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Cement paste colouring in concretes

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Abstract

Tests have been carried out with chemicals that give rise to coloured compounds through a selective reaction with certain mineral species present in cement paste. In the case of carbonated concretes (pH ≅ 9), the reaction with potassium ferrocyanate dyes the cement paste a strong blue colour that disappears when the concrete is treated again with a slightly more alkaline solution. Both in carbonated concretes and in young concretes with an alkaline reserve (pH ≅ 12.5), the tannic acid dyes the cement paste dark brown.

Keywords: Concrete; Cement paste; Image analysis; Coloured compounds

1. Introduction

In the different Spanish Concrete Instructions, including that of 1991 (EH-91), values for compressive strengths were considered an index of the other properties of concrete. The current instruction, EHE [1] indicates, however, that compressive strengths alone are not an index of the other qualities of concrete. A resistant concrete is not necessarily a durable concrete. Achieving an appropriate durability demands, amongst other dosing requirements, the use of concrete with a minimum cement content.

Due to the complexity of the test, no accurate method exists so far to calculate the amount of cement in hardened concrete. The procedure recommended [2], based on the determination of soluble CaO and SiO_2 oxides in hydrochloric or maleic acid, needs frequent corrections because certain aggregates and some cement admixtures may be soluble depending on pH and concrete age.

In 1999 and 2000, some members of Alicante University's Architectonic Constructions Department and the Association of Accredited Laboratories in the Valencian Community (ALACAV) researched with products that react with some cement paste phase to form coloured compounds. A series of reagents were successfully tested, although they only worked with carbonated concretes [3].

The Spanish Institute of Cement and its Applications (IECA) took an interest in these initial results and suggested that we extend our research with the aim of developing a method able to determine the quantity of cement through the application of selective colourings on ∅15 × 30-cm concrete cylinders.

As a result of new research work, we have developed a product that can also dye cement paste in young concretes with an abundant alkaline reserve (with pH values of ≅ 12.5).

This article describes the process followed in this work, from the initial colourings to the most recent ones.

2. The initial colourings

The first colourings to be tested were those used in petrology to distinguish the different types of carbonates (calcite, aragonite) along with those used to differentiate between plagioclases and potassium feldspars.

What we wanted to do was dye all types of aggregates, quantify them in the scanned images and obtain the

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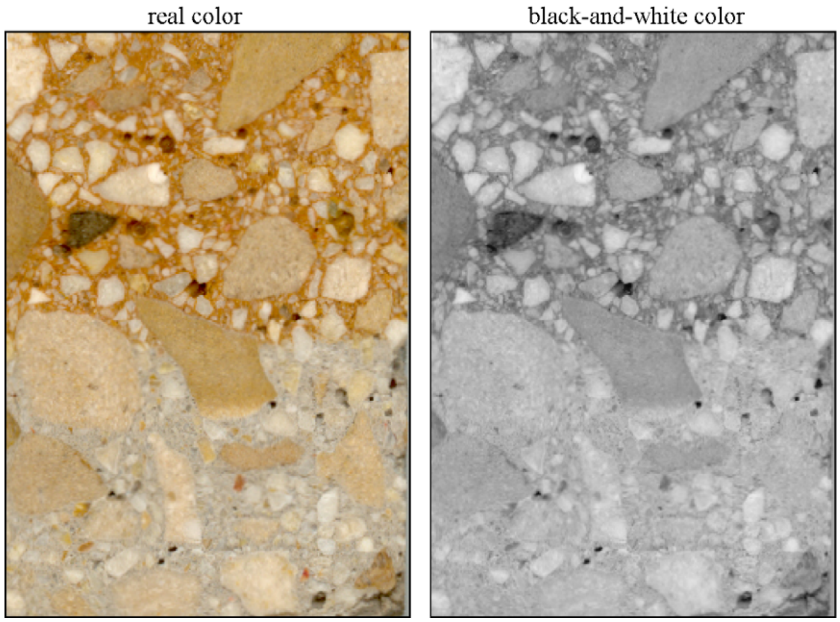

Fig. 1. Concrete section attacked with hydrochloric acid and later with sodium hydroxide.

amount of hydrated cement paste from the difference. With that information in hand, we would only need a simple calculation to obtain the content of cement in the hardened concrete. We had to discard that first idea for two reasons:

1. In the attempt to design a method with wide application, the varied nature of aggregates makes the treatment become very laborious and, in some cases, impossible because the reagents used to dye a type of aggregate may interfere with the ones we use to dye other aggregates.
2. The most important colouring, the one used to colour calcite (alizarine), also hides the cement paste.

This is why we decided to reorient our research towards the development of products that could dye some of the species present in cement paste and, at the same time, leave aggregates unaltered.

In the first treatment, where we managed to dye the cement paste, leaving the aggregate unaltered, we resorted to reagents similar with those used to dye feldspars in geological samples, assuming that the silicate phases in cement paste [C–S–H (calcium silicate hydrate)] would behave very much like those minerals did. Concrete samples were firstly attacked with hydrochloric acid and then with sodium hydroxide.

