

Prediction of Cement Hydration

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ABSTRACT

The solution of many problems of concrete performance (e.g. those relating to curing, carbonation, shrinkage etc.) would benefit from a knowledge of in-situ microstructure and moisture state and how these vary with time and location under realistic exposure conditions. In developing a model of in-situ microstructure and moisture state it is necessary to consider, among other things, how free water diffuses, controls local rates of hydration, is consumed by the reaction and causes gradients of microstructure and moisture content with respect to the exposed surface. A simple method of estimating cement hydration, that can be used in such modelling, is developed in this report. Input parameters include water/cement ratio, moisture history, compound composition and specific surface of the cement. The outputs give the fraction of each compound hydrated, total heat evolved and bound water content as a function of age. The kinetics are considered for each of the four main compounds in cement and suitable factors are then applied to obtain the related bound water and heat evolution contributions. Although not all of the complexities of cement chemistry have yet been considered the approach yields estimates of hydration that are in reasonable accord with experimental data.

INTRODUCTION

This report describes part of a study on the prediction of the microstructure, moisture content and property gradients that develop in concrete exposed to normal environmental moisture conditions. These gradients are thought to be relevant to the quality and mass transport properties of concrete near the exposed surface and in particular to the durability of reinforced concrete. Development of a predictive model encourages the useful assimilation of current and published experimental research and helps to answer technical questions that arise when industrial practices or materials change. For example, Portland cements in the UK have gradually changed over the last 50 years (1) and it is natural therefore to ask if compressive strength is still to be regarded as a satisfactory indicator of concrete quality. Alternatively we might ask if new concrete structures made using modern materials and traditional construction methods and design procedures will remain maintenance-free. Such questions are difficult to answer but if we can identify and model hydration, porosity and diffusion coefficient gradients in concrete the task becomes simpler and the answers will seem more credible. Furthermore the role of basic research as a tool for developing the uses of concrete will become clearer both to the engineer and to the researcher.

An obvious first stage in modelling the in-situ microstructure of concrete is to model the main characteristics of cement hydration and this constitutes the central theme of the present report. Further reports will examine the prediction of porosity and diffusion properties and the synthesis of these components into a model of microstructure, moisture and property gradients in concrete.

SCOPE

A central consideration of the proposed modelling is the role played by water as it

- (a) is lost or gained at a boundary due to environmental factors
- (b) develops concentration gradients with respect to the drying boundary
- (c) is held in pores by capillary condensation and thereby restricts diffusion
- (d) affects the current rate of cement hydration

The last factor will be examined in detail in this report. Although hydration involves chemical binding of water it can also be regarded as the consumption of anhydrous cement compounds. This view has the attraction that the consumption of individual cement minerals can be measured (by x-ray diffraction) and their relative importance assessed. The heat evolved during cement reactions has also been used as a measure of hydration and will be considered in this report. It has the advantage that it can be continuously monitored and furthermore it is of direct technical significance.

The approach developed here will use X-ray diffraction data to assess the different levels of hydration of each cement compound. The chemically bound water and heat evolved is then calculated for each compound. The degree of hydration, bound water and heat evolution for the cement will be estimated on the basis of the relative weight fractions of each compound. The surface area of the cement, the water/cement ratio and a simple indicator of moisture state will be introduced as moderators of the hydration rate.

A wide range of cements will be examined so predictions will normally be based on interpolation. Also the kinetic aspects of hydration will be linked to standard reaction rate equations where possible in an effort to minimise the empiricism of the approach. However, the formulations developed later will still contain a substantial measure of empiricism and they are best regarded as a means for making some of the existing data on cement hydration more usable. An additional function of this report is to provide bases for assessing the importance of potential research topics and for incorporating new results to give additional refinement. Areas that are regarded as important for future refinement, but are not covered here, include the effects of temperature, blended pulverised fuel ash, variations in the reactivity of individual compounds, chemical interactions of tricalcium aluminate with sulphates and alkalis, distribution of compounds within cement grains, and the formation of individual cement hydrates.

METHODS

Published data will be considered together with new experimental data in the later sections of this report. Brief method descriptions are given below as background to the new data.

The cement materials were hand mixed with distilled water and cast in moulds. The moulds were sealed and slowly rotated during setting to avoid sedimentation of the cement.

