Available online at www.sciencedirect.com

ScienceDirect

Cement and Concrete Research 37 (2007) 551–558

Cement and Concrete Research

The role of calcium carbonate in cement hydration

T. Matschei [a,*], B. Lothenbach [b], F.P. Glasser [a]

[a] *Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Old Aberdeen, AB24 3UE Scotland, UK*
[b] *EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Concrete & Construction Chemistry, Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland*

Received 23 February 2006; accepted 18 October 2006

Abstract

Limestone, mainly consisting of calcite, is a permitted additive to Portland cements often up to a 5 wt.% limit. It is shown by experiment and calculation that much, if not all, of this calcite is reactive and affects the distribution of lime, alumina and sulfate and thereby alters the mineralogy of hydrated cement pastes. Calcite affects the mineralogical variant of the AFm phase(s). Calcite additions affect the amount of free calcium hydroxide as well as the balance between AFm and AFt phases, although C–S–H is unaffected in much of the range of compositions. Generic data are shown in graphical form to quantify these mineralogical changes as functions of cement composition and amount of added calcite. Calculations of the specific volume of solids as a function of calcite addition suggest that the space-filling ability of the paste is optimised when the calcite content is adjusted to maximise the AFt content. However, before the calculated data can be used uncritically, certain kinetic constraints on reactivity also need to be assessed. Progress towards the quantification of paste mineralogy suggests that (i) elucidation of the mineralogy of pastes, particularly blended cement pastes, is facilitated by using both theoretical and experimental approaches and (ii) that the ultimate goal, of calculating paste mineralogy from the bulk chemistry, is attainable.

Keywords: Cement paste mineralogy; AFm; AFt; Calcium carbonate; Phase relations; Thermodynamics

1. Introduction

Portland cement consists of a fine-grained assemblage of minerals many of which have low crystallinity and are difficult to quantify by existing methods. Nevertheless, the materials science of other structural solids has advanced through control of the mineralogy and microstructure. At present we are unable to develop quantitative structure-property relationships for cement pastes because the basic first step, phase characterisation, is incomplete. We know in broad outline the nature of the constituent phases, their composition and coexistence. But many important details, necessary for quantification, are often either incompletely known or unknown.

The relationship between composition and mineralogy was essentially solved for Portland cement clinkers by Bogue some 80 years ago. Bogue utilised the known phase equilibrium relationships in the four component system of lime–alumina–ferric oxide–silica to obtain a series of equations to calculate mineral content. Since Bogue's time the calculation has been refined [1–3] but remains unaltered in principle. It is often argued that, because of the extensive metastability in hydrated cement paste systems, it is not possible to use the same approach for pastes. However brief thought is sufficient to demonstrate that this objection has only limited validity. In the original Bogue calculation, provision was made for corrections for non-equilibrium to be applied, for example to correct for the amount of unreacted lime. Bogue was also well aware that the alite phase was thermodynamically unstable at low temperatures and that its persistence to ambient conditions in the course of clinker cooling was entirely metastable. Nevertheless, because the amount of alite developed at elevated temperatures persisted during cooling in a reproducible and consistent manner, its metastability was not relevant to a successful calculation. We assert that the same logic applies to the calculation of cement hydration: phases develop, albeit sometimes metastably, but in a reproducible and

---

* Corresponding author.
E-mail addresses: t.matschei@abdn.ac.uk (T. Matschei), barbara.lothenbach@empa.ch (B. Lothenbach), f.p.glasser@abdn.ac.uk (F.P. Glasser).

0008-8846/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2006.10.013

consistent manner. Hence their amounts are amenable, in principle, to calculation. Of course hydration is a more complex process than clinkering; whereas an adequate description of clinkering can be accomplished by considering only four components, hydration requires that we add at least two more; water and sulfate (or sulfur trioxide; the two are interchangeable if molar units are used) and, if alkalies are included, two more components, Na_2O and K_2O. However the present treatment will not include alkalies. If the impacts of added calcium carbonate are also taken into account, the system complexity is further increased by addition of another component, carbonate. A system of simultaneous equations can in principle be developed to relate chemistry to paste mineralogy but require much more data for their solution than for clinkers.

