THE DISPERSION MODEL FOR HYDRATION OF PORTLAND CEMENT

I. GENERAL CONCEPTS

Torben Knudsen
The Institute of Mineral Industry, Building 204,
The Technical University of Denmark,
DK-2800 Lyngby, Denmark

ABSTRACT

This paper introduces an analytical mathematical model for develop-
ment of the hydration of Portland cement:

$$t_0 + t_1 A + t_2 A^2 = t$$

t is time, and t_0, t_1 and t_2 are time-constants depending on temperature,
cement type, admixtures etc. A is the hydration ratio, i.e. the ratio
of hydrated to unhydrated cement. The dispersion model has been derived
on basis of the typical particle size distribution for tube-milled pro-
ducts. Earlier findings by us have proven the particle size distribution
to be a dominant factor in the correct modelling of cement hydration.
The parameterization of hydration curves, which is easily performed with
the dispersion model, gives a sufficient characterization of these for
purposes of practical interpretations of the effects of factors decisive
for the development of hydration.

Introduction

This paper describes a mathematical model for the development of the hy-
dration of Portland cements. The content of the model differs in many respects
from earlier attempts to model cement hydration, but a comparison to other mo-
dels is outside the scope of this paper. The model of hydration presented here
is the result of our previous work with cement hydration (1,2). These works
were inspired by the works of Taplin (3). He was the first to point to the im-
portance of the particle size distribution (psd) in the modelling of cement hy-
dration. The influence of psd on the shape of the hydration curve has in our
work been brought into explicit form in the dispersion model of hydration. The
model appears in a mathematical analytical form, which can easily be used for
parameterizing hydration curves.
The dispersion in particle sizes in a material like cement is such, that the
state of reaction of the smallest particles is significantly different from the
state of reaction of the largest particles. While the smallest particles may be
fully hydrated, the largest particles may have a low degree of hydration. In
fact, at any time of hydration there exists a distribution of degrees of hydra-

tion, corresponding to one point on the hydration curve. Thus it may be under-
stood, that the development of hydration of a single particle can not directly
be discovered by the hydration curve. For materials with a broad psd like in
cements it can be shown by numerical means, that only gross features in the ki-
netics governing the hydration of a single particle, may be discovered by the
hydration curve. A change for instance from constant rate kinetics to surface
reaction controlled kinetics, both being linear kinetics, makes no significant
change in the hydration curve obtained by calculation. This important observa-
tion will be designated the "dispersion rule".

Thus the influence of psd may be considered a complexity in the study of
hydration kinetics per se. On the other hand, in attempts to model the hydration
development of cements it constitutes a simplifying factor. According to the
dispersion rule differences within a size class in morphorlogy, chemical com-
position etc. can hardly be recognized in the hydration curve. The hydra-
tion curve is sensitive mainly to the psd (with the exception mentioned later),
and the psd-curve for tube-milled products is smooth and simple in form.

Now what is left of kinetic information in the hydration curves?
Mainly two features:

1) When hydration curves are plotted as function of log-t, the position
   of the curve on this axis determines the value of the rate-constant
   (The situation is more complicated when 2 rate-constants govern the
   hydration development).

2) The two important groups: linear and parabolic kinetics, can be recog-
   nized in the hydration curves.

In order to appreciate the last point one should note that all kinetic equations
leaning on the shrinking-core model contain the variables r,t and k, being the
particle size, time and the rate-constant respectively, in either of two com-
binations:

$$\text{linear:} \quad \frac{kt}{r} \qquad ; \qquad \text{parabolic:} \quad \frac{(kt)^{\frac{1}{2}}}{r} \qquad (1)$$