Although the cement paste is dyed a reddish colour (the black-and-white format of the journal makes it become ‘dark’), easy to distinguish from aggregates (Fig. 1), we abandoned the study of this treatment because the samples lose the colour when not moistened and, especially, because the reagents used are highly aggressive, their utilisation being banned in routine tasks.

3. Ferrocyanate colouring

After rejecting the treatment described in the previous section, we oriented our studies towards the search for reagents that could result from C_3A and C_4AF hydration.

The colouring we will describe next arises from the experimentation and preparation for concrete of an iron identification test that is well known and widely documented in any good Analytical Chemistry textbook [4]: Potassium hexacyanoferrate (II) (potassium ferrocyanide) produces with Fe^{3+} a precipitate that has a strong blue colour (known as Prussia blue or Berlin blue). Although the reaction is known to be not selective at all because most cations precipitate with ferrocyanide, the intensity of the blue colour can be clearly appreciated over the usually lighter tonalities of the other ferrocyanides that may precipitate.

Fig. 2 shows a 10×5 cm concrete section in which the upper part has been dyed by immersing the sample for 2 min in a 5×10^{-3} M potassium hexacyanoferrate (II) solution, to which HNO_3 has been added to acidify and obtain a pH value slightly below 1. The strong blue colour (the black-and-white format of the journal makes it become ‘dark’) is due to the formation of ferric ferrocyanide, a process that has been checked through X-ray diffraction. However, that colouring does not work in samples with high pH values, which is why it cannot be used in the case of young concretes with large amounts of portlandite.

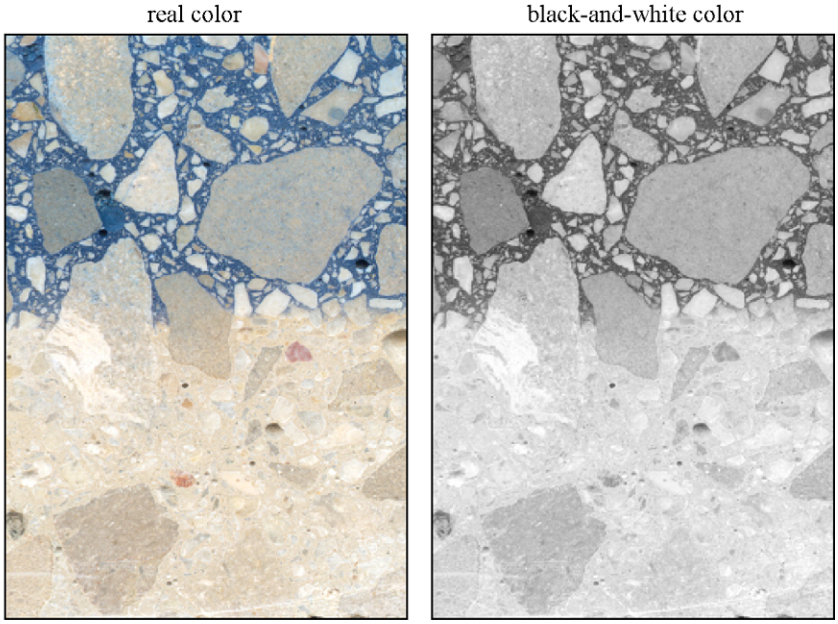

Fig. 2. Concrete section dyed by immersing in a potassium hexacyanoferrate (II) solution.

Because our ultimate objective consists in designing a cement quantification method that can be directly applied to the young concrete cylinders, we approached the problem from a twofold perspective:

1. The study of accelerated concrete carbonations, as well as other reactions, that consume the alkaline reserve, in which case we would apply ferrocyanate colouring.
2. The design of colourings for noncarbonated concretes that can be directly applied to the test tubes used in concrete takes at the building site.

Regarding what is explained in Ref. [1], the treatment of concrete with acids may eliminate the alkaline reserve but substantially modifies the surface that we will have to dye later. Besides, we could not develop accelerated carbonation treatments using CO_2.

4. Tannic acid colouring

For the reasons we have explained in the previous section, we decided to research with compounds able to

