Determination of the cement content of five samples of hardened concrete by means of optical microscopy

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This article presents the results of a microscopic analysis to determine the cement content of five samples of hardened concrete prepared with portland pozzolanic cement and crushed limestone as part of the aggregate. The volume fraction of the coarse aggregate was determined macroscopically from polished plates of the concrete samples. The volume fractions of the cement paste, the fine aggregate and the air voids were determined microscopically from thin sections. Both analyses were carried out by means of point-counting. The mass by volume of the samples was determined according to RILEM Recommendation CPC 11.3. The cement content of the concrete samples was calculated from the point-counting results combined with the estimated water-cement ratio, the estimated mass by volume of the cement paste and the measured mass by volume of the concrete samples. Corrections were made for the resulting value concerning part of the very fine aggregate material (≤ 63 μm) that may have been counted as part of the cement paste during the point-counting analysis.

Key words: **Concrete, cement content, optical microscopy, point-counting analysis, water-cement ratio.**

1 Introduction

1.1 Background

The cement content and especially, the water-cement ratio are the two most important parameters that control the strength and the durability of concrete.

The water-cement ratio is related directly to the capillary porosity of the cement paste which, in turn, is directly related to the strength and particularly, the durability of concrete. In general, a higher capillary porosity of the cement paste or binder will result in a higher permeability which can enhance ingress of aggressive agents such as sulphates, chlorides and alkalis into concrete.

A knowledge of the water-cement ratio and the cement content of hardened concrete is therefore of vital importance for performing quality control of new concrete and for determining the causes of deterioration of concrete in existing structures.

Various standards are available that provide comprehensive guidance and details of procedures for carrying out tests to determine these parameters [1-3]. These methods of analysis are based on physico-chemical analysis and involve initial heating of a sample of the hardened concrete at two temperatures: first at 105 °C and subsequently at about 900 °C. This is followed by hitting the heated

sample with a hammer to loosen the structure, after which the sample is chemically treated with hydrochloric acid. The quantity of silica, SiO_2 or calcium oxide, CaO is determined by simple analytical methods, and if the composition of the cement is known, the cement content of the original volume of the sample can be calculated.
Heating of the sample at 105 °C and about 900 °C makes it possible to determine the capillary water and the bound water respectively. These values are then used to determine the degree of hydration, the original water content and the water-cement ratio of the concrete.

1.2 *Problems associated with traditional methods*

The methods described in the above-listed standards are based on the assumption that the acid is able to dissolve the hardened cement paste completely, that is, the lime, the silicates and the hydration products of the cement as well as any other additions without affecting the aggregate. Concretes containing calcareous aggregate such as limestone or marble cannot be analyzed accurately using these methods. This means that the methods are only suitable for performing analysis of concretes containing siliceous aggregates (river gravels and sands with negligible acid-soluble contents) and prepared with portland cements without siliceous cementitious additions. Concretes prepared with composite cements containing siliceous additions, such as "pozzolana" (volcanic ashes) cannot be analyzed accurately unless a representative sample of the cement is available.
Other analytical methods, such as sulphate analysis of the cement and the concrete and instrumental neutron activation analysis (INAA) also require a fore-knowledge of the composition of the cement used or a sample available for analysis. In addition to the enumerated problems, none of these methods takes into consideration changes in the concrete caused by chemical attack and the presence of other materials such as air-entraining agents.

The standards in which these so-called "classical" or "traditional" methods have been described were prepared in the seventies and early eighties. In those days only relatively few types of cement were available for use in preparing concrete. Most of those cements contained no additions and their chemical and mineralogical compositions were fairly well known. As such, it was possible, using these methods to determine the cement content and the water-cement ratio with a relatively high degree of accuracy. Currently, several types of cement are available for preparing concrete. Most of them contain one or more types of pozzolanic and inert additions. Combinations of more than one kind of aggregate material, such as siliceous gravel and crushed limestone in a single batch of concrete is not uncommon. Uncertainties about the concrete constituents, especially the type and the amount of additions used, make continuous use of these traditional methods without representative reference samples of the cement almost impossible.

