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Kinetics of depletion of a population of hydrating cement particles

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In this paper the effects of the particle size and distribution of a population of hydraulic cement particles, and the rate of growth of the hydrating layer or coating surrounding the individual cement particles on reaction kinetics are presented. The shrinking core model is incorporated to yield a relationship between the volume percentage hydration and the initial particle size distribution. Subsequently, the coating growth velocity as a function of the hydrate layer thickness is deduced.

1. Introduction

The fineness (surface area) of hydraulic cement particles is a useful parameter for proportioning mixtures of cements, mortars and concretes. It is a quantitative measure of the ratio of exposed surface area of a population of cement particles (usually in m^2) to that of a unit weight (usually in kg) of cement.

Particle size distribution (PSD) is another important physical parameter involved in the kinetics of hydration of cement. This parameter is independent of fineness, and cements of equal fineness can have different PSD characteristics [1]. PSD data are normally presented in a graphical form called a number frequency histogram where the ordinate represents the number or population of the particles, and the abscissa represents the size of particles. In addition, cements similar in composition and fineness can possess different hydration characteristics if their PSDs are different. The use of PSD as a tool for mixture proportioning is usually only determined for research purposes [2].

Although the importance of the roles of fineness and PSD in hydration has been established, there is limited quantitative work done on correlating them with hydration kinetics. To the best of the knowledge of the authors, it was Gronau [3] who first published a paper in 1967 in which he correlated PSD and hydration in portland cements. The importance of PSD was again stressed in 1968 by Taplin [4]. Kondo and Ueda [5] assumed a monomodal PSD to simplify derivation of a mathematical model dealing with hydration of tri-calcium silicates (C_3S)*. This model was later expanded and modified by Pommersheim and co-workers [6, 7]. Both of these models considered particle size, thickness of the hydrate layer (coating), and diffusivities through the coating. They also regarded the coating as consisting of a three-layer system; inner, middle, and outer. Bezjak and Jelenic [8] and Bezjak [9] developed a model to determine rate constants of polysize cement particles, specifically C_3S. In their model they claimed that particles belonging to different size groups follow different rate laws during hydration. Thus, different rate laws are involved simultaneously in the overall degree of hydration. Brown *et al.* [10] in deriving their model assumed that the reduction of C_3S particle surface area during hydration does not influence its hydration kinetics. In his paper, Knudsen [11] perceived the existence of an interconnection between cumulative PSD and the hydration–time plot for cements. His conclusion was that weight distributions that follow exponential behaviour have their cumulative PSDs related to the hydration–time curve by a constant that possesses the dimensions of length per unit time (velocity).

The objective of this paper is to derive a quantitative explanation of the kinetics of depletion (a measure of reaction and hydration kinetics) of a population of cement particles in time. Based on Gronau's concept of the shrinking core [3], a rigorous derivation of the theoretical hydration to account for a generalized PSD shall be presented. Following this, a correlation between theoretical and experimental hydration (α) is given which will eventually lead to a relationship between velocity of growth of the hydrate or coating layer and the layer thickness itself. This can offer a valuable tool for identifying different mechanisms that could be involved during hydration.

Several points should be stressed regarding the assumptions. First, the coating consists of one homogeneous layer, unlike the three layers considered in earlier models [5–7]. This assumption is incorporated in order to limit the number of parameters and to simplify derivation of the model. Second, the mode of reaction is independent of the initial particle size and the interdependence of particle size and hydration rate laws [8, 9] is not dealt with directly. However, the

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*Cement chemistry abbreviation: C = CaO, S = SiO_2.

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interdependence can be deduced from mathematical and graphical presentations. In other words, although in the model the coating growth velocity for individual particles, regardless of their size, is assumed similar throughout hydration, the reaction kinetics for varying particle sizes can be advanced from the work presented herein.

2. Mathematical modelling

In accordance with the shrinking core model, we shall take the individual cement particle to be spherical, and whose radius, r, constantly decreases in time, t, until the core disappears (Fig. 1). The rate of reduction in core size shall be denoted by v and given by

$$v = -\partial r(t)/\partial t \tag{1}$$

which has the units of length over time (velocity). Furthermore, assume that v is a function of coating or hydrate layer thickness only and entirely independent of the instantaneous size of the particle core. Subsequently, v will be a function of time only, independent of r, and thereby shall be designated by $v(t)$.

