THE CORRELATION OF STRUCTURE POROSITY AND COMPRESSIVE 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.

Streszczenie

W artykule przedstawiono rozważania teoretyczne i wyniki badań rozwoju właściwości młodego betonu. Zastosowanie betonu wysokowartościowego oznacza wyższą zawartość spoiwa i niższe wskaźniki wodnospoiwowe w porównaniu z betonem zwykłym. W artykule przedstawiono wyniki badań przyrostu wytrzymałości mieszanek betonowych, których wskaźniki wodnospoiwowe miały wartość pomiędzy 0.52 i 0.32. Zaprezentowano także model symulacyjny do predykcji rozwoju stopnia hydratacji i tworzenia się struktury twardniejących tworzyw cementowych, zawierających także domieszki chemiczne i dodatki mineralne. Przedstawiono również model matematyczny ukazujący zależność pomiędzy wytrzymałością betonu na ściskanie i współczynnikiem jego porowatości. Główną ideą tego modelowania jest predykcja wytrzymałości twardniejącego betonu zwykłego i wysokowartościowego.

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. Despite the long-term research, it has not been possible to, unequivocally define sort 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 important building material. Positive and negative experiences with their application were used in subsequent realizations. Boisterous development of material engineering, especially in the last few years, has created 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 modifications of the cement materials structure that rested 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 problems, 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: technological, 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 discussed in these dissertations.

The problem of mechanical properties development in concrete hardening process has a large bibliography. 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 binding 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 concrete are described by relationships of structural parameters that depend on binding materials hydration degree [1], [5], [7], [8], [11], [12], [14], [16], [18].

The process of hardening of new generation concretes (with addition of superplasticizer and microsilica) 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 different concrete mixtures that are presented in Table 1, are considered.

3. GENERAL MODEL ASSUMPTION

Comprehensive specification of mechanical characteristics of hardening concrete, especially of high performance, creates necessity to adopt specific physical model. In this paper it is established, that the concrete 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 established 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 physical 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.

Table 1.
Components and physical characteristic of concretes mixtures [18]

No.	Components and physical characteristics	The type of concretes mixture						
		1 A	**1**	**2**	**3**	**4**	**5**	**6**
1.	W/(C + SF)	**0.52**	**0.52**	**0.47**	**0.42**	**0.42**	**0.37**	**0.32**
2.	C [kg/m^3]	340.0	345.0	363.0	394.0	320.0	348.0	388.0
3.	SF [kg/m^3]	–	–	–	–	36.0	39.0	43.0
4.	SP [kg/m^3]	–	4.310	4.540	4.925	8.900	9.675	10.781
5.	P [kg/m^3]	989.0	982.0	988.0	985.0	1003.0	992.0	988.0
6.	G [kg/m^3]	989.0	982.0	988.0	985.0	1003.0	992.0	988.0
7.	W [kg/m^3]	177.0	177.0	168.0	163.0	144.0	137.0	132.0
8.	ρ_B [kg/m^3]	2495.0	2490.0	2512.0	2532.0	2515.0	2518.0	2550.0
9.	ρ_{SB} [kg/m^3]	2519.0	2514.0	2533.0	2545.0	2552.0	2564.0	2577.0
10.	s [-]	0.990	0.990	0.992	0.995	0.985	0.982	0.990
11.	j [-]	0.001	0.001	0.008	0.005	0.015	0.018	0.010
12.	Va [dm^3/m^3]	10.0	10.0	8.0	5.0	15.0	18.0	10.0
13.	Ve-Be [s]	10.5	7.0	8.0	8.0	9.5	10.5	9.0
14.	$f_{c.\ cube}$ [MPa] after 28 days in hydroisolated condition (18±2°C)	50.4	53.5	63.7	77.80	77.7	86.4	93.5

The table includes: W/(C+ SF) - water binder ratio, C, SF, SP (the 40% water solution of super plasticizer), P, G, W - content of cement, silica fume, superplasticizer, sand, basalt grit, water in 1 m^3 of concrete mixture respectively.
The table includes: ρ_B, ρ_{SB}, s, j, Va, Ve-Be, $f_{c.\ cube}$ – apparent density and density of concrete mixture, tightness and cavity, volume of air pores, consistency of concrete mixture, compression strength of concretes respectively.
SP contains the remaining water in the formula W/(C + SF).