Petrographic analysis by means of optical point-counting both macroscopically on epoxy-impregnated polished plates and microscopically on thin sections is one of the suitable methods for determining the composition of hardened concrete, regardless of the composition of the aggregate or cement. Recently, this technique was used to determine the cement content of five hardened concrete samples prepared using pozzolanic cement (portland clinker and trass as a natural pozzolan) and limestone as the coarse aggregate as well as part of the fine aggregate. All the samples

were taken from one large concrete structure prepared using the same concrete mix composition. The age of the concrete at the time of this investigation was about two months.

2 Samples

Each core had a diameter of about 150 mm and a length of about 120 mm and at the time of delivery were coded I, II, III, IV and V. In addition to the concrete samples, a sample of the portland pozzolanic cement that was used to prepare the concrete samples was also available. The density, ρ_c of this cement was determined using the method of stereo-pycnometry to be 2900 kg/m^3. The usual density of portland trass cement, with 30 respectively 40 % by mass of trass is about 2750 and 2700 kg/m^3 respectively [4]. The comparatively higher value obtained for this cement suggests that the trass content of this cement is probably lower than 30 %.

3 Procedures of optical investigation

3.1 *General*

The optical investigation was performed according to TNO standard procedures [5], which are similar to ASTM Standard C856-88 "Standard Practice for Petrographic Examination of Hardened Concrete" [6]. The TNO standard procedures also allow the determination of the water-cement ratio by means of fluorescent microscopy using (standard) reference thin sections prepared from portland cement concretes with known water-cement ratios [7]. The examination was performed in three phases: visual inspection of the cores, microscopical analysis of thin sections and macroscopical analysis of polished plates to determine the coarse aggregate content.

3.2 *Macroscopical analysis*

A macroscopical analysis by means of point-counting was used to determine the coarse aggregate fraction, that is, the fraction of the aggregate particles larger than 2 mm. For each sample, two specimens were used. Each specimen consisted of a 100 mm × 100 mm × 15 mm polished plate that was taken from the longitudinal direction of the cores. After sawing, the specimens were vacuum-impregnated with an epoxy resin containing a fluorescent dye. The surfaces to be examined were then smoothly polished in order to enhance visibility.

3.3 *Microscopical analysis*

The microscopical analysis was performed by means of Polarising and Fluorescent Microscopy (PFM) on thin sections prepared from the cores. In order to prepare a thin section, a small block was sawn in the longitudinal direction from each core, glued to an object glass, and vacuum-dried and -impregnated at approximately 40 °C with an epoxy resin containing a fluorescent dye. After hardening one thin section with a surface area of approximately 50 mm × 30 mm and a thickness of 20–30 µm was prepared from each block for the PFM-analysis. Impregnation of the blocks with a fluorescent resin makes it possible to study the thin sections by means of transmitted light and fluorescent microscopy. One thin section was prepared per sample.

By means of transmitted light microscopy, the various components (the type of cement and aggregate) in the specimens under investigation can be identified. The fluorescent microscopy enables the homogeneity of the mix and cement paste, the capillary porosity, the air-voids, compaction pores, microcracks and other defects in the specimens to be studied. It also allows the water-cement ratio to be determined by comparison with standard reference thin sections.

Evaluation of these aspects provides clues to the nature and effectiveness of the working methods used in the manufacture of the concrete. The determination of the content of binder, fine aggregate (< 2 mm) and voids (air-voids and compaction pores) was performed by means of point-counting [5]. In general, point-counting on polished surfaces or large thin sections measures the total amount of binder with an error of ≤ 2 %. The total number of points counted, the point spacings used for both the macroscopical and microscopical analyses and the minimum particle size of 2 mm chosen for determination of the coarse fraction by means of macroscopic analysis were established from ASTM Standard C457-95 "Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete" [8].

4 Results

4.1 *Macroscopical analysis*

The results of the macroscopical analysis by means of point-counting to determine the coarse aggregate content are presented in Table 1.

Table 1. Results of the point-counting analysis to determine the coarse aggregate content in two 100 mm × 100 mm plates per sample.

