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Reproducibility of w/c ratio determination from fluorescent impregnated thin sections

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Abstract

The ease and reproducibility of preparing fluorescent epoxy impregnated thin sections for w/c determination of concrete has been studied. Five sets of thin sections were prepared from 6 concrete mixes having different compositions and w/c ratios (0.35 to 0.80). The thin sections were prepared by different technicians and produced over a period of nearly a year. The quality of the thin sections was checked and the w/c ratio determined by seven petrographers using fluorescent light microscopy as a Round Robin test.

The investigation showed that, within a reasonable time, different technicians were able to produce a comparable quality of fluorescent epoxy impregnated thin sections, even though the thin sections were produced from concrete at different ages and using different equipment and chemicals. The petrographers were able to distinguish between the green shades of the fluorescent dye epoxy impregnated cement paste, with sufficient accuracy. The result of the w/c Round Robin test gave standard deviations between 0.02 and 0.03 (average 0.026).

Keywords: w/c determination; Concrete; Microstructure; Petrography; Characterization

1. Introduction

Production of fluorescent impregnated thin sections was commenced in an American laboratory in order to use these as one of their standard ways of examining the micro-structural appearance of concrete, and as a tool for the determination of the w/c ratio.

One of the great advantages of using fluorescent epoxy impregnated thin sections is the possibility to determine the w/c ratio of concrete [1,2]. The w/c can be determined using fluorescent epoxy impregnated thin sections because the fluorescent epoxy fills the capillary pores in the hardened cement paste during vacuum impregnation. The amount of epoxy filling the pores is proportional to the capillary porosity (and therefore the original mix w/c). This causes a dense cement paste with low water to cement ratio to appear darker green while a more porous cement paste with a higher water to cement ratio appears lighter green. By comparing the green shade of the paste to known laboratory mix standards in the range of 0.35 to 0.70 the water to cement ratio (w/c) of the concrete can be determined.

A second but very important advantage of using the fluorescent epoxy impregnated thin sections is that micro-structural features, such as e.g. homogeneity of the cement paste, bleeding, re-tempering, porosity of aggregate, water absorption related to aggregate, zoning (variable w/c through the concrete column) and cracks (especially micro-size cracks less than 10 μm), may be identified immediately if present [3,4]. Thirdly, seen in perspective of quality assurance, training, knowledge building and research, the preparation of fluorescent epoxy impregnated thin sections is very valuable, as these can be permanently archived, not taking up much space, and may be used repeatedly.

In order to test the ease of preparing and analyzing fluorescent epoxy impregnated thin sections, a research program was set up including fluorescent thin section production and w/c determination by both experienced and inexperienced, in-training technicians. The first fluorescent epoxy impregnated thin sections were made by a skilled technician from a laboratory in Denmark. These fluorescent epoxy impregnated thin sections formed a reference for subsequent thin section production. The concrete from six of the jobs performed in Denmark were saved and used for thin section preparation at the American laboratory, at four different periods. The first set of thin section was prepared during an initial

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training session. Three different technicians prepared fluorescent epoxy impregnated thin sections during this session. The next set of thin sections was prepared half a year later by two technicians, after having prepared fluorescent epoxy impregnated thin sections for about 5 months. The last set of thin sections was made by a new technician after a training period of 2 months. All the fluorescent epoxy impregnated thin sections were made using the same thin section machine, the same fluorescent dye, but different vacuum pumps and different brands of epoxy and hardener.

After preparation of the fluorescent epoxy impregnated thin sections one skilled petrographer checked the quality. Always and initially when using the fluorescent technique for w/c determination the petrographer should compare the green intensity of the cement paste with the spacing of the cement grains and e.g. the amount and appearance of calcium hydroxide in the cement paste, voids and cavities. If the green intensity e.g. appears very light and the cement grains are closely spaced something may be amiss since this is contradictory in terms of the w/c ratio. In such a case white pigment may have been used and the w/c ratio cannot be determined with the fluorescent method. This little example shows that it is really important that the petrographer is experienced in optical microscopy as well in concrete technology in order to interpret the microstructural features observed and being able to assess the data obtained. Areas, which were improperly impregnated, damaged from preparation, had an incorrect thickness or carbonated during storage were noted and marked directly on the section in order to insure that all petrographers did their w/c determination on a similar area and on an as good "fresh" area as possible. Ideally if the fluorescent epoxy impregnated thin sections were of poor quality they should not have been used for w/c determination, but in this case the experienced petrographer made sure, by marking the sections, that data was comparable for the study.

