THE CORRELATION OF STRUCTURE POROSITY AND COMPRESSION STRENGTH OF HARDENING CEMENT MATERIALS

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Abstract
The paper presents theoretical and experimental studies of development of early age concrete properties. The use of high-performance concretes means higher content of binders and lower water to binder ratios in comparison with the use of plain concrete. In this paper strength growth of seven concrete mixes with water to binder ratios between 0.52 and 0.32 are presented. A simulation model of early age concrete is presented for prediction of development of the hydration degree and structure formation in cement materials including chemical and mineral admixtures. Mathematical model showing the dependence between concrete compressive strength and porosity coefficient of its structure is presented as well. General idea of modelling is to predict strength growth of early age Plain and High Performance Concretes.

Keywords: Cement matrix; Gel products; Gel pores; Capillary pores; Air pores; Porosity coefficients.

1. INTRODUCTION
Cement and water blending generates chemical reaction that is usually called hydration. Reaction of cement with water is in fact a set of chemical reactions and physical processes. After blending cement with water, reactions take place on the surface of cement grains and as well as components and some other products in the reaction dissolve in liquid phase [4], [6], [8], [12], [15]. Some components of cement dissolve congruently and fall into hydration. Other components dissolve incongruently – with disintegration, falling into hydrolysis [4], [6], [8], [12], [15]. In the analyzed process, there are also reactions of synthesis between compounds created as the result of hydration or hydrolysis of separate cement components. There is also a phenomenon of newly made products hardening. Reaction of cement with water is a very complicated process. Mutual influence of different cement components reacting with water is often complicated by the activity of various supplements [4], [6], [8], [12], [15]. The analyzed process is not only hydration but it is much more complicated process, often called hardening [5], [7], [8] which seems to be adequate and well-founded.
research, it has not been possible to, unequivocally
definesort and character of chemical reactions taking
place during the time of cement materials hardening
process [4], [6], [8], [12], [15].

2. MODELLING OF CEMENT MATERIALS
HARDENING PROCESS

Although cement materials have had more than one
hundred years of history, they are still a very impor-
tant building material. Positive and negative experi-
ences with their application were used in subsequent
realizations. Boisterous development of material
engineering, especially in the last few years, has cre-
ated new possibilities also in the cement materials
technology [6], [8], [12], [18]. This has contributed to
the considerable increase in both: durability of
cement materials and firmness of their structure.
Those effects were possible to attain thanks to modi-
fications of the cement materials structure that rest-
ed mainly on usage of specific chemical admixtures
(superplasticizer) and mineral addition (silica fume).
Modifications of the cement materials structure
allow to reduce water-cement ratio and porosity. As
a result one can obtain a mixture, in which there are
much more active particles that are able to make
structural bonds and much less capillary pores that
create main structural defects.
The essence of the cement materials structure and
the structural theory of concrete have been discussed
in work [18] stressing the importance of the prob-
lems, which are connected with the structural defects
of the analysed materials. In this work the problems
concerning modelling of hardening process have
been presented, with distinction of models: techno-
logical, time-dependent, structural and thermo
dynamical. Moreover, in work [18] the essence of the
temperature function and maturity of hardening
cement materials have been defined.
It may appear that modeling problems have already
been solved. In literature one can find many different
hardening models: technological, time-dependent,
structural and thermodynamical [6], [8], [10], [12],
[18]. The notion of hardening concrete temperature
function and the ripeness of concrete are also dis-
cussed in these dissertations.
The problem of mechanical properties development
in concrete hardening process has a large bibliogra-
phy. The results of considerations are systematized in
form of functional or correlation relationships. It is
possible to mark out two fundamental methods of
hardening process modeling. In one of them the
problems concerning modelling of hardening process
have been presented with distinction of technological
and time-dependent models. In these models
changes of hardening concrete strength are described
by time-dependent function and parameters of bind-
ing material that had been used [2], [3], [7], [8], [9],
[11], [12], [13], [18], [20] CEB-FIP Model Code MC
90 [21].
The second method of concrete hardening process
modelling may be called the structural modelling. In
this case mechanical properties of hardening con-
crete are described by relationships of structural
parameters that depend on binding materials hydra-
tion degree [1], [5], [7], [8], [11], [12], [14], [16], [18].
The process of hardening of new generation con-
cretes (with addition of superplasticizer and micro-
silica) leads to forming up qualitatively different
structure than it takes place in ordinary concretes.
Mineral admixtures and chemical additives also
affect the kinetics of structural processes. In present
paper the structural model which enables prediction
of compressive strength of concrete, especially in
early period of its hardening, is presented. Seven dif-
ferent concrete mixtures that are presented in
Table 1, are considered.

