Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1999–2003

Communication

Indirect determination of the Ca/Si ratio of the C-S-H gel in Portland cements

J.I. Escalante-Garcia*, G. Mendoza, J.H. Sharp

Department of Engineering Materials, The University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

Received 15 December 1998; accepted 25 August 1999

Abstract

An alternative method for the indirect determination of the Ca/Si ratio of the C-S-H gel in Portland cements is proposed. It is based on graphical correlations of experimental determinations of the degree of hydration of alite and the amount of calcium hydroxide formed with theoretical data based on the hydration reactions of the alite and belite present in the cement. The initial composition of the cements is of prime importance in these calculations; the phase composition obtained by use of the Bogue, Taylor's modified Bogue, and quantitative X-ray diffraction methods gave rise to some differences in the results obtained. Ca/Si ratios determined using the Bogue composition were consistently lower than those from Taylor's method and the quantitative X-ray diffraction analysis methods for both the Portland cements studied. The Ca/Si ratios estimated based on the mineralogical phase compositions determined from these latter methods agreed well with those from energy dispersive X-ray spectroscopy measurements.

Keywords: C-S-H; Thermal analysis; Quantitative X-ray diffraction; Portland cement; C/S ratio

1. Introduction

Compositional values for the Ca/Si ratio of the inner product C-S-H in neat Portland cement have been widely reported from several characterisation techniques, with values ranging from approximately 1.6 to 2.0: transmission electron microscopy (TEM), 1.65 to 1.9 [1]; scanning electron microscopy, 1.65 [2] and 1.89 to 2.0 [3]; and calculated 1.74 [4] for several water/cement (w/c) ratios from 0.4 to 0.7 and curing temperatures in the range of 20 to 25°C. It can be noted that these values vary somewhat with the experimental technique used in their determination.

In this paper, we propose an alternative graphical method for the estimation of the Ca/Si ratio of the calcium silicate hydrate (CSH) in Portland cement. The method involves the use of experimental data for the degree of hydration (DOH) of alite, obtained from quantitative X-ray diffraction analysis (QXDA), and the amount of CH formed, determined by thermogravimetric analysis (TGA), after several curing periods. Measured data are graphically matched with the corresponding simulated data in a plot of degree of hydration of alite vs. CH concentration. The simulated data are obtained using the hydration reactions of the calcium silicates, where a Ca/Si ratio is initially proposed and the amount of CH formed is calculated from the chemical equations for the reactions of alite and belite. The Ca/Si ratio is then varied to obtain the best match between the simulated and experimental hydration data.

The key factor in the calculations is the phase composition of the Portland cement, since the amount of CH produced is a function of the relative amounts of alite and belite present in the cement. For this consideration, the most common methods of estimating the potential phase composition of an ordinary Portland cement were employed, namely the Bogue calculation (BC), Taylor's Modified Bogue Calculation (TMBC) [5], and QXDA [6].

2. Methods

2.1. Portland cements and hydration conditions

Two ordinary Portland cements pastes (labelled OPCN and OPCS) were cured under water at 10, 20, 30, 40, and 60°C for up to 1 year. A w/c ratio of 0.5 was employed using freshly boiled distilled water. The hydration products of these samples were characterised after curing periods of 1, 3, 7, 14, 28, 90, 180, and 365 days and the results have been reported elsewhere [7]. Hydration was arrested by hand grinding the samples to produce a relatively fine powder that was placed in a vacuum desiccator for 24 h.

* Corresponding author. Apartado Postal 663, Saltillo, Coahuila, CP. Tel.: +52-84-881019, ext. 265; fax: +52-84-881300/881139.

E-mail address: jieg@saltillo.cinvestav.mx (J.I. Escalante-Garcia)

J.I. Escalante-Garcia is currently at Centro de Investigacion y de Estudios Avanzados (CINVESTAV) Unidad Saltillo, Apartado Postal 663, Saltillo, Coahuila, Mexico, CP 25000.

