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Determination of water–cement ratio of hardened concrete by scanning electron microscopy

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Abstract

A methodology has been developed for the determination of the water–cement ratio (w/c) in hardened concrete using backscattered electron imaging (BEI) by a scanning electron microscope. The method is based on concrete sections that have been vacuum impregnated with epoxy and polished to a flat surface. During impregnation of a dried concrete specimen, epoxy fills capillary porosity, cracks, and voids. The epoxy-impregnated porosity appears dark in BEI, while other phases such as calcium silicate hydrate, unhydrated cement grain and aggregate appear as brighter phases. The backscattered intensity of the epoxy is the lowest compared to all other phases present within a concrete. By using image analysis program and setting an appropriate threshold of the gray scale the capillary porosity of the concrete can be quantified. Reproducible quantitative data is obtained for a concrete sample of unknown w/c by using a set of standardized instrument parameters such as brightness, contrast and working distance. The water–cement ratio, which is directly related to the capillary porosity, can therefore be measured. Signal production, brightness, contrast, sample preparation, and general methodology are discussed. The measured data using this method is compared with data generated by using optical fluorescence microscopy, according to Nordtest NT Build 361-1999.

Keywords: w/c; BEI; SEM; Porosity; Durability

1. Introduction

The water–cement ratio is one of the most important parameters in the concrete mixture proportioning. The original water content in the mixture dictates the rate of strength development and the ultimate strength of the concrete [1]. The water–cement ratio is of crucial importance to concrete durability. Capillary porosity formed from residual spaces occupied by original mix water increases with higher water–cement ratios within Portland cement paste. Increased water content in the original mix results in an increased capillary porosity, lower strength and potential decrease in durability of the concrete.

Petrographers have used a range of methods for determining the water–cement ratios in hardened concrete [2]. These methods include resistance of cement paste to scratching, microhardness, rate of water-drop absorption, optical microscopy using blue-dye epoxy impregnation, fluorescence microscopy and scanning electron microscopy [2–6]. Two methods have been accepted as standards: (1) the fluorescence microscopy method, Nordtest NT Build 361-1999 [6]; (2) measuring the capillary porosity by absorption method and cement content of the concrete and back calculating the original w/c, BS 1881-124:1988 [7].

Scanning electron microscopy (SEM) has proven to be a powerful tool for the analysis of concrete and related materials. With the advent of good quality backscattered electron detectors and digital imaging, it is possible to separate the features pixel by pixel depending upon their backscattered intensity. By using image segmentation, the darker features corresponding to capillary porosity can be separated from the solid components of the cement paste. This study documents a method of determining water–cement ratio in hardened concrete using SEM.

2. Relation between capillary porosity and water–cement ratio

The basis for microscopic methods for determining the w/c is the relationship of capillary porosity to the

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Table 1
Relationship between the capillary porosity of hardened cement paste and the original water–cement ratio [8]

Water–cement ratio by mass	Capillary porosity of cement paste % by volume
0.40	8
0.45	14
0.50	19
0.55	24
0.60	28
0.65	32
0.70	35
0.75	38
0.80	41

amount of original mix water. The data presented in Table 1 shows an increase in capillary porosity with increased original water content in a fully hydrated cement paste. This data was calculated by Christensen et al. [8] by using Powers [9] formula.

Thus, the paste in a mature concrete with a water–cement ratio of 0.65 has a capillary porosity that is four times as high as that in a concrete with w/c = 0.40.

Backscattered electron imaging is sensitive to the differences in atomic number. Phases containing lower atomic number elements appear darker than those possessing higher atomic number elements. Therefore, backscattered electron images of pores filled with carbon-rich epoxy and C–S–H solids in the paste may be separated and measured, based on the gray level intensities. By comparing the area percent of detectable pores in reference samples of concrete of known water–cement ratios, the apparent water–cement ratio can be determined. Perturbing factors that may influence the determination may include homogeneity of the concrete mix, carbonation, and paste deterioration.