3. GENERAL MODEL ASSUMPTION

Comprehensive specification of mechanical charac-
teristics of hardening concrete, especially of high per-
formance, creates necessity to adopt specific physical
model. In this paper it is established, that the con-
crete can be treated as a composite material, where
the dissipate phase – aggregate and grain of non-
hydrated cement is joined by gel with dissipate pores,
which makes a matrix. Assumptions which are estab-
lished here can be the basis for description of
destruction process, which, in the broad scope of
structure’s development, proceeds in the matrix area.
Mechanical characteristic are given by the following
factors [4], [6], [7], [8], [11], [12], [18]: total porosity,
pores size distribution, defect’s existence, diversity of
structure’s level.

4. PARAMETERS OF CONCRETE
STRUCTURE

Concrete materials, because of the character of physi-
cal and chemical processes, occurred in cement grout
included in them, and on the point of contact of filler’s
grains with a cement paste, have a porous structure.
In the hardening process of cement grout, next to capillary pores, molecular (gel) pores, directly connected with gel products, are made. Capacity of capillary pores with reference to the unit of binder mass can be calculated from the formula [12]:

$$\omega_{\text{cap}} = \frac{w}{S} \cdot (\omega_H + \omega_p) \cdot \alpha$$

where \(w\) is initial capacity of water in the unit of cement grout capacity [dm\(^3\)], \(\omega_H\) is chemically tied water in the unit of binder mass [dm\(^3\)/kg], \(\omega_p\) is out of network water which stays in binding gel structure with reference to the unit of binder mass [dm\(^3\)/kg], \(\alpha\) is degree of binder’s hydration, \(S\) is binder mass, \(w/s=\alpha\) is water – binder ratio.

Capacity of molecular (gel) pores with reference to the unit of binder mass amounts [12]:

$$\omega_{\text{gel}} = 0,28 \cdot \alpha \cdot (1 - \frac{\omega_H + \omega_p - V_S}{\rho_S})$$

where: \(\rho_S\) is binder density, \(V_S\) is a change of system volume: water – cement with reference to the unit of cement mass (contraction).

Structures parameters and thermo-physical characteristics of binders that compose the analyzed concretes: 1A (Plain Concrete – PC), 1+3, 4+6 (High Performance Concrete – HPC), are presented in table 2. Value of degree of binder hydration in the process of its hardening is approximated on the basis of own calorimetric research of hardening heat by the equation [18], [19]:

$$\alpha = \exp \left[-c \left(\ln t_a\right)^{-d}\right] \frac{Q_{\text{max}}}{Q_0}$$

where: \(c, d\) are empirically appointed parameters, \(t_a\)
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is reduced time \( [h] \), \( Q_{\text{max}} \), \( Q_0 \) are maximum and theoretical value of heat in binder hardening.

In Table 3 equation parameters (3), assigned to individual type of researched concretes are presented.

Equivalent time is described by the equation (18), (19):

\[
t_a = \int_0^t \frac{E_k}{R} \exp \left[ \frac{T(t) - T_a}{T(t) T_a} \right] \, dt
\]  

(4)

where: \( E_k \) is an energy of chemical process activation, \( R \) is universal gas constant \([J/molK]\), \( T(t) \) is an absolute temperature course of reaction \([K]\) course, \( T_a \) is temperature of reference \([K]\), \( t \) is time \([h]\).

Energy of activation \( E_k \) is an important parameter which characterizes influence of temperature on kinetics of structural transformation of binders process. Raised temperatures of hardening activate structural transformations process in various degrees, depending on binder composition. Higher level of activation energy comes out in concretes which include micro silica \((4+6)\) in comparison with concretes without it \((1A \text{ and } 1+3 \text{ concretes})\). For \(4+6 \text{ and } 1A\) as well as \(1+3 \text{ concretes}\) appropriate values of \( E_k \) amount to: 26 kJ/mol and 23 kJ/mol.

The measure of cement materials structure condition during their hardening determines, put by (11), porosity coefficient, given by an equation:

\[
x = \frac{\omega_{\text{gel}}}{\omega_{\text{gel}} + \omega_{\text{cap}} + \omega_a}
\]

(5)

where: \( \omega_{\text{gel}} \), \( \omega_{\text{cap}} \), \( \omega_a \) adequately stand for gel, capillary and air pores capacity with reference to unit of binder mass \([\text{dm}^3/\text{kg}]\).