	Composition and content (% by volume of concrete)	
Sample	Coarse aggregate (> 2 mm)	Mortar (cement paste, including fine aggregate < 2 mm and voids)
I	44.4	55.6
II	43.1	56.9
III	45.9	54.1
IV	43.8	56.2
V	46.9	53.1
Average	44.8	55.2
Standard deviation	1.6	1.6

4.2 *Microscopical analysis*

The results presented in this section apply to all five core samples unless otherwise stated that they apply to a specific sample or set of samples.

4.2.1 Composition

The coarse aggregate consisted predominantly of fossiliferous limestone, porous and non-porous chert and sericitic sandstone. The fine aggregate was mostly quartz and porous and non-porous chert with minor fragments of fossiliferous limestone, sericitic sandstone, chalcedony, quartzite, mica, feldspars, calcite and oxides.

The cement used to prepare the concrete in each of the five samples consists predominantly of portland clinker and pulverised trass (Figure 1). The degree of hydration was low, but the homogeneity of the cement paste was reasonably good (Figure 2). No air-entraining agents were used to prepare the concrete of any of the samples examined. The water-cement ratio was estimated by fluorescent microscopy to be ≈ 0.70. The cement content is relatively low. The homogeneity of the mix is not optimum. In each sample there are local areas of segregation coupled with bleeding around the aggregate particles. The aggregate is gap-graded. There is apparent lack of the 4–8 mm size range (see Figure 1). The fine aggregate was, however, found to be well-graded and very well-distributed throughout the binder but bonding of the cement paste to the aggregate particles is very poor, indicating poor placement and compaction procedures or the use of a high water-cement ratio in combination with a low binder content.

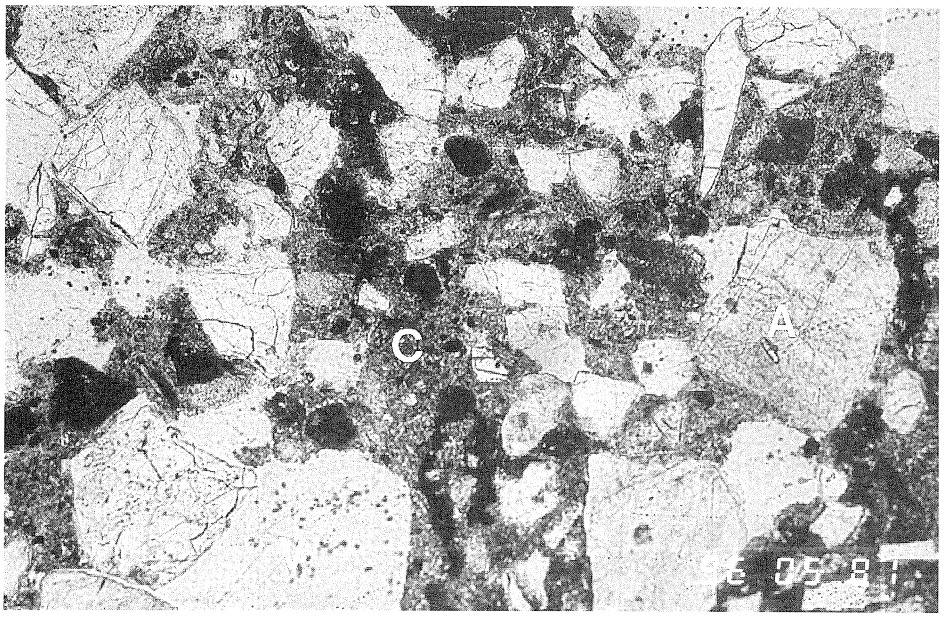

Fig. 1 *Thin section micrograph (transmitted light) showing an overview of the concrete in sample II. A = aggregate; C = cement paste; V = voids. (Size of micrograph is 2.7 mm × 1.8 mm).*

