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Communication

The coloration phenomenon associated with slag blended cements

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Abstract

Blue-green coloration observed in concrete made with slag-blended cement sometimes raises concern mainly due to lack of understanding of the causes. This article presents the results of a study conducted to investigate the various factors that influence the coloration. Five different concrete mixes were studied with water to binder ratio ranging from 0.3 to 0.5 with 50% and 70% slag in the binder. Three different curing regimes were studied, namely, (1) bath curing under constant temperature, (2) sealing with plastic bags to stop any moisture movements under constant temperature and (3) curing in water baths temperature matched to in situ conditions. Extent and intensity of the coloration was also studied in four large-size columns by taking cores from columns at various ages. The compressive strength of the cores was also determined. The results show that the coloration is a function of rate of oxidation, curing conditions and slag content. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Concrete made with slag-blended cement has a tendency to develop a distinct blue-green coloration a few days after casting [1]. Previous researchers have encountered the phenomenon and reported its existence in full-scale structures [2]. Occasionally, its presence can cause some degree of concern due to a lack of knowledge of its cause. Commonly, the concern is associated with speculation of adverse consequences.

This article presents the results of an experimental program, which investigated the extent and intensity of various factors that contribute to coloration phenomenon. Some expla-nations of the reasons behind the coloration are also provided.

2. Proposed explanation

Iron and sulfides are present in blast-furnace slag during the manufacture of iron. The iron and sulfide compounds react at high temperatures to form iron sulfide. This material is oxidized during the granulation process to ferric salts, which are generally black in color.

Granulated slag also forms a vesicular, open structure, and some of the iron oxide material remains in the ferrous state. During the hydration process, the high-temperature iron sulfides decompose to produce limonite (hydrated iron oxide) and iron sulfate crystallites. The iron sulfate crystallites are ferrous sulfate hydrate and are found in two forms:

$FeSO_4{\cdot}5H_2O$ (siderotilate)
$FeSO_4{\cdot}7H_2O$ (rosenite)

The first form, siderotilate, is green in color, while the second form, rosenite, is a blue-green. These materials are responsible for the coloration in moist concrete. Another independent study [3] on the same source of slag confirms the presence of siderotilate and rosenite.

As the concrete dries and oxygen enters the hydrating matrix, the water of crystallization is lost by desiccation and the ferrous salts oxidize to ferric salts. This causes the color to change from blue-green to brown. For a particular concrete, all other factors being equal, the depth of color is a function of the quantity of sulfur

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present in the slag, the blast-furnace conditions and the granulator performance.

The flow diagram, shown in Fig. 1, summarizes the process involved in producing the blue-green coloration encountered in slag-blended concrete.

3. Experimental program

Four concrete columns of 800 × 800 mm in cross section and 1200 mm in height were made as part of this experimental program to study the effect of coloration in in situ concrete and its relationship with compressive strength, if any. All the columns contained 50% Portland cement and 50% slag in the binder and similar levels of workability (slumps within the range of 100–130 mm) and water content (water content within the range of 165–180 kg/m^3). The main variable between the columns is the water to binder (slag + Portland cement) ratio.

Further, standard cylinders (100 mm in diameter and 200 mm in height) were made using a concrete mix with 70% slag in the binder with a water to binder ratio of 0.3, to study the effect of various curing conditions on coloration and compressive strength in a high-slag-content concrete mix.

