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Image analysis: a tool for the characterisation of hydration of cement in concrete – metrological aspects of magnification on measurement

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Abstract

This study aims at seeking what magnification is optimal in view to evaluate the hydration state of cement-based materials. When observing surfaces of flat polished sections of cement paste and mortar under SEM in BSEI mode at 100×, 200×, 400×, 600×, 1000× magnifications, an image analysis procedure, derived from the entropy maximisation, is applied to evaluate the area fraction of the anhydrous remnant cement grains A_A (NH) at a given maturity.

Results show that:

- 200× is sufficient to correctly determine A_A (NH) since higher magnifications induce marginal variations of A_A (NH),
- by calculating the covariance, 200× is also a representative field to describe the dispersion of the anhydrous phase.

The number of fields necessary to obtain a mean value of A_A (NH) with a defined accuracy at 200× is specified according to statistical laws. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Magnification; Image analysis; Area fraction; Anhydrous residues

1. Introduction

Some techniques are available to characterise the hydration of cement-based materials: chemically bound water, X-ray diffraction, heat of hydration [1,2]. Nevertheless, each method can be only used at a given stage of hydration in order to avoid artefacts. For example, at a very young state, the measurement of the heat released by the hydration reactions is able to describe hydration, but the measurement of the chemically bound water is affected by an increase in the rate of hydration due to the elevated temperature between 20°C and 105°C necessary to extract free water. Furthermore, all these physical methods require some assumptions concerning the chemical composition of the mixture so that the degree of hydration is finally indirectly derived.

By comparison with these methods, image analysis is undoubtedly a valuable technique to quantify the hydration whatever the material maturity may be. It makes it possible to achieve local data concerning the size, the shape and the dispersion of the cement grains.

The procedure presented in this paper allows us to measure the area fraction of anhydrous remnant cement grains A_A (NH) from a binarised image, succeeding an operation of segmentation of a digitised image [3]. The technique developed in our laboratory [4,5] is based on the entropy maximisation of the grey level histogram [6]. This latter is obtained by observation of flat polished sections under scanning electron microscope (SEM), using the backscattered electron imaging (BSEI) mode.

The choice of the optimal magnification to get an accurate counting of the pixels identified as anhydrous cement phase is discussed in this paper. Results from cement pastes and mortars are presented and analysed.

2. Experimental procedure

Ordinary Portland cement is used to make up plain cement paste (water-cement ratio by weight W/C = 0.35) and nominal mortar (NF EN 196-1: W/C = 0.5, Quartz sand-cement ratio by weight S/C = 3).

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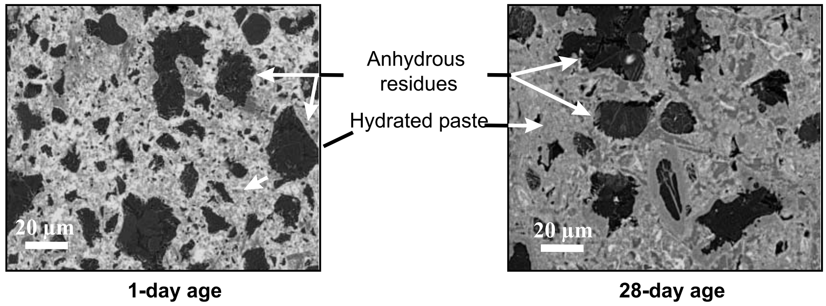

Fig. 1. Digitised images from polished section of cement paste observed under SEM (BSEI).

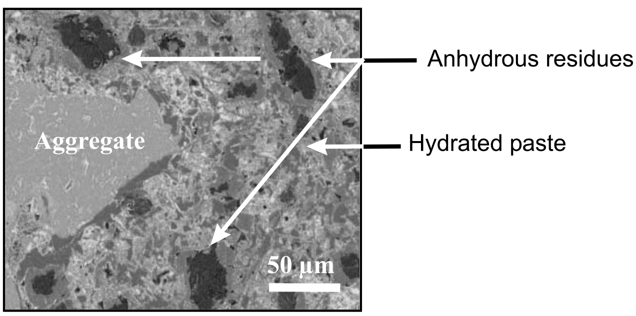

Fig. 2. Digitised image from polished section of 28-day mortar observed under SEM (BSEI).