Due to the reduction of the particle core size in time, the core size distribution function (PSD) is also time-dependent. The core size PSD function, $n(r, t)$, shall be defined to satisfy the following relation:

$$\mathrm{d}N(r, t) = n(r, t)\,\mathrm{d}r \tag{2}$$

where $\mathrm{d}N(r, t)$ is the number of particle cores at time t whose radii fall between r and $r + \mathrm{d}r$. Equation 2 is therefore integrated to give the instantaneous total number of particle cores at time t in the system

$$N(t) = \int_0^\infty n(r, t)\,\mathrm{d}r \tag{3}$$

The expression for the total number of cores at time $t = 0$ can therefore be obtained from Equation 3,

$$N_0 \equiv N(0) = \int_0^\infty n_0(r)\,\mathrm{d}r \tag{4}$$

where

$$n_0(r) \equiv n(r, 0) \tag{5}$$

is the known initial PSD.

An important result deduced from the assumption imposed on the core size reduction rate, $v(t)$, i.e. that it is entirely dependent upon time only and independent of the instantaneous core size, is sketched in Fig. 2. Due to this particular behaviour, the size distribution is shown to move to the left with a wave speed equal to $v(t)$ while the characteristic shape remains unchanged. As a consequence, by following a specified set of particles in time,

$$n(r, t) = n(r + \Delta r, t + \Delta t) \tag{6}$$

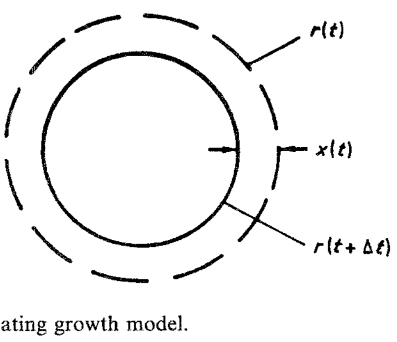

Figure 1 Coating growth model.

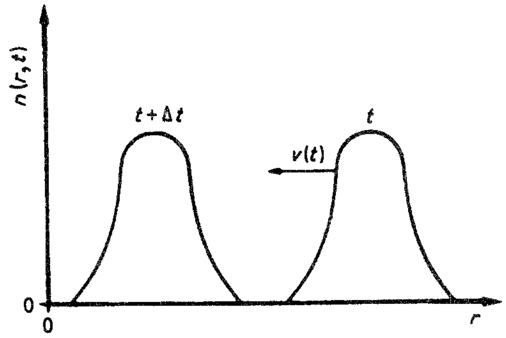

Figure 2 Characteristic behaviour of PSD, $n(r, t)$, with time, t.

In differential form, Equation 6 becomes

$$\mathrm{d}n = 0 = \left(\frac{\partial n}{\partial t}\right)\mathrm{d}t + \left(\frac{\partial n}{\partial r}\right)\mathrm{d}r \tag{7}$$

which upon rearrangement and using the expression for $\partial r/\partial t$ obtained from Equation 1 results in the partial differential equation

$$\frac{\partial n}{\partial t} - v(t)\left(\frac{\partial n}{\partial r}\right) = 0 \tag{8}$$

whose solution acquires the form

$$n(r, t) = n[r + x(t)] \qquad 0 \leqslant x(t) < \infty \tag{9}$$

where $x(t)$ is the coating thickness expressed by

$$x(t) \equiv \int_0^t v(\tau)\,\mathrm{d}\tau \tag{10}$$

The initial condition is simply the PSD, $n_0(r)$, given at time $t = 0$ and which is assumed to be known.

Substitution of Equation 9 into Equation 3 gives the time-dependent core population

$$N(t) = \int_0^\infty n[r + x(t)]\,\mathrm{d}r \tag{11}$$

which after a change in the frame of reference becomes

$$N[x(t)] = \int_x^\infty n(z)\,\mathrm{d}z \tag{12}$$

where

$$z \equiv r + x(t) \tag{13}$$

The wave-like nature of the problem implies

$$n(z) = n_0(r) \qquad \text{for} \qquad 0 \leqslant r = z < \infty \tag{14}$$

so that

$$N[x(t)] = \int_x^\infty n_0(r)\,\mathrm{d}r \qquad 0 \leqslant x(t) < \infty \tag{15}$$

which indicates that, under the imposed assumptions, the core population, $N(t)$, can be calculated given the initial size distribution, $n_0(r)$, and the size reduction rate $v(t)$.

In addition, the volume percentage hydration, α, a parameter of more practical importance than the number density, can also be calculated. By definition, α is the percentage volume reacted. Analytically it is expressible by

$$\alpha(t) = 1 - \frac{V(t)}{V_0} = 1 - \frac{\int_0^\infty n(r, t)\,r^3\,\mathrm{d}r}{V_0} \tag{16}$$

where V_0 is the total volume at $t = 0$ and equal to $\int_0^\infty n_0(r)\, r^3 \mathrm{d}r$.

