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Modelling of the hydration of tricalcium silicate

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A previously developed mathematical procedure is used to illustrate the kinetics and mechanism of cement hydration. By using the experimentally obtained degree of hydration against time curve and the weight percentage particle size distribution (PSD) of a cement, the procedure can isolate an individual cement particle and characterize its different regimes or modes of hydration reaction. Specifically, one can identify an "accelerating mode" followed by a "decelerating mode" of reaction, and the changeover period, "maxima", from one mode to the other.

1. Introduction

Hydration reaction kinetics of portland cement is commonly studied by periodic measurements of the degree of hydration (α) of cement components. The degree of hydration is normally determined by X-ray analysis, a direct method, or by non-evapourable water content or heat of hydration, indirect methods [1]. A plot of the obtained values as a function of time yields the conventional α–t curve where t is time.

Information obtained from an α–t curve, however, is limited in scope. This is due to the influence of size distribution of the cement particles (PSD). In fact, information can even be obscured and misleading.

With a relatively wide PSD curve Knudsen [2] demonstrated that a shift in an α–t curve may not necessarily indicate a shift in the hydration mechanism. The shift may be attributed to the depletion of a particular group of particle size due to the variable group sizes of cement particles, or both, to changes in mechanism and depletion, occurring simultaneously. Very frequently, the shifts are incorrectly attributed to changes in hydration mechanisms, however, this can only be the case for monosized PSD.

The objective of this paper is to apply a previously developed mathematical procedure [3] to characterize the hydration behaviour (kinetics and mechanism) of cement. The procedure will be modified for the case of a discretized weight distribution and applied to the hydration data obtained from Bezjak and coworkers [4] for cements with known initial PSDs.

2. Review of literature

Hydration has been frequently modelled and there are numerous publications dealing with this subject matter. However, models of hydration as a function of PSD are very limited due to the extremely complex nature of the hydration process which makes it even more necessary, and indeed a requirement, for model development.

There are several factors which influence hydration that have historically assumed important roles in model development. These include mainly

(A) mechanism of formation of hydration products (topochemical or through-solution),

(B) mode and morphology of the hydration product layer, and

(C) effects of particle characteristics (size, distribution, composition, shape, and texture).

2.1. Mechanism of formation of hydration products

Topochemical and through-solution hydration mechanisms have been discussed in detail by Kondo and Ueda [5]. Both these modes have independently been considered to be rate-determining and have formed the basis for numerous model developments. Reference [6] provides a thorough review of the models developed.

A combination of topochemical and through-solution reaction modes has also been suggested by Kondo and Ueda [5]. They assumed that a cement particle forms an inner product topochemically and an outer product by through-solution. Other models [6] suggest that the rate-determining step is dynamic, for example it shifts from one mechanism to another.

2.2. Mode and morphology of the hydration product layer

The mode of the hydration product layer or coating has also been considered to consist of one layer [3, 7–9] or more [10, 11]. If there is more than one layer, it is generally assumed that each layer has a distinct physico-chemical characteristic, i.e. chemical composition and diffusivity. Overall, these models are based on a shrinking core model first developed by Jander [12] for sintering of metallic and ceramic powders. Although the shrinking core model is an oversimplification of the actual hydration process, it has been used in a number of models.

The morphology of the hydrate coating layer is also

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not well established, especially during the early seconds or minutes of hydration.

In a review of the hydration process [13] the following scenario was suggested for early hydration – an extremely thin layer ($<2\,\text{nm}$) begins to form within one second of hydration. This coating characteristic varies considerably with respect to the degree of continuity and rate of growth before giving rise to a layer of honeycomb-type material on its outer surface as a result of spalling and cracking.

Most of the modelling related to the latter part of hydration assumes a topochemical reaction mode with the single most important rate-determining step being the diffusion of ions through the ever-thickening hydration product coating [6].

There is no general consensus as to the required number of hydration product layers in modelling. This subject remains open to further research.

2.3. Effects of particle characteristics

The effects of particle size, distribution, composition, shape, and texture on hydration have been taken into consideration for modelling.