The fluorescent epoxy impregnated thin sections were in sets of 5 handed out to 7 different petrographers from 3 laboratories for

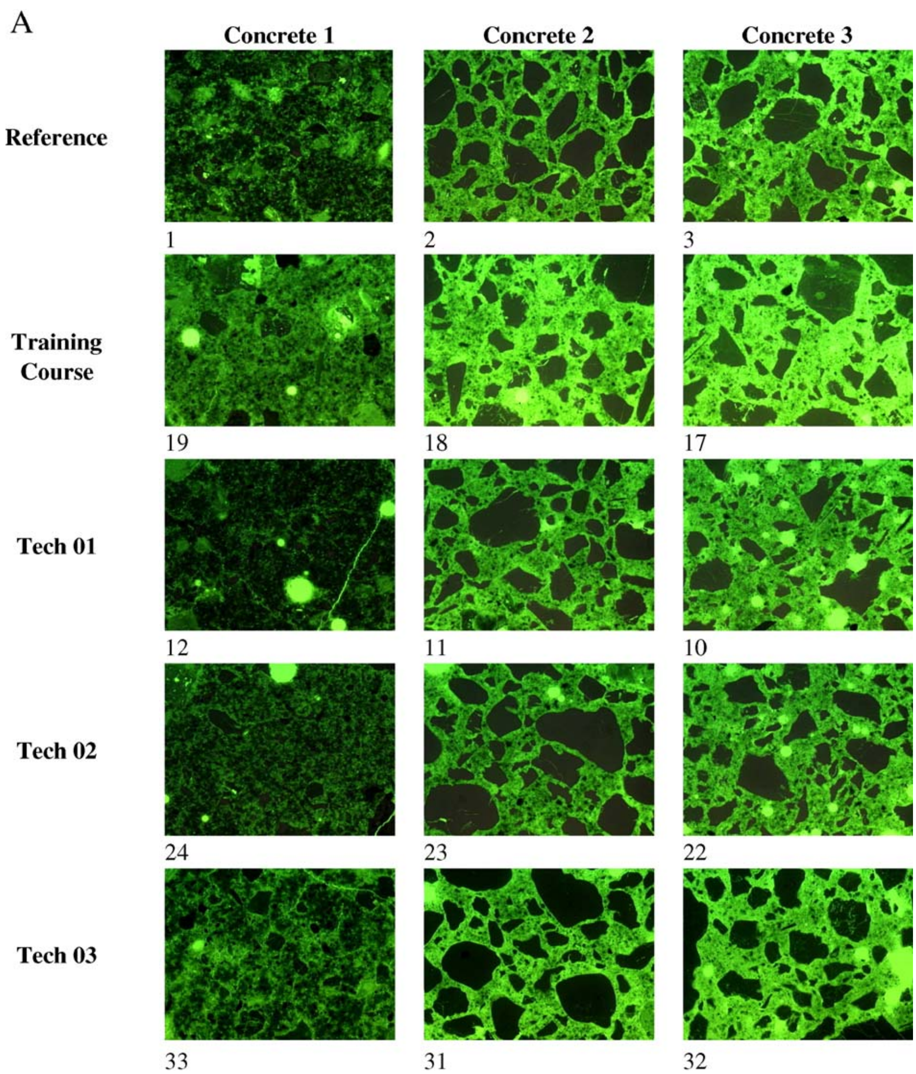

Fig. 1. (A) Images showing the paste structure of 15 of the fluorescent epoxy impregnated thin sections (concretes 1, 2 and 3). The cement paste appears with different green shades depending on w/c ratio, dense aggregate appears dark green/black and air voids or cracks yellow. The images are taken in fluorescent light mode and have a length of 2.6 mm. (B) Images showing the paste structure of 14 of the fluorescent epoxy impregnated thin sections (concretes 4, 5 and 6). The cement paste appears with different green shades depending on w/c ratio, dense aggregate appears dark green/black and air voids or cracks yellow. The images are taken in fluorescent light mode and have a length of 2.6 mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