With $n(r, t)$ given by Equation 9, Equation 16 therefore assumes the form

$$\alpha(t) = 1 - \frac{\int_0^\infty n[r + x(t)]\, r^3 \mathrm{d}r}{V_0} \tag{17}$$

which after a coordinate transformation becomes

$$\alpha[x(t)] = 1 - \frac{\int_x^\infty n_0(z)\,(z - x)^3 \mathrm{d}z}{V_0} \tag{18}$$

where z is defined in Equation 13 and $n_0(z)$ is the initial PSD.

In terms of the weight distribution, $W_0(r)$, where $W_0(r) = n_0(r)\, r^3/V_0$, Equation 18 can be rewritten as

$$\alpha(x) = 1 - \int_x^\infty W_0(z)\left(1 - \frac{x}{z}\right)^3 \mathrm{d}z \tag{19}$$

assuming that the unreacted cement density is uniform over all cores. Equation 19 suggests that indeed, as expected, a relationship does exist between α and the initial weight distribution function, $W_0(r)$.

This brings attention to the work of Knudsen [11]. There the total hydration, $\alpha_i(x)$, with subscript i corresponding to the order of reaction, is given by (Equation 6 in Knudsen [11])

$$\alpha_i(x) = \int_0^\infty \alpha_i(x, r)\, W_0(r)\, \mathrm{d}r \tag{20}$$

where $\alpha_i(x, r)$ denotes the hydration of a single particle core having instantaneous radius r. Equation 20 represents an averaging of the local or single-particle hydration over the weight distribution. It should be mentioned that parameters x and $W_0(r)$ have been substituted for kt and $W(r)$, respectively, of Equation 6 in [11] in order to comply with the nomenclature associated with this paper.

Following Taplin [4] and Kondo and Ueda [5], the local hydration reaction kinetics is given by

$$\alpha_1(x, r) = 1 - \left(1 - \frac{x}{r}\right)^3 \tag{21}$$

Substitution of Equation 21 into Equation 20, dropping the subscript 1, and by definition letting $\int_0^\infty W_0(r)\, \mathrm{d}r = 1$ leads to

$$\alpha(x) = 1 - \int_0^\infty W_0(r)\left(1 - \frac{x}{r}\right)^3 \mathrm{d}r \tag{22}$$

which represents linear kinetics hydration based on Knudsen's averaging technique.

Comparison of the above with the more rigorously obtained Equation 19 shows that the lower limit of the integral in Equation 22 is different. This is merely due to the fact that the averaging scheme proposed by Knudsen does not account for the change of PSD with time. The similarity of the integrands of Equations 19 and 22, however, implies that the present work represents a more detailed development of the hydration equation of a cement with generalized PSD. The step by step derivation also provides an insight to the mechanics of the shrinking core model as applied to the reaction kinetics. Application of the model to actual distributions is carried out in the next section.

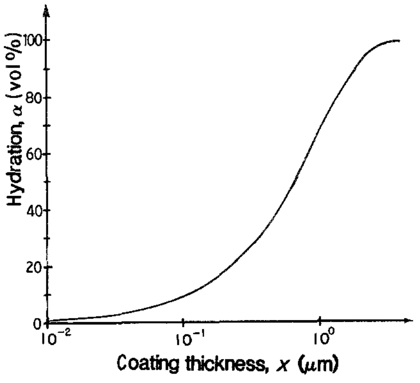

Figure 3 Theoretical $\alpha(x)$ for Specimen 3 of Kondo and Ueda [5].

3. Applications to actual distributions

Equation 19 leads to the calculation of instantaneous hydration as a function of the coating thickness, x, following the shrinking core assumption. Accordingly, should analytical or numerical expressions of $W_0(r)$ be available for a specific cement, $\alpha(x)$ can then be calculated either analytically or by numerical integration of Equation 19. In other words, $\alpha(x)$ is obtainable for any distribution provided that $W_0(r)$ is known. Fig. 3 illustrates an example of such a calculation performed on the uniformly distributed data of Kondo and Ueda [5] for their Specimen 3.

Furthermore, Fig. 4 illustrates the experimentally obtained hydration against time curve for the same cement (Specimen 3 of Kondo and Ueda [5]). With theoretical $\alpha(x)$ from Equation 19 and experimental $\alpha(t)$ pertaining to the same cement sample available, the two graphs can then be matched and reduced to a single plot of x against t, representing the coating thickness as a function of time. Subsequently, the coating growth velocity, v, can be computed by differentiating x with respect to t. From this one can therefore deduce the behaviour of v against x. In summary, for a given initial weight distribution function, $W_0(r)$, and experimental hydration–time plot, $\alpha(t)$, belonging to a cement specimen, the coating growth velocity as a function of coating thickness can be calculated.

