Determining w/c ratio in hardened concrete: an inter-laboratory trial by the Applied Petrography Group

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Summary

In 2017, the Applied Petrography Group in London organised a pan-European inter-laboratory collaboration to measure the water/cement (w/c) ratio in hardened concrete by microscopy to evaluate and compare methods used by participating laboratories. Determination of w/c ratio in hardened concrete is a critical measure of concrete quality and is sometimes a subject of dispute in concrete strength and durability issues. Five separate prism samples with measured w/c ratios ranging from 0.35 to 0.55, but otherwise identical in mix design were prepared. Thick slices were cut from these samples and distributed. Initially, 14 laboratories across Europe agreed to participate but the w/c ratios were withheld. These laboratories used a range of methods that could be broadly divided into visual assessment methods, measurement of fluorescent intensity and backscattered electron microscopy. Some laboratories made the w/c ratio determinations by more than one method or operator. Consequently, 100 individual w/c ratio determinations were collected from 11 of the participating laboratories. Comparing the results it was found that there was little significant difference between visual assessment and quantitative fluorescent methods. Overall, 58% of results were within ±0.05 of the target value and 81% of results were within ±0.10 of the target value.

1. Introduction

The Applied Petrography Group at a meeting in London in 2015 began discussions concerning the organisation of an inter-laboratory collaboration to measure and to compare the w/c ratio in hardened concrete by microscopical methods between participating laboratories.

In October 2016 the steering committee agreed that five separate test concrete samples should be prepared for this trial. Since this was an initial and exploratory trial of the methods in current use it was decided that a simplified concrete mix design should be used containing no chemical or mineral additions. The same mix design should be used for each sample with the only variable for the five samples being the w/c ratio which ranged from 0.35 to 0.55. These samples were prepared by the Tarmac Technical Centre at Lutterworth, UK in May, 2017.

It was fully appreciated that these laboratory prepared samples would be very simplified versions of normal modern concretes and consequently the results obtained by participating laboratories would only be comparable with other laboratories using the same trial samples and any extrapolation of their results to the determination of the w/c ratio of normal concretes should be treated with extreme caution.

1.1. Background

The Applied Petrography Group (APG) is affiliated to the Engineering Group of the Geological Society of London and set up a calibration trial steering (CTS) sub-committee to organise, oversee the trial and produce a report on conclusion of this initial trial. The sub-committee was chaired by Mr Richard Fox and Dr Alan Poole was the Secretary. There were some changes to the sub-committee membership before stabilising as shown under the title heading. They were empowered to seek expert advice as necessary and have received numerous comments from APG members, following the presentation of a first draft to members.

1.2. Objectives

Three objectives of this initial, exploratory first trial were identified by the CTS committee as follows:

(a) An investigation of the validity of optical fluorescence microscopy, visual assessment methods and backscattered electron microscopy for determining the w/c ratio in simplified hardened concretes.

(b) An examination of the precision of the results obtained for each of the five trial specimens through a normal range of w/c ratios.

(c) To compare the results obtained by the participating laboratories and to estimate inter-laboratory precision in determining the w/c ratio of hardened concrete.

1.3 Participating laboratories

Initially contact was made with 29 laboratories across the UK and Europe to enquire whether they would be interested in participating in this trial. 14 laboratories agreed to participate and samples were dispatched to the following:

- Dr Maarten Broekmans, NGU (Norway)
- Dr Alan Bromley (UK)
- Dr Oguzhan Copuroglu, Delft University (Netherlands)
- Mr Mike Eden, Sandberg (UK)
- Dr Isabel Fernandes, University of Lisbon (Portugal)
- Mr James Ferrari, RSK Ltd (UK)
- Dr Gisli Guðmundsson, Mannvit (Iceland)
- Dr Rachel Hardie, Heath & Hardie Geosciences (UK)
- Dr Ulla Jakobsen, Danish Technological Institute (Denmark)
- Mr Kiket Makoubi, Petroclays Materials Ltd. (UK)
- Ms Alice Mitchinson, SLR Consulting (Ireland)
- Mr Phil Raybould, Enterprise Petrography (UK)
- Mr James Strongman, Petrolab Ltd. (UK)
- Dr Hong Wong, Imperial College London (UK)

In order to maintain confidentiality each laboratory was allotted a unique laboratory reference number. Participants were asked to report their findings and methodology on a pro-forma drafted by the Secretary (Appendix 3).

By June 2018, 11 of these laboratories had submitted their sets of 5 results, and some had presented more than one set, either by using more than one analytical method, or by using several different petrographers to produce the w/c ratio results submitted. This multiplicity of individual results and the method used to obtain each result set are summarised in the next Section (see Table 2). In total, 20 complete sets of results, or 100 individual w/c ratio determinations were obtained.

2. Methodology

2.1 Specimen preparation

Taking account of all the initial discussions and the practical matters associated with the preparation of the specimens it was agreed that in this first initial and exploratory trial, the sets of specimens should be a simplified concrete mix, with CEM I Portland cement, 10 mm maximum size coarse aggregate and that no chemical admixtures or mineral additives should be included. It was agreed that the mix design for all the specimens should be standardised, with the only variable being the water/cement ratio.

Five concrete mixes were prepared and tested (Table 1). Details of the mix design were discussed by APG members, but the final mix design was developed in close consultation with Michael Thomas (Tarmac Technical Centre, Lutterworth) who had carried out preliminary mix trials. Their exact w/c ratios were known

only to the Chairman and Secretary of the CTS committee throughout the trial. CEM I 52.5N Portland cement was supplied by Tarmac/CRH, Tunstead. The average Bogue composition was 73.3% C3A, 11.5% C2S, 7.3% C3A and 9.8% C4AF.

Coarse aggregate was Tunstead crushed limestone (4/10 mm) and fine aggregate was Alrewas natural quartz sand (0/4 mm) (Fig. 1). The contents of water and cement were varied to achieve the target w/c ratio. Aggregate to cement ratio was kept constant at 3.99 for all mixes. Aggregate absorption to saturated-surface dry condition was considered in the mix design. The mixes were proportioned to have sufficient workability to be cast without excessive voidage or honeycombing at w/c 0.35, but sufficient cohesion and segregation resistance at w/c 0.55.

The laboratories of Tarmac Ltd., Lutterworth generously agreed to produce the sets of test specimens and after undertaking trial mixes (observed by Dr I. Heritage and Dr A. Poole) a set of 5 prism specimens with w/c ratios of 0.35, 0.40, 0.45, 0.5 and 0.55 were cast on the 16th May 2017 (Fig. 2). The 5 specimen prisms were nominally $75 \times 75 \times 300$ mm in size. The prisms were covered in polythene membrane for the first 24 hours, then demoulded and stored for 28 days at 20°C, 80% RH.

The detailed method statement for sample preparation and mix design data for each specimen was provided by Tarmac and are appended to this report in Appendix 1 and Appendix 2 respectively. Photographs of the fresh concrete mix and cast prism are provided in Appendix 2.

Table 1 Mix proportions at saturated-surface dry condition adjusted for yield (see Appendix 2 for details).

Mix ID	w/c	Free water (kg/m^3)	CEM I (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)	Theoretical density(kg/m^3)
A	0.35	157	450	898	898	2403
C	0.40	176	440	876	876	2369
E	0.45	192	428	853	853	2325
B	0.50	207	414	825	825	2271
D	0.55	230	417	831	831	2307

Fig. 1 Coarse and fine aggregates used (Photo: Alan Poole, 16th May 2017).

Fig. 2 Preparation of concrete prisms at Tarmac Ltd., Lutterworth (Photo: Alan Poole, 16th May 2017).

After 28 days of curing, the prisms were sealed in polythene, packed in plastic containers and dispatched (27th June 2017) to Sandberg Clapham laboratory where each prism was sliced transversely into 14 sub-specimens each 17 mm thick. The first 5 mm at each end of each prism was discarded. The prisms were identified by the letters A, B, C, D and E but the identifications were randomised with respect to their w/c ratios (Table 1). The slices were numbered 1-14, wrapped in cling film and sealed individually in polythene bags to prevent drying and carbonation.