0008-8846/99/$ – see front matter
PII: S0008-8846(99)00191-X

2.2. Characterisation

After every hydration interval, the amount of CH formed was determined by TGA and the degree of hydration of alite was estimated by means of QXDA, using the methods reported previously [6,7]. The DOH was calculated as the ratio of the amount of anhydrous alite remaining at each time interval to the initial amount of alite in the cement. Samples were examined in a fully automatic Siemens D500 diffractometer, Stuttgard, Germany, in the range of 24 to 39° 2 theta in steps of 0.05° 2 theta with a measuring time of 20 s.

The chemical composition of the cements and the phase composition as determined by the three methods (Bogue, Taylor's Modified Bogue, and QXDA) are given in Table 1.

3. Results and discussion

Data for the degree of hydration of alite and the amount of CH formed (from QXDA and TGA) for the five hydration temperatures for OPCN are plotted in Fig. 1. Least squares regression analysis gave good correlation and the index is shown in Fig. 1. Similar data were obtained for OPCS with slopes and correlation coefficients of 0.17, 0.98 and 0.22, 0.93 for CH from QXDA and TGA, respectively. Only data for alite were used since it is present in much greater amounts than belite, and also since the production of CH from alite is much higher. Moreover, as the Ca/Si ratio of the CSH approaches 2, CH formation from belite tends toward zero (according to the chemical reactions given below), in this way minimising its influence on the calculations.

The theoretical amount of calcium hydroxide expected to form can be calculated as a function of the hydration of the silicate phases present from the chemical equations for their hydration. The reactions are shown in Eqs. (1) and (2).

$$\begin{aligned} &C_3S + \mathbf{z}H \rightarrow C_xSH_y + (\mathbf{3}-\mathbf{x})CH \\ &\quad \text{(for the hydration of alite)} \\ &C_2S + \mathbf{z}H \rightarrow C_xSH_y + (\mathbf{2}-\mathbf{x})CH \\ &\quad \text{(for the hydration of belite)} \end{aligned} \tag{1}$$

where $z = y + 3 - x$ for alite and $z = y + 2 - x$ for belite.

$$\%CH_{C_3S} = \%\text{ hydrated } C_3S \cdot \%\text{ initial } C_3S \cdot \left[\frac{CH_{M.W.}}{C_3S_{M.W.}}\right] \cdot \left[3 - \text{proposed } \frac{C}{S} \text{ ratio}\right] \quad \text{molecular weight (m.w.)}$$

$$\%CH_{C_2S} = \%\text{ hydrated } C_2S \cdot \%\text{ initial } C_2S \cdot \left[\frac{CH_{M.W.}}{C_2S_{M.W.}}\right] \cdot \left[2 - \text{proposed } \frac{C}{S} \text{ ratio}\right] \tag{2}$$

Due to its power and simplicity, a spreadsheet program was used to calculate and construct the simulated curves of CH vs. DOH of the calcium silicates. In this way, the amount of CH formed was easily recalculated and plotted, as the Ca/Si ratio was varied. The effect of the variation in the Ca/Si ratio on the simulated CH production is shown in Fig. 2. For every Ca/Si ratio proposed there is a set of separate lines for fixed DOH of belite (i.e., 0, 20, 40, 60, 80, and 100%) and every one of these lines describes the DOH of alite vs. amount of CH formed. From Fig. 2 it can be seen that as the Ca/Si ratio is reduced, the calculated amount of CH formed increases and the belite lines spread out because its production of CH increases. There is also a change in the slope of the set of lines for each Ca/Si ratio.

Under these conditions, by overlapping the experimental data (as shown in Fig. 2) and adjusting the simulated Ca/Si ratio until the two data sets match up, we can obtain a very good approximation of the Ca/Si ratio in the CSH. An example of this is presented in Fig. 3, which displays data for OPCN based on the QXDA phase composition. The experimental data for OPCN are best matched with a Ca/Si ratio of 2.02. For OPCS the best match was at a ratio of about 1.95.