The models, generally, assume that particles react much in the same way regardless of their size [7, 14–16]. Furthermore, Brown and coworkers [17] in constructing their hydration model assumed that the reduction of the surface area of C_3S during its course of hydration does not influence the hydration kinetics.

Other researchers have considered that different particle sizes have different compositions and degrees of crystallinities [18]. Different particle sizes also react at different rates [19] and at the same time obeying different rate laws [4, 20]. Steinharz [19] suggested that water penetration into a cement particle increases with an increase in the size of the particle. Bezjak and coworkers [4, 20] stated that particles belonging to different size groups follow different rate laws, i.e. different rate laws are involved simultaneously in the overall degree of hydration.

Knudsen [8] stated that the degree of hydration of a single particle is inversely related to its radius. However, in the total cement system, the specific reaction mechanism becomes unimportant due to the more important influence of PSD. Thus, it is more important to include PSD rather than individual particle size in modelling. Frigione and coworkers [9], also demonstrated that the particle size parameter could be neglected in modelling.

The inclusion of a parameter describing the influence of particle size on reaction kinetics does not appear to be necessary. This, therefore, adds to the simplicity of model development and mathematical solution.

In real cement systems, cement particles are polymineralic with a high degree of chemical anisotropy, extremely irregular in shape, and rough in surface texture. In modelling, cement particles are assumed to be monomineralic in composition and spherical in geometry, the surface texture does not enter into consideration.

3. Model and application

The procedure used is based on a previously developed quantitative model [3] which followed Gronau's [7] shrinking core principle.

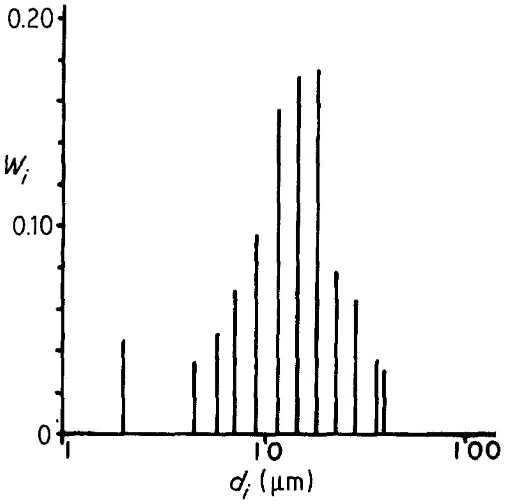

Figure 1 Particle size, $d_i = 2r_i$, plotted against weight distribution, W_i, for sample A (alite).

In the development of the model the following assumptions were made: cement particles are spherical and monomineralic; the hydration layer consists of a single layer and its mode of formation is topochemical.

These assumptions, as demonstrated in the previous section, have formed the basis of numerous hydration models. The values obtained from the model may not represent the real situation, but they probably would yield values adequate for relative or comparative evaluations and thus quantification purposes.

3.1. Mathematical development

It has been shown [3] that the theoretical degree of hydration function of hydrate coating layer thickness can be given as

$$\alpha(x) = 1 - \int_x^{\infty} W_0(r)\left(1 - \frac{x}{r}\right)^3 \mathrm{d}r \qquad (1)$$

where $\alpha(x)$ is the degree of hydration (percentage volume reacted as a function of x), x the thickness of hydrate coating layer (μm), r the initial radius of a spherical particle (μm), and $W_0(r)$ the initial percentage weight distribution of particles.

Given the numerical or analytical expression for $W(r)$ for a specific cement, the theoretical relationship between α and x can be obtained from Equation 1. When α–x is used in correlation with the experimentally obtained α–t curve, values of x as a function of t could be plotted. The slope ($\Delta x/\Delta t$) indicating velocity (V) could then be evaluated and finally plots of V against x, V against α, and V against t, can be obtained.

3.2. Application of the model

In many instances it is more convenient to present the weight distribution in a discretized fashion. One such example is the distribution data of Bezjak and coworkers [4], from which the weight distribution for sample A (alite) is portrayed here in Fig. 1.