In the course of developing compatibility relationships in Portland cements we have initially concentrated on plain cements. A sensitivity analysis disclosed that we had sufficient information on the C–S–H phase to sustain the calculations made here but that the constitution of the minor phases was likely to be very sensitive to clinker sulfate, carbonate and alumina contents. An analysis of the physical chemistry of cement hydration disclosed that this supposition was essentially correct [4]. This reference gives details of the calculations, which were performed using standard computer protocols for the minimisation of free energies of defined systems. Data not in standard compilations but essential for the calculation were obtained and are tabulated in [4]. It was also shown, both by calculation and experiment, that cement pastes were likely to contain several coexisting AFm phases but that normal cements, i.e., those not containing high contents of alkali, had an AFt phase close in stoichiometry to that of ideal ettringite. Hence ettringite could be treated as a phase having essentially constant composition and thermodynamic properties but treatment of AFm was complicated by the need to consider several phases. Other complications emerge but will be dealt with in due course.

The present study, including AFt–AFm phase relations, concentrates on the impacts of calcite on paste mineralogy. Many codes governing the constitution of ”Portland cement” now permit adding up to 5 wt.%. limestone: Portland composite cements may of course contain more than 5 wt.%. Specifications require a minimum calcite composition in limestone: for example, in EN 197, >70 wt.% calcite: in subsequent calculations, we use calcite as a surrogate for limestone. The role of calcite, as inert “filler” or as a reactive admixture (or both), has been much studied [5–12]. Many studies use high levels of calcite, such that most of the calcite acts as a filler. Studies using lower additions, 1–10 wt.%, confirm that mineralogical changes result but are not readily comparable with the approach developed here. An analysis and interpretation of the literature will be presented in a subsequent paper [13].

An unexpected result of the experiments, and of related calculations on the stability of AFm, was to provide new insight into the role of added calcite in cement hydration. We believe this marks an important milestone in understanding the quantitative aspects of cement hydration and report the results here.

2. Results

2.1. *“reactive” vs. “filler” calcite*

Table 1 lists the composition of mainly AFm phases likely to occur in Portland cement and used in the title paper. The particular phase (or phases) of AFm is sensitive to the nature of the characteristic anion — hydroxide, sulfate, or carbonate, or mixtures thereof. It can be seen from the data that low weight percentages of carbonate are sufficient to form hemi- or monocarboaluminate: these phases require only 3.9 and 7.7 wt.% carbonate respectively.

The stability relations as presently understood are shown in Fig. 1, taken from [4] and experimentally proven by Kuzel, et al. [14]. It is important to note that stability relationships were calculated assuming an excess of portlandite: reasons for this will become apparent in the subsequent exposition. Also, that the relations shown in Fig. 1 are unaffected by the presence of “normal” C–S–H; that is, C–S–H having a Ca/Si molar ratio ≥1.7; the exact value probably lies in the range 1.7 to 2.0, such that it also coexists with portlandite, calcium hydroxide. Regions I–III (Fig. 1) involve possibly metastable phases and are delineated by dotted lines. Assemblage III is not only metastable but is also labile in respect of its C_4AH_x content: that is, it is prone to decomposition, especially at high water/solid ratios, over a time scale of days to a few years, depending on temperature.

The diagram, Fig. 1, is constructed for lower temperatures, ~25 °C, such that monosulfoaluminate tends to be persistent, although perhaps not actually stable [4]. The impact of adding calcite on the paste mineralogy can be predicted as follows: select a horizontal line corresponding to the effective sulfur trioxide/alumina ratio, termed the “sulfate ratio”, of the cement.

Table 1
Composition and densities of minerals relevant to Portland cement used in current model

Mineral	Formula	CO_2 [wt.%]	SO_3 [wt.%]	CaO [wt.%]	Al_2O_3 [wt.%]	Density * [g/cm^3]
gypsum	$CaSO_4 \cdot 2H_2O$	–	46.5	32.6	–	2.31
ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	–	19.1	26.8	8.1	1.77
monosulfoaluminate	$Ca_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$	–	12.9	36.0	16.4	2.01
calcite	$CaCO_3$	44.0	–	56.0	–	2.71
monocarboaluminate	$Ca_4Al_2(CO_3)(OH)_{12} \cdot 5H_2O$	7.7	–	39.5	17.9	2.17
hemicarboaluminate	$Ca_4Al_2(CO_3)_{0.5}(OH)_{13} \cdot 5.5H_2O$	3.9	–	39.7	18.1	1.98
hydroxy-AFm	$Ca_4Al_2(OH)_{12} \cdot 7H_2O$	–	–	40.0	18.2	2.05
portlandite	$Ca(OH)_2$	–	–	75.7	–	2.24

* Values taken from Taylor [2].