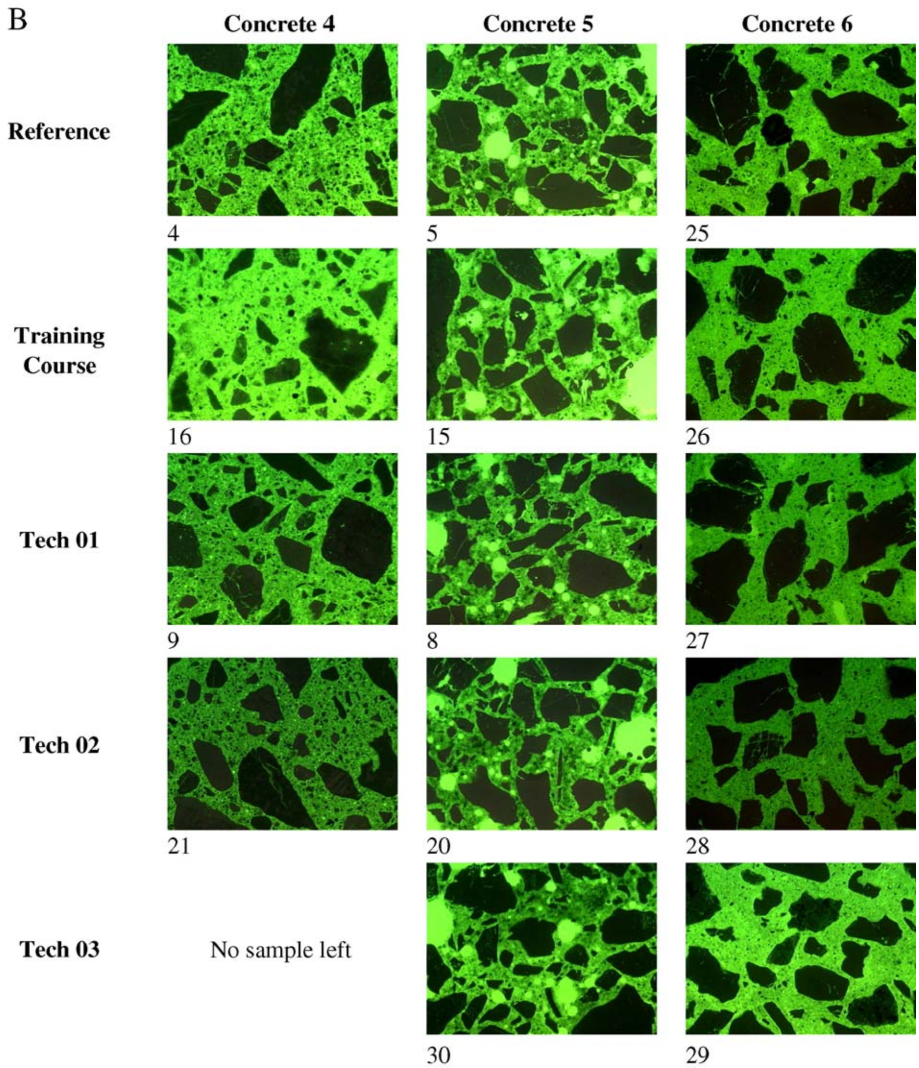

Fig. 1 (*continued*).

analysis; four experienced in fluorescence microscopy and three less so. In order to ensure that the petrographers did not recognize the concrete from one set to the other, they were only supplied with one set at a time. After having determined the w/c ratio of a set of fluorescent epoxy impregnated thin sections the petrographer received a new set after 1 to 2 weeks. All petrographers were asked to use the same set of w/c standards having a w/c range of 0.35 to 0.70, when determining the w/c ratio. In cases were the paste apparently appeared darker than the 0.35 standard the petrographers assigned a lower extrapolated value. This value was solely based on the petrographer's own experience.