This fundamental difference between linear and parabolic kinetic equations
"overrides" the dispersion rule since it constitutes a difference in the way
r and t enters the kinetic equations. The fact that r and t enter the kinetic
equation in ratios is not a mere coincidence. It is a result of shrinking-core
kinetics, and it guarantees that reaction curves belonging to different partic-
le sizes never cross. While the dispersion rule may be said to be primarily
responsible for the simplicity in modelling hydration with the dispersion model,
the simplicity is also the result of a deliberate limitation in its range of va-
lidity. As can easily be verified by noting the form of the dispersion model,
this model does not give a correct description of the early accelleratory part
of the hydration curve, i.e. the interval 0-15% is outside the reach of the mo-
del, and should be left out in numerical work with it. The model in its pre-
sented form models this part by shifting the zero-point of time to t_0. A closer
agreement in the range 0-15% can be obtained by using a more correct formula
for psd (see eq.2 in ref. 1) than used in the derivation presented in this pa-
per. But the new parameter entering the model, as a result of this modification
of the formula for psd, depends only on the correct description of the finest
5% of psd, and contains no further kinetic information. Therefore we feel, that
the loss of close agreement in the first 15% of the hydration curve is not a
serious loss, and the primary goal with the dispersion model is a general and use
ful characterization of hydration curves, and not the optimal accuracy in mo-
delling all parts of the hydration curve.

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Outlines of the derivation of the dispersion model of hydration.

Due to the earlier mentioned effect of the dispersion of particle sizes the crucial point in modelling cement hydration is the transformation from single particle kinetics to the hydration of the total ensemble of particle sizes. By assuming independent reactions of particles this transformation may be represented by:

$$\alpha(t) = \int_{0}^{\infty} w(r) \, \alpha(r,t) dr \tag{2}$$

where $\alpha(t)$ is degree of hydration of the ensemble of particle sizes, $w(r)$ is the frequency psd, and $\alpha(r,t)$ the degree of hydration of a particle of size r.

$\alpha(r,t)$

Much mathematical modelling of hydration in the literature has been concerned with theories about $\alpha(r,t)$. Comparison to experimental data has often been done by putting $r=\bar{r}$, where $\bar{r}$ is the mean particle size of the material in question. This procedure may be very misleading, if the psd of the samples are not sufficiently narrow (2). Theories involving specific assumptions as to the form of $\alpha(r,t)$ must be compared with hydration data from narrow-sized samples. The frequently referenced data presented by Kondo and Ueda in Tokyo symposium (4) is not narrow-sized as far as modelling with $r=\bar{r}$ is concerned. This was shown in ref. (2).

Taplin seems to have been the only author who earlier suggested a solution of eq.2, which was not purely numerical (5). He used a log-normal distribution for psd, and his very elegant index-of-reaction equation for $\alpha(r,t)$, but his solution is in form of a series-development, which can hardly be called analytical in the stricter sense of the word.

Some of the reason for the difficulty in suggesting analytical solutions to eq.2 lies in the form of $\alpha(r,t)$. All suggestions, so far, as to the form of $\alpha(r,t)$ has a time of termination. From that time on the $\alpha(r,t)$-curve is a straight line with $\alpha=1$. Such a curve, composed of an ascending part and a constant part, can hardly be given a simple analytical form, suitfull for the solution of eq.2.

In our case we have chosen an analytical form for $\alpha(r,t)$ with the property $\alpha(r,t)<1$ for all values of t:

$$\alpha(r,t) = \exp(- \frac{r}{(kt)^i}) \quad ; \quad i = \begin{cases} 1 \text{ for linear} \\ \frac{1}{2} \text{ for parabolic} \end{cases} \tag{3}$$

where k is a rate-constant. This form resembles quite closely the "classical" forms up to ca. 70% of hydration, but thereafter ascends more slowly towards the asymptote $\alpha=1$. It is a convenient mathematical form for the solution of eq.2, but so far no direct physical interpretation can be given of it. A choice like this, of an $\alpha(r,t)$ which disregards a physical content, is relying on the dispersion rule, which says that the hydration curve is insensitive to the form of $\alpha(r,t)$. All, which is important, is that the independent variables should appear in the combination as given by eq.1. This is not the whole truth though! The use of the dispersion rule should be seen in the light of the convolution principle as derived in (1), but a closer evaluation of this point is outside the scope of this introductory paper.

<u>w(r)</u>

   As to the form of w(r) appearing in the integral of eq.2 it is a lucky co-
incidence, that the psd of tube-milled product like cement may be modelled in
95% of its range by a form as simple as:

$$w(r) = \frac{1}{r_0} \exp\left(-\frac{r}{r_0}\right)$$ (4)

where r_0 is a constant in the equation depending on fineness. This form is sui-
ted for the integration (eq.2) with $\alpha(r,t)$ given by eq.3. Its major draw-back
is the lack of agreement for the finest 5% of the material. The error is such
that it leads to infinite specific surfaces. This is of no serious practical
consequence though, since experiments show $1/r_0$ to be directly proportional to
Blaine's measure of fineness (6).