For such representations, the weight distribution, $W_0(r)$, of a system containing n discrete particle sizes

TABLE I Phase compositions of industrial clinkers [5]

Phase	C1		C2	
	XRD	Chemical analysis	XRD	Chemical analysis
C_3S	65	63.4	65	58.2
C_2S	12	16.0	12	19.9
C_3A	3	6.0	9	9.8
Ferrite	7	11.1	4	8.6

is given by

$$W_0(r) = W_i\delta(r - r_i) \quad 1 \leqslant i \leqslant n \tag{2}$$

where $\delta(r - r_i)$ is the delta function and W_i is the weight fraction of particles corresponding with size $d_i(2r_i)$. Substitution of Equation 2 into Equation 1 and summation over all radii greater than x (to correspond with the limits of integration) leads to

$$\alpha(x) = 1 - \sum_{\substack{i=j \\ x \leqslant r_j}}^{n} W_i\left(1 - \frac{x}{r_i}\right)^3 \tag{3}$$

which designates the degree of hydration for a discrete set of particle sizes ranging within r_1 and r_n (i.e. $r_1 \leqslant r \leqslant r_n$).

Equation 3 is applied to the data obtained from Bezjak and coworkers [4]: specimens A, C1, and C2. Specimen A is alite, and specimens C1 and C2 are two industrial clinkers. Table I gives the compositions of the two clinkers as determined by XRD and chemical analyses. Both clinkers have a similar calcium silicate content.

The water to cement ratio was held constant at 0.5. The mixing, casting, and curing procedures are described in [4]. XRD analysis was used for the determination of α for C_3S using quartz as standard.

4. Results

Fig. 2, which represents the results of the above calculations performed on sample A, is included here to serve as an example. Subsequently, by matching the experimentally observed $\alpha(t)$ (see Fig. 3 for specimen A) with the theoretically obtained $\alpha(x)$ (Fig. 2), a plot of coating thickness, x, as a function of time, t, is obtained. Numerical differentiation of this yields the hydrate growth velocity, V, as a function of time, t, or coating thickness, x.

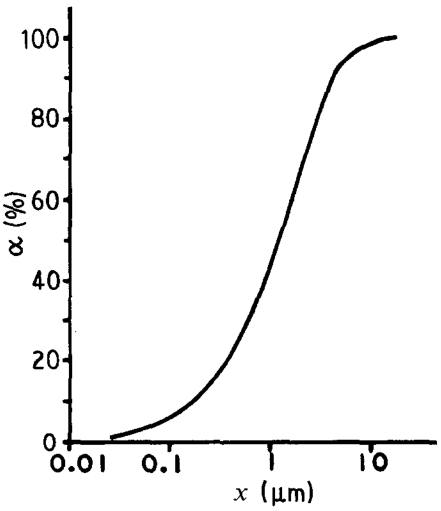

Figure 2 Relationship between degree of hydration (α) and hydrate coating thickness (x) for sample A (alite) obtained theoretically from Equation 3.

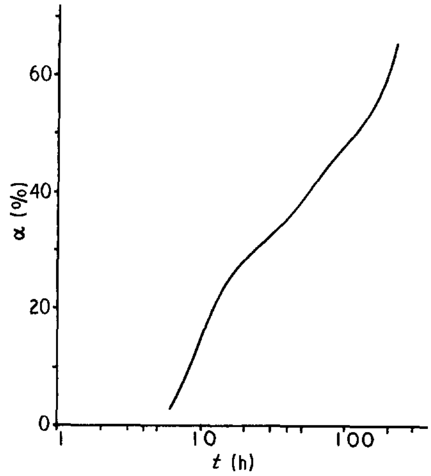

Figure 3 Relationship between degree of hydration (α) and time (t) for sample A (alite) obtained experimentally.

Figs 4 and 5 give, respectively, the V–t and V–x values for specimens A, C1 and C2. These figures account for the PSD of the cement system and represent the hydration kinetics of an individual cement particle.