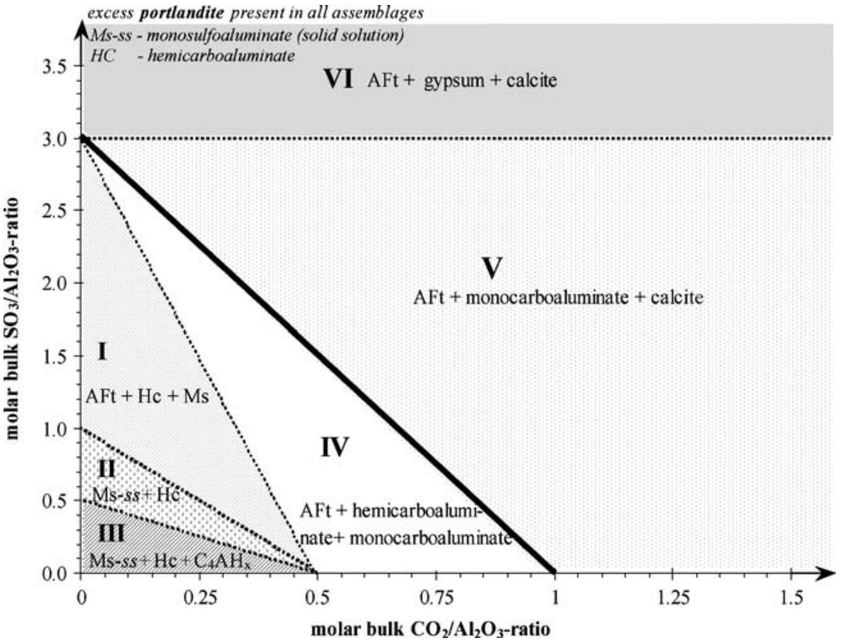

Fig. 1. Calculated phase assemblages of a hydrated mixture consisting of C_3A, portlandite and varying initial sulfate (SO_3/Al_2O_3) and carbonate ratios (CO_2/Al_2O_3) at 25 °C (molar units).

The intersection of this line with a vertical construction line corresponding to the appropriate ratio of carbon dioxide (or carbonate/alumina, termed the "carbonate ratio", will enable the phase assemblage to be calculated with respect to the AFm portion and associated phases, as necessary to preserve mass balances. As can be seen from the slopes of the relevant boundaries, the appearance of hemicarboaluminate and of monocarboaluminate are functions of cement sulfate, carbonate and alumina contents, expressed here as ratios. Calcite totally reacts in regions I, II, III and IV, appearing in excess only in regions V and VI. Since the carbonate content of AFm phases is low and the total content of the phases containing alumina, AFm and AFt is low, not much calcite is required to attain regions V and VI; we calculate this quantity subsequently. Aged hydrated cements are normally undersaturated with respect to gypsum so the phase assemblage corresponding to region VI is not likely to be encountered in practice (altered cements are excepted from this presentation). The boundary between regions IV and V is shown in bold to indicate its special significance as a dividing line between compositions that are either undersaturated or oversaturated with respect to calcite. Compositions to the left of this line are undersaturated: that is, calcite behaves as a reactive admixture and is totally consumed, while those compositions to the right of this line will contain a permanent excess of free calcite; in these regions excess calcite behaves as a filler. Of course the amount of any excess will be less than the total added because some calcite will have reacted. The position of the saturation line (bold) enables the numerical calcite saturation value to be determined in terms of sulfate and carbonate ratios for a given cement composition. Although the figure does not depict the composition of the pore fluid coexisting with solids, we note that an insignificant proportion of the total solids are dissolved in the aqueous phase, assuming realistic water: cement ratios are used: for this reason we do not recommend that the determinative graphs be applied to the very high w/s ratios, $\gg 1$, sometimes used in laboratory simulations.

2.2. Quantification of phases

A disadvantage of Fig. 1 is that it does not enable the amounts of phases to be calculated. Fig. 2 has been constructed to enable this calculation. We present the calculation initially for one ratio, at sulfate/alumina = 1.0. For calculation purposes, a definite amount of portlandite has to be added although the amount in excess is not critical provided an excess is always present. Thus the amount of portlandite can be scaled up or down, as required, without affecting the relative ratios of the other phases except by dilution. It is instructive to begin the explanation with a calcite-free cement by projecting a vertical line at a carbonate ratio equal to zero and subsequently adding carbonate, the impact of which can be visualised by moving the vertical line to the right in small increments, i.e., allowing the calcite ratio to increase. It can be seen that at the outset of calcite addition, very small changes in the calcite ratio result in the rapid consumption and decrease in amount of monosulfoaluminate, while at the same time, the amount of hemicarboaluminate increases rapidly. However sulfate released from monosulfoaluminate does not stay in solution and, because the cement is undersaturated with respect to gypsum, sulfate thus displaced from monosulfoaluminate forms ettringite. This reaction, in turn, requires alumina and consumes portlandite with the result that portlandite contents decrease sharply from the original amount. This is why the calculation needs to be commenced with an excess of portlandite, to avoid its total depletion and thus violate a condition of the calculation. In this specimen calculation, ettringite formation reaction reaches a