3. Background of technique

Backscattered electrons are strongly controlled by the atomic number of the material irradiated. For low atomic number materials, little scattering takes place near the surface and most of the incident electrons are absorbed within the specimen. Materials with a higher atomic number generate much more scattering at the specimen surface and consequently a greater proportion of backscattered electrons are produced. Therefore, in a backscatter electron SEM image brighter regions represent phases of higher atomic number and darker regions represent phases of lower atomic number. The amount of electron backscattering is indicated by the backscattering coefficient (η), which is defined as the fraction of incident electrons that do not remain in the specimen.

For a homogeneous mixture, the backscatter coefficient is calculated based on the weight fractions of the elemental components. In this manner, the weight fraction of each element and its elemental backscatter coefficient is multiplied and the products are summed to provide the backscatter coefficient of the compound. By combining Arnal's [10] and Castaing's [11] formulas, the average backscattering coefficient ($\bar{\eta}$) for a number of phases of relevance has been calculated [12]. They are arranged in order of increasing η in Table 2. The expectation is that the phases with higher η will appear brighter in the backscatter electron image. This is supported by general experience and by the measured relative image intensity.

Many major phases in concrete are easily identified from the backscatter electron image intensity, although some compounds are difficult to distinguish because the intensities are so similar. For example, Fig. 1 shows a

Table 2
Average backscattering coefficient ($\bar{\eta}$) and measured relative brightness of various phases [12]

Phase	Calculated average backscatter coefficient	Relative, measured image intensity
Epoxy	0.081	3.1
Brucite, $Mg(OH)_2$	0.129	71.7
Silica gel, $SiO_2.H_2O$	0.135	82.1
Thaumasite, $CaSiO_3.CaSO_4.CaCO_3.15H_2O$	0.141	111.3
Dolomite, $CaMg(CO_3)_2$	0.143	76.9
Ettringite, $C_3A.3CaSO_4.32H_2O$	0.146	111.9
Quartz, SiO_2	0.147	100.0
Gypsum $CaSO_4.2H_2O$	0.158	113.2
Potassium feldspar, $KAlSi_3O_8$	0.159	119.7
Calcium silicate hydrate, C–S–H	0.160	116.0
Calcite, $CaCO_3$	0.161	131.9
Aragonite, $CaCO_3$	0.161	132.0
Aluminum, Al	0.177	145.2
Portlandite, $Ca(OH)_2$	0.182	147.5
Calcium aluminate, C_3A	0.185	146.9
Belite, C_2S	0.187	158.9
Alite, C_3S	0.193	167.7
Ferrite, C_4AF	0.205	184.9

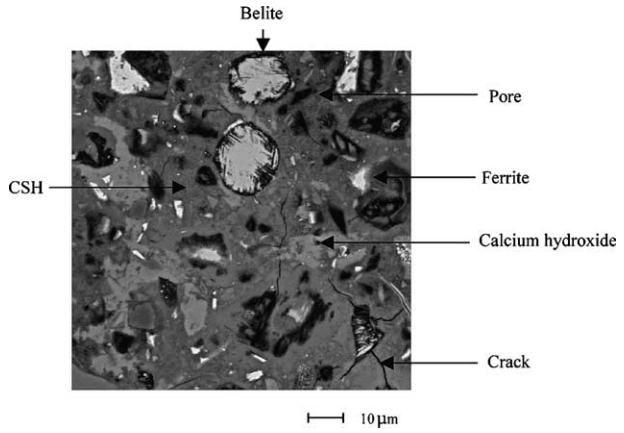

Fig. 1. Representative backscattered electron image of paste area of a Portland cement concrete at 800× showing common phases and structures.

typical Portland cement concrete microstructure at 800 times magnification. The distinctively higher intensity phases such as ferrite are easily distinguished from the rest of the paste due to their higher backscattered intensity. Unhydrated Portland cement phases have higher mean atomic numbers than hydrated cement phases. Therefore, unhydrated phases show a higher intensity and are therefore brighter in the BEI. Cracks and voids are also easily recognized by the low intensity associated with the epoxy resin, which has filled these regions.

Differences in backscatter coefficients therefore allow for the discrimination between phases. It is possible to perform phase quantification by area measurement given adequate resolution of the detector and optimal setup of the SEM. However, even the resolution of phases with large differences in the backscattering coefficient is not entirely perfect and is limited by the image pixel size [13–15].

4. Procedure—sample preparation technique

The method of analysis of hardened concrete for w/c described here is performed using either epoxy impregnated polished sections or epoxy impregnated thin sections without cover slips. Both sample types are acceptable for the technique but the polished sections require much less time for preparation.

