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Cement content determination through selective stain in hardened concrete

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ABSTRACT

A cement quantification method has been developed in Ø 15×30 cm concrete specimens applying selective stain. A tannic acid–tartaric acid solution was used to stain the cement paste.
This paper explains the procedure to determine the quantity of cement in the samples: the reagents utilised for the stain, preparation, cutting and stain of the specimens, the capture and treatment of images of the stained samples, and the preparation of the calibration curves.
Next, we assess the accuracy of this method and include the resolution of a practical case in which a comparison is drawn between the values obtained through the application of this method and those obtained using a 'reference' method.

1. Introduction

Faced with the difficulties involved in calculating the quantity of cement in concretes and, taking into account, however, that in accordance with the current Spanish regulation [1] structural concretes must have a minimum content of cement, research into the development of products that can stain the cement paste leaving the coarse aggregates unaltered has been undertaken. The objective is to quantify the cement on the basis of the cement paste content obtained from the binarised image of the specimen. Studies [2,3] showed a process that had led to the development of a type of stain applicable both to carbonated concretes (pH≈9) and to concretes with an abundant alkaline reserve (pH≈12.5). It was an 8%-in-weight tannic acid solution to which HNO_3 was added until pH=1.

This paper firstly describes the modification applied to the cement paste stain with the solution of HNO_3-acidified tannic acid [2,3], which stained some types of coarse aggregates slightly and thus affected the correct binarisation of images.

Secondly, a description is offered of the process followed during the development of the test methodology, specifying all the stages that make up the protocol of analysis as well as the equipment and software used.

And thirdly, the accuracy of this method is assessed, after which we finally present an example where a comparison is drawn between the cement content values obtained with our method and those obtained with another ASTM method [4].

2. Experimental development of the method

The experimental process used to implement the cement quantification method has been divided in different stages. Research has been conducted into the identification of the optimum solution for stain, into the most suitable morphology and size of specimens, into the actual stain process and into the capture and treatment of the stained specimen images.

The method has equally been verified for concretes manufactured with different types of cement, though it is worth clarifying that a method is proposed for an average concrete, that is, specific patterns will be used for each concrete manufactured with a type of cement. In the example described in this paper, we refer to the concrete that is most commonly used at new construction works in the Alicante area (Spain).

2.1. Solution optimisation for the stain

As said in the Introduction, practice has made it possible to check that, in some cases, the 8%-tannic acid solution acidified with HNO_3 [2,3] stains with a slightly yellow colour certain types of coarse aggregates, the mineralogy of which coincides with that of iron dolomites (Fig. 1). This fact poses a problem when it comes to binarise the specimen images, distorting the results and influencing the accuracy of the method.

At present, this problem has been solved removing HNO_3 and acidifying the tannic acid solution with an organic acid, more precisely, tartaric acid. Tartaric acid —$C_4H_6O_6$— has a low toxicity and is easily degraded and, the same as tannic acid, it shows a strong tendency to form complexes with the Fe^{2+} ion [5–7].

Tannic acid solutions with 8%, 5%, 3%, 2%, 1%, 0.5% and 0.2%-in-weight concentrations along with tartaric solutions with 1%, 2%, 3%, 4% and 5%-in-weight concentrations were prepared and tested in order to obtain the most suitable stain, the best results obtained corresponding to a solution composed by tannic acid (3% in-weight) acidified with tartaric acid (3% in-weight).

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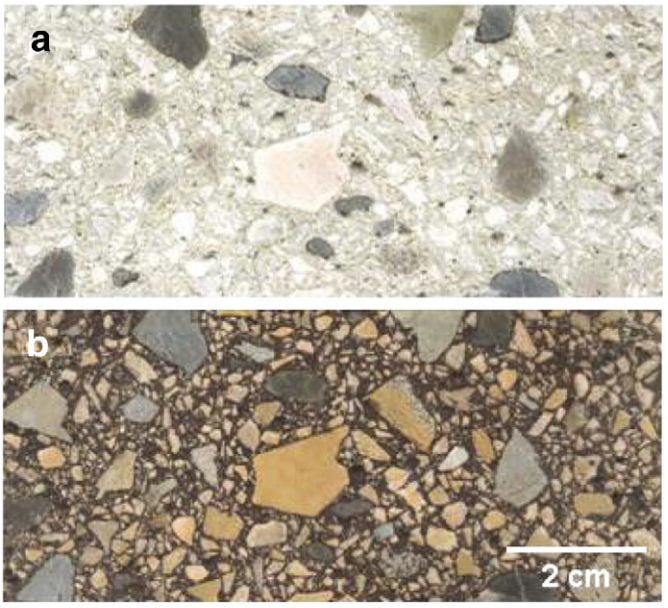