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]:

$$\omega_{cap} = \frac{w}{S} - \left(\omega_H + \omega_p\right) \cdot \alpha \qquad (1)$$

where w is initial capacity of water in the unit of cement grout capacity [dm^3], ω_H is chemically tied water in the unit of binder mass [dm^3/kg,], ω_p is out of network water which stays in binding gel structure with reference to the unit of binder mass [dm^3/kg], α is degree of binder's hydration, S is binder mass, w/s=ω is water – binder ratio.

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

$$\omega_{gel} = 0,28 \cdot \alpha \cdot \left(\frac{1}{\rho_s} + \omega_H + \omega_p - V_s\right) \qquad (2)$$

where: ρ_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 (**P**lain **C**oncrete – **PC**), 1÷3, 4÷6 (**H**igh **P**erformance **C**oncrete – **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]:

$$\alpha = \exp\left[-c\left(\ln t_a\right)^{-d}\right] \cdot \frac{Q_{max}}{Q_o} \qquad (3)$$

where: c, d are empirically appointed parameters, t_a

Table 2.
Parameters of structure and thermo-physical characteristics of binder [18]

No	Concrete mixture	$\omega_t = \omega_H + \omega_p$ cm^3/g	ω_H cm^3/g	ω_p cm^3/g	V_s cm^3/g	ρ_s g/cm^3
1.	1A (**PC**)	0.439	0.252	0.187	0.04690	3.125
2.	Concretes 1÷3	0.439	0.252	0.187	0.04690	3.125
3.	Concretes 4÷6 (**HPC**)	0.395	0.278	0.117	0.04221	2.973

is reduced time [h], Q_{max}, Q_o 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]:

$$t_a = \int_0^t \exp[\frac{E_k}{R}(\frac{T_{(t)} - T_a}{T_{(t)} T_a})]dt \tag{4}$$

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].

Table 3.
Parameters of (3) equation [18]

No	Concrete	c	d	Q_{max} [kJ/kg]	Q_o [kJ/kg]
1.	**1A**	13.448	2.135	430	430
2.	**1**	22.297	2.094	430	430
3.	**2**	24.078	2.167	430	430
4.	**3**	27.129	2.238	411.51	430
5.	**4**	175.659	3.863	387	387
6.	**5**	165.527	4.082	362.51	387
7.	**6**	132.679	4.025	313.47	387

Energy of activation Ek 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 and 1÷3 concretes). For 4÷6 and 1A as well as 1÷3 concretes appropriate values of Ek 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:

$$x = \frac{\omega_{gel}}{\omega_{gel} + \omega_{cap} + \omega_a} \tag{5}$$

where: ω_{gel}, ω_{cap}, ω_a adequately stand for gel, capillary and air pores capacity with reference to unit of binder mass [dm^3/kg].

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

$$x = \frac{0{,}28 \cdot \alpha \cdot (\frac{1}{\rho_s} + \omega_H + \omega_p - V_s)}{0{,}28 \cdot \alpha \cdot (\frac{1}{\rho_s} + \omega_H + \omega_p - V_s) + \omega - (\omega_H + \omega_p) \cdot \alpha + \omega_a} \tag{6}$$

Porosity coefficient x assumes values of < 0.1 > range. For $\alpha = 1$, $\omega_a = 0$ and $\omega = \omega_H + \omega_p$, 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 defloculation 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.