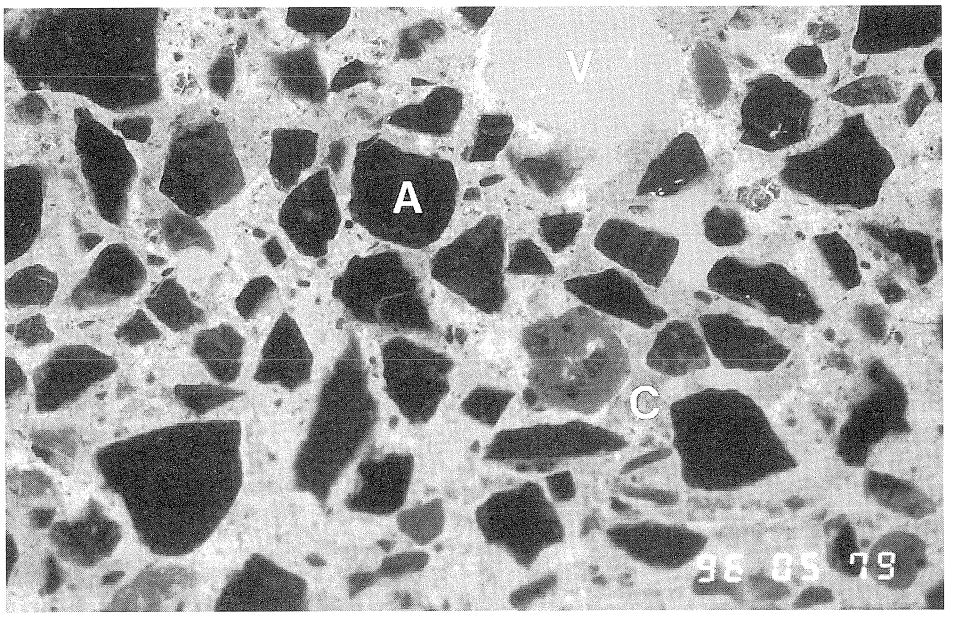

Fig. 2 *Fluorescent thin section micrograph showing an overview of the concrete and the microstructure of the cement paste in sample II. A = aggregate; C = cement paste; V = voids. (Size of micrograph is 2.7 mm × 1.8 mm).*

4.2.2 Principle of the water-cement ratio determination

The principle underlying the determination of the original cement content by this microscopical method is based on the determination of the water-cement ratio from the capillary porosity of the cement paste by means of fluorescent microscopy [5]. The capillary porosity of the cement paste is a function of the cement content, the water-cement ratio and the degree of hydration of the cement. When a hardened concrete sample becomes impregnated under vacuum with an epoxy resin containing a fluorescent dye, all the capillary pores and the air voids become filled with the resin. When a thin section is prepared from such a specimen and then observed with a fluorescent microscope, the intensity of the fluorescence is proportional to the capillary porosity and consequently the water-cement ratio. By comparing the thin sections of the unknown samples to standard thin sections (reference specimens with known water-cement ratios in a normal range of 0.40 to 0.70 in steps of 0.05 for example), the water-cement ratios of the unknown samples can be estimated. Using the above principle, the water-cement ratio of the concrete in the five samples was estimated. A value of about 0.70 was found for the concrete in each sample.

In the present investigation, the water-cement ratio of the samples was estimated using the same principle by comparing the thin sections of the samples to reference thin sections prepared from hardened concrete containing Dutch ordinary portland cement. This Dutch portland cement does not contain any trass or any other pozzolans. Differences between the ordinary portland cement

and the portland pozzolanic cement that was used to prepare the samples in question can cause differences between the values obtained in this investigation and the actual values (see further under Section 5).

4.2.3 Determination of concrete components and constituents

The results of the point-counting analysis performed on the thin sections to determine the components in the mortar fraction of the concrete samples, that is the binder (cement paste), fine aggregate and voids are presented in Table 2. Table 3 shows the combined results of Tables 1 and 2. All the values are expressed as percent by volume of the concrete.

Table 2. Results of the point-counting analysis performed on one thin section per sample to determine the components in the mortar fraction of the concrete samples.

	Composition and content (% by volume of mortar) *		
Sample	Fine aggregate (< 2 mm)	Cement paste	Voids (air voids and compaction pores)
I	40.0	36.3	23.7
II	39.4	38.4	22.2
III	39.8	38.1	22.1
IV	37.6	40.1	22.3
V	38.8	40.3	20.9
Average	39.1	38.6	22.2
Standard deviation	1.0	1.6	1.0

* The fraction of coarse aggregate in each thin section has been deducted from the total value and the resulting values scaled up to 100 %.

Table 3. Results of the point-counting analysis to determine the content of coarse aggregate combined with the results of the point-counting analysis to determine the components in the mortar fraction of the concrete samples.