Care must be taken to ensure complete epoxy impregnation of the surface to be examined. Factors that affect sample impregnation include incomplete drying and poor vacuum. Excessive grinding can remove portions of the impregnated layer, exposing unimpregnated material. Samples of varying water–cement ratios will impregnate to different depths due to varying capillary porosity. It is essential that samples not be ground below the depth of impregnation.

The following should be considered before any w/c analysis [16]:

- The specimen should be reasonably well hydrated, and preferably have a maturity of 28 days or more.
- There should be no signs of damage from sample collection or preparation.
- The capillary pores should be completely filled with epoxy.
- Areas with significant carbonation or deterioration should be avoided.

In this work, the standard concrete samples were made in the laboratory with known water–cement ratios in the range of 0.45–0.85. The samples were cured for 28 days before water–cement measurement were carried out. An additional set of unknown water–cement ratio samples were prepared from cores taken from 8 to 10 year old residential concrete.

5. Procedure—SEM configuration

The instrument employed was a personal scanning electron microscope (PSEM©) operating at 20 keV accelerating voltage. The details of the backscattered electron detector setup are of utmost importance when performing a water–cement ratio analysis.

Proper setup requires standardization of the SEM brightness and contrast settings. In the present work, aluminum and carbon tapes were employed to reproduce the SEM settings between the standards of known water–cement ratio and the samples with unknown water–cement ratios. The backscattered intensity of carbon tape was set at a gray level of 5 (±2), and that of the aluminum tape at 145 (±3).

6. Image acquisition criteria

The selection of areas to be analyzed within a given specimen, magnification and the number of images need to be acquired are important aspects considered during the analysis.

6.1. Selection of magnification

As the intention is to measure the capillary porosity of the paste, an appropriate level of magnification must be established to image only the paste microstructure. It is extremely difficult to image the paste microstructure only, without aggregates, if the magnification is too low. If the magnification is too high, the total measured area is too low. From our experience with various concrete 800× magnification was found to be appropriate.

The porosity of the paste at this level of magnification varies significantly from location to location. To obtain

a representative porosity number a statistically significant number of images need to be collected.

6.2. Selection of location

The locations of the images were random. Care was taken not to collect images from the cast or finished surface. Special care was taken not to acquire images from areas of altered microstructure. This alteration could be due to carbonation, leaching, cracking etc. Since the specified images were selected manually to avoid entrained air voids, air voids are not present in the images. No specific attention was paid to collect images away form the aggregate to avoid the interfacial transition zone (ITZ). That means some images could be close to the aggregate and others away from the aggregate.

7. Water–cement ratio determination

The image analysis software employed in this study can distinguish gray levels ranging from 0 to 255. Using the standardized brightness and contrast settings, pores are readily segmented from solid components at a gray level of 50.

Fig. 2 is a comparison of images of cement paste from concrete made with three different water–cement ratios. The image on the left is the backscattered electron image at 800 times magnification, and the image to the right is the matching binary image separated at a gray level of 50 (i.e. black is 50 or less and white is greater than 50 on a 255 scale).

An automated software was used to calculate the area percent of pixels within the specified range, and comparison of the values to standards. The average area