The procedure described above was applied to the data of Kondo and Ueda [5] and Knudsen [11]. The relatively narrow particle size range of Kondo and Ueda's specimens (2 to 5 and 5 to 8 μm) has been assumed to be uniform in distribution, thereby allowing analytical evaluation of Equation 19. Fig. 3, which is included as an example, is a result of the calculation

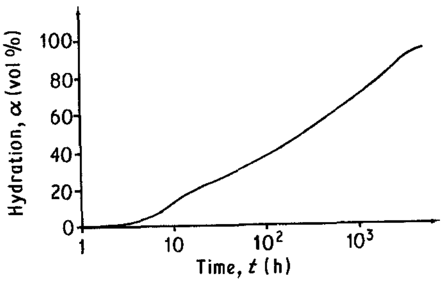

Figure 4 Experimental $\alpha(t)$ for Specimen 3 of Kondo and Ueda [5].

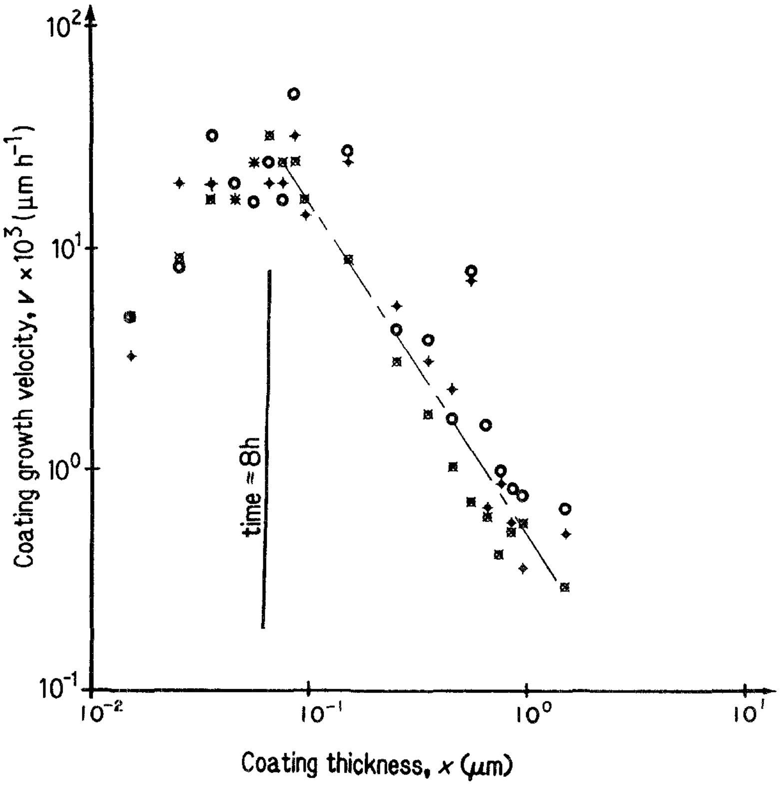

Figure. 5 v against x for (○) Specimen 1, (ɔ) Specimen 2 and (✦) Specimen 3 of Kondo and Ueda [5].

performed on Specimen 3 of Kondo and Ueda [5]. Knudsen's data, however, was comprised of Portland cement characterized by

$$W_0(r) = \frac{BC}{B - C}(e^{-Br} - e^{-Cr}) \qquad (23)$$

where $B = 0.0595$ and $C = 1.28$ [11]. Analytical evaluation of Equation 19 involving $W_0(r)$ given above can be expressed in terms of the exponential integral series. Here, however, numerical integration using Simpson's rule was employed to give $\alpha(x)$.

With experimental $\alpha(t)$ available for both data sets (see for example Fig. 4) it was then possible, by graphical correlation of $\alpha(x)$ and $\alpha(t)$, to compute x against t from which v against x was calculated by numerical differentiation. Final results are illustrated in Figs 5 and 6 for Kondo and Ueda [5] and Knudsen [11], respectively, and are discussed in the next section.

4. Discussion of results

The developed technique has been applied to hydration data obtained from the literature [5, 11], and the results appear in Figs 5 and 6. Fig. 5 represents v against x for the three specimens of Kondo and Ueda [5] listed in Table I.