	Composition and content (% by volume of mortar)			
Sample	Coarse aggregate (> 2 mm)	Effective fine aggregate (< 2 mm)	Effective Cement paste	Effective voids (air voids and compaction pores)
I	44.4	22.2	20.2	13.2
II	43.1	22.4	21.9	12.6
III	45.9	21.5	20.6	12.0
IV	43.8	21.2	22.5	12.5
V	46.9	20.6	21.4	11.1
Average	44.8	21.6	21.3	12.3
Standard deviation	1.6	0.7	1.0	0.8

4.3 *Determination of cement content*

4.3.1 General

The cement content of the hardened concrete samples can be determined in two ways as follows:

a. On the basis of the volume of cement paste, determined from the results of the point-counting analysis, in combination with the estimated water-cement ratio and the determined density of the dry, unhydrated cement.

b. On the basis of the dry density of the concrete samples, determined according to RILEM Recommendation CPC 11.3, in combination with the total aggregate content obtained from the results of the point-counting analysis. In this case, the difference between the dry density value and the total aggregate content of each sample gives the cement paste content in each sample.

4.3.2 Principle of the cement content determination from the paste volume and the water-cement ratio

The hardened concrete samples examined in this study consist essentially of four components: coarse aggregate (> 2 mm), fine aggregate (< 2 mm), cement paste and voids (entrained air voids and compaction pores or entrapped air voids).

The point-counting method used in this investigation is based on the fact that the volume of the hardened cement paste is equal to the original volume of the cement, that is, the volume of the unhydrated cement powder and the quantity of water employed. If the water-cement ratio is known, the cement paste content can be used to determine the cement content. This method of

determining the cement content does not take the chemical shrinkage of the cement paste during hydration into consideration, because this is reflected in the amount of capillary pores which eventually is used in the determination of the effective cement paste fraction. Using the above principle, the cement content (original volume of cement) can be determined from the cement paste volume, the water-cement ratio and the densities of cement and water from Equation 1.

$$V_c = \frac{V_{cp}}{1 + w/c \cdot \rho_c/\rho_w} \quad (1)$$

where,

V_c = original volume fraction of cement
V_{cp} = cement paste fraction or proportion obtained by point-counting
w/c = water-cement ratio
ρ_c = density of the cement in kg/m^3
ρ_w = density of water in kg/m^3

Using the same principle, the cement content and the coarse and fine aggregate contents can be determined from Equations 2 and 3.

$$M_c = \rho_c \cdot V_c \quad (2)$$

$$M_{cagg} = \rho_{cagg} \cdot V_{cagg} \quad (3)$$

$$M_{fagg} = \rho_{fagg} \cdot V_{fagg} \quad (4)$$

where,

M_c = cement content in kg/m^3
M_{cagg} = coarse aggregate content in kg/m^3
V_{cagg} = coarse aggregate fraction obtained by point-counting
ρ_{cagg} = density of the coarse aggregate in kg/m^3
M_{cagg} = fine aggregate content in kg/m^3
V_{cagg} = fine aggregate fraction obtained by point-counting
ρ_{fagg} = density of the fine aggregate in kg/m^3

Using Equations 1-4, the estimated water-cement ratio value of 0.70 and the measured density of the portland pozzolanic cement (ρ_c = 2900 kg/m^3), the volume fraction of cement and its corresponding content in each of the concrete samples were determined.
Using the same procedure (ρ_{cagg} = 2700 kg/m^3, average value for limestone and ρ_{fagg} = 2650 kg/m^3, average value for quartzitic sand) and Equations 3 and 4, the coarse and fine aggregate contents in the concrete samples were determined. The results are presented in Table 4.

4.3.3 Principle of cement content determination from the dry density and total aggregate volume

From Table 4, the difference between the dry mass by volume and the total aggregate volume (coarse and fine aggregate content) of each sample gives the mass of cement paste in each sample. In other words,

$$\text{Cement paste content} = \text{Dry density (DD)} - \text{Total aggregate volume (TAV)} \quad (5)$$

Table 4. Composition of concrete in each of the samples determined from the cement paste and the water-cement ratio from Equations 1 to 4.