Thermogravimetric analysis (2) was performed on samples that had been dried by solvent exchange techniques (3) or by direct drying in a desiccator at 33% relative humidity, 20°C. 20 mg samples were heated at 2°C/minute in dry nitrogen up to 750°C. A less refined method of estimating chemically bound water was also used wherein the loss of weight was measured between 105 and 900°C. These two thermogravimetric methods yielded similar estimates of bound water.

The quantity of each unreacted cement compound was determined by X-ray diffraction with Cu K α radiation using a Siemens D500 Automatic powder diffractometer (4). Heat evolution at 20°C was measured continuously from the time of water addition up to 28 days using a conduction calorimeter (5).

MODELLING HYDRATION

The progress of hydration is estimated by integration of equations that represent the rate of hydration of each compound. Thus for each compound we can write

$$D_t = D_{t-1} + \Delta t \cdot R_{t-1}$$

where D is the degree of hydration based on compound consumption

Δt is the time interval for integration

R is the rate of hydration

A series of equations can be used to estimate values of R in terms of D (6) and the lowest value of R (i.e. the rate controlling value) is selected for calculating the new value of D. The equation that yields the lowest rate will vary with the degree of hydration. The literature on hydration of cement compounds and cements suggested that the following rate equations might prove useful.

$$\text{Nucleation and Growth} \quad R = \frac{K_1}{N_1} (1-D) (-\ln(1-D))^{(1-N_1)} \quad (1)$$

$$\text{Diffusion (3 dimensional)} \quad R = \frac{K_2 (1-D)^{2/3}}{1 - (1-D)^{1/3}} \quad (2)$$

Preliminary trials suggested that the diffusion equation could not predict the later stages of hydration. Other standard equations were worse than this diffusion equation so the following equation was tried and found to be successful with a range of hydrating materials:

$$R = K_3 (1-D)^{N_3} \quad (3)$$

Our knowledge of the later stages of hydration suggests that a coating develops around the grains of unhydrated cement thus creating a barrier that slows down the transport of dissolved species. Equation 3 is an empirical representation of this process.

The constants K and N in equations 1, 2 and 3 are estimated from the available experimental data for the hydration of individual compounds in Portland cement. Although the data from various experiments were scattered, Figures 1 to 4, a reasonable representation was obtained using the coefficients in Table 1.