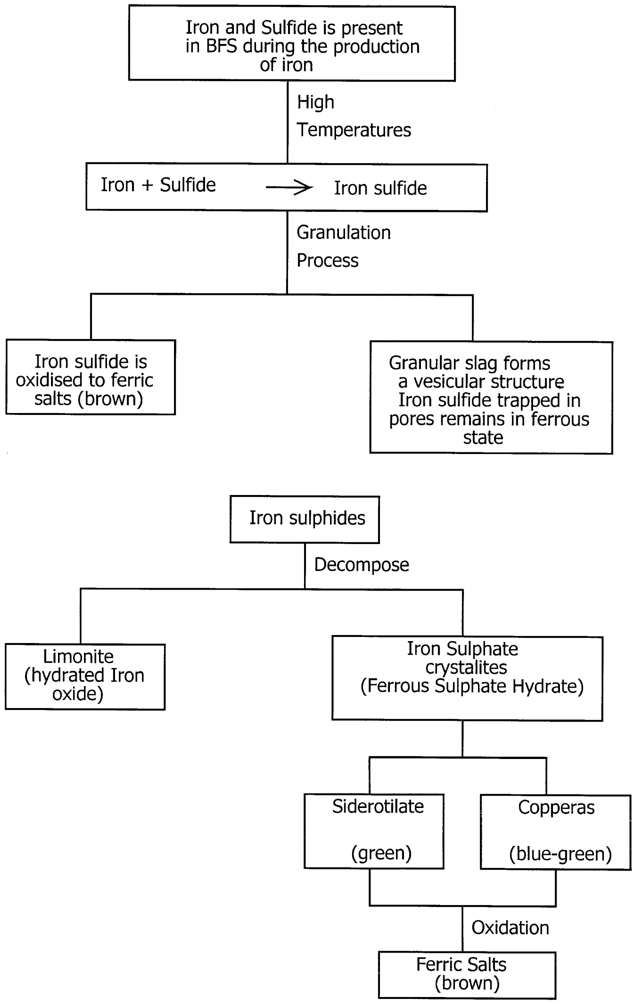

Fig. 1. Process involved in producing the blue-green coloration.

Table 1
Mixture proportion per cubic meter

	Mixture type				
Material	A	1	2	3	4
Cement (kg)	165	275	250	200	180
Slag (kg)	385	275	250	200	180
Water (kg)	165	165	175	180	180
Coarse aggregate (kg)	1320	1320	1240	1300	1120
Fine aggregate (kg)	510	510	600	630	820
SP[a] (kg)	9.5	9.3	5	2.2	–
W/B[b]	0.3	0.3	0.35	0.45	0.5
Slump (mm)	130	130	130	120	100

[a] Superplastizer in liquid form.

[b] Water/binder ratio.

3.1. Concrete mixes and materials

Five different mixture proportions were investigated in this study as presented in Table 1. The term water to binder ratio is used instead of the water to cement ratio to refer to both the slag and Portland cement in the binder. The Mixture Type A, a high-strength mixture with 70% slag in the binder, is used for the study of cylinders. Mixture Types 1, 2, 3 and 4 were used for the study of the columns. Mixture Type 1 is identical to the Mixture Type A, except the percentage slag content in the binder is changed to 50%. All the column Mixture Types 1, 2, 3 and 4 contained 50% slag in the binder. The main variable parameter in these mixture types is the water to binder ratio, which was progressively increased from 0.3 in Mixture Type 1 to 0.5 in Mixture Type 4. The binder content was adjusted accordingly to maintain similar water content and hence the workability.

The coarse aggregate used in this investigation was a basalt with a maximum size aggregate between 10 and 14 mm. The specific gravity and absorption of this aggregate are 2.95% and 1.2%, respectively. The fine aggregate was Lyndhurst sand with a fineness modulus of 2.18. The specific gravity and absorption of the fine aggregate are 2.65% and 0.5%, respectively. The details of chemical and physical properties of other materials used in this investigation are provided in Table 2.

3.2. Cylinder testing

To examine the influence of moisture and temperature on the development of coloration and compressive strength in a high-slag-content mix, standard-size cylinders (100 mm ϕ × 200 mm) were made. The cylinders were divided into three groups, and each group was subjected to a different curing regime. The curing regimes are described as follows.

Table 2
Chemical and physical properties of materials

Material	Chemical contents (w/w %)	SG[a]	LOI[b] (%)	SSA[c] (m^2/kg)
Cement[d]	SiO_2 (19.9); Al_2O_3 (4.62); Fe_2O_3 (3.97); MgO (1.73); CaO (64.27); K_2O (0.57); SO_3 (2.56)	3.15	1.2	350
Slag[e]	SiO_2 (33.21); Al_2O_3 (12.58); Fe_2O_3 (0.22); MgO (5.87); CaO (39.29); Na_2O (1.27); TiO_2 (0.42); K_2O (0.36); SO_3 (3.38)	2.85	1.7	430
Superplasticizer[f]	Formaldehyde condensate type, 40% solids	1.2	–	–

[a] Specific gravity.
[b] Loss of ignition.
[c] Specific surface area.
[d] Ordinary Portland cement.
[e] Ground granulated blast-furnace slag with 5% gypsum processing addition.
[f] Rheobuild 1000.