Sample	Composition and content (mass by volume, kg/m^3)				Dry mass by volume (dry density)
	Coarse aggregate (> 2 mm)	Fine aggregate (< 2 mm)	Cement	Total	
I	1199	702	194	2095	2110
II	1164	755	209	2128	2110
III	1239	663	197	2099	2110
IV	1183	689	215	2087	2150
V	1266	673	206	2145	2130
Average	1210	696	204	2111	2120
Standard deviation	42	25	9	25	18

The cement paste contains both hydrated and unhydrated clinker particles. At any given time, the extent to which the cement has hydrated is expressed by the degree of hydration, m and is defined as the fraction of the original cement that has become hydrated at that particular time. The value of m ranges between 0 (no hydration) and 1 (full hydration or fully hydrated cement).

For a fully hydrated cement, that is for $m = 1$, the fraction of chemically bound water (that is water chemically incorporated in the C-S-H phase in the cement paste = 0.25 and the fraction of physically bound water (water held in voids and the capillary pores) is 0.15. The physically bound water, however evaporates during the determination of the dry density value of the samples by drying the concrete specimens at 105 °C. This leaves only the chemically bound water. Using this principle, the amount of cement in the cement paste can be determined from the following relationship:

$$\text{DD - TAV} = \text{Cement content} + m \cdot (0.25).\ \text{Cement content}$$

$$\text{Cement content} = \frac{\text{DD - TAV}}{1 + m \cdot (0.25)} \quad (6)$$

From the microscopical analysis (see Section 3.3), the degree of hydration of the cement used in the concrete samples was found to be low. A value of $m = 0.60$ is a reasonably good estimation. This value was chosen on the basis of experience and data from the literature [9].
Using Equation 6, the degree of hydration of the cement and the aggregate content given in Table 4, the original cement content of the concrete in each sample was determined. The results have been presented alongside with those obtained on the basis of water-cement ratio in Table 5.

Table 5. Cement contents of the concrete samples determined on the basis of water-cement ratio and the dry density values.

	Cement content, kg/m^3	
Sample	Determined from the cement paste volume and the water-cement ratio	Determined on the basis of the dry density-total aggregate volume
I	194	182
II	209	166
III	197	181
IV	215	242
V	206	166
Average	204	187
Standard deviation	9	32

5 Discussion

From Table 5, the following deductions can be made about the cement content values obtained by the two methods:

- The values obtained for each sample in each group compare reasonably well with each other and the average values. The results of the two separate methods used are also in good agreement.
- The average value obtained on the basis of cement paste volume and water-cement ratio is higher than the value obtained on the basis of the dry density-total aggregate content value. A possible cause of this effect may be an underestimation of the water-cement ratio for the samples. This effect is likely to have been caused by the difference between the portland pozzolanic cement used to prepare the samples and the portland cement in the reference thin section specimens and lack of reference thin sections with water-cement ratios greater than 0.70; the maximum water-cement ratio that can be estimated using thin sections from our reference collection is 0.70.
- The results obtained by means of the cement paste volume and the water-cement ratio possibly give relatively high values compared to the actual values of the samples. The reason for this is

that part of the very fine material in the aggregate (that is, part of the very fine fraction ≤ 63 μm occurring as clay or carbonate minerals and intermixed with the cement paste) is not easily distinguishable and may have been counted as part of the cement paste during the point-counting analysis, thereby increasing the fraction of the cement paste in the samples. Assuming that 1.0 % (by mass) of the aggregate content in this case, was counted as part of the cement paste during the point-counting analysis, this would be equivalent to 19 kg/m3 of cement paste (see Table 4) or 17 kg/m3 of cement. Thus, correcting for this error, the effective average cement content would be 187.

- The standard deviation of the results obtained on the basis of the cement paste volume and the water-cement ratio is considerably lower than that obtained on the basis of the dry density-total aggregate content value. An explanation for this is that the former method is based directly on the point-counting results of the cement paste, which gave a low standard deviation value (see Table 3). The dry density-total aggregate content method, on the other hand, is based on the results of the total aggregate content, which as shown in Table 4, gave a high standard deviation-value.
  (Note: The exceptionally high cement content (from water-cement ratio) value of sample IV also exerts a considerable effect on the resulting average value).