It is noteworthy that the data for the formation of CH from QXDA were consistently lower than those from TGA for both cements. However, QXDA and TGA data displayed linear correspondence; the regression coefficients (for the five hydration temperatures) are shown in Eq. (3):

$$\begin{aligned} &[\%CH]_{TGA} = 3.86 + 1.02[\%CH]_{QXDA} \qquad R = 0.96 \\ &\quad \text{(for OPCN)} \\ &[\%CH]_{TGA} = 2.47 + 1.04[\%CH]_{QXDA} \qquad R = 0.96 \\ &\quad \text{(for OPCS)} \end{aligned} \tag{3}$$

Table 1
Chemical composition and phase composition determined by three methods for the Portland cements studied

	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	SO_3	Total	Free CaO
OPCN	63.6	20.6	4.6	3.1	0.5	0.9	1.6	3.5	98.4	1.1
OPCS	64.4	20.9	5.7	2.9	0.6	0.6	1.9	2.4	99.4	1.0

	OPCN			OPCS		
Phase	Bogue	QXDA	Taylor	Bogue	QXDA	Taylor
Alite	52.6	71.6	72.3	50.0	65.6	69.4
Belite	19.4	10.9	5.1	22.2	16.4	7.6
C3A	6.9	3.7	4.2	10.2	8.0	8.7
C4AF	9.4	10.7	10.7	8.8	7.4	8.8
Gypsum	7.5	3.1	4.3	5.2	2.4	2.7
MgO	1.6		0.4	1.9		0.6

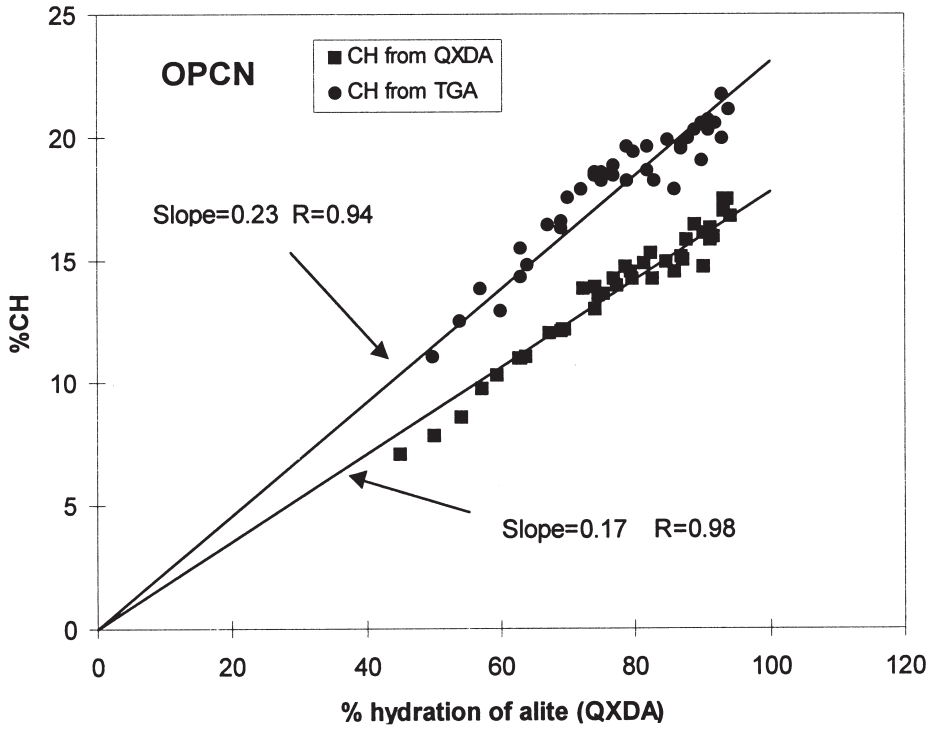

Fig. 1. Percent CH from thermogravimetry and X-ray diffraction analysis vs. percent of hydration of alite from QXDA for OPCN for the five hydration temperatures.