Mixing sequence and curing conditions comply with specifications of the standard NF EN 196-1. Specimens (20 mm × 50 mm cylinders for cement paste, 4 cm × 4 cm × 16 cm prisms for mortar) are sealed and cured under controlled laboratory conditions for the first 24 h. After stripping, they are stored in a water tank at 20°C until testing.

Cement paste is observed at 1, 7, 28 and 120 days. Mortar is only observed at 28 days. The following experimental programme is carried out before using the image analysis procedure.

Specimen extraction. Specimens are taken from the core of slices (3 mm thick) sawn out from the middle of either cement paste cylinders or mortar prisms.

Drying. The removing of free water from specimens is different in accordance with the maturity.

At 1-day and 7-day ages, samples are first immersed in liquid nitrogen for 5 min, then dried, first under primary vacuum (10^{-3} Torr) for 2 days, second at 105°C for a night. The combination of freeze-drying and of oven-drying techniques is reported to be "gentle", because it limits the cracking of the microstructure [7].

At 28-day and 120-day ages, samples are dried at 50°C for 5 days.

Resin impregnation. Whatever their maturity may be, specimens are impregnated with an epoxy resin under lower vacuum.

Polishing. Samples are dry-polished with silicon carbide grits from 30 to 4 µm. Material dust accumulated is cleaned out ultrasonically in alcohol, after 4 µm grit. The polishing is finished using a 1-µm impregnated diamond cloth to which an oil-based lubricant is added. The ultrasound cleaning is then repeated.

Observation conditions. Carbon-coated surfaces are examined under SEM with an accelerating voltage of 15 kV and a working distance of 15 mm. Backscattered electron imaging by inverse polarity is used so that the densest phase (anhydrous cement grains) appears black on the TV screen (Figs. 1 and 2).

Image acquisition. Each image obtained from the SEM is 8-bit digitised in a hexagonal lattice into a 740 × 625 matrix of pixels with 256 grey levels.

3. Image analysis process

The image analysis is carried out from the procedure implemented by E. Ringot in the library Imglib of our laboratory. This procedure is based on the entropy maximisation of the grey level histogram of the image in order to extract the area fraction of cement residues as a scarce phase on the image. In a few words, the entropy maximisation involves a maximisation of the contrasts between grey level classes in order to find out one or several critical thresholds in the grey level histogram.

Concerning cement pastes, four steps are necessary to perform the automated procedure:

- light filtering (FAS) of the initial image,
- thresholding by the entropy maximisation of the grey level histogram so that a binarised image corresponding to the anhydrous particles is obtained,
- hole closing of the anhydrous phase which may be hidden by unremoved grits for example; no further filtering is carried out,
- rebuilding of the image, just for illustration.

Concerning mortar, the procedure is the same as above but two thresholds are necessary to discriminate anhydrous, hydrated and aggregate phases, in so far as the degree of hydration α is concerned. Indeed, α is deduced from the anhydrous phase-paste phase area ratio A by the relation $\alpha = 1 - \frac{A}{\Gamma}$, where Γ is the initial volume fraction of cement grains present in the fresh paste of mortar. Unfortunately, in some cases, the grey level values of the hydrated paste are almost the same of those of aggregates (see Fig. 2). Consequently, it is not always possible to separate hydrated paste and aggregates as previously said [5]. This difficulty is emphasised by the fact that aggregates cannot be considered like scarce objects. On the contrary, the remnant cement grains are distinctly dark. Since this phase is in the minority in the mortar (area fraction of a few % only), it is always discriminated by the entropy maximisation. So, even though this procedure applies very well to measure A_A (NH), it is not always convincing to evaluate the degree of hydration because, in some cases, the perimeter of critical aggregates has to be manually drawn so that A can be determined [5].

Further to this difficulty, the ISODATA technique [8] is applied with one parameter (radiometric level) and for five classes of grey level. The method, which seems to be more adapted, makes it possible to discriminate, in the rising order of the radiometric level: anhydrous cement grains (class1 C1), calcium hydroxide (C2), aggregate (C3), C–S–H (C4), porosity (C5). The ISODATA technique with five classes practically gives the same A_A (NH) value as the one determined by the entropy maximisation. The corresponding relative variation is always lesser than 5% for the fields studied in this paper.