The 14 sets of 5 sub-specimens were then stored in a humidity cabinet until dispatch (28th July 2017) to Imperial College London, where they were photographed (back & front), repacked and distributed to participating laboratories. Figure 3 shows an example photographs (flatbed scanner) of the sub-specimens from set #3.
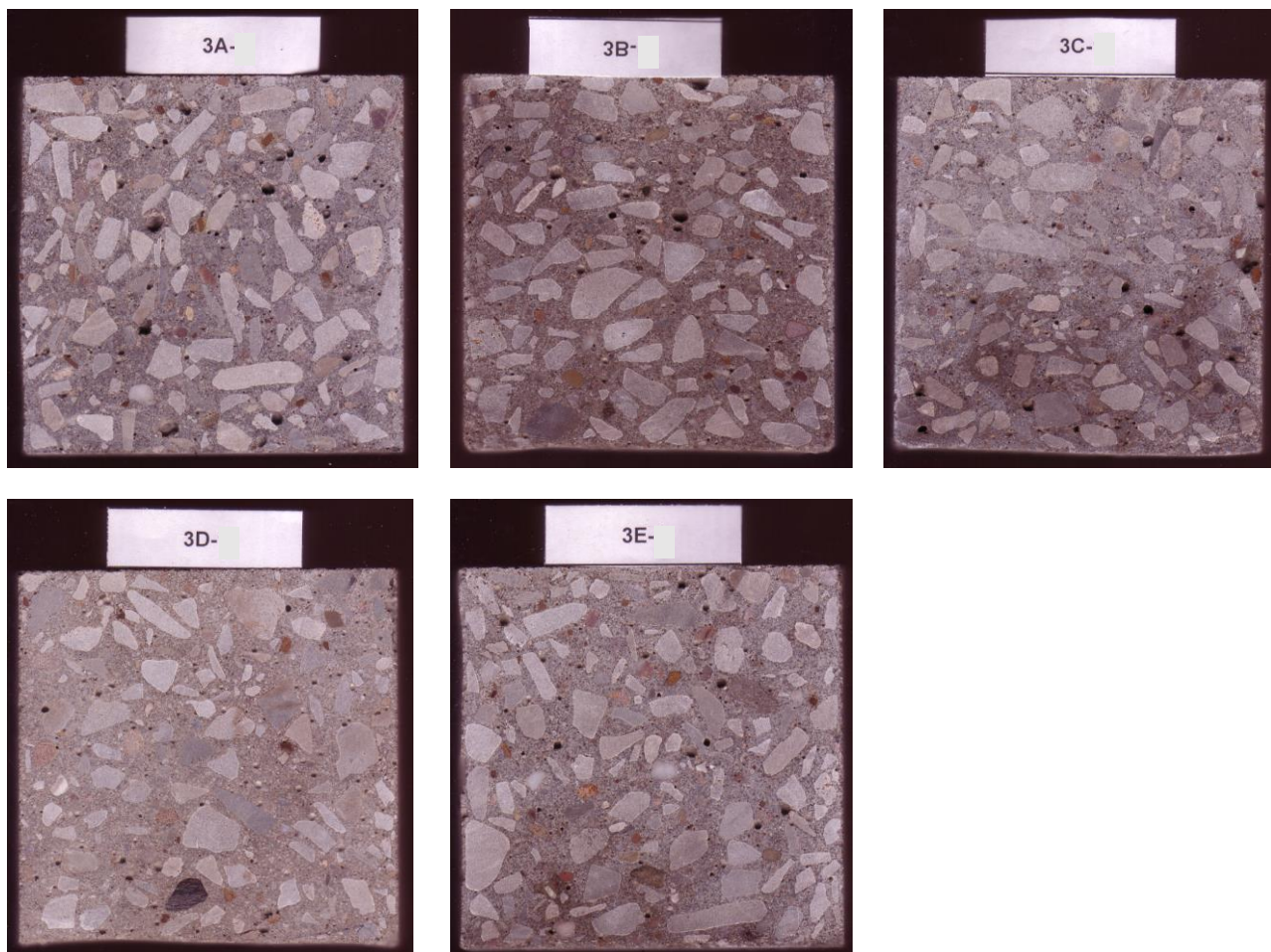

Fig. 3 Example photographs of the as received sub-specimens (set #3 from each prism). Cross-section of each specimen was approximately 75 × 75 mm.

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2.2   Methods for determining w/c ratio

Each participating laboratory was required to measure w/c ratio using their routine, in-house methodology. The methods employed fall into three main groups as follows:

a) Determining w/c ratio by visual assessment of cement paste characteristics.
b) Determining w/c ratio by visual (qualitative) or quantitative assessment of microporosity using fluorescence microscopy.
c) Determining w/c ratio by measuring the unreacted cement, hydration products and capillary porosity using quantitative backscattered electron microscopy.

The above techniques are described in the following sections of this report. It is important to note that trial concretes would not have been affected by deterioration since placement and were simple concretes without cement replacement materials and admixtures.

2.2.1   Visual assessment (VA)

The basis of this technique is that variations in free w/c ratio lead to variations in micro-texture, degree of cement hydration and microporosity in cement paste in concrete that can be readily observed petrographically using thin sections. The principal parameters used to assess w/c ratio by this method are as follows:

- Physical appearance of cement paste: The effects of very high w/c ratios of 0.65 or more are usually obvious in the hand specimen and might include weak and friable cement paste, segregation and excessive bleeding. Very low w/c ratios may result in dark-coloured cement paste due to an increased abundance of unhydrated cement.

- Portlandite: As a general rule increases in w/c ratio result in increased cement hydration and increased amount of portlandite in cement hydrates.

- Cement hydration: As a general rule increases in w/c ratio result in corresponding increases in the degree of cement hydration and reduced quantities of unhydrated cement.

- Microporosity: As a general rule increases in w/c ratio result in increases in the microporosity of the cement paste.

An important principal of this method is that no one parameter can be viewed in isolation. This is because there are many factors that might lead to one or more of the parameters listed above being unreliable if used to determine w/c ratio. Such factors might include:

- Water reducing admixture (plasticiser): Especially at high dosages, plasticisers can reduce the degree of cement hydration and can also influence microporosity.

- Low temperature curing: Low temperature curing can affect rates of cement hydration and can lead to increased quantities of unhydrated cement and the formation of unusually coarsely crystalline portlandite.

- Curing duration: Curing affects the degree of cement hydration, which in turn affects the amounts of porlandite, unreacted cement and microporosity, irrespective of w/c ratio.

The above list is by no means exhaustive. It is important to note that an experienced petrographer should be able to recognise conflicts between the degree of cement hydration and microporosity that could lead to uncertainty in the petrographic assessment of w/c ratio. It is also important to note that this method is highly dependent on the experience of the petrographer carrying out the method.

The use of reference concretes of different types made with known w/c ratios can greatly assist in w/c ratio measurement by this method.

2.2.2   Fluorescence microscopy (FM-V)

The principal of this method is that the microporosity of the cement paste in reference concretes of similar type to the unknown concrete and made with differing w/c ratios is compared with the microporosity of the cement paste in the unknown concrete [1-5]. The comparison can be made in two ways:

- Visual comparison of fluorescent intensity using fluorescence microscopy. (FM-V)

- Quantitative measurement of fluorescent intensity using fluorescence microscopy. (FM-Q)

Visual comparison of fluorescence microscopy is one of the most commonly applied techniques in the UK and this technique was employed by the majority of the labs using the fluorescence method in this trial. Quantitative measurement of fluorescence intensity has the potential to be more precise than visual assessment as very small differences in fluorescence intensity can be detected that may not be visible to the human eye.

The method of thin section preparation is especially critical to the precise application of this method as it is highly sensitive to very small variations in thin section preparation methodology. Using automated methods of thin section preparation, however, in conjunction with quantitative measurement of fluorescent intensity, much higher degrees of precision are likely to be achievable than by the methods adopted by many of the participants in this trial.

It is important to note that this method is especially sensitive to factors other than w/c ratio that can influence microporosity and some experience is required in assessing whether or not this technique is appropriate for a given type of concrete.

2.2.3   Backscattered electron microscopy (BSE)

The basis of this method is that the original cement content, water content and free w/c ratio of an unknown concrete can be calculated from the microstructural phase assemblage at any time after setting. This is achieved by measuring the volume fractions of capillary pores, hydration products and unreacted cement of the hardened concrete using scanning electron microscopy in the backscattered mode [6-8].

Epoxy impregnated flat polished blocks or petrographic thin sections are prepared from the unknown concrete and imaged at high magnification (typically 500× or more). A large number of images are collected per sample in a random and uniform manner so that bulk paste and paste near aggregate particles (interfacial transition zone) are sampled. Image analysis is used to segment and measure the volume fractions of capillary pores, unreacted cement and hydration products. Sufficiently large number of images is analysed until the cumulative average reaches a steady value, thereby indicating representative sampling. The measured volume fractions are then used to calculate the original cement and free water contents, and free w/c ratio.

The main advantage of this method is that it is quantitative and does not require comparison with reference standards made of the same materials and cured to the same hydration degree as the unknown concrete. The method is only applicable to concretes that have not experienced physical or chemical degradation such that significant volumetric changes have occurred since hardening.

It should be noted that the calculated value is the free w/c ratio. The method assumes that aggregate absorption has been accounted in the mix design and that no water is lost through bleeding and/or evaporation from the fresh concrete. Lab studies [6, 9] have shown that the latter occurs in concretes at high w/c ratios (≥ 0.5) and that the method tends to underestimate the mix design w/c ratio unless water lost to bleeding and/or evaporation is accounted.

Table 2 Summary of sample type and methods used for estimating w/c ratio.

Lab Ref.	Result Set	Method *				Sample type *	Reference standards	Notes *
		VA	FM-V	FM-Q	BSE			
01	(a)		√			TS, 30 × 50 mm, 30 μm thick, with coverslip. Struers resin + EpoDye (2 g per 400 ml)	None.	TL. 6-10 images per sample.
02	(a)	√	√			TS, 20 × 20 mm, 20 μm thick, with coverslip. Caldofix + EpoDye (0.6%, 5g/L)	None, but comparison was made against published fluorescence images of concretes and mortars at w/c ratios 0.30 to 0.70, from Poole & Sims (2016) and Ingham (2011).	TL. Full area visually assessed. Lower w/c ratio was estimated with samples prepared using Epofix. Report noted heterogeneity of paste due to bleeding and segregation.
	(b)	√	√			TS, 20 × 20 mm, 20 μm thick, with coverslip. Epofix + EpoDye (0.6%, 5g/L)		
04	(a)			√			Measured green intensity was compared against lab reference concrete standards of w/c ratios: 0.35, 0.40, 0.45, 0.50, 0.60 & 0.70, prepared with CEMI 52.5 according to NT Build 361 ed. 2, 1999.	RL. Estimation was carried out by 5 operators. Each result is an average of 10 fields at 50× magnification (∅ 4 mm FOV). Also observed cement grains spacing, amount and morphology of CH in cross-polarised light. Noted inhomogeneous paste with many "plastic defects".
	(b)			√		TS, 35 × 45 mm, 20 μm thick with coverslip. Conpox Harpilks BY158 from Condor Kemi + Struer EpoDye (1% wt. of epoxy)		
	(c)			√				
	(d)			√				
	(e)			√				
05	(a)			√		TS, 30 × 40 mm, 30 μm thick with coverslip. CondorChemie + EpoDye (1%)	Comparison was made against concrete standards of w/c ratios 0.35 to 0.65, 3 months cured.	RL. Each result is an average of 30 images at 20× magnification (725 μm FOV). Two thin-sections per sample.
07	(a)	√	√			TS, 30 × 45 mm, 30 μm thick with coverslip. Resiblend + Pelcon dye (0.75%)	Comparison against mortar standards of w/c ratios: 0.3, 0.4, 0.5 & 0.6.	RL. Multiple visual inspections at 5× and 10× magnifications (4 and 2 mm FOV).
08	(a)	√				TS, 24 × 46 mm, 30 μm thick with coverslip. Araldite + Epodye	None. Comparison was made against table from Danish Technological Institute (U.H. Jakobsen) to grade features.	TL.
09	(a)		√				Two sets of mortar standards made with CEM I and natural quartzitic sand, w/c ratios: 0.3 to 0.6	RL. Multiple visual inspections were carried out, minimum 10 per sample using 5× and 10× objectives. Two thin-sections per w/c ratio. Operators held 4 to 9 years professional experience in concrete petrography, all postgraduates with BSc or MSc in Geology.
	(b)		√			TS, 35 × 50 mm, 30 μm thick with coverslip. Epofix + EpoDye (5 g/L)		
	(c)		√					
	(d)		√					