Such differences in CH determination have been reported previously by Midgley [8] and Dalziel and Gutteridge [9]. Midgley proposed that amorphous CH is present and determined by TGA but not by QXDA, hence the higher value for CH from thermal analysis. Dalziel and Gutteridge [9], on the other hand, suggested that the lower values from QXDA might be due to the presence of microcrystalline material and preferred orientation in the powdered sample. Although a possible source of errors in the determination by TGA arises because of the continuous dehydration of the CSH gel present in the paste, we favour the TGA method since it is very difficult indeed to totally eliminate the preferred orientation of CH in the QXDA method. Matching the calculated data shown in Fig. 3 to the CH determined from QXDA gives a Ca/Si ratio of 2.19. This value requires CH to be a reactant rather than a product in the hydration of belite.

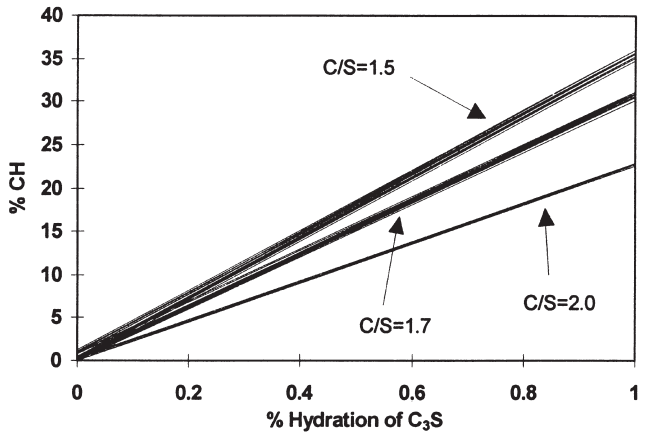

Fig. 2. Simulated CH production as a function of alite and belite hydration for several Ca/Si ratios.

Alternatively, the Ca/Si ratio can be estimated by interpolation using the same data as above. A plot is constructed using pairs of data, i.e., the slope of every set of simulated lines, as shown in Fig. 2 (for every Ca/Si ratio), vs. the corresponding Ca/Si ratio. This is represented in Fig. 4. The Ca/Si ratio can be interpolated by using the slope of the experimental linear fitting of CH concentration vs. DOH of alite (as seen in Fig. 1, i.e., slope = 0.23 for OPCN). A plot like that seen in Fig. 4 has to be constructed for the Ca/Si estimations from each of the cement phase compositions.

The estimated Ca/Si ratios based on the three potential phase compositions are presented in Table 2, which shows estimates using the CH determined from both TGA and QXDA data. Values from the graphical method, which are shown in Fig. 3, were very similar to the interpolated estimates shown in Fig. 4. The interpolated values were slightly lower because the method does not consider the hydration of belite. As the Ca/Si ratio is reduced, the sets of lines tend to spread out (see Fig. 2) and the interpolation uses the lowest alite hydration line. The plots shown demonstrate how small the contribution from the hydration of belite is to the