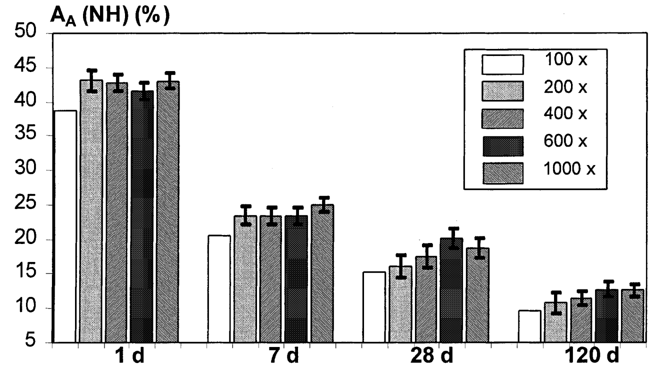

Fig. 3. A_A (NH) mean values and corresponding 95% confidence interval – cement paste.

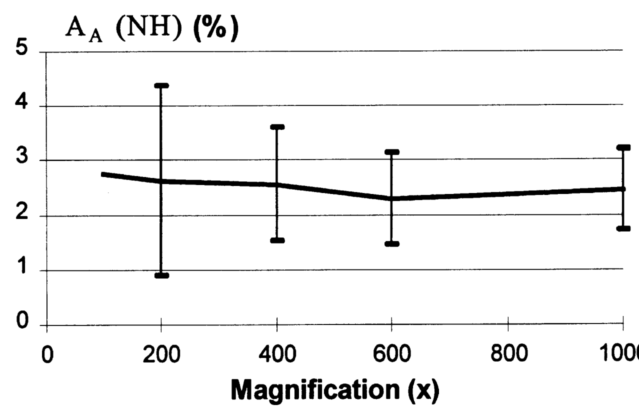

Fig. 4. A_A (NH) mean values and corresponding 95% confidence interval – 28-day mortar.

4. Local study

A field at 100× magnification, is digitised at one go as the reference area. This surface, randomly chosen on the total specimen area, is examined at 200× which results in four fields, next at 400× (16 fields), 600× (36 fields), 1000× (100 fields). Even though an automated image acquisition is available, a manual and constant fitting for each acquisition is needed to maintain a correct adjustment (brightness, contrast) of the SEM during the whole acquisition.

The 100× magnification is only used to determine the zone of interest in this local study. Hence, no measurement is done at 100× because the low resolution hides details less than 2 μm. The purpose of this study is to assess how magnification affects the estimation of A_A (NH) mean value in that zone. Figs. 3 and 4 present A_A (NH) versus magnification.

Some points have to be detailed to clarify the presentation of the results.

- The error lines visible on these graphs correspond to the 95% confidence interval for A_A (NH) mean value, using coefficient t_β of Student's law (see Fig. 9).
- Student's t-test is used to determine if two mean values of A_A (NH) corresponding to two distinct magnifications are significantly different at the significance level of 0.01. Usually, the difference is said to be probably significant at the significance level of 0.05.

4.1. Cement paste results (Fig. 3)

First of all, it can be seen that A_A (NH) obviously decreases with the maturity of the paste, due to the progress of the hydration with time. Results of Student's t-test are shown in Table 1.

Whatever the time of observation may be, A_A (NH) mean values:

- are always not significantly different between 200× magnification and the other ones,
- are globally comparable with each other between 400× and 600× magnifications, between 400× and 1000× magnifications, between 600× and 1000× magnifications.

4.2. Mortar results (Fig. 4)

No significant differences are found between A_A (NH) mean values obtained at distinct magnifications (see also Table 1).