Fig. 1. Image of the specimen stained (b) with a (8%) tannic acid and nitric acid solution in which a yellowish colouring can be appreciated in some coarse aggregates compared to the image of the non-stained specimen (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Specimen morphology and size

Using a CEM I 52.5 R cement and lime coarse aggregates, we manufactured a series of eighteen Ø15×30 cm normalised specimens and another eighteen 20×20 cm cubic specimens with dosing levels comprised between 200 and 400 kg of cement per m^3 of concrete and variations every 25 kg/m^3 (2 specimens per dosing). Each specimen was prepared individually so as to ensure that the dosing was accurate.

The samples were cured in a wet chamber for 28 days following the procedure indicated in the UNE-EN 12390-2 norm [8]; they were cut into two equal halves with a diamond disc saw; they were cleaned in an ultrasound bath; they were stained and, finally, the real and experimental results for each series were assessed.

Better results were obtained for the series of Ø15×30 cm cylindrical specimens than for the 20×20 cm cubic ones.

2.3. The stain process

Different ways to stain specimens were tested: pulverising the reagent onto the specimen, applying the solution with dressings, and submerging the specimen into the stain solution. Optimum results were only obtained using the method where the surface to be stained was immersed in the solution.

The application of the stain will be carried out through the immersion of the specimen surface for 2 min, using to that end a flat container manufactured with a material that does not react with the solution (Fig. 2). Once the stain time has elapsed, the stained surface is washed with running water.

In order to assess the effect that the whitish patinas resulting from concrete carbonation have on the stain process, we prepared a number of specimens that were cured for 28 days and later cut and washed. The samples were stained at 24-hour intervals. This study brought as a result that a specimen can be stained within 7 days of being cut with a diamond disc saw without that causing any problems on its surface.

This process was tested for portland cement pastes with the main admixtures (CEM I 52,5 R, CEM II/A-L 32,5 N, III/A 42,5 N/SR, IV/A 32,5 N/SR) and a homogeneous, stable-over-time stain was obtained in all cases.

2.4. Image capture and treatment

The images from the stained specimen surfaces can be captured using various processes: conventional photography, digital photography or through specimen scanning. In this method, it is advisable to use a scanner because it permits to control important parameters such as: a) light, as the type of illuminator is always the same; b) inclination, since the image is always taken perpendicularly to the surface of the specimen; and c) distance to the surface, which remains constant.

A specific computer program called CuantiCem® [9] has been developed for image treatment thanks to which the cement quantification process can be automated by means of images to prevent the calculation of the result from depending on the operator (Fig. 3).

At the process of colour segmentation of the images from the software designed, we used the Matlab program, which permits to use images as matrices in a simple way, thus making the mathematical calculation process easier. The CuantiCem® program works with