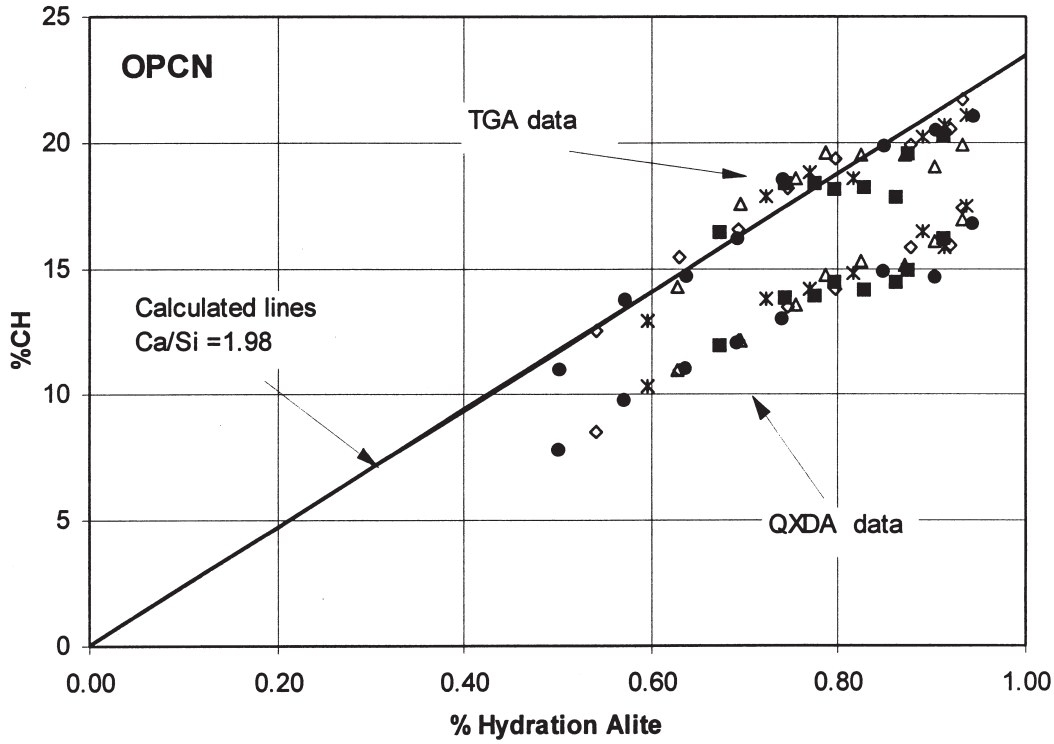

Fig. 3. Example of graphical estimation of the Ca/Si ratio for OPCN and QXDA phase composition. The symbols represent the different hydration temperatures.

amount of CH formed, and hence how little the amount of belite present affects the Ca/Si ratio. This would become more important at lower ratios, such as 1.5, but the errors are negligible at Ca/Si ratios approaching 2.

The Ca/Si ratios estimated from QXDA and TMBC phase composition data, using values for CH determined from TGA, give rise to closely similar values in the range of 1.95 to 2.00 for the two cements. A significant change is observed when the phase compositions from the Bogue calculations are used; the Ca/Si ratios are lower, with values around 1.6 to 1.7. The reason for these reduced ratios, from those obtained when the Bogue calculation was used, is that the method leads to higher belite and lower alite percentages than the alternative methods. Since alite is the major producer of CH, a lower alite content means less CH produced; therefore, the calculated CH data will plot in a lower region, as in Fig. 2. Thus, to obtain higher simulated values of CH, the proposed Ca/Si ratio for the hydration reactions has to be reduced to match the experimental data.

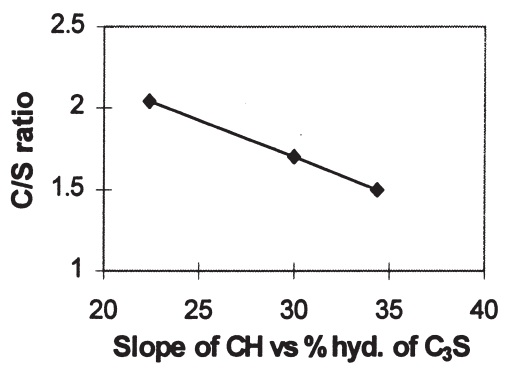

Fig. 4. Estimation of the Ca/Si ratio using the slope method. Data as in Fig. 3.

There is also good agreement between the Ca/Si ratios from QXDA and TMBC (cement composition) with energy dispersive X-ray spectroscopy (EDS-SEM) measurements on the inner products of these cements, which gave Ca/Si ratios averaging 2.06 and 2.07 for OPCN and OPCS, respectively [10]. The methods presented do not have sufficient resolution to detect variations of the Ca/Si ratio with the curing temperature, but perhaps the results presented here indicate that the Ca/Si ratio does not vary much with curing temperature. The variations observed when the composition from the unmodified Bogue method was used were due to the inherent deficiencies of that method, which delivers results of lower accuracy.

It has also to be remembered that the present estimations are for the overall Ca/Si ratio of the CSH as a whole, whereas the EDS data to which the results have been compared related to the inner hydration products only. Also, the method can only be applied to neat cements. It cannot be applied to blended cements, with pozzolanic or hydraulic additions, because of the chemical interactions of the replacement materials with the CH produced by the cement hydration.