This paper comments on the quality of the 29 fluorescent epoxy impregnated thin sections as well as presenting data from the Round Robin test on the w/c determination of the concretes. This study does not have any intention of studying the absolute accuracy of the fluorescent method since it does not contain any laboratory-controlled samples with known w/c. The samples used were all complaint field samples of various compositions and the data solely represent different technicians capabilities of producing fluorescent epoxy impregnated thin sections and petrographers capability to obtain similar w/c ratios based on the green colour of the cement paste.

2. Method

The fluorescent epoxy impregnated thin sections used for this study were prepared by different technicians but all following the procedures described in the Nordtest Standard [5] and by an ACI Special Publication [2]. The concrete samples were cut into small blocks measuring 35×45 mm. The blocks were vacuum impregnated using a low viscosity yellow fluorescent epoxy resin (e.g. products from Ciba Geigy and Struers), containing 1% (w/w) fluorescent dye. This impregnation step ensured the concrete was consolidated in order not to damage it during processing. After hardening one face of the block was made flat using grinding equipment, which ensured plane parallel grinding throughout the subsequent process. After grinding the block was impregnated a second time, in order to ensure proper impregnation of the capillary porosity. After hardening, the excess epoxy and 7 μm of the concrete beneath the impregnation surface was removed by

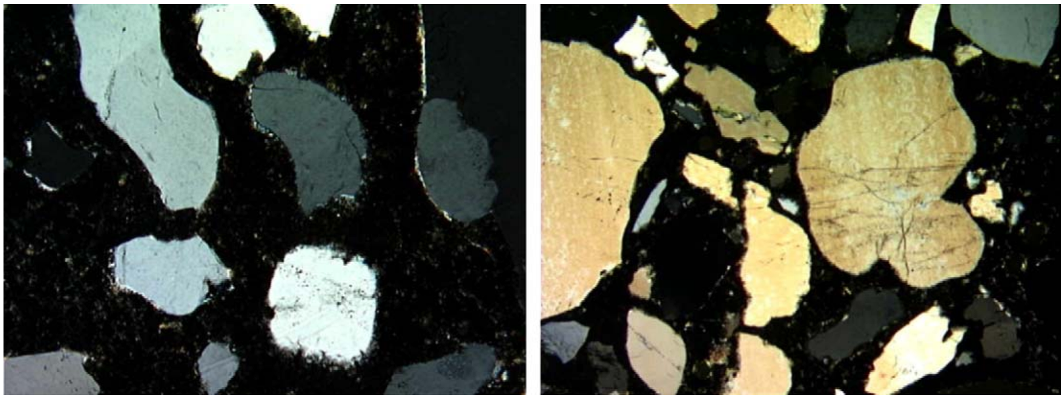

Fig. 2. Images showing correct (left) and incorrect (right) thickness by the use of the birefringence of quartz. The image to the left with grey quartz is taken from a thin section prepared in Denmark, the image to the right with yellow quartz from a thin section prepared during the training session. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

grinding. An object glass was then glued onto the fully impregnated concrete and the block cut in such a way that about 0.5 to 1 mm of the impregnated concrete was left on the glass. The concrete slice was ground to thickness of 20–25 μm. The thickness was controlled partly by the equipment itself but also manually by watching the birefringence colour change of quartz. As the last step a cover glass was glued onto the section prior to analysis.