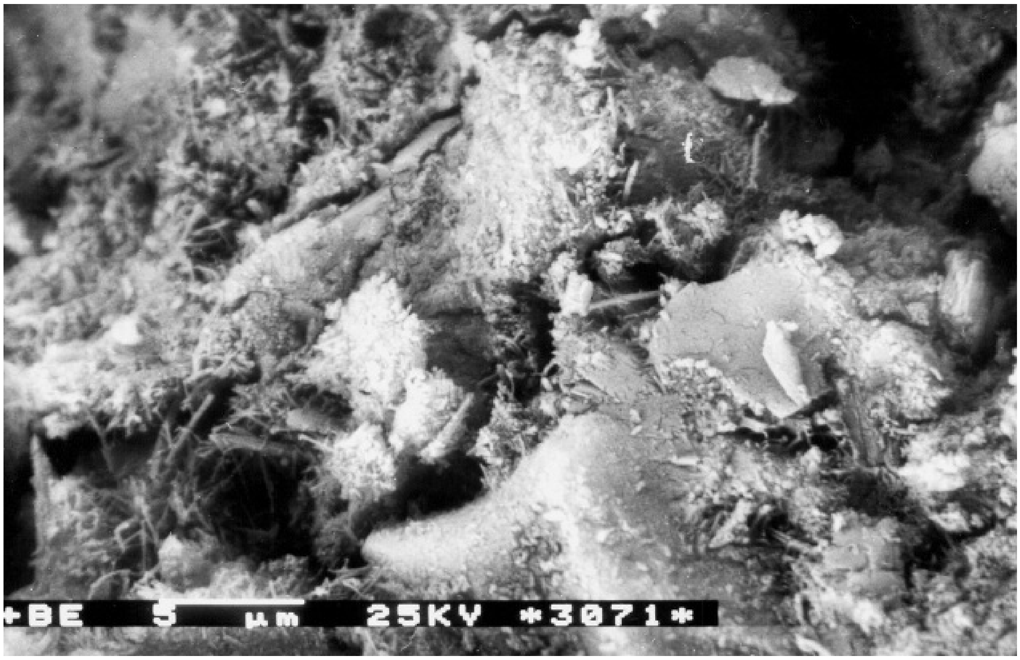

Figure 1.
A microscopic picture (magnification x 4000) of a hardened 1A cement paste (own research). There are crystal needles of phase C – S – H in porous places [18]