#		VA	FM-V	FM-Q	BSE	Sample	Reference standards	Notes
11	(a)				√	PB, 17 × 40 × 8 mm, Epofix + EpoDye (5 g/L)	Not required.	30 images per sample at 500× magnification (228 x 171 μm FOV). Two replicate polished blocks per w/c ratio. Heterogeneous paste microstructure noted. Estimated values are "free" w/c ratio, i.e. assuming no water lost to bleeding and evaporation in fresh concrete.
12	(a)			√		TS, 45 × 67 mm, 30 μm thick without coverslip. Araldite + EpoDye (0.2% wt.)	Comparison was made against concrete standards at w/c ratios: 0.35, 0.40 0.45, 0.50, 0.55, 0.60, 0.65 & 0.70.	RL + TL, Entire thin section was scanned and 5-10 representative areas examined in detail at 200× (2 mm FOV). Porosity distribution suggests mix water not uniformly distributed.
13	(a)	√				TS, 45 × 60 mm, 30 μm thick with coverslip. Epotek + Epoye (0.5%)	No reference standards. Determination was based on extrapolation from Fig. 4.62 of Poole & Sims (2016).	RL. One observation per sample at 10× magnification (2.6 mm FOV).
14	(a)				√	TS, 50 × 75 mm, 30 μm thick with coverslip. MSDS + EpoDye (5 g/L)	Two sets of concrete standards with w/c ratios: 0.30 to 0.60 at 0.05 increment.	RL, 7 repeat measurements per thin-section, averaged over 952 measurements. Noted large standard deviation and standard error, such that the results are not reliable. This suggests there are variables, in addition to w/c ratio, that may have affected results e.g. differences in sample preparation, and differences between unknown sample and reference standards.
	(b)	√				TS, 50 × 75 mm, 30 μm thick with coverslip. Robnor + Orasol Blue (0.7g/100g)		RL

* VA = Visual assessment of cement paste characteristics; FM-V = Visual assessment of fluorescent intensity; FM-Q = Quantitative assessment of fluorescent intensity; BSE = Quantitative backscattered electron microscopy; TS = Thin-section; PB = Polished block; RL = Reflected light; TL = Transmitted light, FOV = Field of view.

2.3 Analysis of results

The secretary copied all the sets of w/c ratio results, together with the methodologies that had been used by the participating laboratories to CTS committee members on 6th April 2018 (with one additional late result sent on 23rd June 2018). A generalised update concerning the results was also circulated to all APG members on 16th May 2018 which read as follows:

> *11 organisations/laboratories across the UK and Europe (identified only by a reference number) have provided sets of results. 100 individual test specimen determinations of w/c ratio have been collected. Some laboratories provided sets of results by more than one method.*
>
> *A first appraisal of the results suggest that the large majority are within ± 0.1 of the mix design target values and near to 2/3 come to within ± 0.05 of the target value. Differences in the particular methods used does not appear to make significant differences to the precision of the results obtained, but a more accurate and thorough evaluation of the results will be provided by the CTS committee in due course.*

3. Results

Table 3 summarises the results obtained. Fig. 4 shows a plot of the estimated w/c ratios against target mix design w/c ratios. Note that some of the estimated w/c ratios were reported as a range. If a laboratory returned a w/c estimate as ranging from x to y, then the average (= $(x + y)$ / 2) was plotted. If a lab estimated w/c as $< x$ (or as $> x$), then x was plotted as the returned value.

Table 3 Estimated w/c ratios from all participants.

Lab Ref.	Method	Mix ID (Target w/c ratio)				
		A (0.35)	C (0.40)	E (0.45)	B (0.50)	D (0.55)
01	FM-V	0.5	> 0.45	0.60	< 0.65	0.55
02 (a)	VA, FM-V	0.40 ± 0.1	0.50 ± 0.1	0.45 ± 0.1	0.55 ± 0.1	0.65 ± 0.1
02 (b)	VA, FM-V	0.35 ± 0.1	0.40 ± 0.1	0.50 ± 0.1	0.55 ± 0.1	0.65 ± 0.1
04 (a)	FM-Q	0.35	0.40	0.50	0.60	0.70
04 (b)	FM-Q	0.43	0.47	0.56	0.70	0.78
04 (c)	FM-Q	0.35	0.40	0.50	0.55	0.60
04 (d)	FM-Q	0.37	0.40	0.53	0.65	0.75
04 (e)	FM-Q	0.35	0.40	0.50	0.60	0.70
05	FM-Q	0.35 ± 0.04	0.38 ± 0.03	0.47 ± 0.06	0.51 ± 0.03	0.61 ± 0.03
07	VA, FM-V	0.30 ± 0.05	0.40 ± 0.05	0.45 ± 0.05	0.50 ± 0.05	0.55 ± 0.05
08	VA	< 0.35	< 0.35	0.45-0.55	> 0.55	0.45-0.55
09 (a)	FM-V	< 0.3 ± 0.1	0.35-0.4 ± 0.05	0.4-0.50 ± 0.05	0.50 ± 0.1	0.60 ± 0.1
09 (b)	FM-V	0.4 ± 0.05	0.45 ± 0.05	0.5 ± 0.05	0.6 ± 0.05	0.65-0.7 ± 0.1
09 (c)	FM-V	0.35 ± 0.1	0.4 ± 0.1	0.45 ± 0.1	0.5 ± 0.1	0.6 ± 0.1
09 (d)	FM-V	0.4 ± 0.1	0.45 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.7 ± 0.1
11	BSE	0.35 ± 0.02	0.41 ± 0.02	0.44 ± 0.02	0.46 ± 0.02	0.49 ± 0.02
12	FM-V	0.46 ± 0.1	0.42 ± 0.1	0.50 ± 0.1	0.55 ±0.1	0.60 ± 0.1
13	VA	0.50	0.55	0.60	0.65	0.70
14 (a)	FM-Q	0.35 ± 0.1	0.35-0.4 ± 0.1	0.45-0.5 ± 0.1	0.55-0.6 ± 0.1	0.55 ± 0.1
14 (b)	VA	0.35 ± 0.05	0.40 ± 0.05	0.50 ± 0.05	0.60 ± 0.05	0.55 ± 0.05

Some of the results were provided with an estimate of error or precision i.e. w/c ± confidence interval. However, it is unclear how this was defined or obtained in all cases except for Lab #5 (based on standard deviation of the estimates from two thin-sections per series) and Lab #11 (based on 95% confidence interval). The estimated errors reported by Labs #07, #09, #12 and #14 were based on previous work experience. Some labs returned more than one precision. All of this in addition to variations in the test methods used further complicate data analyses.

It is noted that of the 20 sets of w/c ratio results, 14 sets (70%) from 6 laboratories (i.e. 55% of participating labs) gave the correct order of sample w/c ratios from low to high regardless of the absolute error. The frequency and cumulative histograms in Fig. 5 show that 81% of the estimated w/c ratios are within +/- 0.1 of the target mix values and 58% of the estimated w/c ratios are within +/- 0.05.

Fig. 6 shows that error in the estimated w/c ratio ranged from -0.058 to +0.23 or from -14% to +43%. The magnitude of error does not appear to be strongly dependent on w/c ratio. However, of the 100 individual determinations, 61% gave positive errors while only 10% were negative. The data show that w/c ratio tend to be over-estimated, this is particularly the case for the VA and FM methods.

Fig. 7 shows the maximum, minimum and average error in the estimated w/c ratio, according to test method.