The above description of thin section preparation may appear easy, but of course as with all other types of sample preparation it is something which has to be practiced before gaining experience. A number of things may go wrong as described in [2] and it is therefore a good idea, as done in this study, that unskilled technicians are trained onsite by skilled personnel. One thing which may go wrong (but which definitely should be avoided) is improper impregnation of the cement paste (into the capillary porosity). If a sample (thin section) is improperly impregnated for any reason or if it is too thin or too thick it *cannot* be used for w/c determination and it has to be further prepared or repeated. If on the other hand minor damages such as cracking of the edges of the thin section have been created during preparation, it may be used but caution should be taken when evaluating the cause of features such as the cracks.

The w/c determination was performed using the same set of standards containing Type I Portland cement, and sea dredged aggregate with a max. size of 8 mm. No supplementary cementitious materials were present in the standards or the test concretes. The standards covered a w/c range of 0.35 to 0.70. Standard and field concrete were all more than 28 days when prepared for thin sections. The determination was performed using an optical polarizing microscope (transmitted light mode) equipped with a GB21 blue filter and a K530 yellow blocking filter as described in [2].

3. Results and discussion

3.1. Thin section quality

All fluorescent epoxy impregnated thin sections were, as mentioned earlier, examined for defects before initiating the w/c determination. Representative photographs of the impregnated cement paste were taken of each of them using the fluorescent light mode and magnifications of 25 times (Fig. 1A and B). The thickness was checked and the average thickness measured by the use of birefringence colours. Where the thickness varied though the section this was noted with a marker pen on the section in order to insure that all 7 petrographers did their w/c determination in fully impregnated paste and at a correct thickness as possible. The general appearance of the paste of the 29 thin sections when viewed in fluorescent light mode is shown in Fig. 1A and B.

The upper row shows the appearance of the paste of the reference thin sections; row #2 the paste of the sections prepared during the training course; rows #3 and #4 the paste of the sections performed later by two different technicians, and row #5 the paste of the sections prepared by a newly trained technician. Overall, except for the fluorescent epoxy impregnated thin sections prepared during the training session, the paste green shade appears very similar and the photographs illustrate well the improvement of the unskilled technicians from the time of the training session to the end of the period.[1] Most of the thin sections produced during the training course were too thick (30–40 μm) and resultantly they appear somewhat lighter green compared to the thin sections having correct thickness. At the time of the training session the laboratory did not have proper grinding equipment for the final stage of bringing the section to the proper thickness of 20–25 μm, and consequently these sections were too thick (Fig. 2). Later, a special grinding disk (the so-called pellet disk) was purchased which makes it easier to achieve the proper thickness of the fluorescent epoxy impregnated thin sections.

Another reason for the higher apparent w/c ratio of the thin sections from the training course is that the sections were not properly cleaned of excess epoxy as seen by a yellow haze on the aggregates. On properly cleaned fluorescent epoxy impregnated thin sections dense aggregates should appear dark green such as those seen at the images of the other columns of Fig. 1A and B. When epoxy is present on the backside of the sections it results in

[1] Colour is clearly a critical element of the techniques used in this study, so the text and images of this paper have not been modified to reflect the fact that images in Cement and Concrete Research are printed in black and white. A full colour copy of this paper is available online at http://www.sciencedirect.com/.

Table 1
The seven petrographers (PE) w/c readings on the 29 different thin sections