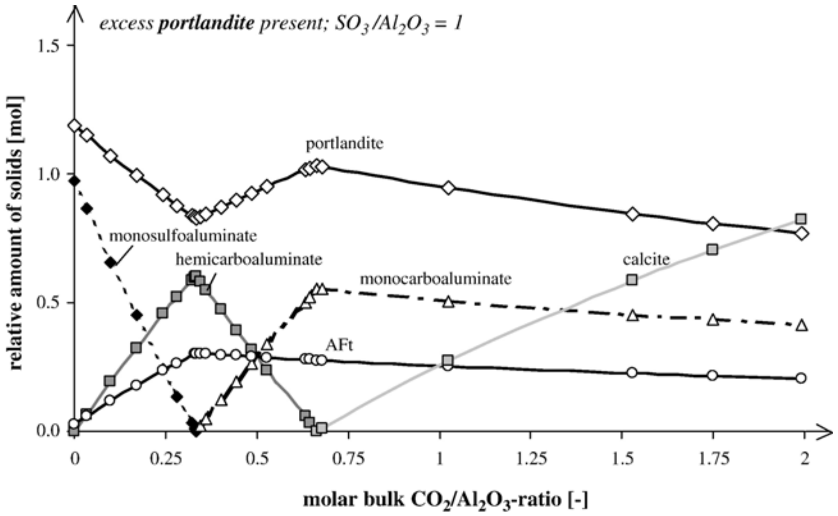

Fig. 2. Relative amount of hydrate phases of a hydrated model mixture consisting of C_3A, portlandite and with fixed sulfate ratio ($SO_3/Al_2O_3 = 1$) in dependence of changing carbonate ratios (CO_2/Al_2O_3) at 25 °C (constant total amount of solids, $C_3A + CaSO_4 + CH + Cc = 3.25$ mol, reacted with 500 g water; data are expressed in molar units).

maximum at a carbonate ratio equal to about 0.33. Thereafter, upon continued addition of calcite, hemicarboaluminate is progressively replaced by monocarboaluminate: the trend of portlandite consumption is reversed and it is now liberated by calcite additions at carbonate ratios in the range between 0.33 and 0.66, approximately. At carbonate ratios at or above 0.66, calcite saturation is achieved and increasing amounts of free calcite will appear as the calcite ratio is increased. This calcite effectively dilutes the other solids and their amounts gradually but slowly decrease as calcite amounts increase. However, because of the scale of the Figure, the dilution effect is only just perceptible.

Of course not all cements will have a sulfate/alumina ratio equal to 1.0. Figs. 3 and 4 are presented to enable the boundary between “reactive” and “filler” calcite to be determined for other ratios; that is, to make the calculation generic. Because the industry tends to work in terms of wt.%, the alumina and sulfate ratios of Figs. 3 and 4 are shown in weight units. Fig. 3 shows how the maximum reactive wt.% of calcite varies with amount of alumina and the sulfate ratio.

It can be seen that for a fixed alumina content, the amount of reactive calcite increases with the amount of sulfate present. Fig. 4 shows a similar plot, of reactive calcite shown as functions of the sulfate ratio and amount of sulfate, as sulfur trioxide. The discussion contains further guidance to appropriate applications of these diagrams to cement proportioning.

2.3. Space filling by cement paste solids

It is instructive to compare the space-filling ability of the solids arising in the course of hydration and the chemical bound water demand of the hydration products. In the example calculation, results of which are shown in Fig. 5, the volume contribution of C–S–H remains essentially constant throughout