Solving the integral

   By insertion of eq.3 and eq.4 into integral of eq.2 we arrive at the
solution:

for linear: $$\alpha(t) = \frac{t}{t + t_1} \quad ; \quad t_1 = \frac{r_0}{k_1}$$ (5a)

for parabolic: $$\alpha(t) = \frac{\sqrt{t}}{\sqrt{t} + \sqrt{t_2}} \quad ; \quad t_2 = \frac{r_0^2}{k_2}$$ (5b)

Both eq. 5a and eq.5b are simple hyperbolas in t and $\sqrt{t}$ respectively. The time-
dependency in eq.5a is well-known in drying shrinkage and creep, and has been
suggested a few times for modelling the strenght development of concrete (7,8,9).
Why it has never found wide-spread application in practice within hydration mo-
delling may be due to two reasons. Firstly, eq.5a covers only one group of hydra-
tion curves encountered in practice. The other group obeying eq.5b is equally
important. We find that hydration curves for normal Portland cement are modelled
by eq.5a, whereas eq.5b should be used when modelling the hydration development
of for instance white cement. Secondly, the importance of introducing the correct
zero-point for time has not been recognized in much mathematical modelling of
hydration (10), (Carino in ref. (9) correctly introduces t_0). The proper use of
eqs.5 depends on the correct choice of zero-point. Thus the time appearing in
eqs.5 is "reaction time", and should be understood as $t_m - t_0$, where t_m is the time
from mixing. The reason for the introduction of t_0 in modelling of hydration is
the obvious one, that the dormant period is not included in the modelling, ex-
cept as a delay in the start of the hydration development. (In the equations to
follow t_0 will appear explicitly and t takes on the meaning of time from mixing).
   In most practical cases the use of eqs.5 is dependent on another adjustable
parameter besides t_1 (or t_2) and t_0. This parameter appears in connection with
the definition of α. Since very few data in the literature contain direct mea-
surement of α (as obtained with XRD), properties like heat evolution, non-eva-
porable water, chemical shrinkage, etc. have to be relied on. The use of such
data for the modelling of hydration require a knowledge of P_∞ (the property mea-
sured after infinitely long time) or the estimation of this parameter by adju-

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sting $\alpha \equiv P/P_\infty$ until the best fit with eqs.5 is obtained. How this is done in prac
tice will be described in the following chapter.

The final form of the dispersion model

For the purpose of arriving at the final form of the dispersion model we pre
fer to rewrite eqs.5:

$$\text{linear:} \qquad t_0 + t_1 A = t \qquad\qquad (6a)$$

$$\text{parabolic:} \qquad t_0 + t_2 A^2 = t \qquad\qquad (6b)$$

where $A \equiv \alpha/(1-\alpha) = P/(P_\infty - P)$, and t in contrast to eqs.5 take on the meaning of
time from mixing, since t_0 is now explicitly entering the equations. Written in
this way the designation linear and parabolic take on a direct formal meaning,
besides refering to the underlying kinetics. A is called by us the hydration
ratio as opposed to α the hydration degree.

Experiments in this laboratory using chemical shrinkage of Portland cement
paste, with the admixture $CaCl_2$, triggered the fusion of eq.6a and eq.6b to the
final form (11):

$$t_0 + t_1 A + t_2 A^2 = t \qquad\qquad (7)$$

Eqs.6a and 6b are still contained as limiting cases of eq.7, when either t_1 or
t_2 takes on the value 0.

The hydration experiment with additions of $CaCl_2$ showed, that by adding from
2 to 6% by weight of cement, kinetics changed from linear (eq.6a) to parabolic
(eq.6b). In between none of these limiting cases could produce satisfactory
fits. The combinatory eq.7 gave excellent fits for all additions: 2,4 and 6%
(see fig. 1). The parameters t_1 and t_2 changed in this interval in such a way,
that the ratio t_1/t_1+t_2 changed its value from approximately 100% to approxi-
mately 0%. We defined this ratio as degree of linearity:DL.