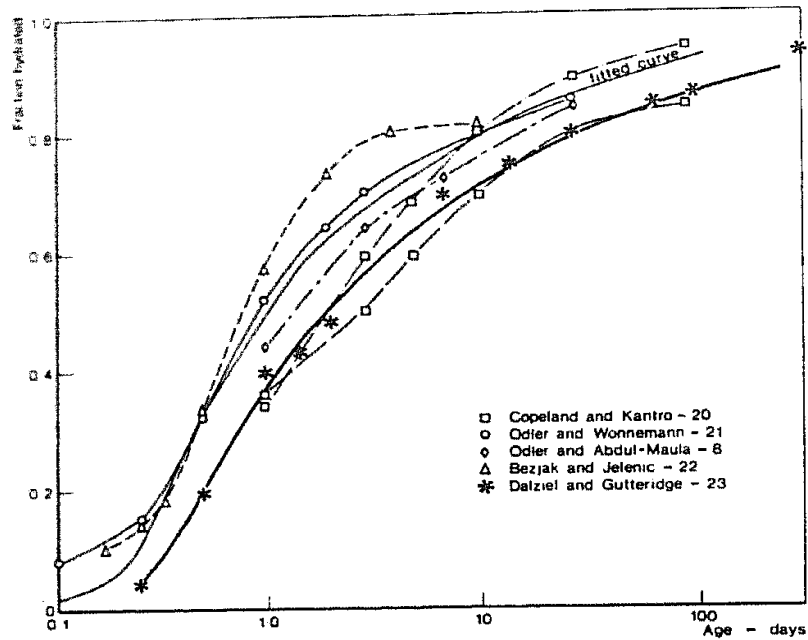


Fig. 1: Hydration of alite by x-ray diffraction

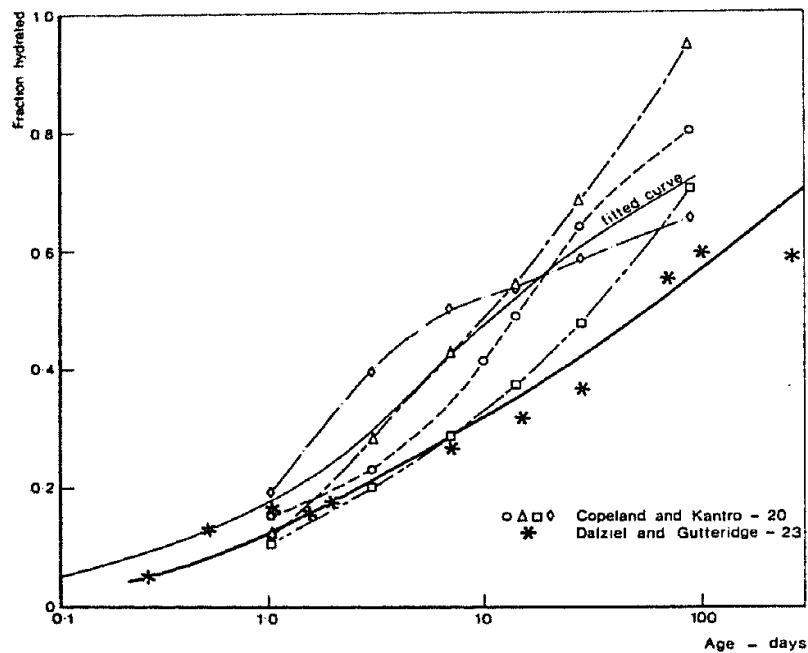


Fig. 2: Hydration of belite by x-ray diffraction

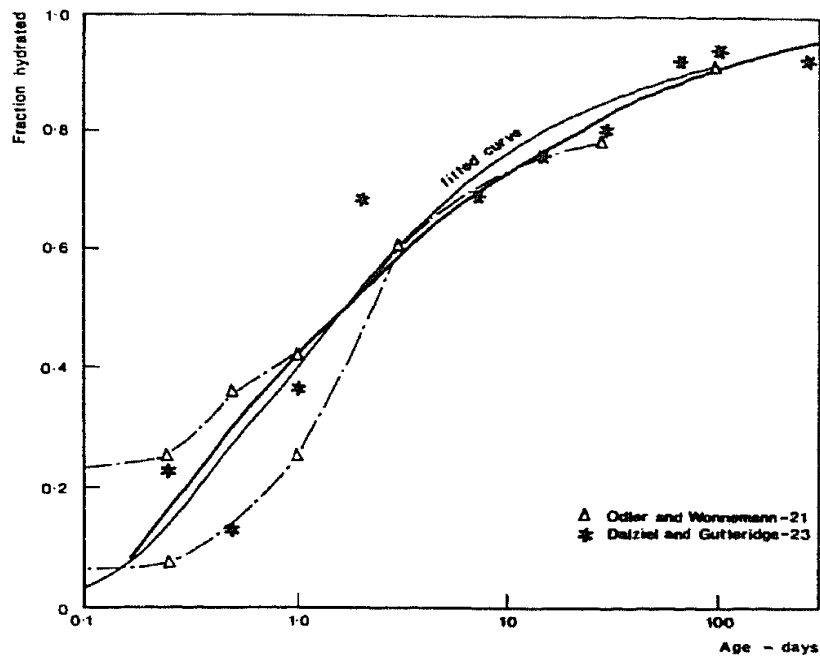


Fig. 3: Hydration of tricalcium aluminate by x-ray diffraction

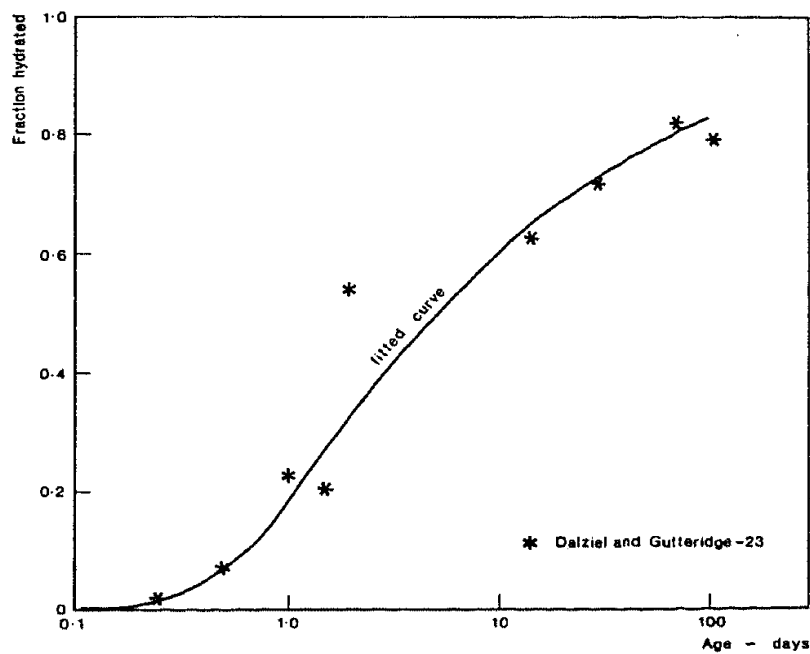


Fig. 4: Hydration of tetracalcium aluminoferrite by x-ray diffraction

TABLE 1 VALUES OF K AND N FOR CEMENT COMPOUNDS

Cement compound*	Equation 1		Equation 2	Equation 3	
	K1	N1	K2	K3	N3
Alite, C ₃ S (8,20,21,22,23)	1.5	0.7	.05	1.1	3.3
Belite, C ₂ S (20,23)	0.5	1.0	.006	0.2	5.0
Tricalcium aluminate, C ₃ A (20,23)	1.0	0.85	.04	1.0	3.2
C ₄ AF (23)	.37	.7	.015	0.4	3.7

Early age data are scarce for all compounds and there are very few data pertaining to C₃A and C₄AF hydration in Portland cement at later ages. Thus the constants in Table 1 should be revised as more data become available.

The degree of hydration of each compound is used to estimate the degree of hydration of the cement (D_{opc}), the bound water content (WN_{opc}) and the heat evolved (H_{opc}) by substitution in the following equations:

$$D_{opc} = DA \times A + DB \times B + DC \times C + DF \times F \quad \dots (4)$$

$$WN_{opc} = WNMA \times DA \times A + WNMB \times DB \times B + WNMC \times DC \times C + WNMF \times DF \times F \quad \dots (5)$$

$$H_{opc} = HMA \times DA \times A + HMB \times DB \times B + HMC \times DC \times C + HMF \times DF \times F \quad \dots (6)$$

where A, B, C and F are the relative weight fractions of alite, belite, C₃A and C₄AF initially present in the cement

DA, DB, DC, DF are the degrees of alite, belite, C₃A, and C₄AF hydration