Table 1
Students's t-test results of A_A (NH) mean values at the significance level of 0.01 (S) and of 0.05 (PS)[a]

	1-day age	7-day age	28-day age (cement paste/mortar)	120-day age
200×/400×	NS	NS	NS/NS	NS
200×/600×	NS	NS	NS/NS	NS
200×/1000×	NS	NS	NS/NS	NS
400×/600×	NS	NS	PS/NS	NS
400×/1000×	NS	NS	NS/NS	NS
600×/1000×	NS	NS	NS/NS	NS

[a] S: significant, PS: probably significant, NS: not significant.

5. Discussion

The whole of the result shows that for a given maturity the variations of A_A (NH) mean values are not significant between 200× and 1000× magnifications.

Hence, in this experimental context, 200× magnification seems to be sufficient to correctly quantify A_A (NH). At 200× magnification, the resolution is limited to 1.033 μm. When the magnification is increased, the discrimination of the microscopical features is made easier, particularly for the small anhydrous residues. But, when the area fraction of anhydrous grains ranging from 0.2 μm (limit of the resolution at 1000×) to 1.033 μm (200×) in size is taken into account, a marginal variation of A_A (NH) mean values is induced. This leads us to conclude that A_A (NH) solely depends upon the discrimination of the "largest" remnant cement grains.

Finally 200× magnification gives enough accurate measurement of A_A (NH) and in the same time enables to reduce the number of fields to be analysed in a given area.

Now, it remains to determine:

- if 200× magnification is actually representative of the structure of cement paste and mortar,
- how many fields at 200× magnification are needed to have a satisfactory representation of the analysed sample.

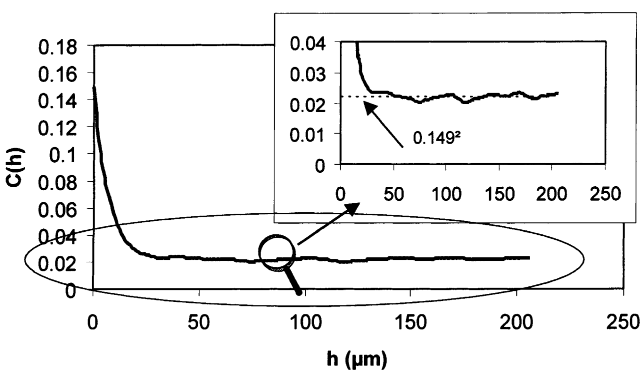

Fig. 5. Typical covariogram of surface of cement paste (28-day age) observed at 200× magnification.

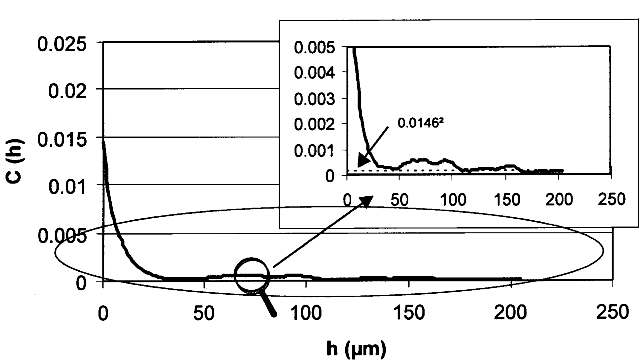

Fig. 6. Typical covariogram of a mortar surface (28-day age) observed at 200× magnification.

5.1. Calculation of the covariance at 200× magnification

The covariance C(h) is useful to describe the phase dispersion in a material [9]. C(h) represents the probability that 2 points distant of h belong both to the anhydrous phase. Considering the material anisotropy, the covariance is a mean value which is determined in 6 directions corresponding to those of the hexagonal lattice of the digitised image. Each direction is probed by a bi-point structuring element whose size h varies from 1 to 200 pixels. Figs. 5 and 6, respectively, present typical covariograms from an image of cement paste and an image of mortar at 200× magnification.

In the case of cement paste (Fig. 5), A_A (NH) is equal to 0.149, and C(h) converges on the theoretic asymptote $(0.149)^2 = 0.0222$ for a displacement h of 150 μm. Concerning mortar (Fig. 6), A_A (NH) is equal to 0.0146, and C(h) converges on $(0.0146)^2 = 2.13 \times 10^{-4}$ for a displacement h of 105 μm. So, according to these h values, 200× magnification is representative of the structure of both materials, since the image area is equal to 765 × 645 μm.