The derivation of eq.7 from first principles is not complicated, but will
not be given in this paper. In brief, it considers two separate resistances de-
pending on the linear and parabolic part, and makes series-coupling as with re-
sistances in an electrical curcuit. This is done for kinetics of the individual
particles, whereafter the transformation by means of the integral in eq.2 is
performed. The fact that eq.7 comes out as a linear combination of eqs.6a and
6b is a result of the particular form assumed for linear and parabolic kinetics
in eqs.3.

Concluding this chapter we find it important to stress, that although
the form for eq.7 is such, that the parabolic element $t_2 A^2$ will be governing
for sufficiently long times, numerous hydration curves modelled by us could
in practice be considered 100% linear. A change from linear to parabolic ki-
netics as pictured by eq.7 may come so late (small values of t_2) as to have
no practical implication.

Parameterizing hydration curves with the model

In the following a brief description will be given of the use of the dis-
persion model for parameterizing hydration curves. Examples of the success of
the dispersion model in modelling hydration curves for cement will not be given
in this paper, except for the example presented in fig.1. Reference will be
made to earlier presentations concerning the applicability of the dispersion
model in the form of eqs.6 (1,2,12), and to a recent Ph.D. thesis for a more
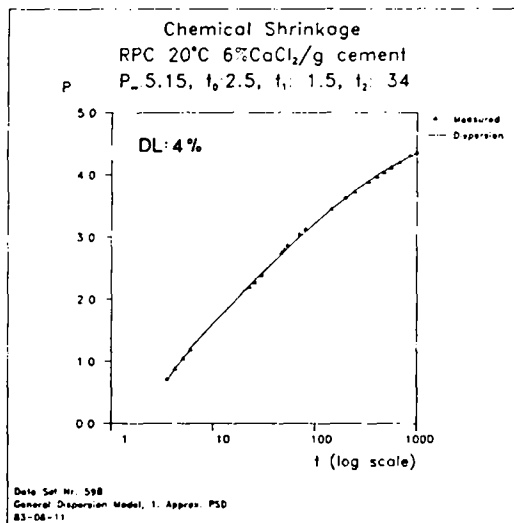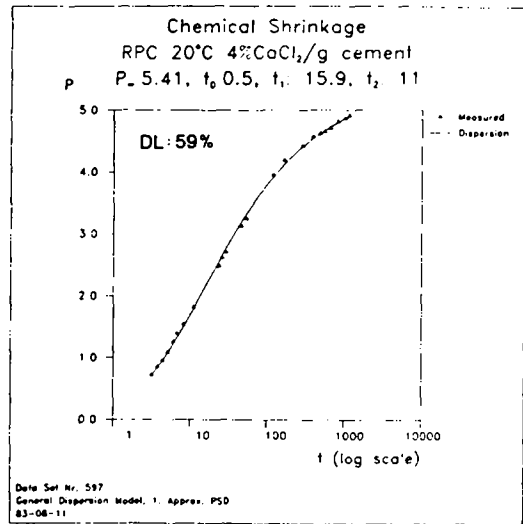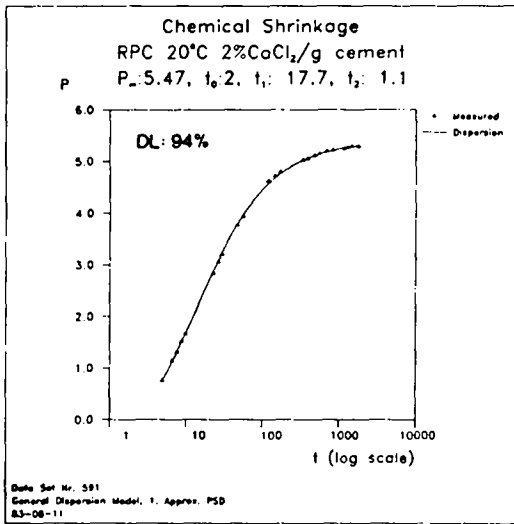thorough documentation including the final form eq.7 (11).