3.2.1. Bath-cured (BC)

The BC cylinders were demolded 24 h after casting and cured under standard conditions, i.e., in a lime-saturated water bath at 23 ± 2°C.

3.2.2. Sealed-cured (SC)

The SC cylinders were demolded 24 h after casting, sealed in plastic bags and cured at 23 ± 2°C in a constant-temperature room. Comparisons of the SC cylinders with BC cylinders are expected to show the effect of continuous moist-curing.

3.2.3. Temperature matched cured (TMC)

The TMC cylinders were used to simulate the temperature conditions experienced by the in situ concrete. The cylinders were subjected to the temperature–time curve experienced at the center of an 800 × 800 mm square column made of the same concrete (Mixture Type A). The temperature–time curve obtained from the center of the column is shown in Fig. 2. The cylinders were sealed in plastic bags and placed into the TMC bath 20–30 min after casting. A computer connected to the thermocouples and heaters in the bath controlled the temperature of the bath water as specified in Fig. 2, based on the feedback from the thermocouples located in the bath. At the end of 72 h, the cylinders were moved from the bath to the constant-temperature room at 23 ± 2°C, while still being kept inside the sealed plastic bags.

Comparisons of TMC and SC cylinders are expected to show the effect of curing temperature.

3.3. Column tests

Concrete columns, 800 × 800 mm in cross section and 1200 mm in height were cast in three layers. Each 400-mm thick layer was separated using a boundary separator consisting of a 5-mm-thick masonite sheet sandwiched between two corrugated sheets of cardboard. The segmental form-

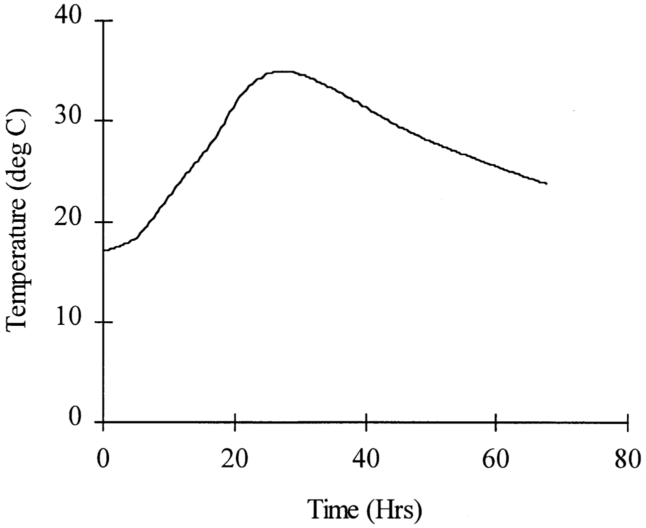

Fig. 2. Temperature profile for TMC cylinders.

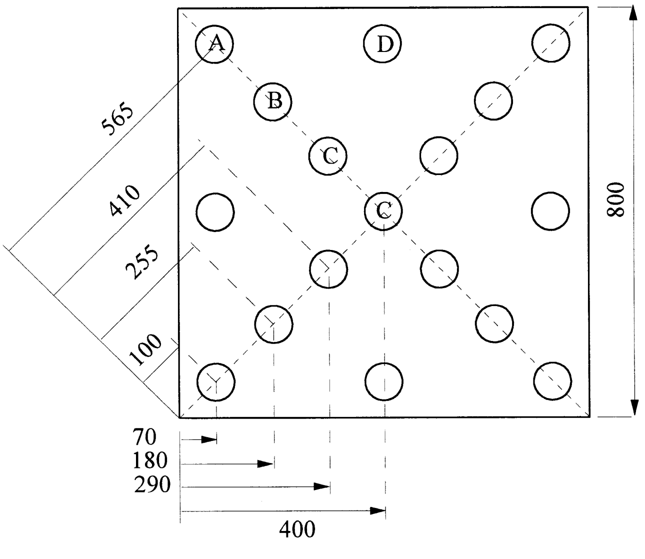

Fig. 3. Column coring pattern.

work used to cast the columns was made from 3-mm mild steel plates welded to angle sections.

The layered casting scheme was adopted to facilitate core sampling throughout the cross section of each column. Cores were taken from bottom, middle and top layers at 28, 56 and 91 days, respectively. Access to the concrete at different elevations in the column was obtained simply by separating individual layers. Fig. 3 shows the drilling pattern adopted for each concrete layer, as well as the labeling system used to identify core locations. The diameter of the cores was 95 mm. The cores were cut to a length of twice the diameter (i.e., 190 mm) before the strength tests.