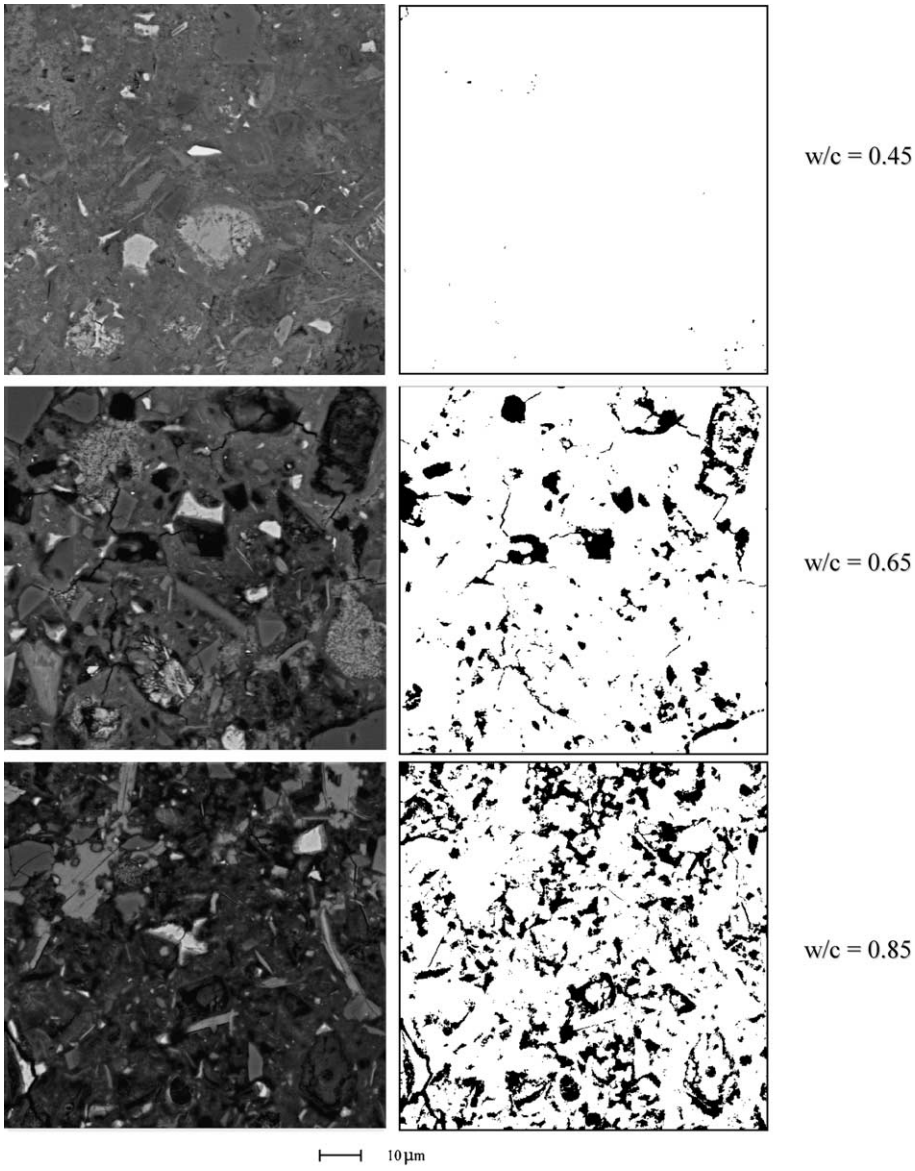

Fig. 2. Comparisons of 28 days old Portland cement concrete polished sections in BEI and matching binary image with a 50/255 threshold.

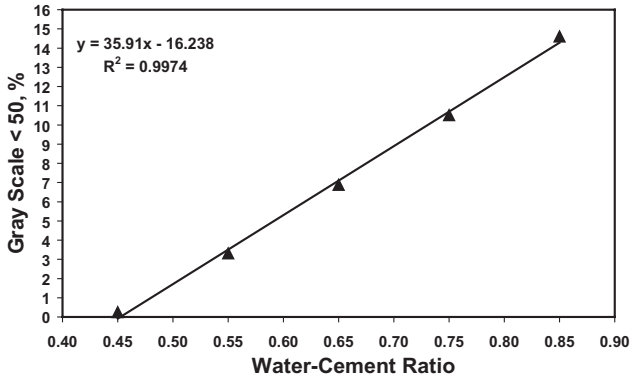

Fig. 3. Plot showing the relation between water–cement ratio and gray scale $\leqslant 50$.

percent of pixels at gray level 50 or less is plotted vs. w/c for the set of known w/c ratio concretes in Fig. 3. It is apparent that the two are linearly related, and that the percent of pore pixels can be used as a measure of the w/c for unaltered concrete. Many analytical techniques utilize this general procedure of measuring an index property of standards with differing characteristics and plotting the measured values as a calibration curve for use with unknown samples.

The average pore areas (gray scale $\leqslant 50$) of images collected from each standard samples are plotted in Fig. 3. The straight-line relationship between the average value of the % of pore pixels and the water–cement ratio was established to be linear, with $y = 35.91x - 16.238$. This equation was then used to calculate the water–cement ratio of the unknown samples, as discussed later.