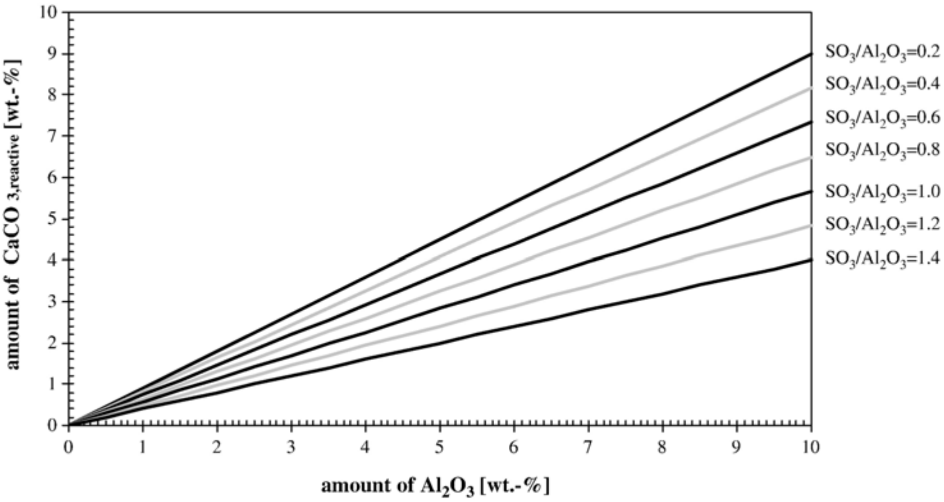

Fig. 3. Calculated amount of reactive $CaCO_3$ in dependence of the initial amount of initial solid Al_2O_3 content and bulk SO_3/Al_2O_3-ratio of the paste (data are expressed in weight units).

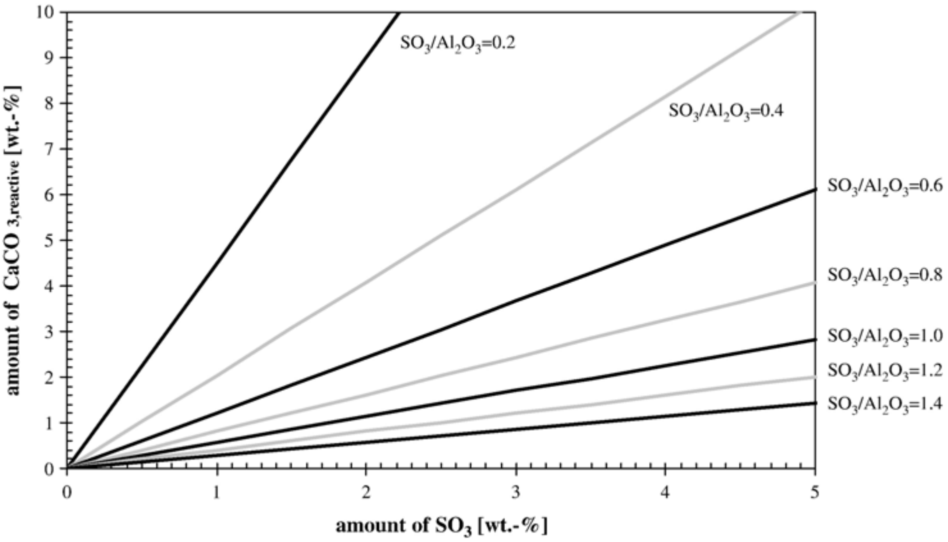

Fig. 4. Calculated amount of reactive $CaCO_3$ in dependence of the initial amount of initial solid SO_3 content and bulk SO_3/Al_2O_3-ratio of the paste (data are expressed in weight units).

(except in regions where calcite is present in excess, where slight dilution occurs). Because of this constancy, or near constancy, the volume occupied by C–S–H is not shown. Moreover, while the numbers selected for the calculations will be affected by the exact composition of the cement as well as the water:cement ratio. But changing the water:solid ratio affects the calculation only in the sense that the amount of free water changes. However the solid phase ratios remain essentially unaffected by the excess water content, up to w/s ~1 and the calculated trends are therefore of general applicability for all practical formulations. The calculation, like that of Fig. 2, depicts changes in mineralogical balances as a function of the carbonate ratio. Data for the densities of phases have been compiled from the literature and are given in Table 1. Results of the calculation show that, commencing with a calcite-free cement (carbonate ratio = 0.0), addition of calcite and its subsequent reaction initially increases the molar volume of the solids and consumes water. Because calcite has a greater density than most cement hydrates, this trend, of increasing the volume of solids by diluting the cement with calcite, seems counterintuitive. But low calcite additions are reactive; free calcite is consumed and, as carboaluminates form, sulfate displaced from the AFm phase forms ettringite. Both AFm and ettringite have lower physical densities than calcite, although the low physical density and high water demand of the ettringite product are mainly responsible for the increase in the volume of