5. Discussion

It is interesting to note from the observations in Figs 4 and 5 that the hydration of C_3S in all specimens occurs in two distinct regimes or modes; an "acceleratory mode" and a "deceleratory mode" separated by a distinct "maxima". For clarity only the points in the deceleratory regime are connected with a straight line. The term "maxima" is used in the context of this paper because it appears as a maximum point on the V–t and V–x curves. It corresponds to the changeover from the acceleratory to the deceleratory periods. It may very well correspond to the same peak for the rate of heat liberation against time curve (see [5], Fig. 31). However, this needs to be substantiated since the rate of heat liberation curves have not been given in the reference [4]. Moreover, the heat curve data must account for PSD and for the sake of comparison the particles should be monosized.

It is interesting to note here that when this procedure was used for Kondo and Ueda's data [5] for C_3S hydration (2–5 μm, water to cement ratio = 0.5), the changeover time was calculated to be about 8 h. This time corresponded well to the time of peak of the

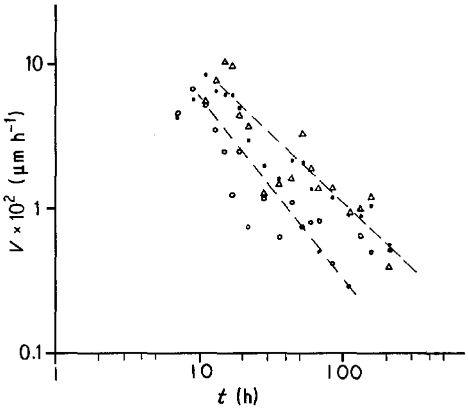

Figure 4 Relationships between hydrate coating growth velocity, V, and time (t) for samples A (○) (alite), C1 (●) (industrial cement) and C2 (△) (industrial cement).

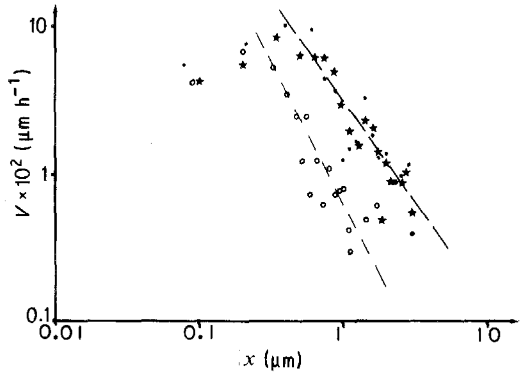

Figure 5 Relationships between hydrate coating growth velocity, V, and coating thickness (x) for samples A (○) (alite), C1 (★) (industrial cement) and C2 (●) (industrial cement).

rate of heat liberation against time curve for the same specimen and water to cement ratio.

After the initial wetting, hydration stages of C_3S have been classified into three general regimes: induction, acceleratory, and deceleratory (decay). In the procedure used here, the induction period is not identified or it may be well integrated in the early part of the acceleratory regime. This is due to lack of hydration data for the very early part of hydration (< 4 h) when the induction period most likely occurred. Nevertheless the changeover period and the deceleratory regime are clearly distinguishable from one another.

Application of this procedure to Kondo and Ueda's data [3, 5] for C_3S hydration clearly showed similar regimes. Due to lack of data for the first hour of hydration the induction period could not be clearly identified. It also appears, from the rate of heat liberation against time curve, that the induction period is over before the first hour after hydration.

The existence of the two hydration regimes have been discussed by numerous other investigators. Lea [1] reviewed the literature on this subject matter and cited the works of zur Strassen [21] and Tsumura [22]. Zur Strassen suggested that during the initial reaction diffusion through hydrate coating is so rapid that the reaction rate is controlled by solid–water reaction. When the solid–liquid reaction becomes fast, the diffusion through hydrate coating controls and reaction slows down. The changeover time for C_3S is 30 days. Tsumura also found two stages of hydration but suggested that the changeover time for C_3S is 15 h, much less than zur Strassen's value.