Laboratory	PE	Concrete 1	Concrete 2	Concrete 3	Concrete 4	Concrete 5	Concrete 6
Reference	*1*	0.33	0.50	0.55	0.58	0.60	0.70
	2	0.35	0.55	0.62	0.63	0.65	0.70
	3	0.32	0.60	0.65	0.55	0.60	0.75
	4	0.35	0.60	0.63	0.50	0.62	0.70
	5	0.35	0.55	0.60	0.54	0.60	0.80
	6	0.33	0.55	0.58	0.65	0.58	0.72
	7	0.34	0.58	0.60	0.58	0.60	0.72
Training	*1*	0.40	0.60	0.70	0.65	0.70	0.70
	2	0.42	0.65	0.70	0.65	0.68	0.70
	3	0.45	0.55	0.65	0.60	0.75	0.65
	4	0.45	0.60	0.75	0.73	0.70	0.75
	5	0.50	0.60	0.72	0.63	0.73	0.70
	6	0.43	0.60	0.72	0.70	0.70	0.80
	7	0.58	0.60	0.68	0.70	0.70	0.72
Tech 1	*1*	0.30	0.55	0.65	0.55	0.60	0.70
	2	0.35	0.55	0.65	0.58	0.65	0.70
	3	0.30	0.55	0.65	0.55	0.65	0.75
	4	0.30	0.63	0.64	0.65	0.60	0.75
	5	0.30	0.57	0.60	0.54	0.52	0.68
	6	0.33	0.52	0.68	0.58	0.58	0.72
	7	0.32	0.54	0.68	0.56	0.60	0.74
Tech 2	*1*	0.35	0.50	0.60	0.45	0.55	0.70
	2	0.35	0.42	0.58	0.37	0.55	0.68
	3	0.30	0.48	0.55	0.40	0.55	0.60
	4	0.33	0.57	0.65	0.43	0.55	0.68
	5	0.32	0.45	0.62	0.36	0.45	0.55
	6	0.33	0.45	0.58	0.35	0.50	0.70
	7	0.32	0.54	0.60	0.44	0.56	0.70
Tech 3	*1*	0.38	0.65	0.70	NA	0.60	0.73
	2	0.40	0.70	0.70	–	0.65	0.73
	3	0.45	0.55	0.70	–	0.65	0.73
	4	0.42	0.63	0.69	–	0.62	0.75
	5	0.45	0.60	0.72	–	0.68	0.74
	6	0.43	0.62	0.75	–	0.60	0.72
	7	0.45	0.62	0.70	–	0.55	0.74
Estimated thickness (μm)		30–35	35– 40	Wedged	Improper impregnated		

The estimated thickness of the sections is indicated by different shadings. White columns indicate correct thickness.

a lighter green appearance of the paste and therefore it will push the w/c determination in a higher direction when compared to standards.

The paste of a few of the fluorescent epoxy impregnated thin sections, such as nos. 21 and 28 (Fig. 1B), was somewhat darker green compared to the paste of its companion fluorescent epoxy impregnated thin sections. The reason for this was an improper impregnation of the capillary pores, resulting in a darker green colour. Both these thin sections were prepared by a technician trained for half a year (Technician 2) and this technician generally had some problems getting the epoxy into the capillary pores resulting in a bit darker green colour for all the fluorescent epoxy impregnated thin sections. Possible reasons for such a problem could be that the samples were not properly dried and vacuumed before application of the epoxy, or the re-grinding of the epoxy impregnated surface was too deep, leaving the analyzed surface non-impregnated.

The largest green colour difference was observed between the fluorescent epoxy impregnated thin sections made from concrete 1 (Fig. 1A). All these fluorescent epoxy impregnated thin sections also had the darkest green colour among the 6 sets of concrete, indicative of a rather low w/c ratio. The different green colour of the paste of this concrete explains very well the difficulty impregnating concrete with low w/c ratio and that the technician has to be very careful when encountering such concrete. The samples have to be properly dried and under proper vacuum before epoxy impregnation starts. Also the technician has to be very careful when making the thin section, and not to re-grind too deeply thus removing the impregnated paste. The above shows that it indeed is important that the technician is capable of evaluating the quality of the thin section before handing the thin section to the petrographer, but it is also important that the petrographer is capable of the same evaluation before performing the w/c determination.

3.2. Operator dependence of measurement

The primary data as well as the average and standard deviation for the 7 petrographers participating in the test are presented in Tables 1 and 2. Each petrographer determined the w/c of 29 concrete thin sections by examining the green colour of the paste within the marked areas and comparing that colour to the standards used. The number and comments were noted and when all data was available the data treatment was performed. As can be seen from the data of Table 2 the standard deviation generally varies from 0.02 to 0.03 with an average of 0.026 for the whole population.