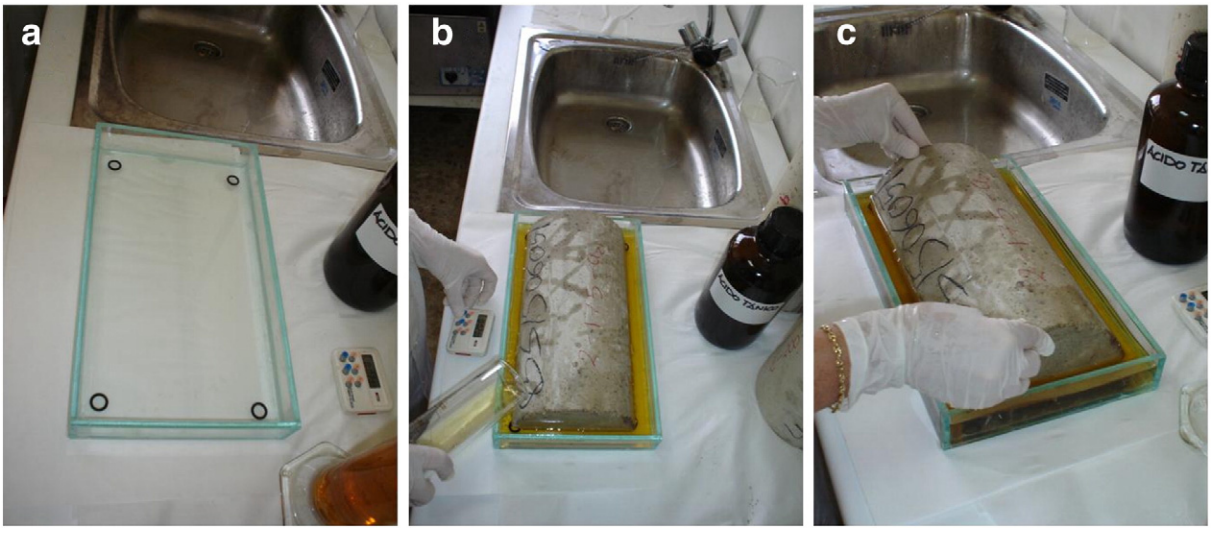

Fig. 2. Stain process: a) Inert stain device; b) Addition of the stain solution; and c) Lateral movements for the evacuation of possible bubbles trapped in the lower part of the specimen.