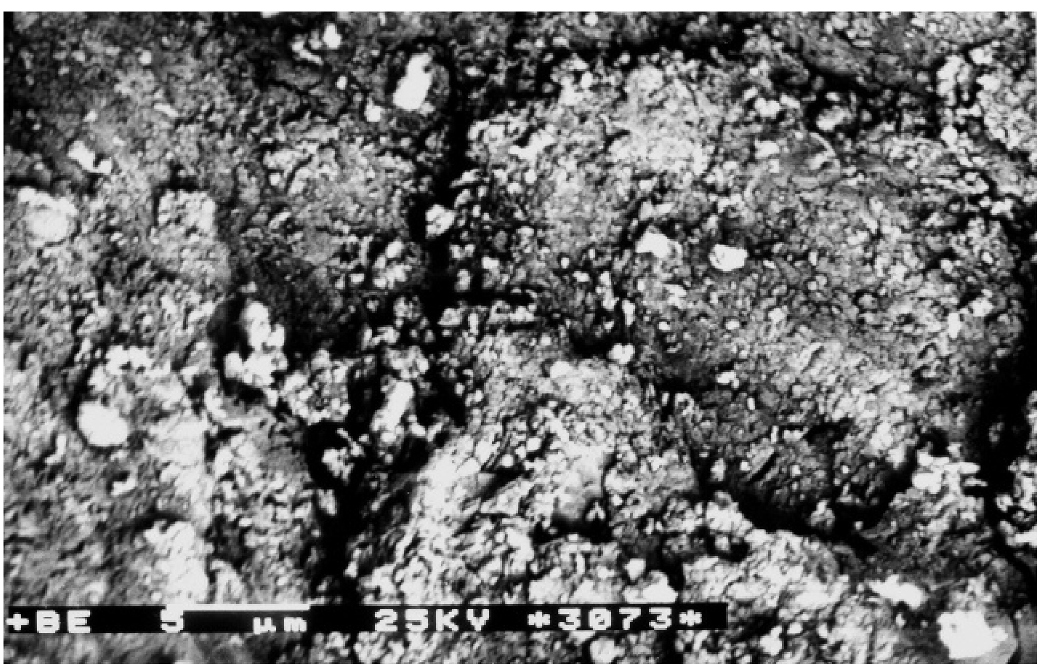

Figure 2.
A microscopic picture (magnification x 4000) of a hardened 6 cement paste (own research). Hydration products in the form of compact gel of the phase C – S – H [18]

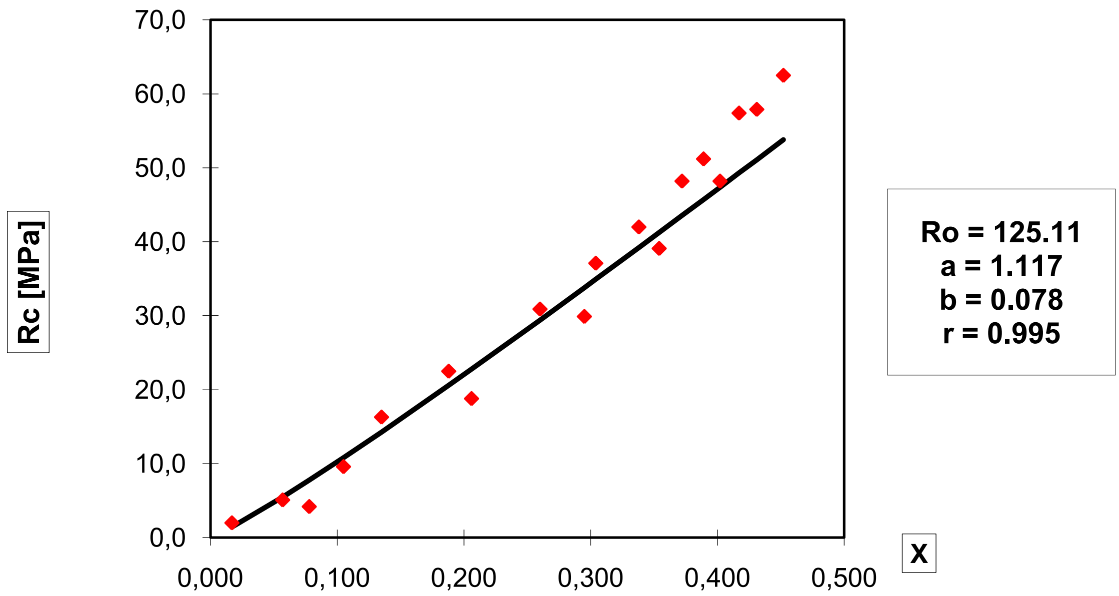

Figure 3.
Graph of formula (7) for concrete 1A [18], [19]