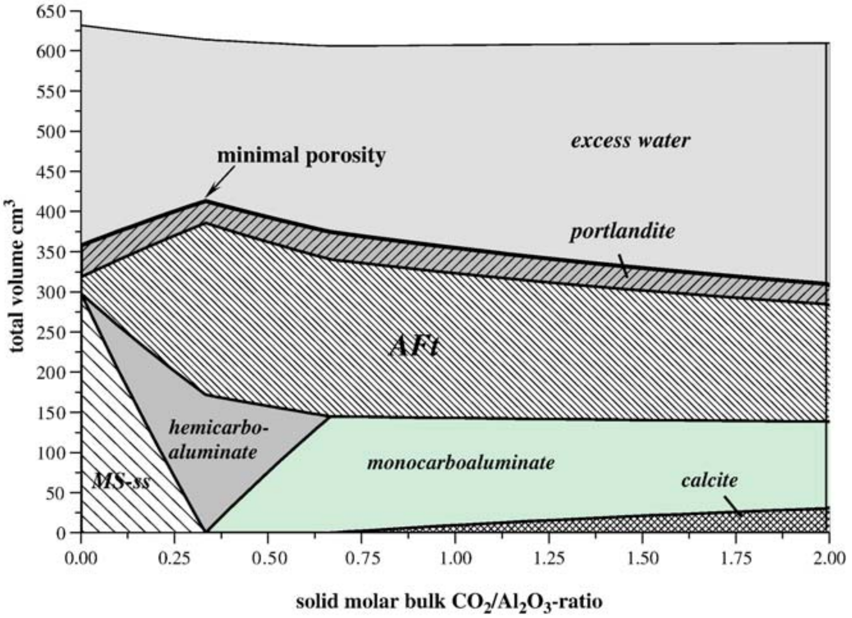

Fig. 5. Volume changes of hydrate phases of a hydrated model mixture consisting of C_3A, portlandite and with fixed sulfate ratio ($SO_3/Al_2O_3 = 1$) in dependence of changing carbonate ratios (CO_3/Al_2O_3) at 25 °C (constant total amount of solids, $C_3A + CaSO_4 + CH + Cc = 3.25$ mol, reacted with 500 g water).

the solids. The bound water content is also increased because calcite, essentially anhydrous, is converted to hydrated phases, thereby binding more water. In this example, the maximum solid phase volume is achieved at a carbonate ratio approximately 0.33, i.e., considerably less than the maximum amount of reactive calcite; the latter occurs at a carbonate ratio approximately 0.66. Thus the point of maximum volume is sensitive to composition and does not necessarily coincide with the maximum amount of reactive calcite. Note also that the volume of portlandite also changes because it is either consumed or produced in the course of reactions, as was explained previously. In commercial cements, where C–S–H develops, C–S–H dilutes the volume change effects arising from calcite reactions but its presence as a diluent does not affect the general conclusions or trends of numerical values described above. Other limitations to the applicability of the data are described in the discussion.

3. Discussion

3.1. Hydration kinetics

The foregoing calculations are based on the simplistic assumption that the chemical components of the cement, as revealed by a bulk chemical analysis, are available for reaction. This is probably not true for real cements. Clinker grains have a range of sizes and complex internal microstructures, with the result that different clinker phases hydrate at different rates and may be partly protected from hydration, perhaps by occlusion within phases with low reactivity. Thus, for example, alumina in tricalcium aluminate may become available at an earlier stage of hydration than alumina in ferrite. Sulfate, nominally in the form of added calcium sulfate and alkali sulfates, is typically available for reaction at an early stage of hydration, although it is not unknown for sulfates to be physically occluded within clinker grains only becoming available for hydration at longer ages [15]. Thus key components, including alumina, sulfate and carbonate are present in clinker in a range of forms and while these range in dissolution rates, with few exceptions, all sulfate becomes available early (hours, days) in the hydration process: typically most of the gypsum interground with clinker is consumed within the first few days of hydration whereas some of the alumina becomes available only over much longer time scales. Therefore detailed and realistic calculations would have to make use of the reactive fraction of these phases: the “composition” that determines the hydrate mineralogy is not necessarily the bulk composition as determined from a total chemical analysis but is instead the sum of the time-dependent reactive fractions of each component liberated from the clinker solid phases. To quantify these amounts requires a series of “snapshots” on the state or condition of the system with changing time. While the relevant hydration kinetics are not sufficiently well known– and indeed almost certainly vary with non-chemical factors such as clinker granulometry and microstructure of the individual grains– we know in general that sulfate ratios tend to be high at the outset of hydration owing to the ready solubility of gypsum, and to decrease as hydration progresses. We do not know how carbonate ratios are affected by these practical considerations and an important task for those who determine reaction kinetics is to quantify how reactive fractions change as a function of time, as well as with changing bulk composition and formulation. In summary, the foregoing calculations assume that the bulk chemistry is relevant but, almost certainly, kinetic controls operate somewhat to modify the picture presented here. Typically the effective sulfate ratio will be somewhat higher during early hydration than is assumed in the calculations. Reference to the Figures shows that, other factors remaining unchanged, increasing the sulfate ratio decreases the potential for consuming calcite. Thus calcite will initially react in response to the effective sulfate ratio, leaving potential for slower secondary reactions to occur. These slow reactions will result in continuing calcite consumption with time as clinker hydration approaches completion.