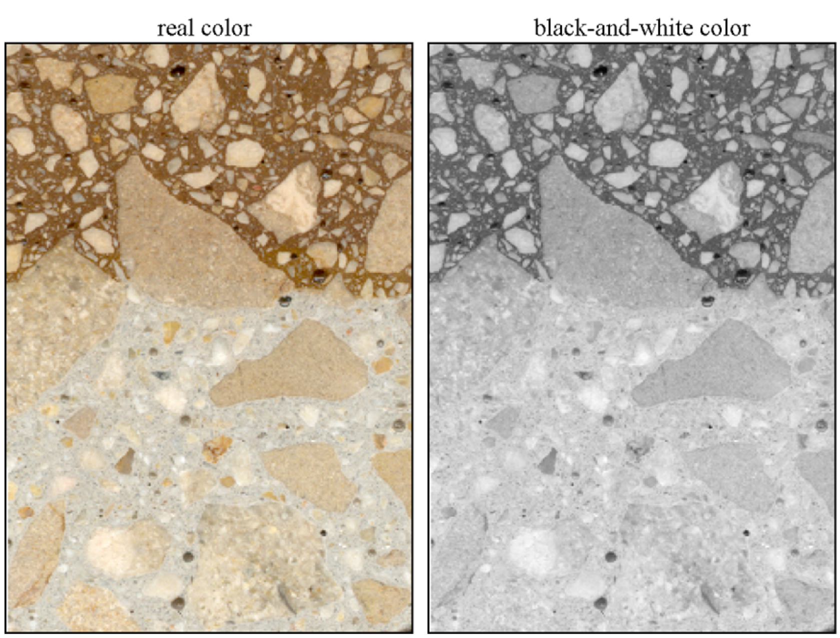

Fig. 3. Concrete section dyed by immersing in a tannic solution.

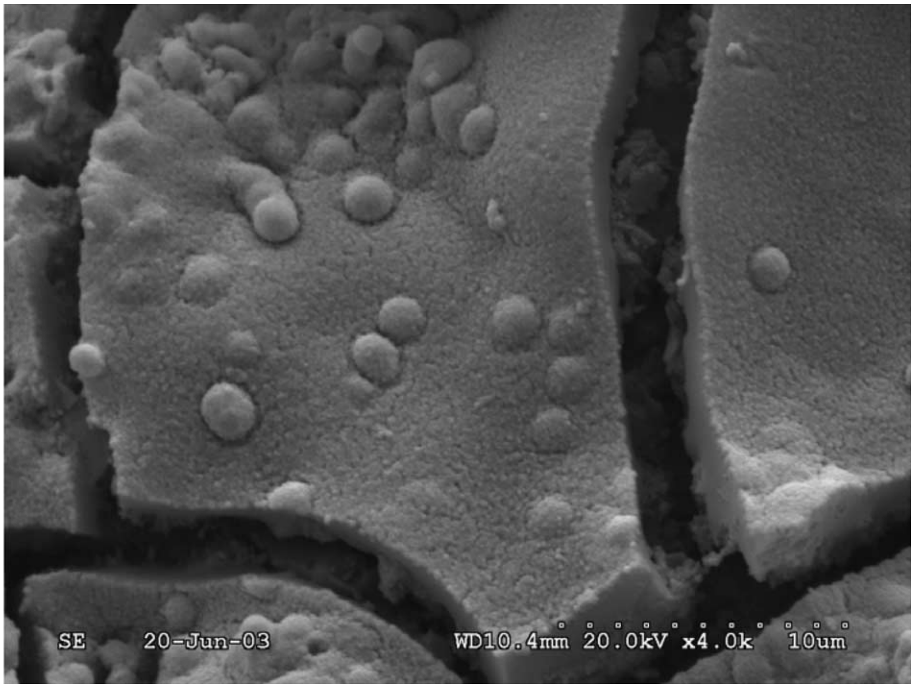

Fig. 4. SEM picture of a cement paste treated with a tannic solution.

dye the cement paste in young concretes with an abundant alkaline reserve. We managed to do it by treating concrete with an 8% in weight (approximately 0.051 M) tannic acid solution, to which HNO_3 was added until reaching a pH value of 1.

Fig. 3 shows a concrete portion that was immersed in the tannic acid solution for about 2 min and then washed with abundant water.

We started to do research with tannic acid above all on the basis on the scientific documentation collected in the works published by a group of researchers of the Spanish National Metallurgic Research Centre [5,6] along with the works of another group at Panamá University's Chemistry Department [7,8]. All these works focus on the interaction of tannic acid with the iron of concrete steels and discuss the nature of the compounds formed.

In the electronic microscopy picture we provide (Fig. 4), which shows a cement paste treated with the tannic acid solution, we can see the growth of amorphous iron hydroxides (goethite) on an iron tannate patina. These compounds are formed as a result of the reaction between tannic acid and the products resulting from C_4AF hydration and are responsible for the colour the paste takes.

5. Results and discussion

Different reagents have been developed that dye the cement paste selectively. The images of the dyed concrete can be easily binarised, which allows to calculate the proportions of cement paste and aggregate in a simple way.

The tannic acid solution dyes concretes with large quantities of portlandite, and we are using it in the design of a method that allows us to know cement content in Ø15 × 30 cm concrete cylinders in different Spanish concrete plants.

The treatment of concrete with the hexaferrocyanate solution does not work in samples with high pH values, which is why it cannot be used with young concretes that have large amounts of portlandite. On the contrary, in the case of old (carbonated) concretes, the solution can be used and helps to know aspects related to the wrought structures that must be concreted directly at the building site. Once the dyed areas have been studied and photographed, the blue colour of concrete disappears by treating it with a slightly alkaline solution (e.g., 0.025 M of NaOH).

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