Expanded polystyrene foam sheets of 50-mm thickness were placed at the top and bottom of the column to improve thermal insulation and simulate a long column. Formwork removal took place 24 h after casting. The columns were then allowed to air dry until required for testing. The casting and curing of the columns took place in the basement of the laboratory where the temperature fluctuation was minimum (17–23°C all year).

4. Results

The compressive strength of the cylinders cured at BC, TMC and SC regimes were determined at 7, 28, 56 and 91 days and are presented in Fig. 4. Each result is an average of three cylinder tests. The TMC and SC cylinders, both sealed from moisture movement, develop notably less strength than the corresponding BC cylinders. The effect of higher temperature during the first 72 h seems to have little influence on the long-term strength, except at early ages. At 7 days, the TMC cylinders demonstrated strengths higher than the BC and SC cylinders.

Fig. 5 shows the strength development of cores from the column made of Mixture Type 4. To evaluate the strength variations within a cross section, average core strengths from each strength zone were compared. The strength zones are denoted as A, B, C and D to identify the location from which they were derived, i.e., A (corner), B (intermediate), C (center), D (side; Fig. 3). Comparisons were made at 28, 56 and 91 days. It can be seen that the core strengths were not uniformly distributed across the column cross section. The highest compressive strengths were found at the center of the column, and a progressive reduction in core strength was observed towards the periphery. Loss of moisture as a result of evaporation near the perimeter of the column impedes the development of strength in this region. Although Zones A and D were both located near the surface of the columns, their curing conditions were markedly different. Zone A is exposed on two surfaces, while Zone D is exposed only on one. Consequently, it is expected that Zone A will have a higher moisture loss than Zone D.

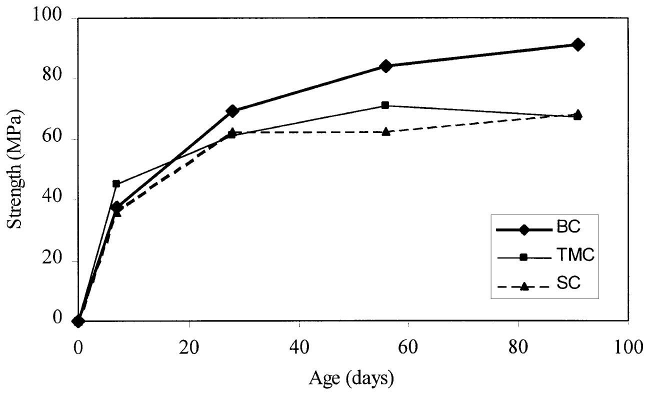

Fig. 4. Cylinder strengths of Mixture Type A.

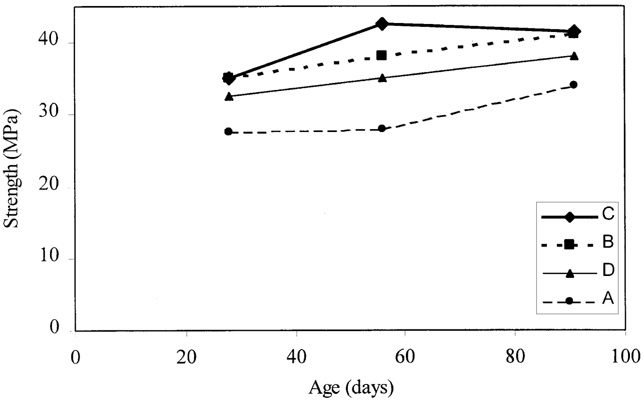

Fig. 5. Core strengths of column made with Mixture Type 4.

The core strengths of columns made of Mixture Types 1, 2, 3 and 4 were tested at 91 days and are presented in Table 3. The results are average core strengths in each zone as described earlier.