3.2. Volume changes

We calculate volume changes attending calcite additions in the expectation that these calculations, or very similar calculations, will eventually be used to develop property-composition correlations for hardened cement pastes. The calculations implicitly assume that the volume changes attending reaction of calcite with cement components occur after the paste has hardened but do not lead to changes in external dimensions of a paste monolith i.e., they are not expansive. If this supposition is correct, calcite addition can be used creatively, to improve space filling by solid hydration products and thereby lower product porosity. Because the relationships between porosity and permeability are complex, lowering porosity will not necessarily reduce permeability, but a literature survey [5–12] suggests that calcite does affect both the porosity and permeability of Portland cement pastes, although no consistent patterns seem to emerge. Nevertheless the property-composition correlations developed here should give fresh direction and focus to these studies leading, for example, to focus investigations on the impact of calcite additions in the lower concentration range, perhaps up to a maximum 5–10% replacement, and of optimising the % of calcite from knowledge of the cement composition.

3.3. Thermal factors and relevant databases

At present, data are only sufficient to sustain calculations at about 25 °C. Nevertheless, cements experience a wide range of service temperatures and may encounter strong self-heating early in their life cycle, as the heat of hydration is not always readily dissipated. The temperature dependence of the thermodynamic properties of AFm phases are known to impact significantly on phase development: for example hydroxy AFm is unstable but persistent at low temperatures, less than 20 °C but is increasingly decomposed at elevated temperatures. More data on the stability of carboaluminates, especially for hemicarboaluminate, are needed before the calculation of paste properties can usefully be extended across the range of temperatures relevant to normal civil engineering applications, 0–50 °C. Finally, just as the Bogue calculation has been modified as more knowledge of phase compositions accrues, so the database used in this study will need periodic assessment which, in turn, will enhance the accuracy of calculations. For example, in the Bogue calculation, including the *actual* compositions of alite, belite, etc, rather than ideal formulae, has been found to improve agreement with other methods for the determination of clinker mineralogy [1,2]. Thus the present set of calculations will eventually require modification to take into account factors such as sorption by C–S–H of sulfate, alumina and possibly carbonate. In anticipation of these needs studies of sulfate sorption by C–S–H have been commenced and will be reported in due course.

Data obtained in the course of this study also apply to the reactivity of coarse limestone aggregate. In theory, limestone aggregate is predicted to be reactive with cement in the same way as high specific surface limestone. The same conditions apply to aggregate; except that for coarse aggregate, the kinetics of reaction with cement are likely to be appreciably slower: not only is the surface area available for reaction much reduced but diffusion paths for other species, e.g., alumina, tend to lengthen as reaction progresses. When clinker is interground with limestone, the many observations in the literature showing rapid formation of monocarboaluminate in hydrating pastes suggests that reaction is rapid. It is also likely that the potential of coarse limestone aggregate to react with cement can be reduced or even eliminated by saturating the cement matrix in carbonate, as may occur when sufficient fine-grained reactive calcite is included in the cement formulation. Thus if the matrix is calcite saturated, the potential for subsequent reaction of cement with limestone aggregate can be reduced to zero, with consequences for the development of bonding between aggregate and paste.

We do not treat carbonation from external sources in this presentation. All the processes described here occur at low carbonate activities, many orders of magnitude less than typically obtain in the course of atmospheric carbonation. Nevertheless cements undergoing carbonation develop gradients in carbonate and, even if not made with carbonate admixtures, may experience the mineralogical changes described here. Spatially low carbonate mineralogical zones are most likely to develop ahead of the main carbonation front. The mineralogical zonation developed in the course of atmospheric carbonation has also been calculated and will be presented in [16].

It is also noteworthy that adding carbonate in the form of calcium carbonate to cement slightly reduces its buffering capacity towards subsequent carbonation, for example in atmospheric carbonation. If protection of embedded steel is important, it is desirable that improvements in cement performance, for example reduced permeability arising from calcite addition, should outweigh the loss in buffering capacity.