WNM and HM are the bound water content and heat evolved at full hydration

It should be noted that these equations imply an independence of compound hydration from the presence of other compounds and that a given increment of hydration produces the same effect regardless of the level of hydration. These points will be discussed in more detail in the next section. An attraction of equations 4, 5 and 6 is the unity achieved by the recurrent terms that represent the degree of hydration and the relative weight fraction of each compound. The WNM and HM terms in equation 5 and 6 define how the different measures of hydration are related. Table 2 gives values

* standard cement oxide notation C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃

for the WNM and the HM terms that were based upon published literature and new experimental data.

TABLE 2 BOUND WATER AND HEAT OF HYDRATION FOR FULLY HYDRATED CEMENT COMPOUNDS

Cement Compound	Bound water (kg/kg cement) (Ref. 7, 8, 9, 10)	Heat of hydration (kJ/kg) (Ref. 11, 12, 13)
Alite	WNMA = .235	HMA = 490
Belite	WNMB = .20	HMB = 222
Tricalcium aluminate, C_3A	WNMC = .55	HMC = 1355
C_4AF	WNMF = .25	HMF = 448

Three more variables are included in the modelling of hydration and these are specific surface area of the cement, moisture conditions and water/cement ratio. Surface area affects the rate of hydration and as a first approximation it is assumed that the hydration rate of each compound is proportional to the surface area of the cement. Previously unpublished data on heat evolution suggests that this is a reasonable approximation at low degrees of hydration but at later stages the effect of surface area upon rate of hydration is small enough to be ignored, Figure 5.

