered free of risk for human health and the environment.
- ▶ As the origin of the colouring is now known, a specific study of its impact on health and the environment will be undertaken in order to confirm its innocuity.