Application of the model gave values of 8 h for C_3S using Kondo and Ueda's data [3, 5] and 8–9 h for Bezjak and coworkers data, specimen A [4]. Odler and Dorr [23] also determined a similar changeover time, 8 h, for the hydration of C_3S. The changeover time was defined [23] as the time of transition from a period when reaction between C_3S and water is autocatalytic to a period when reaction becomes diffusion controlled.

Bezjak and coworkers [4], however, in modelling hydration have considered the possibility that cement particles of different sizes in a system can react simultaneously in three rate determining mechanisms; nucleation and growth, boundary interaction, and diffusion. At each instant of hydration a certain group of particles is hydrating according to one of these mechanisms. Normally, the early stages of hydration is dominated by nucleation and growth and the final stage by diffusion. The boundary interaction occurs during the intermediate stage of hydration but may not necessarily be dominating. Bezjak and coworkers' model show that transition from one hydration mechanism to another is gradual and not rapid.

TABLE II Depth of hydration coating for C_3S (μm)

Specimen/ Reference	Time					
	1 day	3 days	7 days	10 days	28 days	6 months
[3]	0.3	0.5	0.7		0.8	2
[24]	2.25		4.32		4.44	
[25]		3.5	4.7		7.9	15.0
A [4]	0.6	1.03	1.48	1.93		
C1 [4]	1.02	1.82	2.8	3.2		
C2 [4]	0.93	1.81	2.9	3.18		

The thickness of hydration coating around C_3S was analysed experimentally by researchers. The thickness at the changeover time was given as 0.4 μm at 15 h by Tsumura from X-ray measurements [22]. Using a microscope, Kondo and Ueda [5] measured a thickness of 0.2 μm at 8 h at what appears to be the changeover period. This value is larger than the range of 0.08–0.1 μm at 8 h obtained using this model [3]. If the limitations of this model are recognized, one reason for the difference in the thickness values may be due to the difference in the hydrating systems. The value of 0.2 μm [5] was for hydration of a single C_3S particle immersed in a liquid medium. The semi-theoretical value of 0.08–0.1 μm [3] was determined for paste. In this research a thickness of about 0.2 μm at 8–9 h is calculated for the alite specimen (A).

Table II gives the coating thickness of specimen A at various times of hydration during the deceleratory regime. The values are compared with other references. Influence of other compounds (i.e. C_3A, C_2S, ferrite) on C_3S hydration coating is also given (specimens C1 and C2).

The deceleratory regime (Figs 4 and 5) is seen to be governed by the following empirical relations

$$V(t) = B'x^{-S'} \tag{4}$$

and,

$$V(x) = Bx^{-S} \tag{5}$$

where B', B, S', and S are constants.

For specimen A,

$$V(t) = 1.15t^{-1.28} \tag{4a}$$

and

$$V(x) = 8.2 \times 10^{-3}x^{-1.63} \tag{5a}$$

Specimens C1 and C2 appear to behave similarly as

$$V(t) = 0.91t^{-0.96} \tag{4b}$$

and

$$V(x) = 2.8 \times 10^{-2}x^{-1.26} \tag{5b}$$

Equation 5a can be related to the equation obtained previously; $V(x) = 5.74 \times 10^{-4}x^{-1.66}$ [3]. Although the coefficients are different by one order of magnitude, the exponents are very similar.

Alkali addition to cement influences these values. However, all specimens still exhibit the acceleratory and deceleratory modes. Analysis of the effects will be presented in a forthcoming paper.

6. Conclusions

A procedure is used to demonstrate the hydration kinetics of cement accounting for its PSD. The procedure clearly identifies the acceleratory and deceleratory regimes of hydration and the changeover (maxima) period separating the two regimes.

For the hydration of C_3S, a changeover period of 8–9 h has been calculated. This corresponds to a hydration coating thickness of 0.2 μm. The deceleratory regime is also found to follow the relationships $V(x) = 8.2 \times 10^{-3} x^{-1.63}$ and $V(t) = 1.15 t^{-1.28}$. These values are in agreement with other data.

The procedure can be applied to demonstrate and quantify the effects of other compounds and admixtures on hydration behaviour.

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