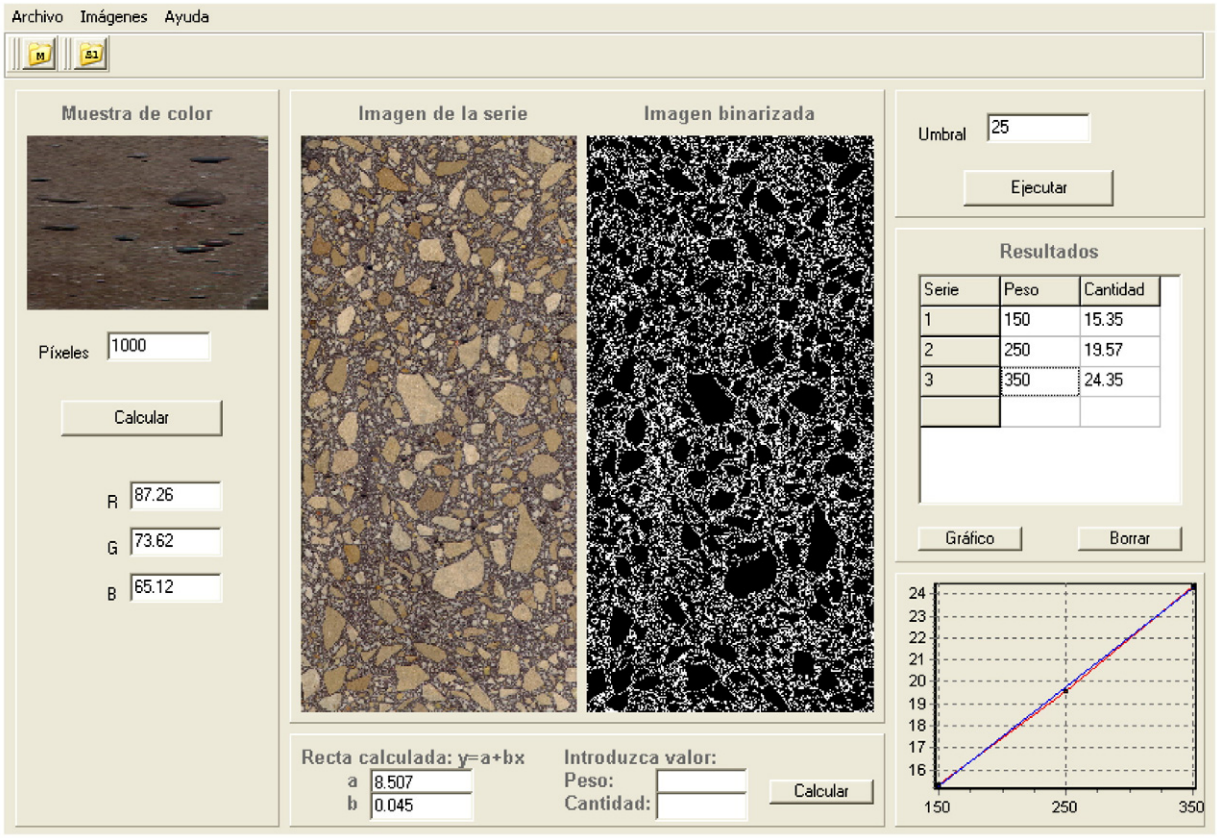

Fig. 3. Image segmentation process using the CuantiCem® program for cement quantification.

images in RGB format and the algorithm constructed is going to receive two images: the image to be segmented and the image of the pattern colour sample prepared as is explained in the following section. It calculates the colour average of the pattern sample in RGB coordinates. With these colorimetric coordinates, the algorithm goes through the specimen image, pixel by pixel, segmenting the image with a 25% threshold difference. After this process, the program shows the resulting binarised image on the screen, as well as the percentage in the paste obtained.

This calculation is made on the images of the non-stained and the stained specimens. Thus, subtracting the percentage obtained in the non-stained sample from the total of the stained sample, we remove the possible error associated with the presence in the concrete of coarse aggregates that have the same colour as the stained cement paste.

2.5. Preparation of the colour pattern sample

Different binary mixtures of cement and fine aggregates ('fine aggregates' are the fraction that passes a 0.063 mm sieve) were prepared in order to identify the best colour pattern sample. More specifically, we manufactured 'mortars' with cement/fine aggregate ratios similar to the dosing levels of 200, 250, 300, 350 and 400 kg/m^3. The best results were obtained with the one manufactured with the same proportion of fine aggregates and water/cement (W/C) ratio as the specimen with the highest dosing (400 kg/m^3). Table 1 shows the masses composing the mortar for the colour pattern sample which was mixed following the procedure indicated in the UNE-EN 196-1 norm for cements [10], using a 15-cm-diameter plastic cast. After a 28-day curing period in a wet chamber, it was subjected to the stain process shown in Fig. 2 and the stained image was registered, the RGB coordinates being calculated too.

Table 1
List of masses for the preparation of mortar for the colour sample pattern.

Dosing (kg cement/m^3)	CEM I 52,5 R	Fine aggregates	Water	W/C
400	1000 g	287.8 g	450 g	0.45

3. Results

The results obtained with the stain method proposed have been verified in different ways: firstly using specimens prepared in the lab and then with samples obtained at a concrete plant, comparing the results achieved with the stain method and with the ASTM method [4].

3.1. Tests in the lab

Ø 15×30 cm cylindrical specimens with different dosing levels were manufactured for the drawing of the calibration curve. The homogenised and dried raw materials used were the following:

- Cement: CEM I 52,5 R
- Lime coarse aggregates: AF-T-0/4-C-L; AG-T-6/12-C-L; AG-T-12/20-C-L
- Additive: Melcret CX

A total of six series of specimens with dosing levels comprised between 200 and 400 kg/m^3, with variations every 25 kg/m^3, were manufactured. Each specimen was mixed individually in a floor mixer and the cast-filling processes in three layers, compacting, conservation in the cast for 24 h, and curing in a wet chamber during a period of up to 28 days were carried out following the indications of the UNE-EN 12390-2 norm [8]. On Table 2 can be found the masses of all the materials for each dosing.

Table 2
Theoretical masses (in g) of all the materials for the mixing of a specimen in each dosing.