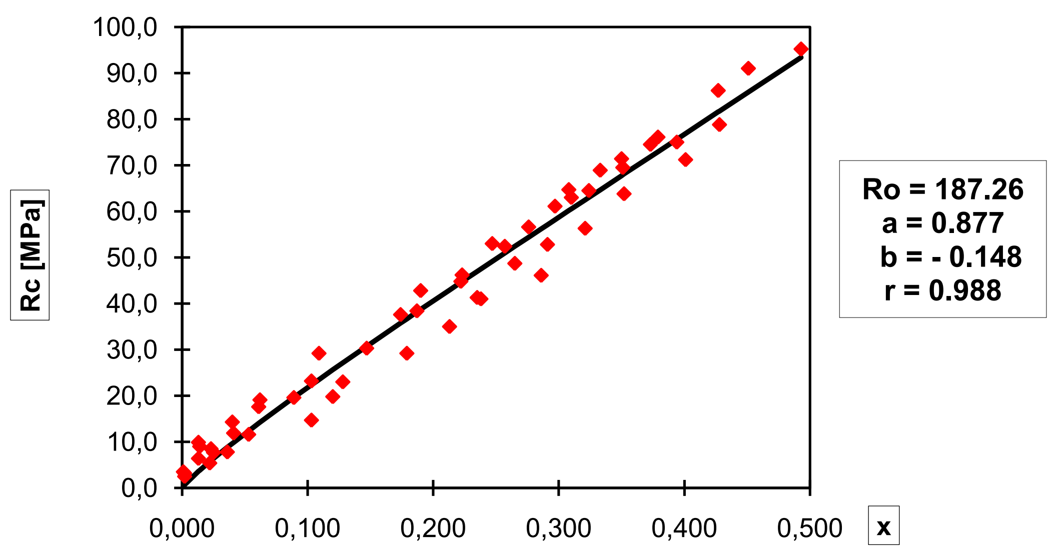

Figure 4.
Graph of formula (7) for concretes 1, 2, 3 [18]

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]:

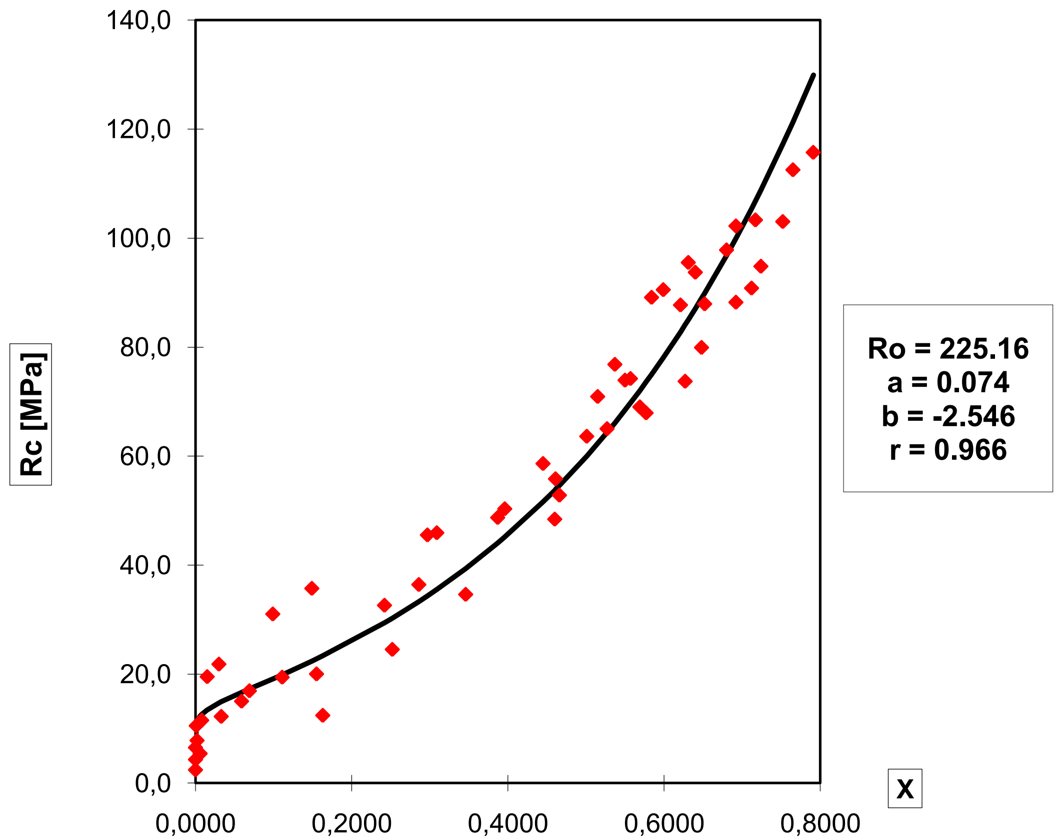

Figure 5.
Graph of formula (7) for concretes 4, 5, 6 [18], [19]

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

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.