Fig. 8 compares the results from laboratories that did not use actual reference standards to results from laboratories that did, the latter divided to those that used FM-V and FM-Q methods.
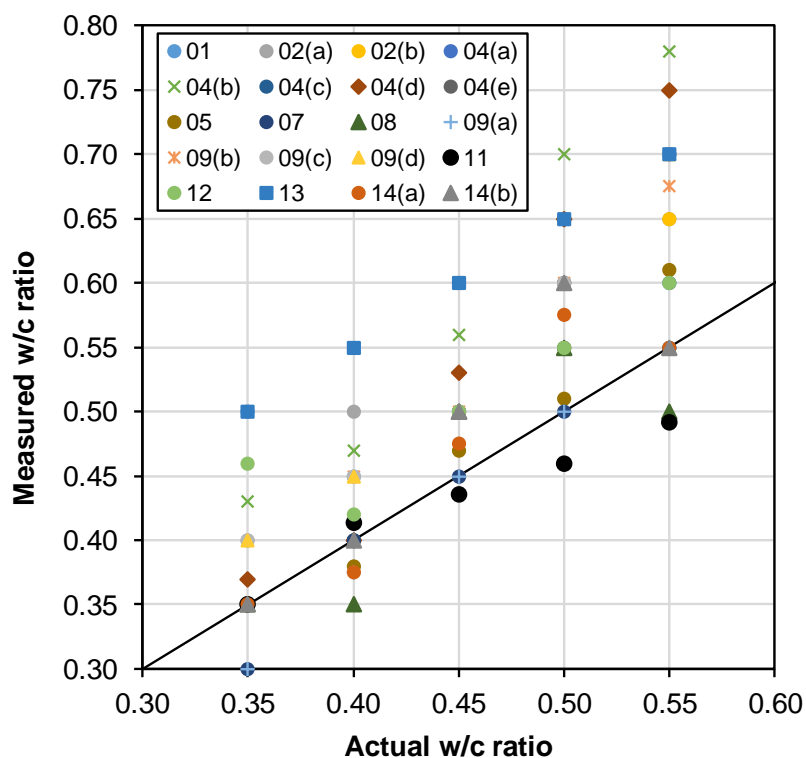
Fig. 4 Comparison between measured and estimated w/c ratios for five concrete mixes. Data from 20 complete result sets (100 individual w/c ratio determinations) from 11 participating laboratories.
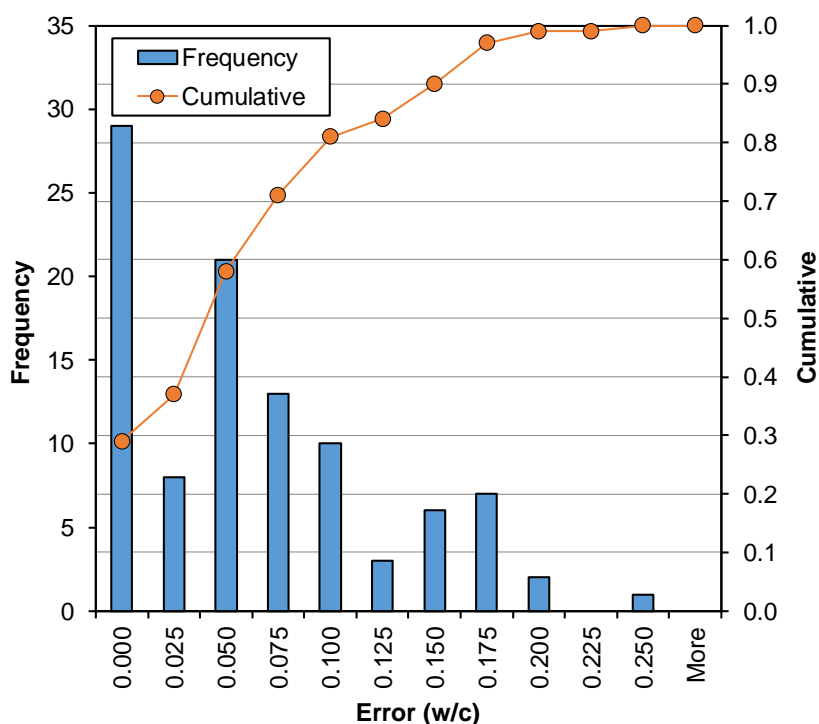
Fig. 5 Frequency and cumulative histograms of the estimation error (w/c) show that 81% of the estimated w/c ratios are within +/- 0.1 of the target mix values and 58% of the estimated w/c ratios are within +/- 0.05.
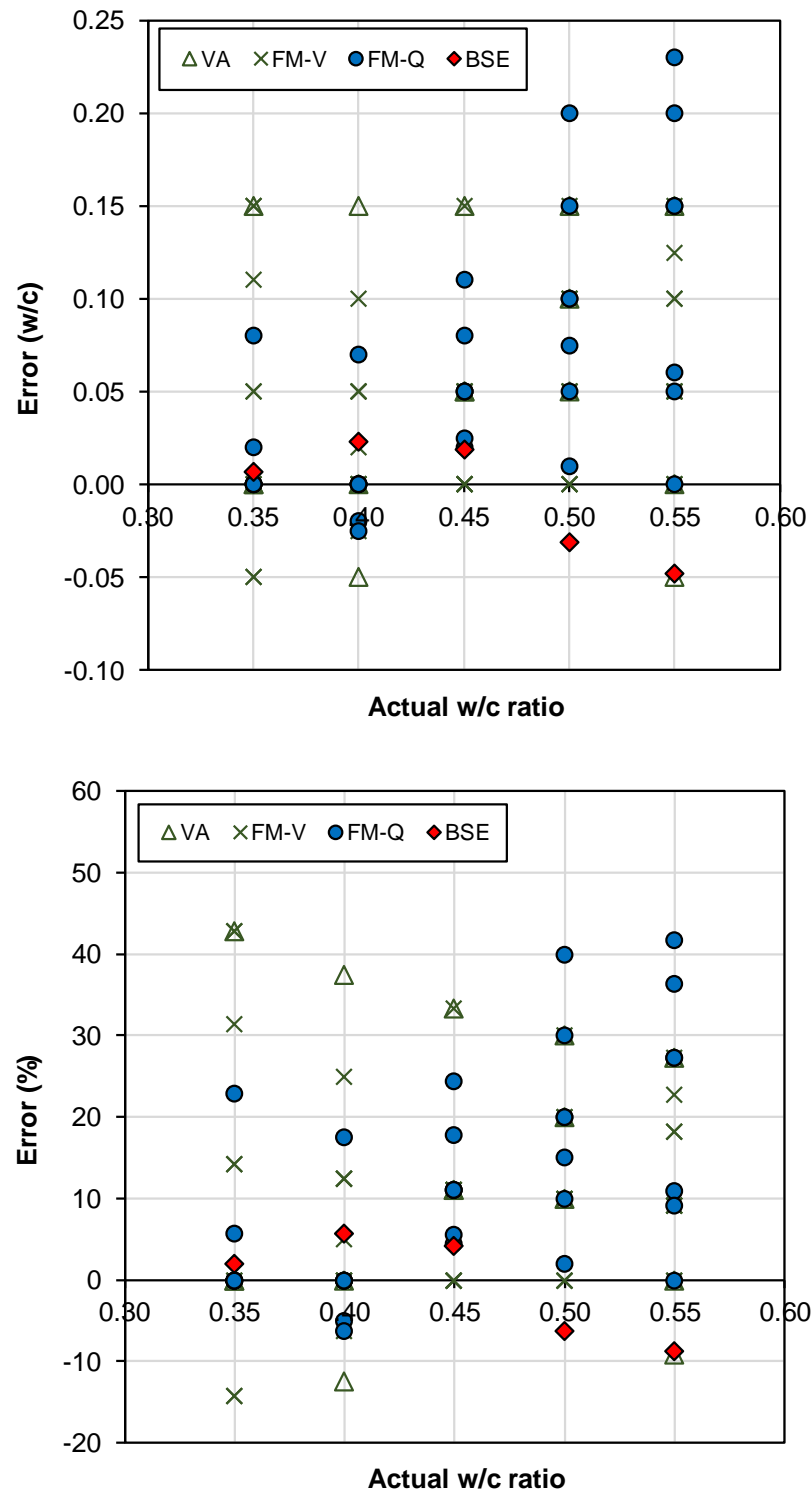
Fig. 6 Error in estimated w/c ratio plotted against target w/c ratios (VA = Visual assessment of paste characteristics; FM-V = Visual assessment of fluorescent intensity; FM-Q = Quantitative assessment of fluorescent intensity; BSE = Quantitative backscattered electron microscopy).
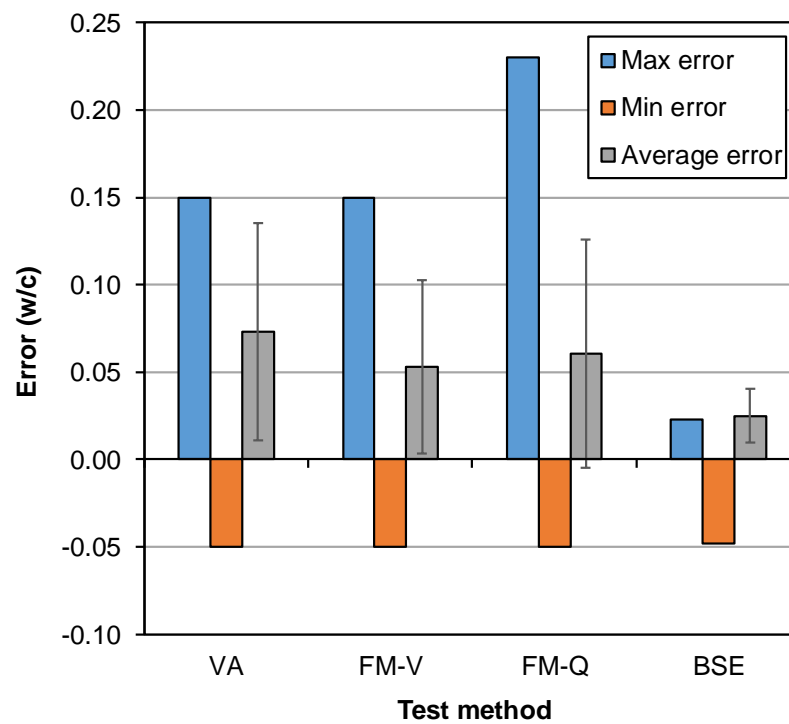
Fig. 7 Maximum, minimum and average error in the estimated w/c ratio. Error bars represent +/- standard deviation (VA = Visual assessment of paste characteristics; FM-V = Visual assessment of fluorescent intensity; FM-Q = Quantitative assessment of fluorescent intensity; BSE = Quantitative backscattered electron microscopy).