Dosing (kg cement/m^3)	CEM I 52,5 R	Coarse aggregate 6/12	Coarse aggregate 12/20	Coarse aggregate 0/4	Melcret additive	Total water	W/C
200	900	1134.0	3046.5	5013	9.00	810.0	0.90
225	1012.5	1210.5	3024.0	4864.5	10.13	810.0	0.80
250	1125	1287.0	2992.5	4711.5	11.25	810.0	0.72
275	1237.5	1363.5	2974.5	4567.5	12.38	810.0	0.65
300	1350	1435.5	2947.5	4414.5	13.50	810.0	0.60
325	1462.5	1512.0	2925.0	4266.0	14.63	810.0	0.55
350	1575	1588.5	2898.0	4117.5	15.75	810.0	0.51
375	1687.5	1665.0	2871.0	3964.5	16.88	810.0	0.48
400	1800	1741.5	2844.0	3816.0	18.00	810.0	0.45

Table 3 shows the values for the proportion of the cement paste stained for each dosing in the six series of specimens, as well as the average values. A simple linear relationship exists between the amount of the cement paste stained (average value for the six series of specimens) and the dosing of concrete, within the range of 200-to-400 kg/m^3 (Fig. 4). The calibration equation that fits the model is: $y = 0.0607x - 9.9049$ and the correlation coefficient equals 0.9802. On Table 4 are collected the real cement content values and those calculated experimentally using our method.

3.2. Comparison between the stain method and the ASTM method

As a second example to assess the results, we applied the stain method to a concrete manufactured at a plant that uses the same materials with which the specimens were made in the lab; according to the data provided by the company, the dosing is 250 kg of cement per m^3 of concrete. To that end, six Ø15 × 30 cm cylindrical specimens were manufactured following the UNE-EN 12390-2 norm [8], which then went through the operating procedure described in the preceding sections. The cement content was calculated using the equation described in Fig. 4.

Those same specimens were later analysed in accordance with the protocol of the ASTM C 1084-02 norm [4].

Table 5 summarises the results obtained using both methods with very similar values.

4. Conclusions

A method for the quantification of cement in Ø 15 × 30 cm concrete specimens similar to those used to calculate resistance to compression has been developed.

The specimens are cut into two equal halves with a diamond disc saw, two flat surfaces of ca. 14 × 30 cm being obtained. The samples resulting from this process are stained through immersion in a solution of tannic acid (3% in-weight) acidified with tartaric acid (3% in-weight). This stain process is equally valid for young concretes with an abundant alkaline reserve and for old concretes with an advanced carbonation degree.

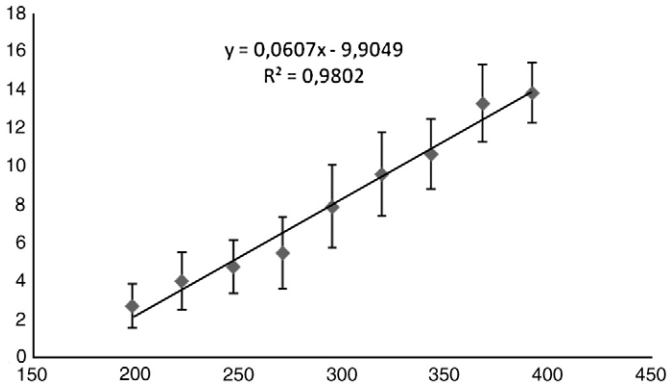

Fig. 4. Representation of the calibration curve: percentage of stained cement paste (y axis) vs. concrete dosing in kg of cement per cubic meter (x axis).

The images from the stained specimens are captured by means of a scanner and are treated using a software program developed by us (CuantiCem®), though other commercial software programs such as Corel or Photoshop can be employed too. In order to use the binarised image, we take a colour pattern sample that results from hydrating a binary mixture of cement and fine aggregates (fraction that passes a 0.063 mm sieve).

The method is applicable to a concrete manufactured with a specific type of cement. For that purpose, it is necessary to have available beforehand a calibration curve made with pattern specimens that relates cement content to the percentage of the image stained.

The method can equally be used for concretes manufactured using cements with admixtures (blast furnace slag, fly ashes, etc.) as long as there is a calibration curve prepared using specimens manufactured with this type of cement and a specific colour pattern sample is used to binarise images.

It can be inferred from the tests performed that the method presented can be applied with a sufficient degree of reliability to control the quality of plant concretes. For the example developed in this study we have chosen concretes similar to those most frequently used in the Valencian Autonomous Region (Spain).

The discussion finishes saying that the results obtained with the selective stain method are similar to those achieved by the ASTM reference method, but we think it is worth highlighting that the selective stain method has significant advantages, among others:

Sample analysis is much faster. Once the calibration graph has been built and the colour pattern sample manufactured, it is possible to obtain results from three concrete specimens within approximately 1 h.