REFERENCES

[1] *Bergström S.G.*; Byggnadsmateriallära, (Building Materials), FKI. Lunds Tekniska Högskola, VBV, Lund, 1967

[2] *Byfors J.*; Plain concrete of early ages. Swedish Cement and Concrete Research Institute, Of 3, Stockholm

[3] *Bresson J.*; Prediction of strength of concrete products. RILEM International Conference on Concrete at Early Ages, Paris, 1982, vol.I, p.111-115

[4] *Czarnecki l., Broniewski T., Henning O.*; Chemia w budownictwie. (Chemistry in Civil Engineering). Arkady, Warszawa 1994

[5] *Hansen T.C.*; Physical Structure of hardened Cement Paste-A Classical Approach. Materials and Structure, 19, 114, 1986, p.423-436

[6] *Jasiczak J., Mikołajczyk P.*; Technologia betonu modyfikowanego domieszkami i dodatkami. Przegląd tendencji krajowych i zagranicznych. (Technology of concrete modified by additives and admixtures. Overview of domestic and foreign trends). Wydawnictwo Politechniki Poznańskiej, Poznań 1997

[7] *Kiernożycki W.*; Compressive and shearing strength of hardening concrete. Archives of Civil Engineering, XXXIX, 1, 1993, p.61-76

[8] *Kiernożycki W.*; Betonowe konstrukcje masywne. (Massive Concrete Structures). Polski Cement, Kraków 2003

[9] *Kishi T., Shimomura T., Maekawa K.*; Thermal crack control design of HPC. Proceedings of the International Symposium held by RILEM, E&FN SPON, Belgium 1991

[10] *Kucharska L.*; Kształtowanie struktury wysokosprawnych betonów. Rola dodatków i domieszek. (Shaping the structure of high-performance concrete. The role of additives and admixtures). Przegląd Budowlany, 8-9/1992

[11] *Mikoś J.*; Wytrzymałość betonu w funkcji współczynnika porowatości. (Concrete strenght as a function of porosity ratio). Archiwum Inżynierii Lądowej. Tom XXX z. 1-2/1985

[12] *Neville A.M.*; Properties of Concrete. Pearson Education Limitem. Fourth Edition, 1995

[13] *Popowics S.*; Generalizations of the Abram's law-Prediction of strength developments of concrete from cement properties. ACI Journal, 78, 1981, p.123-129

[14] *Powers T.C.*; The physical structure and engineering properties of concrete. Portl. Cem. Assoc. Res. Dept. Bull. 90, 1958

[15] *Reul H.*; Handbuch der Bauchemie. (Handbook of Chemistry in Civil Engineering). Verlag für Chemische Industrie. Ziolkowsky AG, Augsburg 1999

[16] *Rostasy F.S, Laube M., Onken P.*; Zur kontrolle früher Temperaturrisse in Betonbauteilen. (Control of early thermal cracking in concrete elements) Bauingenieur, 68, 1993, p.5-14

[17] *Spriggs R.M., Vasilos T.*; Effect of grain size on transverse bond strength of alumine and magnesia. J.AM.Ceram.Soc.46,224,1963

[18] *Ślusarek J.*; Model twardnienia tworzyw cementowych. (The cement materials hardening model). Zeszyty Naukowe Politechniki Śląskiej Nr 1513, seria Budownictwo, z.92, Wydawnictwo Politechniki Śląskiej, Gliwice 2001

[19] *Ślusarek J.*; Hardening concrete effects in massive structures. EJPAU-CIVIL ENGINEERING (Electronic Journal of Polish Agricultural Universities), 11 (2), 2008

[20] *Weber J.W.*; Empirische Formeln zur beschreibung der Festigkeitentwicklung und der Entwicklung des E-Modulus von Beton. (Empirical formulas for description strength and elasticity modulus). Betonwerk+Fertigteil-Technik, 12, 1979, p.753-756

[21] CEB-Comitte Euro-International du Beton-CEB-FIP Model Code 1990. Bulletin D' Information, 213/214, Lausanne, 1993