4. Conclusions

Phase relations amongst AFm phases in Portland paste cement are complex: depending on activities of the principal substituent anions, carbonate, hydroxide and sulfate, several AFm phases may coexist. Although not all the AFm phases are stable, most are persistent in pastes. However carbonate AFm phases are thermodynamically more stable than hydroxy or sulfate phases and it is not surprising that hydroxide and sulfate anions are released from AFm even at the low carbonate activities conditioned by the presence of added calcite (or other calcium carbonate form). With the prevalence of "filled" cements made using up to 5% calcite, it is important to accept that much, perhaps all, of the added calcite will be reactive with cement. Thus calcite has two functions, one as an active participant in the hydration process, the other as an inert filler. The boundary between "active" and "inert" calcite can be calculated on a generic basis: graphical solutions and specimen calculations are presented. The calculations also disclose that sulfate, liberated from sulfoaluminate in the course of carbonation, reacts with water, calcium hydroxide, etc., with formation of ettringite. The additional ettringite formation increases the molar volume of paste solids and it is proposed that this mechanism can be deployed to enhance the space-filling properties of paste, possibly leading to reduction of porosity and permeability of hardened cement pastes. The space-filling reactions occur rapidly, within a few days, using calcite-containing rocks (e.g. limestone) interground with clinker to cement fineness but may be much slower with limestone aggregates.

Acknowledgement

The support of NANOCEM, a European industrial/academic partnership for fundamental research on cementitious materials, is acknowledged.

References

[1] L.P. Aldridge, Accuracy and precision of phase analysis in Portland cement by Bogue, microscopic and X-ray diffraction methods, Cement and Concrete Research 12 (1982) 381–398.

[2] H.F.W. Taylor, Cement Chemistry, 2nd edition, Thomas Telford Publishing, London, 1997.

[3] T.I. Barry, F.P. Glasser, Calculation of Portland cement clinkering reactions, Advances in Cement Research 12 (2000) 19–28.

[4] T. Matschei, B. Lothenbach, F. P. Glasser. The AFm-phase in Portland cement. Cement and Concrete Research, in press.

[5] K.D. Ingram, A review of limestone additions to Portland cement and concrete, Cement and Concrete Composites 13 (1991) 165–170.

[6] P. Livesey, Strength characteristics of Portland-limestone cements, Construction and Building Materials 5 (1991) 147–150.

[7] T. Vuk, V. Tinta, R. Gabrovsek, V. Kaucic, The effects of limestone addition, clinker type and fineness on properties of Portland cement, Cement and Concrete Research 31 (2001) 135–139.

[8] S. Tsivilis, G. Batis, E. Chaniotakis, Gr. Grigoriadis, D. Theodossis, Properties and behavior of limestone cement concrete and mortar, Cement and Concrete Research 30 (2000) 1679–1683.

[9] S. Tsivilis, E. Chaniotakis, G. Kakali, G. Batis, An analysis of the properties of Portland limestone cements and concrete, Cement and Concrete Composites 24 (2002) 371–378.

[10] S. Tsivilis, J. Tsantilas, G. Kakali, E. Chaniotakis, A. Sakellariou, The permeability of Portland limestone cement concrete, Cement and Concrete Research 33 (2003) 1465–1471.

[11] N. Voglis, G. Kakali, E. Chaniotakis, S. Tsivilis, Portland-limestone cements. Their properties and hydration compared to those of other composite cements, Cement and Concrete Composites 27 (2005) 191–196.

[12] H. El-Didamony, T. Salem, N. Gabr, T. Mohamed, Limestone as a retarder and filler in limestone blended cement, Ceramics-Silikaty 39 (1995) 15–19.
[13] T. Matschei, F.P. Glasser, Role of ground limestone in cement hydration — a review with new data, Proceedings of Nanocem Workshop on Limestone in Cement, Copenhagen, April 2006.
[14] H.J. Kuzel, H. Poellmann, Hydration of C_3A in the presence of $Ca(OH)_2$, $CaSO_4 \cdot 2H_2O$ and $CaCO_3$, Cement and Concrete Research 21 (1991) 885–895.
[15] A. Kurdowski, Role of delayed release of sulphates from clinker in DEF, Cement and Concrete Research 32 (2002) 401–407.
[16] T. Matschei, F.P. Glasser. Interactions between Portland cement and carbon dioxide. Submitted for publication to Proceedings of the 12th Intern. Congress on the Chemistry of Cements, Montreal.