Chemical Shrinkage
RPC 20°C 2%CaCl₂/g cement
P∞:5.47, t₀:2, t₁: 17.7, t₂: 1.1

DL: 94%

Chemical Shrinkage
RPC 20°C 4%CaCl₂/g cement
P∞:5.41, t₀:0.5, t₁: 15.9, t₂: 11

DL: 59%

Chemical Shrinkage
RPC 20°C 6%CaCl₂/g cement
P∞:5.15, t₀:2.5, t₁: 1.5, t₂: 34

DL: 4%

Fig.1 Measurements of chemical
shrinkage of rapid hardening
Portland cement (w/c=0.5), fit-
ted by the dispersion model.
The degree of linearity DL is
seen to change from 94% to 4%
by addition of from 2-6% $CaCl_2$
by weight of cement. Time-
constants are in hours and
chemical shrinkage P in ml/loo g
cement.

Regression calculation

The dispersion model of hydration, as given in eq.7, presents itself as a
parabola in A and t. The fitting to experimental data may therefore be performed
as a simple polynomial regression, higher order than 2 being discarded. The pa-
rameter P_∞, entering the definition of A, can be determined by stepwise, re-
peated regression calculations until a value of P_∞ produces a minimum in the
residual variation calculated at each step. As mentioned in the introduction,
points belonging to the interval 0-ca. 15% in degree of hydration should not
be included in the modelling.

Our experience with regression analysis using eq.7 has shown, that the cor-
rect assignment of dependent and independent variables is a crucial point in
the analysis. We found, that if t is used as dependent and A as independent va-
riables, too much emphasize is put on points with large t's on the expense of
the lower part of the hydration curve. Thus for purposes of regression calcu-
lation we rewrite eq.7:

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$$1 = t_0(1/t) + t_1(A/t) + t_2(A^2/t) \tag{8}$$

When this form is used in regression, approximately equal weight is put on all points.

Sometimes a visual inspection of points in the late part of the curve may prove useful. Points deviating too much from a smoothly drawn curve may be detrimental to regression in this part of the curve, and are better left out of the analysis.

A graphical method

A graphical method may be applied for the determination of the parameters t_0, t_1, t_2 and P_∞ in the dispersion model. This method uses a double-log paper and a transparent sheet. Place the sheet on top of the log-paper, and draw a smooth curve through the data points. Now translate the sheet along the log-P axis (P is the measured property) until the following equation is satisfied:

$$t_{80} = 16t_{20} - 27t_{40} + 12t_{60} \tag{9}$$

where t_{20}, t_{40}, t_{60} and t_{80} are times (as read from the curve) corresponding to 20,40,60 and 80% hydration. Now P_∞ is the value on the sheet falling at 100% on the double-log paper, and t_0, t_1 and t_2 may be calculated by:

$$t_0 = 1.4t_{20} - .44t_{50} + .022t_{80}$$

$$t_1 = -1.8t_{20} + 1.9t_{50} - .11t_{80} \tag{10}$$

$$t_2 = .36t_{20} - .44t_{50} + .089t_{80}$$

Inaccurate or incomplete data sets

The success of modelling with eq.7 depends on the accuracy and completeness of the data set. Data sets may often be encountered, which consist of few points or do not cover a sufficient range in α to be useful in the above mentioned methods of parameterizing. In that case it is wiser to resort to the forms given in eqs.6a and 6b. With these forms a graduated characterization of hydration curves in degree of linearity has been abolished, and substituted for an estimation in either linear or parabolic kinetics. A simple graphical procedure is to plot $1/P$ against $1/(t-t_0)$ in the linear case, and against $1/\sqrt{t-t_0}$, in the parabolic case. In both cases a straight line is produced giving $1/P_\infty$ by extrapolation to infinite time. Since t_0 is entering the variables plotted, this adjustable parameter must be determined by trial and error until the best straight line is being produced.

For data sets from hydration experiments which are not carried far enough, it is often found that plotting against $1/(t-t_0)$ or $1/\sqrt{t-t_0}$ produces equally good straight lines. In this case linear or parabolic kinetics may be selected by considering the two different values of P_∞ obtained. One may be in closer agreement with expectation than the other. If an expectation value of P_∞ is not known, it must be concluded that the data set at hand is insufficient for parameterizing.