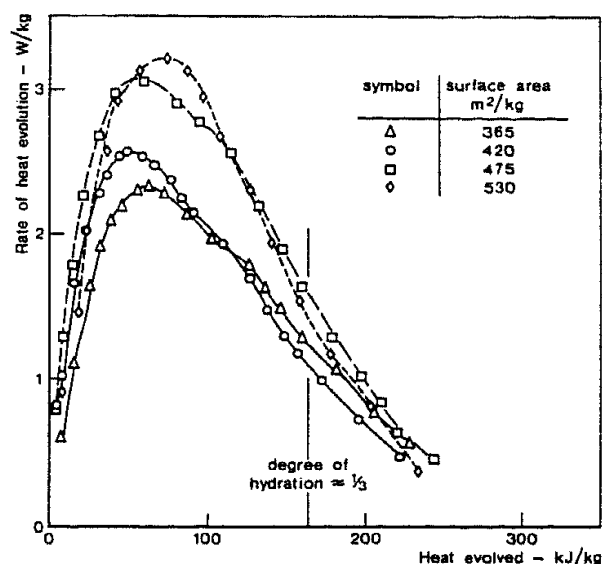


Fig. 5: Effect of surface area of cement upon hydration of Portland cement (Alite = 0.50, Belite = 0.22, C_3A = 0.065, C_4AF = 0.102, w/c = 0.5)

Thus it will be assumed that only equation (1) should be supplemented with a surface area term. It should be mentioned that the effect of surface area upon hydration was not consistent for all cements and in one case there was no significant change of hydration rate as the surface area was increased from 365 to 585 m²/kg. The relationship used to represent the effect of surface area upon hydration rate was based upon a range of cements.

The effect of moisture content upon hydration rate has not been researched in any detail in spite of the fact that concrete is often subjected to drying conditions. A review of published papers (14-17) suggests that hydration rates of Portland cement drop rapidly with a reduction in ambient relative humidity. The following equation is shown in Figure 6 to give a reasonable representation of the available data

$$f(r.h.) = \left[\frac{rh - .55}{.45} \right]^4$$

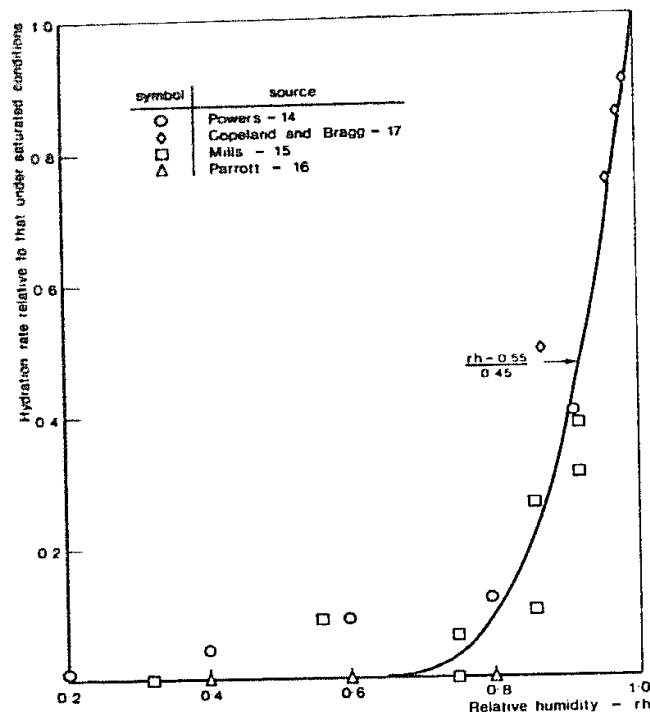


Fig. 6: Effect of relative humidity upon relative rate of Portland cement hydration

It is assumed that this function is applicable to the hydration rate of each compound since no data for individual compounds hydrating in Portland cement are known to be available.

Taplin (18) has shown that the rate of cement hydration is significantly reduced at later ages with low water/cement ratios. This effect seems to relate to the lack of larger pores in which new hydration products can readily form (15) and possibly it could be modelled in terms of an appropriate critical porosity. Since we are not dealing with porosity in this report another approach is adopted wherein the hydration is reduced by

a factor, $f(w/c)$ when a critical degree of hydration, DCR is exceeded. The critical degree of hydration is given by

$$DCR = 1.333 (w/c)$$

$$\text{and for } D > DCR \quad f(w/c) = (1 + 4.444 (w/c) - 3.333D)^4$$

where w/c = water/cement ratio

D = current degree of cement hydration

For values of $D < DCR$ the factor $f(w/c)$ is unity.