Table 3
Stained cement paste content values (%) obtained for the six series using as pattern colour the one corresponding to the fine aggregates mortar with the highest dosing (400 kg/m^3).

Dosing	% Stained cement paste						
(kg cement/m^3)	T-1	T-2	T-3	T-4	T-5	T-6	Mean
198	1,87	1,75	2,74	4,31	3,80	1,62	2,68
222	1,86	3,35	2,66	4,62	5,15	6,27	3,99
247	2,09	4,48	4,73	4,72	5,81	6,59	4,74
271	2,54	3,06	6,62	6,99	7,09	6,43	5,46
295	3,95	6,46	7,79	9,13	10,51	9,36	7,87
319	5,72	8,26	9,11	10,77	11,59	11,98	9,57
343	7,99	9,42	9,52	12,26	13,41	11,10	10,62
368	9,34	12,22	14,09	14,46	13,81	15,72	13,27
392	12,22	12,91	11,80	14,74	16,09	15,16	13,82

Table 4
Real cement content values and those calculated experimentally through our method using the equation in Fig. 4.

Real values	Experimental values (kg cement/m^3)						
(kg cement/m^3)	T-1	T-2	T-3	T-4	T-5	T-6	Mean
198	194	192	208	234	226	190	207
222	194	218	207	239	248	266	229
247	198	237	241	241	259	272	241
271	205	214	272	278	280	269	253
295	228	270	292	314	336	317	293
319	257	299	313	341	354	361	321
343	295	318	320	365	384	346	338
368	317	364	395	401	391	422	382
392	364	376	358	406	428	413	391

Table 5
Cement content results determined using the selective stain method and the ASTM method for the six plant concrete samples.

Sample		ASTM	Stain method
1		256	248
2		235	242
3		234	249
4		235	237
5		250	227
6		254	243
	Mean value	244	241
	s	10	8

The analysis is more economical. The reagents used (tannic acid and tartaric acid) are not only harmless but also very cheap.

The method developed has no dependence on the composition of the coarse aggregates, whereas the ASTM method presents complications when concretes manufactured with coarse aggregates containing low-crystallinity acid-soluble silica are analysed.

Acknowledgments

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References

[1] EHE. – Instrucción de Hormigón Estructural. Real decreto 2661/1998. *BOE* [Official Gazette] 11 de 13/01/99. Pages 1525, 1526 and Annexe.
[2] S. Chinchón, et al., Cement paste colouring in concretes, Cement and Concrete Research 34 (2004) 1987–1991.
[3] Proyecto PETRI N°PTR1995-0319-OP (1999–2000): Cuantificación de cemento en hormigón endurecido mediante microscopía óptica. Financing institution: *MCYT* [Ministry of Science and Technology] Patent P2000102618.
[4] American Society for Testing and Materials (ASTM) C 1084–02, Standard Test Method for Portland-Cement Content of Hardened Hydraulic-Cement Concrete, 2002.
[5] G.K. Gomma, "Mechanism of corrosion behaviour of carbon steel in tartaric and malic acid in the presence of Fe^{2+} ion", Materials Chemistry and Physics 52 (3) (1998) 200–206.
[6] S.R. Gadakh, C.H. Bhosale, Effect of concentration of complexing agent (tartaric acid) on the properties of spray deposited Sb_2S_3 thin films, Materials Chemistry and Physics 78 (2) (2003) 367–371.
[7] J.A. Jaén, et al., Reactivity of tannic acid with common corrosion products and its influence on the hydrolysis of iron in alkaline solutions, Hyperfine Interactions 148/149 (2003) 199–209.
[8] Asociación Española de Normalización y Certificación, Norma UNE-EN 12390-2:2001, Madrid, Spain, 2001, equal to the EN 12390-2:2000 European Standard.
[9] CuantiCem®. – Program for cement quantification using image segmentation process. Patent A-385-06.
[10] Asociación Española de Normalización y Certificación, Norma UNE-EN 196-1:2005, Madrid, Spain, 2005, equal to the EN 196-1:2005 European Standard.