Taking into consideration equations (1) as well as (2) and providing \( \omega = w/s \), we will get (18), (19):

\[
x = \frac{0.28 \cdot \alpha \left( \frac{1}{\rho_s} + \omega_{\text{H}} + \omega_p - V_s \right)}{0.28 \cdot \alpha \left( \frac{1}{\rho_s} + \omega_{\text{H}} + \omega_p - V_s \right) + \omega - \omega_{\text{H}} - \omega_p \cdot \alpha + \omega_a}
\]

(6)

Porosity coefficient \( x \) assumes values of \(< 0.1 >\) range. For \( \alpha = 1 \), \( \omega_a = 0 \) and \( \omega = \omega_{\text{H}} + \omega_p \), porosity coefficient \( x = 1 \), which means that hardened binder grout consists of hardened gel only.

Proprietary research on 1A, 1+6 (compare tab. 1.) concrete made it also possible to identify the influence of the modification of cement matrix on its microstructure. The results of the analysis indicate that there is a close relationship between the properties of cement matrix and the porosity coefficient \( x \). A visible influence of superplasticizer effect was observed for 1A and 1 types of concrete that are characterized by identical values of a water-binder ratio. Superplasticizer’s molecules adsorb on the surface of cement grains and lead to their deflocculation and in this way the use of cement is better [4], [5], [6], [10], [14], [15].

Participation of capillary pores in 1+3 types of concrete decreases in a matrix structure according to decreasing value of water-binder ratio. The effect of a combined action of a superplastificator and microsilica in concrete types 4+6 is similar to the one which was observed in concrete types 1+3.
Figure 1.
A microscopic picture (magnification x 4000) of a hardened 1A cement paste (own research). There are crystal needles of phase C – S – H in porous places [18]

Figure 2.
A microscopic picture (magnification x 4000) of a hardened 6 cement paste (own research). Hydration products in the form of compact gel of the phase C – S – H [18]
The effects of a cement matrix modification are especially visible in the analysis of inner microstructure. The research made by means of a scan microscope showed that microstructure of hardened cement paste in concrete 6 is very consistent, well packed and definitely less porous in comparison to 1A concrete. The essential differences are presented in the structure of phase C – S – H of these types of concrete as well.

5. STRUCTURE PARAMETERS IN CONNECTION WITH COMPRESSION STRENGTH

Mathematical model showing the dependence between concrete compressive strength and porosity coefficient of its structure (given by 6 formulas), assumed in this paper, is depicted by general equation [18], [19]:

\[ R_c = Ro + a \times P - b \]

where:
- \( R_c \) is the compressive strength of concrete [MPa]
- \( Ro \) is the initial porosity coefficient of the concrete [dimensionless]
- \( a \) is the coefficient of compressive strength [MPa/porosity]
- \( b \) is the coefficient of compressive strength [dimensionless]
- \( P \) is the porosity coefficient of the concrete [dimensionless]

The correlation coefficient, \( r \), in equation (7) is equal to 0.995 for concrete 1A and 0.988 for concretes 1, 2, 3.

Figure 3. Graph of formula (7) for concrete 1A [18], [19]

Figure 4. Graph of formula (7) for concretes 1, 2, 3 [18]
The correlation of structure porosity and compressive strength of hardening cement materials

where: $R_c$ is current compression strength of concretes in a given stage of structure’s development, $R_o$ is theoretical compression strength of concrete, when $x = 1$, $a$, $b$ are empirically characterized parameters, dependent on the type of concrete mix. The symbols $R_c$ and $R_o$ were used because strength of concrete was tested on nonstandard cubes.

General structure of formula (7) refers to both: conception of specification of concrete strength in porosity coefficient function [11] and ceramic material model given by [17]. Exponential part of formula (7) expresses influence of grain size, thus pores structure, on material strength. $A$ and $b$ parameters of equation (7) for an individual groups of concrete blends are given by the method of multiple regression with simultaneous definition of correlation coefficient. The results of computations for individual groups of concrete are depicted in Fig. 3, 4 and 5.

6. CONCLUSIONS
Formulas, shown on the basis of established model assumptions, permit expectation of development of concrete strength under compression in wide range of changes of its structure, defined by porosity coefficient. This coefficient, giving the ratios between molecular (gel) pores capacity and total pores capacity in hardening concrete, is good description of structures – formed processes character, integrally connected with structure of porosity of hardening binding gel. The analysis of graphs shown in figures nr 3, 4 and 5 permit statement that various concretes show various characteristics at the same value of porosity coefficient. It means that there is an influence of mineral additives and physical and chemical active admixtures on development of hardening concrete strength. In the established model the fundamental influence on concrete strength in the period of its structural changes, exerts the cement gel with dissipated, molecular, capillary and air pores.

$R_c = R_o \cdot x^a \cdot \exp[b(1-x)]$ (7)

Figure 5.
Graph of formula (7) for concretes 4, 5, 6 [18], [19]

$R_o = 225.16$
$a = 0.074$
$b = -2.546$
$r = 0.966$
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