The extent of the coloration in the column cross sections became evident upon trimming the top and bottom ends off the cores. The off-cuts were then arranged in the same pattern as they had been extracted from the columns to give an indication of the extent of the coloration throughout the column cross section. Pictures of the samples were then taken immediately after all the cores had been arranged and are shown in Fig. 6. A light spray of water was used to dampen the cores prior to photographing them. The water

Table 3
Column core strengths at 91 days (MPa)

	Mixture type			
Zone	1	2	3	4
A	70.0	62.0	40.5	34.0
B	80.0	65.0	45.0	41.0
C	83.5	64.0	44.5	41.5
D	75.5	61.0	40.0	38.0

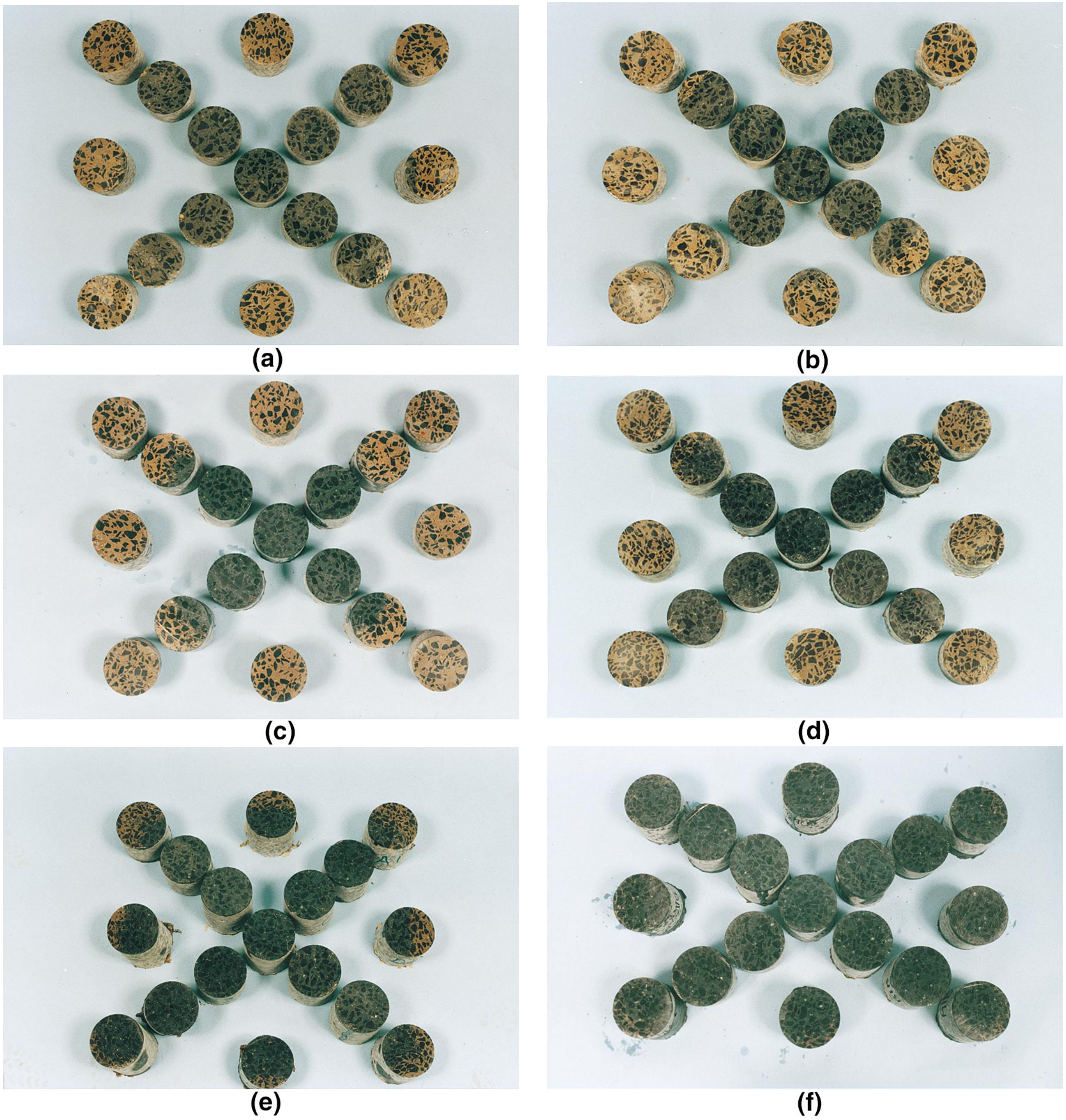

Fig. 6. Column cores arranged in the coring pattern. (a) Mixture Type 4 cores at 28 days, (b) Mixture Type 4 cores at 56 days, (c) Mixture Type 4 cores at 91 days, (d) Mixture Type 3 cores at 91 days, (e) Mixture Type 2 cores at 91 days, (f) Mixture Type 1 cores at 91 days.

aided in highlighting the contrasting shades of brown and blue-green.