Some variation of the w/c is observed among the 4–5 fluorescent epoxy impregnated thin sections produced from the 6 concretes (Tables 1 and 2 and Fig. 3). The variation in w/c can as already been discussed be explained by variation in thickness of the thin sections, carbonation of the paste during storage, and the general preparation flaws made by the unskilled technicians (Table 1). Despite this variation, each of the 6 concretes can, with minor exceptions, be distinguished by their determined w/c ratios.

Table 2
Average w/c and standard deviation measured on the 29 different thin sections prepared by 5 different persons/laboratories for 6 different concrete samples

	Concrete no./laboratory					
	1	2	3	4	5	6
Average						
Reference	0.34	0.58	0.61	0.58	0.61	0.72
Training	0.45	0.60	0.69	0.65	0.71	0.72
Technician 1	0.31	0.55	0.64	0.56	0.61	0.72
Technician 2	0.33	0.52	0.60	0.42	0.54	0.68
Technician 3	0.43	0.63	0.71	–	0.63	0.73
Std. deviation						
Reference	0.012	0.023	0.023	0.027	0.022	0.022
Training	0.038	0.021	0.025	0.038	0.023	0.022
Technician 1	0.020	0.020	0.034	0.015	0.027	0.028
Technician 2	0.018	0.027	0.018	0.028	0.031	0.057
Technician 3	0.034	0.035	0.020	–	0.038	0.010

The numbers are based on the w/c determination performed by the 7 different petrographers who participated in the study.

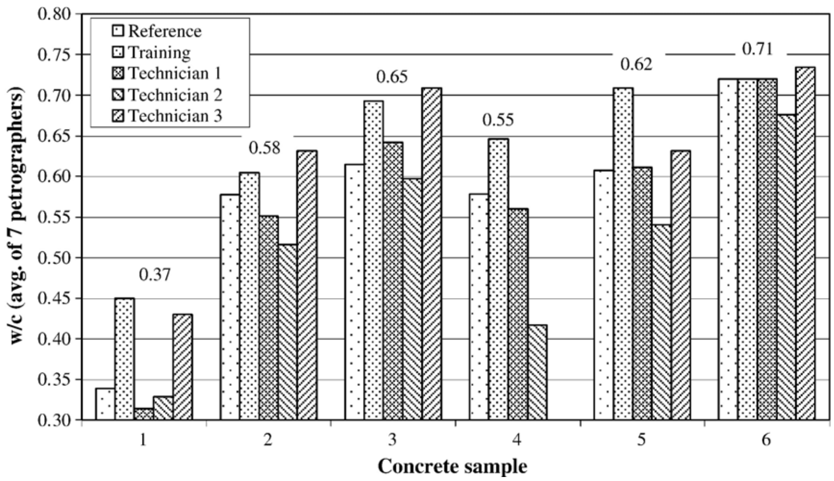

Fig. 3. The figure shows the average w/c determined for the individual fluorescent epoxy impregnated thin sections as well as the variation on 6 different concrete samples. The average w/c of the 4 or 5 sections prepared from each of the 6 concrete samples is shown above the columns.

An example of a thin section, which appears very different from its companion fluorescent epoxy impregnated thin sections, is the section made from concrete 4 by Technician 2. This section was determined to have a w/c of 0.42 whereas the three other fluorescent epoxy impregnated thin sections made from this concrete had a much higher number. Checking this section in the optical microscope showed that the paste was improperly impregnated resulting in a darker green shade, as also seen in Fig. 1B. Symptomatic for all fluorescent epoxy impregnated thin sections produced during the training session, when the laboratory was not fully equipped, is higher w/c determinations. This feature results in the generally lighter green colours of all these fluorescent epoxy impregnated thin sections when compared to their companion sections (Fig. 1A and B). Fig. 3 shows the average and standard deviation of the 7 petrographers on each thin section combined with representative photographs of the cement paste when viewed in fluorescent light mode. As can be seen the average w/c numbers match very well the green colours of the paste e.g. a high w/c determination also matches a light green colour indicative of a high capillary porosity and vice versa.