Following the discussion above and using Equation 7, corrections were made for the values of the cement content determined on the basis of the cement paste volume and the water-cement ratio. The results have been presented in Table 6.

$$\text{Cement content} = C_{wcr} - CORR_{agg} \tag{7}$$

where,

C_{wcr} = cement content obtained on the basis of the estimated water-cement ratio
$CORR_{agg}$ = correction for fraction of very fine aggregate material (≤ 63 μm) in cement paste.

After the corrections, the cement content values for the two methods show a better agreement. The small variations in each group and between the two methods are likely to arise from the inhomogeneity of the mix, the presence of local areas of segregation and bleeding around the aggregate particles and problems associated with the estimation of the water-cement ratio. Statistical analysis of the data shows that no significant difference exists between the means of the two methods. The average original cement content for the five samples and the associated standard deviation are reported in Table 7.

Table 6. Cement contents of the concrete samples after correcting for the fraction of very fine aggregate material (≤ 63 μm) in the cement paste.

	Cement content, kg/m^3	
Sample	Determined from the cement paste volume and the water-cement ratio	Determined on the basis of the dry density-total aggregate volume
I	177	182
II	192	166
III	180	181
IV	198	242
V	189	166
Average	187	187
Standard deviation	8	32

Table 7. Original cement content of the concrete samples.

Samples	Cement content, kg/m^3
I	180
II	179
III	180
IV	220
V	178
Average	187
Standard deviation	16

6 Conclusions

The cement content of five samples of hardened concrete has been determined by means of optical microscopy. All the samples were taken from one large concrete structure prepared using the same concrete mix composition. The concrete in each of the five samples was prepared with portland pozzolanic cement. The degree of hydration of this cement was found to be low. No air-entraining agents were used to prepare the concrete in any of the samples.

The volume fractions of the cement paste, the fine aggregate (< 2 mm) and the air voids were determined microscopically from thin sections by means of point-counting. The volume fraction of the coarse aggregate (> 2 mm) was determined macroscopically from polished plates by means of point-counting. The mass by volume of the samples was determined according to RILEM Recommendation CPC 11.3.

The cement content of the concrete samples was calculated from the point-counting results ombined with the estimated water-cement ratio, the estimated mass by volume of the cement paste and the measured mass by volume of the concrete samples. Corrections were made for the resulting value concerning part of the very fine aggregate material (≤ 63 μm) that may have been counted as part of the cement paste and the possible error associated with the methods used. The resulting original cement content value of the five samples ranged between 178 and 220 kg/m^3 with an average of 187 kg/m^3 and a standard deviation of 16 kg/m^3.

This investigation has shown that it is possible to determine the composition of hardened concrete samples by means of optical microscopy. This method can be applied in cases where the traditional chemical methods fail.

References

1 British Standards Institution, United Kingdom. Testing concrete: Methods for Analysis of Hardened Concrete. BS 1881, Part 124, BSI, London, 1988.

2 German Standard DIN 52170 "Bestimmung der Zusammensetzung von erhärtetem Beton" (inGerman).

3 Belgische Norm NBN B 15-250, Belgium. "Chemische onderzoek van verharde mortel en beton" (in Dutch), october 1991.

4 Trasszement: seine Eigenschaften und Anwenddung im Bauwesen, (in German), 1954, pp. 55.

5 HEIJNEN W.M.M. and LARBI J.A. Microscopy of concrete (in Dutch). Materialen, No. 10, 1992, pp. 9-16.

6 American Society for Testing and Materials. ASTM Standard C856-95 "Standard Practice for Petrographic Examination of Hardened Concrete", 1995, pp. 405-416.

7 CHRISTENSEN, P., THAULOW, N., DAMGAARD JENSEN, A., CHATTERJI, S., and GUDMUNDSSON, H. Struktur- og bestandelanalyse af beton (in Danish). Nordisk Betong, Vol. 3, 1979, pp. 4–10.

8 American Society for Testing and Materials. ASTM Standard C457-95 "Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete", 1995, pp. 229–241.

9 HANSON, T.C. Physical structure of hardened cement paste: a classical approach. Materials and-Constructions, Vol. 19, No. 114, 1986, pp. 423–436.