HYDRATION OF INDIVIDUAL COMPOUNDS

The data shown in Figures 1 to 4 relate to the hydration of individual compounds in Portland cement. Hydration of single compounds and powder blends of selected compounds has also been studied experimentally to clarify chemical and physical interactions. Physically the surface available for the reaction of a compound is restricted in Portland cement by the formation of a C_3A plus C_4AF matrix around grains of alite and belite (19). No such restriction is present with compounds hydrated individually or in powder blends. The hydration of a particular compound may also be affected by the presence of other compounds via their effect upon the chemical environment. This can be checked by comparing the hydration of a single compound with hydration of the same compound in a Portland cement or an appropriate powder blend.

An interesting feature of alite hydration is that hydration in isolation and in powder blends does not differ markedly from that in Portland cement. Alite is the major compound in Portland cement and this lack of interaction supports the additive hydration approach used in the modelling.

Belite hydration, on the other hand, is affected by the presence of other compounds. Generally belite hydration seems to be accelerated by other compounds both in Portland cement and in powder blends. However, Figure 2 and the results of Odler and Schuppstuhl (17) suggest that within the limited range of belite contents normally encountered in Portland cement (i.e. 10-30%) belite hydration can be regarded as independent of other compounds. Errors associated with such an assumption will not be large when estimating hydration of Portland cement since they will usually be moderated by the low weight fraction of belite present in cement.

C_3A and C_4AF hydration in isolation or in the presence of sulphates are very rapid but their hydration rates are much slower in Portland cement. Also when C_3A was powder blended with alite the C_3A hydration rate was reduced (unpublished data). Following the same logic as for belite it will be assumed that in typical Portland cements the hydration of C_3A or C_4AF is independent of other compounds. It may be possible to amend these assumptions when more experimental data become available: in particular it may become possible to account for interactions between C_3A and sulphates.

COMPARISON BETWEEN PREDICTED AND MEASURED DATA

Comparison of prediction with measurement is not appropriate for published hydration data based upon x-ray diffraction since they were used in the development of the model. Figures 1 to 4 show the fitted curves obtained with the coefficients in Table 1 and equations 1, 2 and 3.

Data from Verbeck and Foster for 20 cements were analysed with the aid of the prediction model and the heat evolution results are shown in Table 3. The coefficient of correlation between the observed and predicted data,

TABLE 3 OBSERVED (13) AND PREDICTED HEAT EVOLUTION

Age (days)	3	7	28	91	365
Observed mean (kJ/kg)	234	297	364	397	423
Predicted mean (kJ/kg)	234	285	356	397	423
Standard deviation of prediction error (kJ/kg)	26	18	12	8	8

based upon 100 data sets, was 0.97. The good agreement between observed and predicted data is encouraging since the range of cements used by Verbeck and Foster covered a wide range of compositions and surface areas. Predictions at early ages were less good than those at later ages.

Verbeck and Foster also reported bound water results and the corresponding analysis is shown in Table 4. The coefficient of correlation between

TABLE 4 OBSERVED (13) AND PREDICTED BOUND WATER

Age (days)	7	28	91	365
Observed mean (g/g ign. $\times 10^{-3}$)	137	166	187	200
Predicted mean (g/g ign. $\times 10^{-3}$)	131	166	189	205
Standard deviation of prediction (g/g ign. $\times 10^{-3}$)	12.5	9.7	8.1	9.9

the observed and predicted data, based upon 73 data sets, was 0.95.

The predicted effect of water/cement ratio is illustrated in Figure 7 together with experimental data from Taplin (18). The predicted data are in reasonable general agreement with the measured bound water data. Direct correspondence between predicted and measured data was not observed because the definitions of bound water were different.

Figure 8 suggests that further refinement of the modelling may be necessary at early ages although the effect of surface area upon heat evolution seems to be adequately accounted for. Early age predictions of heat evolution were high for a number of modern cements but the source of this discrepancy is not known. A limited range of bound water content measurements for the same cements have not shown the same trends so it is possible that the values of HM in Table 2 should be revised. Current studies at the Cement and Concrete Association include parallel measurements of heat evolution, bound water and hydration of individual compounds for a range of Ordinary Portland Cements. The results from these studies should help to isolate the cause of the discrepancy, assist with revision of the

data in Tables 1 and 2 and indicate the overall accuracy that can be expected from the present, simple model. It may prove necessary to introduce additional input parameters if significantly better early age predictions are required.