The 7 petrographers were very much in agreement about the w/c ratio of the individual fluorescent epoxy impregnated thin sections as seen from the relatively low standard deviations. Only in few cases, such as one of the sections made from concrete 6, was there some variation resulting in a standard deviation of 0.057 (Table 1). In fact it was only one of the petrographers who was somewhat adrift.

An attempt to correlate the determined w/c with the thickness of the thin section has been done as seen in Fig. 4. Despite the relative sparse data there is a clear indication that the thicker the thin section the higher the w/c determined which indicates that the thickness of the fluorescent epoxy impregnated thin section is of utmost importance for the correct w/c determination. The fluorescent epoxy impregnated thin sections made from field samples must therefore always be produced with the same thickness as the standards, i.e. 20–25 μm.

Based on the above results and discussion there is no doubt that a well-trained petrographer can distinguish between the different green colours of the cement paste and when having a good set of w/c standards the petrographer is therefore also capable of

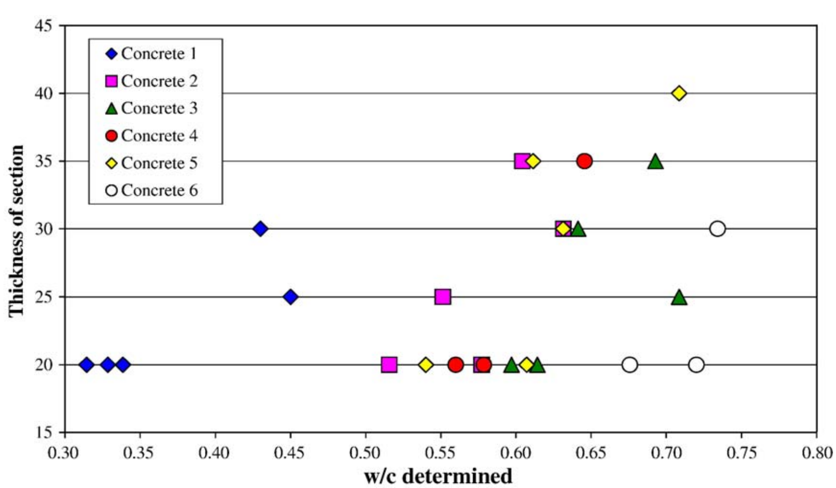

Fig. 4. Correlation between the determined w/c ratio and the thickness of the thin section. Thickness is in μm.

determining the w/c ratio of the field samples. As shown by this study the w/c determination can be performed with a standard deviation of 0.02 to 0.03 when dealing with field samples. The petrographer must however be aware of the limitations of the method when determining the w/c. Some limitations could be lack of good or proper standards, the use of pigments, and general features such as carbonated or leached paste, or a poor degree of hydration. In such cases the w/c determination should be performed with caution (if possible at all) using common sense and experience. As mentioned earlier the spacing of the cement grains may be used to back up the w/c determination. If determining the w/c of field concrete and having standards not matching the mineral composition of the field concrete the w/c should be given as ‘apparent’ w/c.

As mentioned earlier no attempt has been done to verify the fluorescent method on laboratory made samples with controlled w/c ratio. Based on the results of this study there is in the authors mind no doubt that if laboratory samples with controlled w/c ratio were prepared the results would have been very similar to those presented with an accuracy of about ±0.02 as earlier stated by [2].

4. Conclusion

The present study shows that it is indeed possible for a petrographer to distinguish between different green colours of the cement paste and by using proper w/c standards it is possible to determine the w/c ratio with a standard deviation of 0.02–0.03. Also it is shown that it is very important that the petrographer is experienced and not solely uses the green shade to determine the w/c but also uses other information present when determining the w/c of concrete.

The study furthermore shows that the most critical part of this method is to correctly produce the fluorescent epoxy impregnated thin sections, and that the technician as well as the petrographer must be able to evaluate the quality of a thin section before using it for w/c determination. It is however possible, within a reasonable time, as shown in this study, to learn to produce the fluorescent epoxy impregnated thin sections with some supervision from a skilled person. Additionally the laboratory must be properly equipped.

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