Cores obtained from the columns provided ample evidence that both the intensity of the coloration and the rate at which it diminishes with time are a function of the concrete strength grade, the level of slag replacement and the curing conditions. It was noticed that the surface of the cores was predominantly blue-green, and that depending on the geometric location from which the cores were taken, the proportion of the surface, which was colored blue-green, varied.

The fractured surfaces of the cylinders after compression test were examined for coloration. The extent of the coloration of the cylinders varied depending on the curing regime employed. Fig. 7 shows the fracture surfaces of three cylinders that had been subjected to BC, TMC and SC curing regimes.

Further evidence of the effects of moisture availability and exposure to air on coloration can be found in the interior portions of slag stockpiles. A blue-green coloration is often observed in the interior portions of slag stockpiles, where there is a high moisture content and insufficient air to oxidize the trapped ferrous oxide. Fig. 8 shows the blue-green coloration as observed at the base of a slag stockpile. The inset in the photograph shows a closeup of the base of the stockpile in which the coloration can be clearly seen. In this instance, a front-end loader was used to expose a fresh face of the stockpile that was immediately photographed.

Fig. 7. Fractured surfaces of cylinders subjected to the three curing regimes.

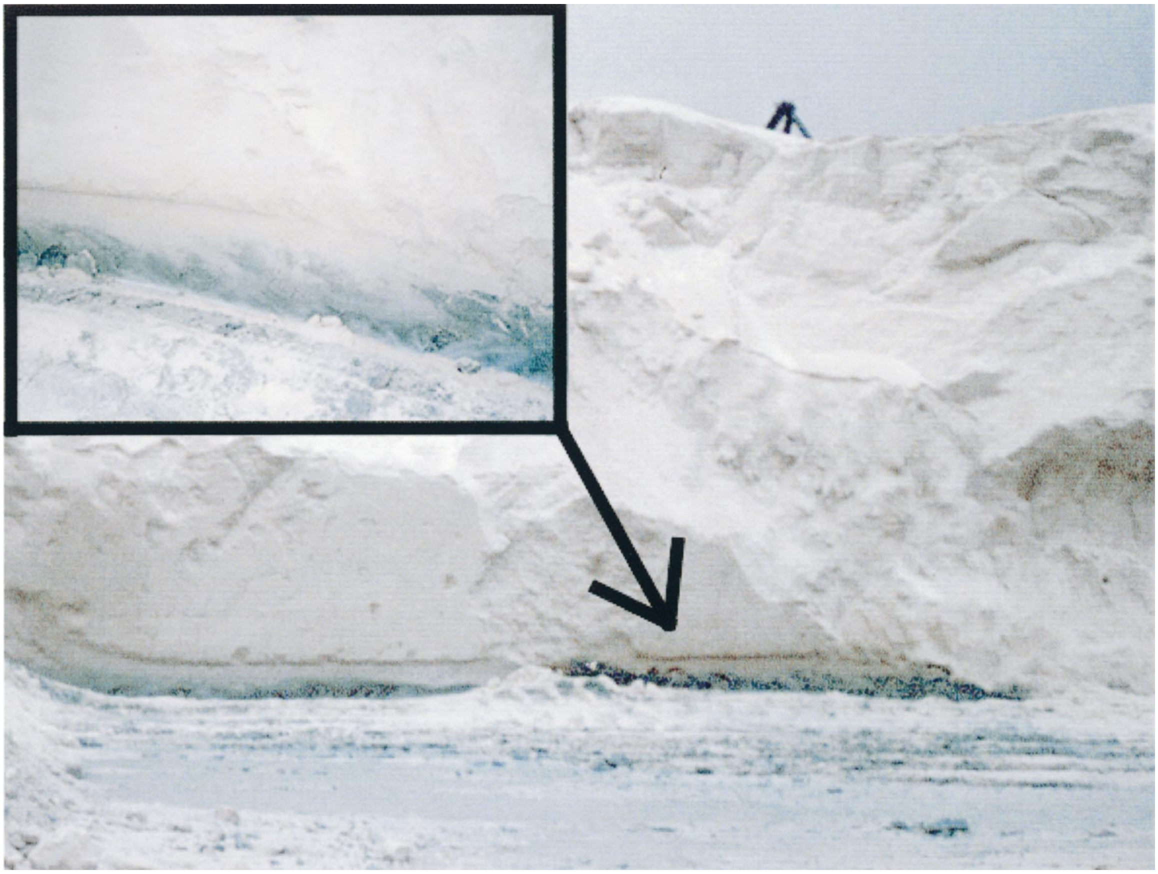

Fig. 8. Exposed face of slag stockpile showing the blue-green coloration at the base.