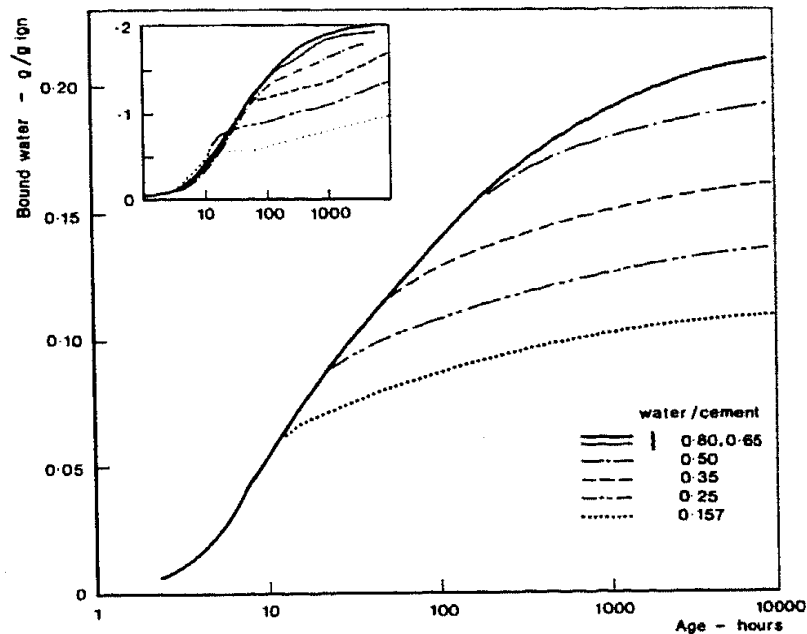


Fig. 7: Predicted effect of water/cement ratio upon bound water development (experimental data of Taplin (18) shown inset)

Although it will not be reviewed in detail here the function relating the rate of hydration and relative humidity, $\left[\frac{rh - .55}{.45}\right]^4$, has

been used to predict successfully the gradients in hydration that were measured near to the exposed face at a drying section of concrete. The dependence of hydration rate upon relative humidity is critical in controlling microstructural gradients in drying concrete and thus influences the quality of the concrete that provides cover for reinforcing steel.

CONCLUSIONS

A predictive model of Portland cement hydration has been developed wherein the fraction of clinker reacted, the water bound in hydrates and the heat evolved are calculated. The required input data are the compound composition of the cement, the surface area, the water/cement ratio and the relative humidity history. The model gives reasonable predictions of different measures of hydration with a coefficient of variation that is generally less than 10%. The model is thus suitable for incorporation in a larger model of the moisture content, microstructure and property gradients that are induced by drying, although further refinement is desirable.

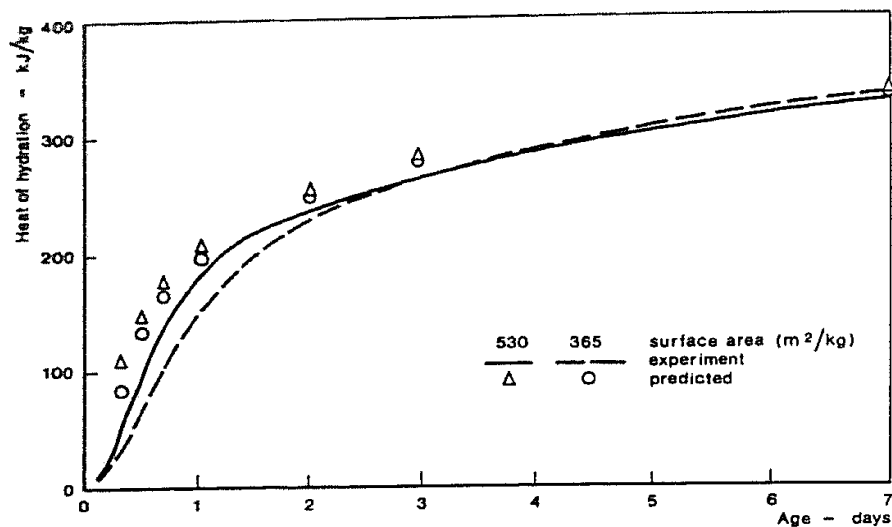


Fig. 8: Effect of surface area upon heat evolution on an Ordinary Portland cement

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