Interestingly, all three samples possess similar behaviours in that the layer growth velocity varies over a range of approximately three orders of magnitude. In addition, all three curves are characterized by two distinct modes of hydrate layer growth separated by

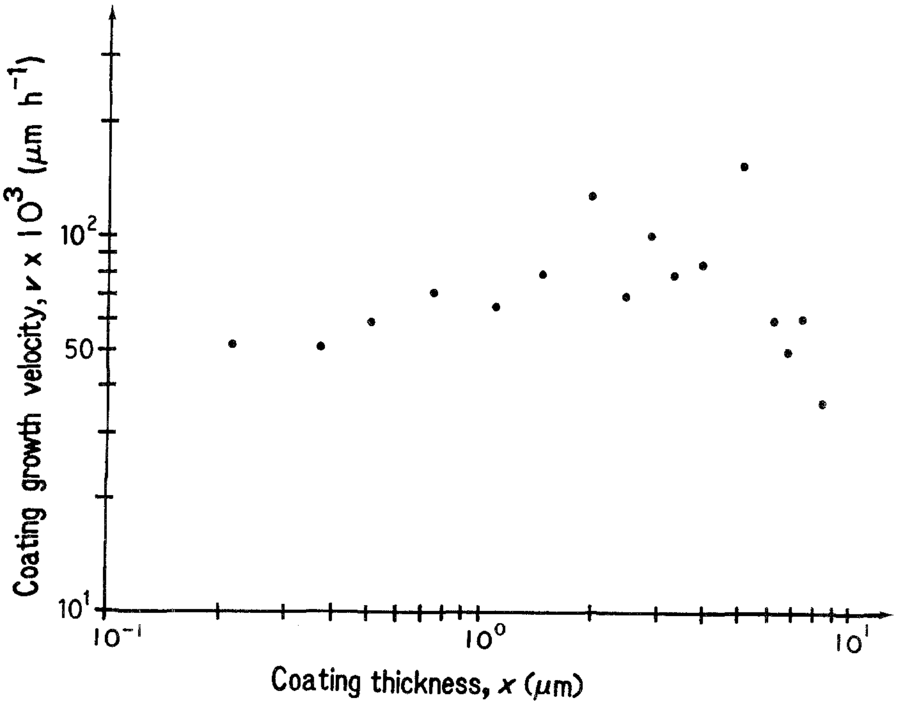

Figure 6 v against x computed from Knudsen's data [11].

TABLE I Specimens of Kondo and Ueda [5]

Specimen No.	Type	Size range (μm)	Water/cement ratio
1	C_3S	2 to 5	1.0
2	C_3S	2 to 5	0.5
3	C_3S	5 to 8	0.5

a maximum that occurs at a coating thickness of approximately 0.08 μm and a coating growth velocity of 0.04 μm h^{-1}, corresponding to about 8 h of reaction. It is also evident that the initial stage of hydration reaction (before 8 h) is an "accelerating mode" where velocity increases with increasing thickness, and since all points effectively lie on one line, it can be argued that this regime is independent of the initial PSD and water/cement ratio. The "decelerating mode" also appearing to be independent of the initial PSD and water/cement ratio, follows after 8 h and is seen to be governed by the following empirical relation

$$v(x) = Ax^{-s} \tag{24}$$

where constants A and s are approximately equal to 5.74×10^{-4} and 1.66, respectively.

On the other hand, Fig. 6 which represents Knudsen's data leads to a different finding. Here it is seen that the coating growth velocity changes by a factor of about 4 while the variation in the coating thickness covers almost two orders of magnitude. This, therefore, deems velocity to be almost constant (independent of x) with a mean value of about 0.07 μm h^{-1}.

5. Conclusion

It was shown that under the given conditions of reaction kinetics, cement hydration can be visualized as being the movement of the PSD curve to the left with its characteristic shape remaining unchanged. The wave speed with which this occurs is essentially the velocity of hydrate layer or coating growth. The model, in effect, signifies the importance of using the initial PSD to characterize cements hydration kinetics.

Graphical matching of theoretical hydration (given in terms of coating thickness, x) and experimental hydration (given in terms of time, t) allows one to compute the hydrate layer thickness as a function of time. This, subsequently, leads to a more useful plot relating growth velocity, v, to coating thickness, x. The plot enables one to determine the effect of coating thickness on the speed of hydration, and also to distinguish regions of abrupt changes in hydration behaviour (as evidenced by the maximum in Fig. 5).

Application of the model to actual cement hydration data led to Figs 5 and 6. At this stage, due to the lack of more data, only a qualitative explanation of cement hydration in terms of v against x was presented. More conclusive results can be achieved only through further data collections and analyses.

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