5. Discussion

Three factors are identified to have the most significant influence on the degree and extent of the coloration exhibited in the columns and the cylinders: (1) the curing conditions, (2) oxidation rate, (3) level of slag replacement.

5.1. Curing conditions

The influence of curing conditions is amply demonstrated by the coloration present in the fracture surfaces of the BC, SC and TMC specimens tested to failure, as shown in Fig. 7.

The fracture surface of the BC cylinders exhibited a deep blue-green coloration that extended throughout the cross section of the specimen. In contrast, the interior portion of the SC specimens was predominantly brown in color. Some light green coloration was evident, but this was confined to the center region of the cylinder. The TMC cylinders also exhibited the blue-green coloration, although a brown ring encompassed the green portion around the circumference of the cylinder.

The three distinct patterns of coloration indicate that the curing regime has a considerable effect on both the intensity and extent of the coloration. Continual submergence of the concrete in water promotes the preservation of the blue-green coloration for an extended period of time. This is because air cannot readily enter the concrete to oxidize the ferrous salts to ferric salts. On the other hand, the SC specimens, which were sealed in plastic bags, had access to the air trapped inside the plastic bag. Consequently, oxygen could enter the matrix of these cylinders from an early age, and this resulted in the bulk of the cross section being oxidized.

The TMC specimens were submerged in water during the first 3 days after casting as required for the TMC process. This resulted in the following: (1) lack of exposure to air at a young age when they are most vulnerable to oxygen permeation due to their incompletely developed pore structure and (2) acceleration of strength development and improved pore structure when initially exposed to the air (4 days), such that the permeation of air was hindered. In comparison, the SC specimens were exposed to the air immediately after demolding at 24 h.

5.2. The rate of oxidation

The rate of oxidation is a function of how readily the oxygen can enter the concrete matrix to convert the ferrous salts to ferric salts. This depends on the denseness of the pore structure, which in turn, relies on the water to binder ratio of the concrete mix, among other factors [4]. Considering water to binder ratio is directly related to concrete strength, the strength of concrete is indicative of the rate at which the oxidation process proceeds.

Fig. 6 shows the concrete off-cuts, arranged in the coring pattern adopted to obtain the cores. The progression of the oxidation front with time is depicted in Fig. 6(a–c), which shows the extent of the coloration at 28, 56 and 91 days, respectively for the Mixture Type 4 column cores. The gradual recession of the blue-green from the column surface with time gives an indication of the rate at which the concrete is being oxidized and that, in fact, the extent of the coloration is a function of time.

Fig. 6(c–f) provides pictorial evidence that the strength of concrete influences the rate at which the ferrous salts are oxidized. It can be seen that the blue-green coloration extends through to the perimeter cores in higher strength columns (Mixture Types 1 and 2), while in the lower strength columns (Mixture Types 3 and 4), the coloration has receded further towards the interior portion of the concrete. This indicates that at the same concrete age of 91 days, and at the same level of slag replacement of 50%, the higher the strength of concrete, the higher portion of the blue-green coloration throughout their cross section.

This is attributed to the more permeable pore structure of the lower-strength concrete, which allows the oxygen to more readily enter the matrix and oxidize the ferrous salts as indicated by the larger portion of brown concrete.

5.3. Level of slag replacement

Comparisons of cylinders of Mixture Types A and 1 show that the degree or intensity of the coloration increases with the increasing slag content. This is anticipated, since the blue-green coloration originates or results from the compounds present in the slag, namely, the iron and the sulfides. It follows then that when a larger portion of slag is present, the greater the abundance of the compounds responsible for the coloration and therefore, the greater the intensity of the coloration.

6. Conclusions

The observed coloration in the concrete is attributed to a complex reaction, which proceeds between the iron sulfide in the slag and certain compounds found in the cement. The results presented indicate that the extent and degree of coloration is a function of the slag content, the curing conditions and the rate of oxidation.

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