a) No reference standards

b) With reference standards (FM-V)

c) With reference standards (FM-Q)
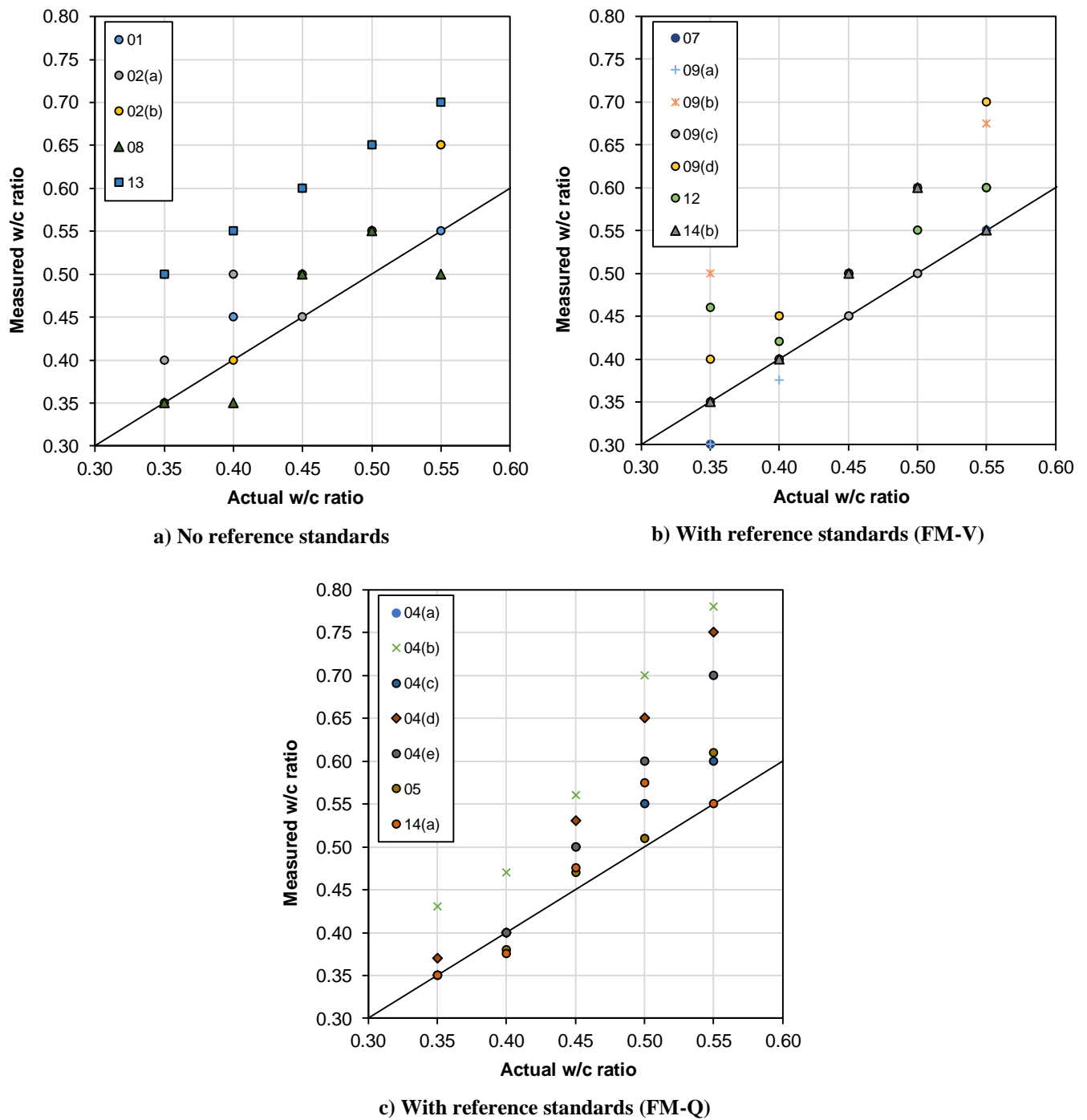
Fig. 8 Comparison between measured and estimated w/c ratios for: (a) laboratories that did not use actual reference standards, and (b, c) laboratories that used actual reference standards.

4. Statistical analysis

4.1 Preliminary considerations

4.1.1 Accuracy

Accuracy measures were claimed for many of the results submitted. However, reading the detailed submissions indicated that, whilst some measures were based on a statistical analysis of many estimates, many were non-quantifiable. It was therefore decided not to use this information. Additionally, it has little bearing on the main objective of the study.

4.1.2 Ranges

Some measurements are reported as ranges, e.g. '0.1 - 0.2' or '> 0.1'. There are various statistical options for dealing with such values but it is decided based both on the nature of the tests and the main objective of the study, to treat each true range, i.e. a reported result shown as a minimum and a maximum, as the mid-point; and to treat inequalities, i.e. less than or more than, as the actual value.

Additional information arising from responses to 'The Enquiry to Laboratories Participating in the APG Inter-laboratory w/c ratio in Concrete Trial - sent out 02/10/2018' does shed further light on the claimed error bars, including one derived from the standard deviation of replicates and others based on experience. It is suggested that any future work should collect more background data and hence to try to incorporate ranges, which could give better results, including analysis of variance.

Starting with summary statistics we look at distribution-free (non-parametric) statistical tests. These are analytical tools that do not require the data to satisfy certain behavioural constraints, i.e. they make minimal assumptions about the data. We then move on to those tests which do make assumptions about the data or, more accurately, about the conditions under which the experiments were run.

4.2 Summary Statistics

4.2.1 Outliers and stragglers

It is impossible to unequivocally identify outliers as being anomalies which should be ignored, as opposed to what might, in this case, be indicators of unreliability in either a laboratory or the process. However, routine outlier analysis did identify some transcription errors (typographical errors) that occurred when the raw data was transferred from the results form and complied, which were corrected. This point is noted in part to indicate how easy it is for mistakes to enter into a data set, which can only be in small part be offset by using robust statistics. In the following, we frequently 'top and tail' the dataset as a rough form of robust estimation but ideally a more thorough provenance analysis would be undertaken. In the following, reference to a robust calculation is simply ignoring the lowest and highest values in the set.

4.2.2 Non-parametric statistics

The most basic non-parametric test is order: did the labs correctly order the samples? We can follow this with a rank test and a measure of how different each result was from the correct value.

Only 7 out of 80 pairs were out of order, which implies that this is a good relative test, whether or not it is a good absolute test. Furthermore, the arithmetic averages (over all labs) were in strict order and showed remarkable consistency: all five averages of measured results were over-estimates and the errors (of each mix) were well correlated with the results, cc 0.997 (confidence >99.99%). This implies that a simple linear calibration could provide very good absolute accuracy, in addition to the extant relative accuracy, if given access to a sufficient number of replications.

That is as far is we should try to take the non-parametric analysis of the whole data set. Additional analysis, still without making assumptions about distributions, could include a between-labs test, to order the labs by accuracy, or between-methods tests. Since the stated aim of the experiment was to judge methods, not labs, we will look only at the latter.

4.2.3 Comparison of methods

There are 4 methods listed (Table 2): VA, FM-V, FM-Q and BSE. Splitting initially at the top level, into F and V, where F is just FM-Q and V is all results using methods VA or FM-V (and temporarily disregarding BSE because there is only one set of results) we find that method F has a rank order of 2/36 whereas method

V has a rank order of 5/16. This is sufficient difference to justify undertaking tests to establish the significance and whether there is a statistical basis for declaring one method is better than the other. However, the arithmetic mean error (Table 4) shows that there is not a clear distinction between the accuracy of the methods. There is also no significance difference in the accuracy of the methods between method F and method V at 80% level on a student's T-test for means (unknown variance).

When the results at each w/c ratio are analysed individually, there is a noticeable difference between the methods (Table 5). Method F shows increasing error with increase in w/c ratio, while method V shows relatively consistent positive error. This does warrant further investigation, which, externally to statistical analysis, could include examination of the standards used for visual comparison, the ability of the method to determine correctly at high w/c ratios, and whether the physical basis for the method scales linearly with w/c ratio. However, it should be noted that this observed effect (of error increasing with w/c ratio) is based on a small number of observations.

Further subdividing V into VA and FM-V does not introduce any further significant differences in these statistical tests.

Table 4 Arithmetic mean error.

Method	Arithmetic mean error (all)	Arithmetic mean error (robust)
F (FM-Q)	0.061	0.053
V (VA & FM-V)	0.056	0.052
BSE	0.025	N/A (only one sample)

Table 5 Percentage error (robust) at individual w/c ratio.

Method	Mix ID (Target w/c ratio)				
	A (0.35)	**C (0.40)**	**E (0.45)**	**B (0.50)**	**D (0.55)**
F (FM-Q)	1.1%	-1.3%	11.3%	19.0%	20.0%
V (VA & FM-V)	8.9%	5.5%	10.0%	12.5%	9.5%
BSE (only one sample)	0.00	0.01	-0.01	-0.04	-0.06

4.3   Standards

An apparently promising line of statistical enquiry is to subdivide the results into those with standards and those without. This would be interesting in its own right but particularly apposite given the analysis of prediction efficiency (later section). Preliminary results were compiled but the rationale seemed to be invalidated by responses received to enquiries sent out 02/10/2018. Of these, there is at least one that said "no standards, we used Poole & Sims" and one that said "our standards are those in Poole and Sims". Further analysis and questioning of the trialists may be required in order to justify this analysis. It is potentially of critical importance for consideration of the prediction efficiency.

Additionally, we could, if required, check the significance of the rank order statistics using a Wilcoxon signed rank test.

4.4   Calibration

Having noted that the errors for Method F and V appear to be linearly related to the data values, once subdivided into top-level method (F, V), we could investigate the possibility that each could be corrected using a straight line calibration, based on a least squared error fit within its own subdivided data set. Whilst this is the same underlying principle (a least squared errors) as underpins bivariate regression, which is a parametric

test, we are not making any assumptions about distributions if we simply fit a straight line by minimising the errors of the points from the line.

As compared with the results in Table 5, this reduces the errors to those shown in Table 6. This is an indication that calibration and the formalisation of standards may have the potential to effect a considerable increase in accuracy of the methods.