Table 2
Estimated Ca/Si ratios for the CSH gel for OPCN and OPCS cements by means of graphical and interpolation methods

	Graphically estimated Ca/Si ratios			Interpolated Ca/Si ratios		
Cement	QXDA	Taylor	Bogue	QXDA	Taylor	Bogue
Using CH (TGA)						
OPCN	1.98–2.03	1.98–2.04	1.73	2.00	2.00	1.63
OPCS	1.92–1.95	1.95–2.00	1.70	1.94	2.00	1.61
Using CH (QXDA)						
OPCN	2.19–2.22	2.20–2.24	1.95–1.98	2.22	2.23	1.94
OPCS	2.11–2.14	2.16–2.20	1.91–1.94	2.18	2.22	1.92

4. Conclusions

A graphical method for the estimation of the Ca/Si ratio of neat cements has been described. It is based on matching experimental data for the degree of hydration of alite from QXDA and determinations of the amount of CH formed from TGA with calculated data from chemical equations describing the hydration reactions of the calcium silicates. Two ways of performing the estimates were proposed; one involves graphical overlapping of the experimental and calculated data, while the other involves interpolation of the estimated Ca/Si ratio in a predictive model from the calculated data.

Estimated Ca/Si ratios from QXDA and TMBC were very similar and consistently higher than the Ca/Si ratio obtained using the classical Bogue calculation. The Ca/Si ratios from the first two agree with data obtained from EDS [10]. Data obtained using the Bogue calculation gave lower Ca/Si ratios since the predicted content of alite in the cement was lower.

Acknowledgments

JI Escalante-Garcia wishes to thank the Mexican National Council of Science and Technology (CONACYT) for a grant that enabled him to carry out this research. The University of Sheffield wishes to acknowledge the gift of the Siemens X-ray diffractometer by the British Cement Association. We are grateful to Walter Gutteridge, David Spooner, and Renhe Yang for helpful discussions.

References

[1] I.G. Richardson, G.W. Groves, Microstructure and microanalysis of hardened ordinary cement paste, J Mat Sci 28 (1993) 265–277.
[2] S.A. Rodger, G.W. Groves, Electron microscopy study of an ordinary portland cement and ordinary portland cement-pulverized fuel ash blended pastes, J Am Ceram Soc 72 (6) (1989) 1037–1039.
[3] A.M. Harrisson, N.B. Winter, H.F.W. Taylor, An examination of some pure and composite portland cement pastes using scanning electron microscopy with X-ray analytical capabilities, in: 8th Int. Cong. Chem. of Cem., Vol. IV, Rio de Janeiro, 1986, pp. 170–175.
[4] W.A. Gutteridge, J.A. Dalziel, The effect of a secondary component on the hydration of portland cement, Part I: A fine non-hydraulic filler, Cem Concr Res 20 (1990) 778–782.
[5] H.F.W. Taylor, Modification of the Bogue calculation, Adv Cem Res 2 (8) (1989) 171–179.
[6] W.A. Gutteridge, Quantitative X-ray powder diffraction in the study of some cementive materials, in: British Ceramics Proceedings No. 35, The Chemistry and Chemical Related Properties of Cement, Glasser F.P., ed., The British Ceramic Society, Stoke on Trent, UK, 1984, pp. 11–23.
[7] J.I. Escalante-Garcia, J.H. Sharp, Effect of temperature on the hydration of the main clinker phases in portland cements: Part I, neat cements, Cem Concr Res 28 (1998) 1245–1257.
[8] H.G. Midgley, The determination of calcium hydroxide in set portland cements, Cem Concr Res 9 (1979) 77–82.
[9] J.A. Dalziel, W.A. Gutteridge, The influence of pulverized fuel-ash upon the hydration characteristics and certain physical properties of a portland cement paste, Cem. Concr. Association, Technical Report 560, 1986.
[10] J.I. Escalante-Garcia, J.H. Sharp, Variation of the composition of the C-S-H in neat portland cements cured at different temperatures, J Am Ceram Soc (in press).