As is seen in Fig. 3, high w/c concretes exhibit progressively higher content of measured pore space.

8. Statistical evaluation of measured data

A statistical evaluation of the porosity data (area percent gray scale $\leqslant 50$) of the standard samples is presented in Table 3. The evaluation makes the common assumption that the data are normally distributed, which is not necessarily the case since some indications of bimodal distributions have been found. The data suggests that with an increase in water–cement ratio both the standard deviation and standard errors increase, suggesting that the inhomogeneity of paste increases with increase in water–cement ratio. However, the coefficient of variation decreases, suggesting the measurement of w/c may be slightly more precise at higher w/c ratio.

9. Optical and backscattered electron microscopy

The water–cement ratio of the set of field concretes mentioned previously were independently determined by two different methods. One of these was the fluorescent light microscopy procedure as described in [16] according to Nordtest NT Build 361-1999 [6]. Water–cement ratios on the same thin sections were also separately measured by using the SEM technique described here (Fig. 4).

In the fluorescent microscopy technique, the intensity of the green tone observed is controlled by capillary porosity. A low w/c sample has lower green color intensity as compared to a higher w/c ratio sample. In backscattered SEM examination, a lower w/c sample has

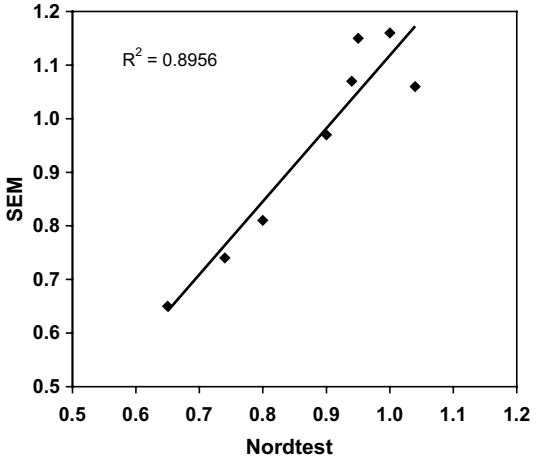

Fig. 4. Relation between water–cement ratios measured by SEM and Nordtest methods on the same samples.

Table 3
Statistical analyses for % pore pixels in 40 repeat determinations for each w/c tested

w/c	Mean	Standard deviation	Standard error	Minimum	Maximum	Coefficient variance	Median
0.45	0.25	0.21	0.03	0.00	0.90	0.86	0.20
0.55	3.07	2.34	0.35	0.10	9.00	0.76	2.40
0.65	6.87	3.49	0.50	1.00	15.70	0.51	6.80
0.75	10.41	2.85	0.42	4.90	17.00	0.27	10.50
0.85	14.60	8.90	1.26	3.70	41.80	0.43	17.50

Table 4
Comparisons of water–cement ratio determined by SEM and fluorescent light microscopy (Nordtest NT Build 361-1999)

Sample no.	SEM	Nordtest
1	0.65	0.65
2	0.74	0.74
3	0.81	0.80
4	0.97	0.90
5	1.06	1.04
6	1.07	0.94
7	1.15	0.95
8	1.16	1.00

a smaller area percent of pore pixels; thus the two measurements are fundamentally similar. However, different relationships apply to the overall brightness of the image in the two modes. Lower w/c specimens are darker in the optical fluorescence mode images, but brighter in the backscatter SEM images.

The w/c determined for the field concretes are presented in Table 4. Note that none of the concretes examined appeared to have w/c below 0.65. It is apparent that the data obtained using the two methods show close linear correlation with each other ($R^2 = 0.89$). The correlation is particularly good for the w/c range between 0.65 and 1. For the extreme w/c ratios above 1, it appears that the fluorescence method gives lower values than the SEM method.

10. Conclusions

The water–cement ratio of hardened concrete can be determined by scanning electron microscopy with associated backscattered electron imaging and image analyses software. The technique has been tested for laboratory specimens of known w/c ratio and shows good linear correlation. w/c ratios determined on field concretes show very good correlation with results obtained on the same specimens using the standardized fluorescence microscopy Nordtest method (NT Build 361-1999) except in the range of extremely high water–cement ratios exceeding 1.

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