Table 6 Percentage error (robust) at individual w/c ratio, after correction using a simple linear calibration.

Method	Mix ID (Target w/c ratio)				
	A (0.35)	**C (0.40)**	**E (0.45)**	**B (0.50)**	**D (0.55)**
F (FM-Q)	4.4%	-6.2%	0.0%	2.6%	-0.6%
V (VA & FM-V)	2.3%	-2.1%	-1.3%	0.9%	0.3%

5. Discussion

The application of fluorescence microscopy to measuring water/cement ratio is based on the scientifically rigorous principal that for a simple concrete, the microporosity of the cement paste in concrete increases as water/cement ratio increases. The term "simple concrete" refers to non-deteriorated and non-carbonated concrete of recent origin without plasticisers or other admixtures that can influence the microporosity of the cement paste in concrete. Using fluorescence microscopy, it is possible to directly establish the microporosity of the cement paste rather than the concrete as a whole, and this is a significant advantage over other porosity based test methods such as that given in BS 1881, Part 124 (2015) that cannot distinguish microporosity in cement paste from porosity due to aggregate porosity and porosity resulting from entrapped and entrained air voids in cement paste.

The relationship between fluorescence and apparent microporosity in thin sections becomes much less linear at the extremes. The reasons for this are that at very low water/cement ratios the fluorescence levels become much harder to detect. Similarly, at very high water/cement ratios the fluorescence becomes saturated and it becomes increasingly difficult to detect differences in microporosity where the water/cement ratio exceeds about 0.60.

The results from the participating laboratories using quantitative fluorescence microscopy (FM-Q) gave a mean error of 0.06. The value for mean error does not, however convey the trend for the FM-Q method to overestimate w/c ratio by a much greater extent compared to other methods when w/c ratio exceeds 0.50.

There are many potential sources of error unrelated to concrete type that can affect the measurement of water/cement ratio by fluorescence microscopy many of which can be mitigated by technicians and petrographers skilled in the preparation and examination of concrete thin sections. Possible sources of error in the fluorescence determination of water/cement ratio include:

- Variation in the quality of impregnation with resin containing fluorescent dye
- Size of the thin section used for the determination
- Accidental, partial removal of the fluorescent resin-impregnated zone during preliminary flattening
- Variation in thin section thickness

Many modern concretes do not fall within the definition of "simple concrete" given above. This means that in many situations it would not be possible to rely wholly on fluorescence microscopy without taking into consideration the many factors that can interfere with the relationship between microporosity and water/cement ratio such as the use of plasticisers, cement replacement materials and silica fume. For these reasons it is usually necessary to consider other indicators of water/cement ratio such as:

- Degree of cement hydration / quantities of unhydrated cement
- Evidence for the presence of plasticisers

- Portlandite size and abundance

- Porosity increase due to leaching or other processes of deterioration

- The effects of aggregate dust including micaceous dust

- Colour of the paste

- Excessive weakness / friability

- Segregation / bleeding

The assessment of water/cement ratio from the wide range of parameters listed above describes the "visual" method of water/cement ratio assessment.

The results from the visual test methods not including FM-Q show a slightly lower mean error of 0.05 compared to 0.06 for FM-Q. There is however a systematic trend for the visual test methods to overestimate w/c ratio by about 10% over the entire range of 0.35-0.55. The FM-Q method, in contrast gave lower errors at w/c ratios of ≤0.40 or less (-1.1 to -1.3%) and much higher errors at w/c ratios of ≥ 0.50 (19.6 to 21.8%).

Taking all test results obtained, irrespective of test method, more than 80% of the results obtained achieve an accuracy of ≥ +/- 0.1. A small proportion of the results, mostly from one of the participating laboratories are inexplicably high.

An important observation from several participants was the non-uniform distribution of microporosity in some of the samples. This probably reflects inadequate mixing or possibly artefacts from the compaction of the test samples and this may be factor in some of the outlying results. It is also possible that there may be variations between the reference concretes used by some laboratories and the trial mix concretes such as those caused by differing curing conditions and curing times.

One of the outcomes of this study is that it would form a useful basis for a more in-depth trial. Some considerations for further work would include:

- Modifying the range of w/c ratios of the test specimens to include w/c ratios of 0.60 and possibly greater. This may require increasing fines content to control bleeding.

- Using larger test specimens that could be cored. This would help mitigate variation in microporosity and mix water dispersion caused by compaction effects at the contacts between the moulds and the concrete.

- There was much variation in the methodology and types of information provided by each participating lab that have hindered the statistical analysis of the test results. The present trial would inform future studies of the types of information required in order to carry out a rigorous statistical appraisal of future w/c trial studies.

6. Conclusions

a) 5 simple concrete mixes with w/c ratios 0.35, 0.40, 0.45, 0.50 & 0.55 were prepared and cured for 28 days. Sub-sections from each mix were distributed to 14 organisations / laboratories across the UK and Europe for w/c ratio determination using petrographic methods.

b) The methods included visual assessment (VA) of paste characteristics (e.g. colour, quantities of unreacted cement, portlandite, microporosity), visual assessment of fluorescent intensity (FM-V), quantitative assessment of fluorescent intensity (FM-Q) and quantitative backscattered electron microscopy (BSE).

c) 11 organisations / laboratories provided 20 sets of complete results. In total 100 individual test specimen determinations of w/c ratio were received.

d) The majority (81%) of the test results are within +/- 0.1 of the target mix w/c ratios and 58% of the results come to within +/- 0.05 of the target value. Error in the estimated w/c ratio ranged from -0.058 to +0.23 or from -14% to +43%.

e) 14 sets of results from 6 laboratories gave the correct order of sample w/c ratios from low to high regardless of the absolute error.

f) 3 of the 11 participating laboratories measured w/c ratios of 0.70 or greater for the trial sample with an actual w/c ratio of 0.55. Further work is required to understand the reasons for these outliers given that these results are significantly outside of the range of w/c ratios that can be used in most structural concrete types without generating substantial segregation, bleeding and laitance development.

g) Further work is required to compare the two fluorescence techniques for measuring w/c ratio (described in Section 2.2.2 of this report).

h) Statistical analysis show that 73 of the 80 pairs were correctly ordered and the arithmetic averages over all labs were in strict order and showed remarkable consistency. Visual assessment methods (VA & FM-V) tended to over-estimate w/c ratio while quantitative fluorescence method (FM-Q) showed increasing error with increase in w/c ratio.

Appendix 1: Method statement for the casting of the APG w/c ratio trial specimens

Location:	**Tarmac Technical Centre**
	Gibbet Lane
	Shawell
	Lutterworth
	Leicestershire
	LE17 6AA

Proposed Casting Date: **18th May 2017**

Objective:

Cast 5*no. concrete prisms of dimension 300mm*80mm*80mm with w/c of 0.35, 0.40, 0.45, 0.50, and 0.55 respectively, and cure for 28 days at 20ºC and 80% RH.

Method:

The concrete mixture for casting the prisms to be composed of cement type CEMI, 4/10mm crushed limestone coarse aggregate, 0/4mm natural quartz sand, and water only.

With the exception of the water content, the mass and proportion of the constituents to be kept constant for each prism.

The concrete mixture to be proportioned to have sufficient workability to be cast without excessive voidage or honeycombing at the 0.35 w/c, but sufficient cohesion and segregation resistance at the 0.55 w/c.

Having arrived at a suitable mixture to satisfy the above, the following detail to be followed:

1. Not more than 24 hours before casting the prisms, oven dry the crushed limestone and sand and allow to cool to ambient temperature in a controlled atmosphere. Record temperature and humidity.
2. Calibrate the prism moulds.
3. Starting with the 0.35 w/c mix, using a calibrated and checked balance, pre weigh the CEMI, limestone, sand, and water into separate containers.
4. Add the limestone and sand to the mixing bowl of a 5 litre capacity "Hobart" mixer and, uniformly distribute by hand, and then add 2/3 of the mixing water.
5. Cover the bowl with a damp cloth and allow to stand/soak for 10 minutes.
6. Remove the cloth from the bowl, attach the mixing blade and mix at low speed (setting 1) for 15 seconds. Add the CEMI and start the timer. Add the remaining 1/3 of the mixing water and mix at low speed for 30 seconds until the CEMI is fully incorporated into the mixture. Increase speed to medium (setting 2) and mix for a further 5 minutes.
7. Stop the mixer, remove the blade and, using a metal spatula, scrape any unmixed material from the sides and base of the bowl and incorporate into the mixture. Re-attach the blade and continue mixing for another minute.
8. Remove the blade and bowl from the mixer, visually check the mixture for homogeneity.
9. Locate the prism mould on the vibrating table, and fill to 2/3rds depth as uniformally as possible. Vibrate for 90 seconds, or until no air bubbles appear. Avoid over-vibrating and segregation of the mixture. Fill the mould to the top and again vibrate for 90 seconds, adding additional material to keep the mixture slightly proud of the mould.
10. Transfer the filled mould to the curing room and cover with polythene membrane. Label and leave to stand undisturbed for 24 hours.
11. Repeat items 4 to 10 for the 0.4 w/c mixture, but reduce the time on the vibrating table to 60 seconds for each layer.

12. Repeat items 4 to 10 for the 0.45 w/c and 0.50 w/c mixtures, but DO NOT vibrate. Hand tamp as required to achieve full compaction.
13. Repeat items 4 to 10 for the 0.55 w/c mixture. DO NOT vibrate or hand tamp. Fill the mould in two layers and lightly tap the mould with a rubber mallet at each fill.
14. 24 hours after casting carefully strip the moulds, remove any flashings. Visually check the prisms for satisfactory compaction, and photograph. Apply an identification label before transferring to the humidity cabinet. Ensure this process is carried out one prism at a time to eliminate any possibility of miss-identification of the prisms.
15. Record the max/min temps and RH of the curing room.
16. At the beginning and end of each work shift, record the temperature and RH of the humidity cabinet for the duration of the curing period.
17. When ready for collection, remove the prisms from the humidity cabinet and seal in polythene before packing in plastic containers for transport. Ensure adequate packaging to guard against damage to the prisms.