5.2. Estimation of the mean value of A_A (NH) at 200× magnification

Figs. 7 and 8 give the evolution of the mean value A_A (NH) according to the number p of fields ($p = 1$–50) for cement paste and mortar respectively. On each figure, the three curves correspond to three random sets of values taken from the 50 measurements available in this study. The comparison between these curves shows that it is obviously hazardous to determine A_A (NH) mean value by this method.

The number of fields necessary to get A_A (NH) with accuracy has to be determined by the use of statistical laws such as the Tchebychev law and the central limit theorem. In fact, the local value of A_A (NH) can be considered as a random variable x which can be characterised by its statistical moments such as its mean m and its variance v. For the purpose of this study, it must be remembered that the estimation $\tilde{m}$ of the mean of a set of p values x_i is

$$\tilde{m} = \frac{\sum_{i=1}^{p} x_i}{p}$$

and the Tchebytchev law assesses that $\tilde{m} = m$. The unbiased variance of the initial variable x is given by

$$\tilde{v} = \frac{\sum_{i=1}^{p} (x_i - \tilde{m})^2}{p-1}.$$

Often, only the mean value presents some interest so the following discussion focuses on it. The problem is to know what is the accuracy of the estimation $\tilde{m}$. The response is that it depends on the number p of measurements, and if $\tilde{m}$ is considered as a random variable, its variance is linked to p according to the relation $v_{\tilde{m}} = \frac{v}{p}$ so that $\tilde{m}$ tends to m when p increases indefinitely.

Is it theoretically possible to compute the optimised number of measurements necessary for obtaining an accurate evaluation of A_A (NH)? Here, an answer has to be found by considering the confidence interval, i.e., the probability that $\tilde{m}$ is situated between two limits around m. So, a value ε has to be searched, for which the probability β that $|\tilde{m} - m| < \varepsilon$ is fixed to a large enough value (typically 95% in material science). Theory of probability states that the value ε is given by $\varepsilon = t_\beta \sqrt{\frac{\tilde{v}}{p}}$, where the coefficient t_β derives from the Student's law $S_{p-1}(t)$ with $p-1$ degrees of freedom such that $2\int_0^{t_\beta} S_{p-1}(t) \cdot \mathrm{d}t = \beta$ (Fig. 9).

Following the above reasoning, Table 2 presents results for cement paste and mortar at 28-day age. For example, concerning cement paste, 30 random measurements involve a mean value of A_A (NH) equal to 16.15% with the 95% probability that the true mean

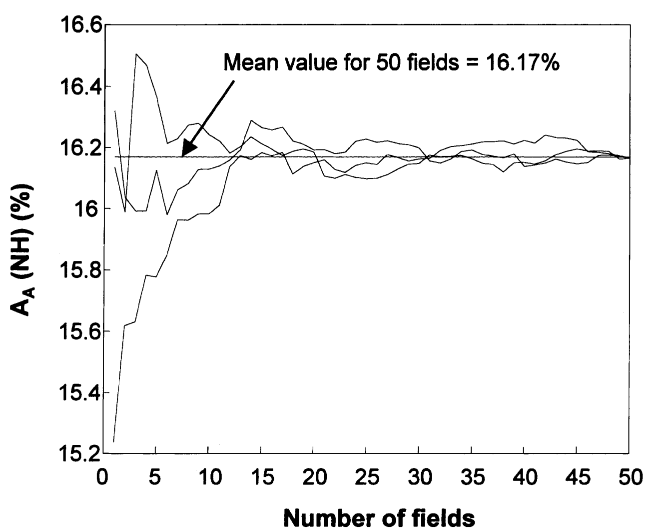

Fig. 7. Evolution of the A_A (NH) mean value according to the number of fields at 200× magnification – 28-day cement paste.