Chemical shrinkage as a source of hydration data

Measurements of chemical shrinkage have been found by us to be an extremely valuable source of information on cements hydration. Much of our success with the use of eq.7 has depended on the completeness of data sets obtained with this method. Measurements of chemical shrinkage can easily be obtained as continous curves and can be carried out for as long as neccesary to provide the

completeness required for successful modelling. The measurement is simple, and
the number of samples studied is not limited by cost or labour. By adjusting
the sample-size depending on the water/cement-ratio we have found no trouble in
securing unhindered suction of water into the samples and thus securing accu-
rate measurements of hydration. A full documentation of the use of chemical
shrinkage in the study of cement hydration can be found in Mette Geiker's Ph.D.
thesis (11).

Discussion on the model

It is the ultimate goal of any mathematical model of hydration to be able
to predict the out-come of future hydration experiments. To achieve this goal
the relations between the factors decisive for the development of hydration
and the parameters entering the model should be searched for. In the case of
the dispersion model two important relations are built into the model. Prima-
rily the effect of fineness is explicitly given by the model, as seen from
eqs.5, and has been experimentally verified in (6), at least for the linear
case. The effect of temperature on the parameters t_1 and t_2 is given in so far
as its effect on the rate constants k_1 and k_2 can be assessed. The applicability
of the Arrhenius eqation for this purpose has been demonstrated in ref.(12).
Concerning the effect of chemical composition of the cement and the effect
of chemical admixtures we have been greatly concerned with the question of
what factors determine the underlying kinetics, linear or parabolic. Our obser-
vations so far seem to indicate, that high degree of "available" Ca^{++}-ions in
the beginning of the hydration favors parabolic kinetics. These Ca^{++}-ions may
come from sources such as gypsum in the cement or from added $CaCl_2$ etc. Ca^{++}
-ions may become "unavailable" for the hydration of the clinker particles by
precipitation with C_3A in the well-known double salts of the form $C_3A(CB)_y$
$(H_2O)_x$, (where B stands for an anion). Thus small ratios of Ca^{++}-ions to the
amount of free C_3A (C_3A not bound in the interior of the clinker particle) pro-
duces linear kinetics and for large ratios we get parabolic kinetics. Many
experiments (to be published later) performed in our laboratory seem to reveal
this pattern. In some intermediate range of ratios we get a joint kinetics as
already explained with the additions of $CaCl_2$ to Portland cement pastes. An-
other example is white clinker which hydrates almost linear whereas white ce-
ment is parabolic, and with additions of gypsum we experience the same gradual
change from linear to parabolic kinetics with decreasing values of DL. It
should be mentioned that the factors influencing the "order of kinetics" (whe-
ther linear or parabolic) influence the length of the dormant period as well, as
modelled by t_0 in eq.7. Linear kinetics generally comes together with long dor-
mant periods and vice versa.
These observations of the influence of available Ca^{++}-ions during the early
period of hydration have lead us to a tentative mechanistic interpretation.
According to these speculations linear kinetics is the result of a membrane
highly resistant to transport of water, and which maintains its stability and
resistance throughout hydration. When the membrane formed is weak (or absent!)
diffusion through the inner (and probably outer) zone of hydration products be-
comes rate-controlling and parabolic kinetics results. The state of membrane,
we believe, is highly dependent on the available Ca^{++}-ions (alkali-ions seem to
have the same effect, although to a lesser extent) in the pore-solution, large
amounts of Ca^{++}-ions favoring a weak membrane. Since the membrane consists of
colloidal particle bound together with polar attractive forces, it is tempting
to speculate that Ca^{++}-ions (in combination with available anions) substitutes
the highly polar silanol groups, thus leading to weaker attractive forces be-
tween the colloidal particles. This last point is pure speculation, but might
act as a contemporary model to aid in proposing further experiments to eluci-
date this point.

An interesting article concerning the aforementioned has appeared recently (13). N.L.Thomas et al performed experiments with EDTA in hydration of cement. Their findings and conclusions are in good agreement with our lines of thinking concerning the influence of Ca^{++}-ions on the length of the dormant period and on the C/S-ratio of the membrane.

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