Collate all records and make available to APG.

End of Method Statement.

Michael L. Thomas
Technical Optimization Manager - RMX

Appendix 2: Mix design

Mix A (w/c 0.35)

Standard Concrete Trial-Mix Form			v5mlt30sep16		
	JOB	**TRIAL MIX NO.**	**OTHER**		TARMAC A CRH COMPANY
Trial Mix Ref. No.	1900	R8			
Description	w/c 0.35				
Pot Volume(litres)	1.646				
Pot Number			**Moisture Content (%)**		
Aggregate/Cement Ratio	3.99		Coarse Aggregate 1	0	
Cement Content	450		Coarse Aggregate 2	0	
Extender %	0		Fine Aggregate 1	0	
Trial Mix Volume (litres)	3		Fine Aggregate 2	0	
Target Slump(mm)					
Fine Aggregate %	0.0		Date	18/05/2017	
Water/Cement Ratio	0.35				
Operator :		Dipak Mistry	Trial Attended by:		
Cube Reference Numbers					

Material	Theoretical ssd m³ Batch Weights (kg)	Theoretical m³ Batch Weights (kg) (Adjusted for Moisture in Aggregates)	Trial Mix Batch Weights (kg)		SSD m³ Batch Weights (adjusted for yield) (kg)
CEM I	450	450.0	**1.350**		450
0	0	0.0	**0.000**		0
0	0	0.0	**0.000**		0
Filler	0	0.0	**0.000**		0
Coarse Aggregate 1	897	883.5	**2.651**		898
Coarse Aggregate 2	897	896.1	**2.688**		898
Fine Aggregate 1	0	0.0	**0.000**		0
Fine Aggregate 2	0	0.0	**0.000**		0
	0.000	0.0	**0.000**		0
	0.000	0.0	**0.000**		0
	0.000	0.0	**0.000**		0
Microsilica slurry	0	0.0	**0.000**		0
Water in Aggregates (kg)		-14			
Water added to achieve target Slump		0.515			
Total Free Water (litres)				157	157
Theoretical Density (kg/m³)				2401	2403
Mass of Fresh Concrete in Pot (kg) A		3.955			
Plastic Density (kg/m³)					2403
Yield		1.00	Cube age (days/No.)	Stress (N/mm²)	Density (Kg/m³)
					2403
Air Content (%)					

Constituents				
Material	**Lab Ref No.**	**Supplier**	**Source**	**Type**	**Absorption (%)**
Cement		CRH	Tunstead	CEM I	N/A
Extender 1					N/A
Extender 2					N/A
Filler					N/A
Coarse Aggregate 1		Tarmac	Tunstead	110L0410C	1.5
Coarse Aggregate 2		Tarmac	Alrewas	110S04MCW	0.1
Fine Aggregate 1					
Fine Aggregate 2					
	Lab Ref No.	**Supplier**	**Type**	**Dose (% by mass of cement)**	**S.G.**
Admixture 1					
Admixture 2					
Admixture 3					
Microsilica slurry					

Notes:

- "Coarse Aggregate 1" refers to 4/10 crushed limestone coarse aggregate.
- "Coarse aggregate 2" refers to the 0/4mm natural quartz sand.
- "Water in aggregate" refers to the water added to bring the oven-dried aggregates to saturated surface dry state.
- "Water added to achieve target slump" is the total water used in the trial mix.

Mix C (w/c 0.40)

Standard Concrete Trial-Mix Form		v5mlt30sep16				TARMAC A CRH COMPANY
	JOB	**TRIAL MIX NO.**	**OTHER**			
Trial Mix Ref. No.	1900	R9				
Description	w/c 0.40					
Pot Volume(litres)	1.646					
Pot Number			**Moisture Content (%)**			
Aggregate/Cement Ratio	3.99	Coarse Aggregate 1	0			
Cement Content	440	Coarse Aggregate 2	0			
Extender %	0	Fine Aggregate 1	0			
Trial Mix Volume (litres)	3	Fine Aggregate 2	0			
Target Slump(mm)						
Fine Aggregate %	0.0	Date	18/05/2017			
Water/Cement Ratio	0.40					
Operator :		Dipak Mistry	Trial Attended by:			
Cube Reference Numbers						

Material	Theoretical ssd m³ Batch Weights (kg)	Theoretical m³ Batch Weights (kg) (Adjusted for Moisture in Aggregates)	Trial Mix Batch Weights (kg)		SSD m³ Batch Weights (adjusted for yield) (kg)
CEM I	450	450.0	1.350		440
0	0	0.0	0.000		0
0	0	0.0	0.000		0
Filler	0	0.0	0.000		0
Coarse Aggregate 1	897	883.5	2.651		876
Coarse Aggregate 2	897	896.1	2.688		876
Fine Aggregate 1	0	0.0	0.000		0
Fine Aggregate 2	0	0.0	0.000		0
	0.000	0.0	0.000		0
	0.000	0.0	0.000		0
	0.000	0.0	0.000		0
Microsilica slurry	0	0.0	0.000		0
Water in Aggregates (kg)		-14			
Water added to achieve target Slump		0.584			
Total Free Water (litres)				180	176
Theoretical Density (kg/m³)				2424	2369
Mass of Fresh Concrete in Pot (kg) A		3.899			
Plastic Density (kg/m³)				2369	
Yield		1.02	Cube age (days/No.)	Stress (N/mm²)	Density (Kg/m³)
Slump @ T10 (mm)					2369
Air Content (%)					

Constituents					
Material	Lab Ref No.	Supplier	Source	Type	Absorption (%)
Cement		CRH	Tunstead	CEM I	N/A
Extender 1					N/A
Extender 2					N/A
Filler					N/A
Coarse Aggregate 1		Tarmac	Tunstead	110L0410C	1.5
Coarse Aggregate 2		Tarmac	Alrewas	110S04MCW	0.1
Fine Aggregate 1					
Fine Aggregate 2					
	Lab Ref No.	Supplier	Type	Dose (% by mass of cement)	S.G.
Admixture 1					
Admixture 2					
Admixture 3					
Microsilica slurry					

Notes:

- "Coarse Aggregate 1" refers to 4/10 crushed limestone coarse aggregate.
- "Coarse aggregate 2" refers to the 0/4mm natural quartz sand.
- "Water in aggregate" refers to the water added to bring the oven-dried aggregates to saturated surface dry state.
- "Water added to achieve target slump" is the total water used in the trial mix.

Mix E (w/c 0.45)

Standard Concrete Trial-Mix Form			v5mlt30sep16		
	JOB	**TRIAL MIX NO.**	**OTHER**		
Trial Mix Ref. No.	**1900**	**R10**			
Description	w/c 0.45				
Pot Volume(litres)	1.646				
Pot Number			**Moisture Content (%)**		
Aggregate/Cement Ratio	3.99		Coarse Aggregate 1	**0**	
Cement Content	428		Coarse Aggregate 2	**0**	
Extender %	0		Fine Aggregate 1	**0**	
Trial Mix Volume (litres)	3		Fine Aggregate 2	**0**	
Target Slump(mm)					
Fine Aggregate %	0.0		Date	**18/05/2017**	
Water/Cement Ratio	0.45				
Operator :		Dipak Mistry	Trial Attended by:		
Cube Reference Numbers					

Material	Theoretical ssd m³ Batch Weights (kg)	Theoretical m³ Batch Weights (kg) (Adjusted for Moisture in Aggregates)	Trial Mix Batch Weights (kg)		SSD m³ Batch Weights (adjusted for yield) (kg)
CEM I	450	450.0	1.350		428
0	0	0.0	0.000		0
0	0	0.0	0.000		0
Filler	0	0.0	0.000		0
Coarse Aggregate 1	897	883.5	2.651		853
Coarse Aggregate 2	897	896.1	2.688		853
Fine Aggregate 1	0	0.0	0.000		0
Fine Aggregate 2	0	0.0	0.000		0
	0.000	0.0	0.000		0
	0.000	0.0	0.000		0
	0.000	0.0	0.000		0
Microsilica slurry	0	0.0	0.000		0
Water in Aggregates (kg)		-14			
Water added to achieve target Slump		0.650			
Total Free Water (litres)				202	192
Theoretical Density (kg/m³)				2446	2325
Mass of Fresh Concrete in Pot (kg) A		3.827			
Plastic Density (kg/m³)				2325	
Yield		1.05	Cube age (days/No.)	Stress (N/mm²)	Density (Kg/m³)
Slump @ T10 (mm)					2325
Air Content (%)					

Constituents					
Material	Lab Ref No.	Supplier	Source	Type	Absorption (%)
Cement		CRH	Tunstead	CEM I	N/A
Extender 1					N/A
Extender 2					N/A
Filler					N/A
Coarse Aggregate 1		Tarmac	Tunstead	110L0410C	1.5
Coarse Aggregate 2		Tarmac	Alrewas	110S04MCW	0.1
Fine Aggregate 1					
Fine Aggregate 2					
	Lab Ref No.	Supplier	Type	Dose (% by mass of cement)	S.G.
Admixture 1					
Admixture 2					
Admixture 3					
Microsilica slurry					

Notes:

- "Coarse Aggregate 1" refers to 4/10 crushed limestone coarse aggregate.
- "Coarse aggregate 2" refers to the 0/4mm natural quartz sand.
- "Water in aggregate" refers to the water added to bring the oven-dried aggregates to saturated surface dry state.
- "Water added to achieve target slump" is the total water used in the trial mix.