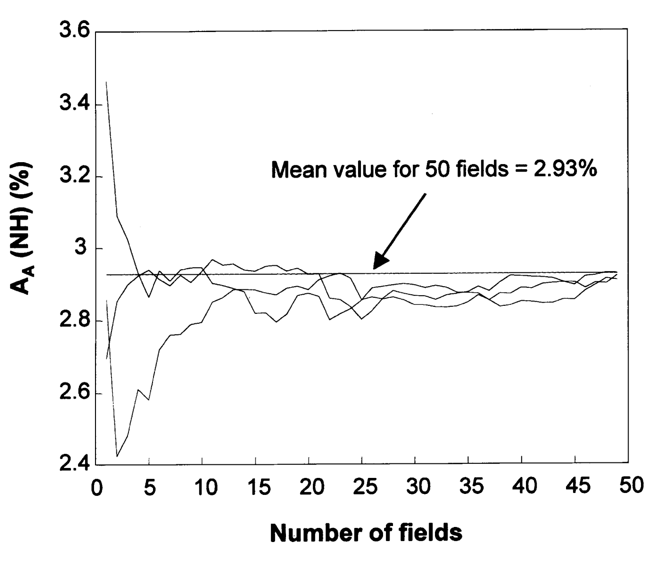

Fig. 8. Evolution of the A_A (NH) mean value according to the number of fields at 200× magnification – 28-day mortar.

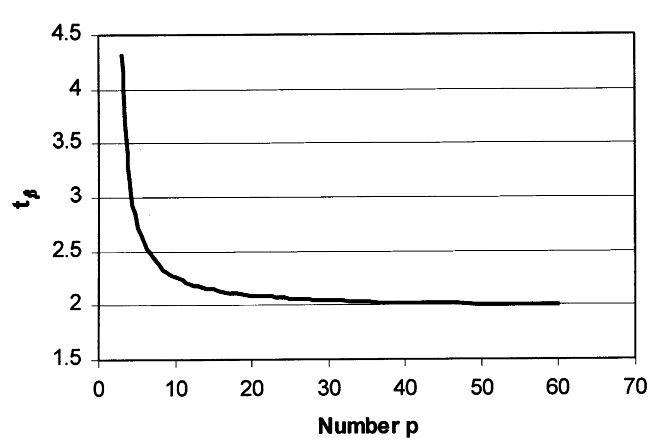

Fig. 9. Coefficient t_β (Student's law) versus the number of fields p for $\beta = 95\%$.

Table 2
Statistical results – mean value $\tilde{m}$ of A_A (NH) and corresponding variance $\tilde{v}$ according to the number of fields p at 200× magnification

	p	$\tilde{m}$	$\tilde{v}$	$\varepsilon = t_\beta\sqrt{\frac{\tilde{v}}{p}}$
Cement paste	5	16.36	0.47	0.85
	10	16.24	0.31	0.40
	20	16.19	0.20	0.21
	25	16.10	0.27	0.21
	30	16.15	0.24	0.18
	40	16.15	0.27	0.17
	50	16.17	0.27	0.15
Mortar	5	2.93	0.24	0.61
	10	2.86	0.26	0.36
	20	2.90	0.18	0.20
	25	2.88	0.17	0.17
	30	2.96	0.17	0.15
	40	2.89	0.23	0.15
	50	2.93	0.20	0.13

value does not differ from this experimental estimation by more than ±0.18%. Concerning mortar, A_A (NH) is equal to 2.96% with an accuracy of ±0.15% when 30 random fields are observed.

6. Conclusion

In this investigation, the influence of the magnification on the evaluation of the area fraction of the anhydrous remnant cement grains A_A (NH) was studied. A_A (NH) was determined by image analysis (entropy maximisation of the grey level histogram) of polished sections observed under SEM by BSEI mode. In order to test the homogeneity of a sample (cement paste or mortar), a given surface was analysed at 100×, 200×, 400×, 600× and 1000× magnifications. Following conclusions were obtained.

1. Using Student's *t*-test, no significant difference is visible between 200× and 400×, 200× and 600×, 200× and 1000×. Consequently 200× magnification is sufficient to correctly quantify A_A (NH) for cement paste as well as for mortar.
2. The calculus of the covariance of the fields studied at 200× magnification shows that 200× is representative of the structures of cement paste and of mortar.
3. For a given sample of cement paste or a given sample of mortar observed at 200× magnification, the number of fields necessary to get a mean value of A_A (NH) with a defined accuracy is specified by means of statistical laws.

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