Mix B (w/c 0.50)

Standard Concrete Trial-Mix Form			v5mlt30sep16		TARMAC A CRH COMPANY
	JOB	TRIAL MIX NO.	OTHER		
Trial Mix Ref. No.	1900	R11			
Description	w/c 0.50				
Pot Volume(litres)	1.646				
Pot Number			Moisture Content (%)		
Aggregate/Cement Ratio	3.99		Coarse Aggregate 1	0	
Cement Content	414		Coarse Aggregate 2	0	
Extender %	0		Fine Aggregate 1	0	
Trial Mix Volume (litres)	3		Fine Aggregate 2	0	
Target Slump(mm)					
Fine Aggregate %	0.0		Date	18/05/2017	
Water/Cement Ratio	0.50				
Operator :		Dipak Mistry	Trial Attended by:		
Cube Reference Numbers					

Material	Theoretical ssd m³ Batch Weights (kg)	Theoretical m³ Batch Weights (kg) (Adjusted for Moisture in Aggregates)	Trial Mix Batch Weights (kg)	SSD m³ Batch Weights (adjusted for yield) (kg)
CEM I	450	450.0	1.350	414
0	0	0.0	0.000	0
0	0	0.0	0.000	0
Filler	0	0.0	0.000	0
Coarse Aggregate 1	897	883.5	2.651	825
Coarse Aggregate 2	897	896.1	2.688	825
Fine Aggregate 1	0	0.0	0.000	0
Fine Aggregate 2	0	0.0	0.000	0
	0.000	0.0	0.000	0
	0.000	0.0	0.000	0
	0.000	0.0	0.000	0
Microsilica slurry	0	0.0	0.000	0
Water in Aggregates (kg)		-14		
Water added to achieve target Slump		0.717		
Total Free Water (litres)			225	207
Theoretical Density (kg/m³)			2469	2271
Mass of Fresh Concrete in Pot (kg) A		3.738		
Plastic Density (kg/m³)				2271
Yield		1.09	Cube age (days/No.)	Stress (N/mm²)	Density (Kg/m³)
Slump @ T10 (mm)					2271
Air Content (%)					

Constituents				
Material	Lab Ref No.	Supplier	Source	Type	Absorption (%)
Cement		CRH	Tunstead	CEM I	N/A
Extender 1					N/A
Extender 2					N/A
Filler					N/A
Coarse Aggregate 1		Tarmac	Tunstead	110L0410C	1.5
Coarse Aggregate 2		Tarmac	Alrewas	110S04MCW	0.1
Fine Aggregate 1					
Fine Aggregate 2					
	Lab Ref No.	Supplier	Type	Dose (% by mass of cement)	S.G.
Admixture 1					
Admixture 2					
Admixture 3					
Microsilica slurry					

Notes:

- "Coarse Aggregate 1" refers to 4/10 crushed limestone coarse aggregate.
- "Coarse aggregate 2" refers to the 0/4mm natural quartz sand.
- "Water in aggregate" refers to the water added to bring the oven-dried aggregates to saturated surface dry state.
- "Water added to achieve target slump" is the total water used in the trial mix.
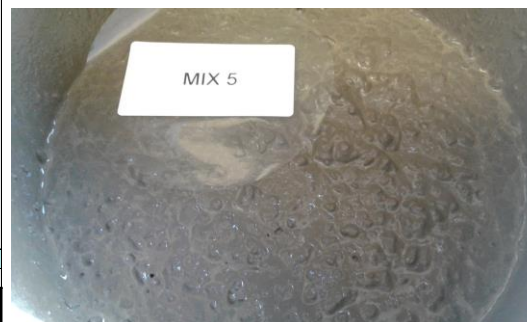
Mix D (w/c 0.55)

Standard Concrete Trial-Mix Form		v5mlt30sep16			○ TARMAC
	JOB	**TRIAL MIX NO.**	**OTHER**		A CRH COMPANY

Trial Mix Ref. No.	1900	R12		
Description	w/c 0.55			
Pot Volume(litres)	1.646			
Pot Number			Moisture Content (%)	
Aggregate/Cement Ratio	3.99	Coarse Aggregate 1	0	
Cement Content	417	Coarse Aggregate 2	0	
Extender %	0	Fine Aggregate 1	0	
Trial Mix Volume (litres)	3	Fine Aggregate 2	0	
Target Slump(mm)				
Fine Aggregate %	0.0	Date		18/05/2017
Water/Cement Ratio	0.55			
Operator :		Dipak Mistry	Trial Attended by:	
Cube Reference Numbers				

Material	Theoretical ssd m³ Batch Weights (kg)	Theoretical m³ Batch Weights (kg) (Adjusted for Moisture in Aggregates)	Trial Mix Batch Weights (kg)	SSD m³ Batch Weights (adjusted for yield) (kg)
CEM I	450	450.0	**1.350**	417
0	0	0.0	**0.000**	0
0	0	0.0	**0.000**	0
Filler	0	0.0	**0.000**	0
Coarse Aggregate 1	897	883.5	**2.651**	831
Coarse Aggregate 2	897	896.1	**2.688**	831
Fine Aggregate 1	0	0.0	**0.000**	0
Fine Aggregate 2	0	0.0	**0.000**	0
	0.000	0.0	**0.000**	0
	0.000	0.0	**0.000**	0
	0.000	0.0	**0.000**	0
Microsilica slurry	0	0.0	**0.000**	0
Water in Aggregates (kg)		-14		
Water added to achieve target Slump		0.787		
Total Free Water (litres)			248	230
Theoretical Density (kg/m³)			2492	2307
Mass of Fresh Concrete in Pot (kg) A		3.798		
Plastic Density (kg/m³)			2307	

Yield	1.08	Cube age (days/No.)	Stress (N/mm²)	Density (Kg/m³)
Slump @ T10 (mm)				2307
Air Content (%)				

Constituents					
Material	Lab Ref No.	Supplier	Source	Type	Absorption (%)
Cement		CRH	Tunstead	CEM I	N/A
Extender 1					N/A
Extender 2					N/A
Filler					N/A
Coarse Aggregate 1		Tarmac	Tunstead	110L0410C	1.5
Coarse Aggregate 2		Tarmac	Alrewas	110S04MCW	0.1
Fine Aggregate 1					
Fine Aggregate 2					
	Lab Ref No.	Supplier	Type	Dose (% by mass of cement)	S.G.
Admixture 1					
Admixture 2					
Admixture 3					
Microsilica slurry					

Notes:

- "Coarse Aggregate 1" refers to 4/10 crushed limestone coarse aggregate.
- "Coarse aggregate 2" refers to the 0/4mm natural quartz sand.
- "Water in aggregate" refers to the water added to bring the oven-dried aggregates to saturated surface dry state.
- "Water added to achieve target slump" is the total water used in the trial mix.

Appendix 3: Results form

The Applied Petrography Group Inter-Laboratory w/c Ratio in Concrete Calibration Trial

A set of 5 individually identified calibration trial sub-specimens are now available for your laboratory

To insure confidentiality your laboratory will only be identified by its laboratory reference number.

Please Note that Your **LABORATORY IDENTIFICATION REFERENCE NUMBER is: xx**

LABORATORY METHOD(S) AND RECORD OF RESULTS

(Please complete with as much detail concerning methods used as possible. Extend the form if necessary. The headings below are suggested as guidance for the sorts of information that would be useful).

1. OPTICAL FLUORESCENCE METHOD(S) AND RESULTS OBTAINED

1.1 Details of the Equipment Used

Microscope: ………………………………………………………………………………………..

UV source: ………………………………Filters used: …………………………………………………

Wavelength/frequency of band of optical radiation used: ……………………………………

Detector type/make: ……………………………………………………………………………..

Measurements made in: Reflected light: ……. Transmitted light: ………. (Please tick)

1.2 Thin Section Manufacture Method Used

Resin used in thin section manufacture: …………………………Refractive Index ……………

Yellow fluorescent dye used in the thin section: ……………………………………………….

Concentration of dye in the resin: ……………………………………………………………….

Thin section thickness in μm: ……………… Cover slip used: Yes/No ……… (Please tick):

1.3 The Measurement Strategy Used

Comparison against standards?   Details of comparative standards: w/c ratios: …………………..

…………………………………… Details of the standards cement/concrete type: …………………………..

Fluorescent measurement: Integrated over:……..seconds/Instantaneous measurement : …

Number of repeat measurements: …… Averaged over …… measurements

Results: Standard Deviation, (2σ): …………………..   /or estimated error: ± ……………………

Fluorescence Results Obtained

Sub-Specimen & Sub-script number	Measured Intensity	No. of Repeat Readings	w/c Ratio determined by Laboratory: xx	Estimated Error
A				
B				
C				
D				
E				

LABORATORY METHOD(S) AND RECORD OF RESULTS

LABORATORY IDENTIFICATION REFERENCE NUMBER: xx

2. OTHER METHOD(S) AND RESULTS OBTAINED

2.1 Basis of Method(s): …………………………………………………………………………………..

2.2 Brief Summary of Equipment used ……………………………………………………………

………

………

2.3 Sample Type and Preparation: …………………………………………………………………..

………

2.4 The Measurement Strategy Used: …………………………………………………………

………

Comparison against standards? ....   Details of comparative standards: w/c ratios: …………….

………………………………………… Details of standards cement/concrete type: …………………………………..

………

………

Number of Repeat Measurements: …………………………. Results are Averages of: ………………….

 Results, Standard Deviation, (2σ): …………………..   /or estimated error: ± ……………………

Method Type & Results Obtained

Sub-Specimen & Sub-script number	Basis of Measurement	No. of Repeat Readings	w/c Ratio determined by Laboratory: xx	Estimated Error
A				
B				
C				
D				
E				

3. Any Other Relevant Comments Concerning the Methods Used or the Results Obtained?

………

………

………

………

Please complete this form with as much information as you consider relevant and return it to CTS Secretary (abpoole@tinternet.com) as soon as possible please.

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