

**MATHEMATICAL MODELLING OF THE COMPOSITION OF A HIGH-STRENGTH
COMPOSITE CONCRETE CONTAINING BLENDED CARBONATE ADDITIVE**

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Abstract

A new high-strength concrete has been developed on the basis of the utilization of the blended carbonates as an active additive (BCA). The main technological features are the preliminary mechanical-chemical activation of this natural mineral product and the stage method of production.

A three-parameter polynomial model has been developed for determining the amount of the main formulation components – Portland cement, BCA and water/cement ratio by evaluation of their influence on the changes of the compressive strength for one-year time period of the hardening. The experimental plan contains 27 tests. The regression equations have been calculated for five ages. The obtained regression coefficients reflecting the trend and the effect of the three factors on the output data during the investigated period have been analyzed. The compressive strength depending on two factors has been plotted for the ages of 28 and 365 days, the value of the third factor being constant. They are important for the construction practice and they display the whole spectrum of possibilities for variation of the formulation parameters, achieving at the same time the specified design strength.

Key words: *high-strength composite concrete, blended carbonate additive, polynomial model, regression, compressive strength*

1. INTRODUCTION

The existence of sustainable and ecologically clean environment depends on the rational utilization of natural and secondary mineral products from various industrial branches and on a number of other measures too, [1-4]. Natural carbonates are one of the most widely applied raw materials for concretes with improved properties. The high activity increases their application. The fast advance of building industry during the last two decades is a basic precondition for the successful utilization of natural carbonates as topical mineral raw materials in the production of highly effective cement construction materials, [5]. Until now, the carbonates make used only as a fillers for concretes, but since 2001 year (application of EN 197-1), they may use like as active mineral additives in composition of blended cements and composite concretes, [6].

Using the present knowledge on the mechanism of structure formation and hardening of the Portland cement systems, this property of increasing the activity of the blended carbonate-containing binder substances is solved in the created new high-strength composite concrete (HCC). The silicate matrix is filled with Portland cement, medium-grained artificial sand and blended carbonate additive (BCA). So obtained non-metallic construction composite concrete possesses increased density, high mechanical characteristics and operation durability, [7, 8]. The development of this composite concrete contributes to the achievement of considerable social, economic and ecological effects.

It is known that there are two methods for faster determination of cement and concrete strength: by express strength testing and by applying suitable mathematical models [9-10]. Models for describing

the hydration processes [11], the microstructure [12], the electrochemical extraction of chlorides from concrete [13] as well as the cement setting when using CaCl_2 as an accelerator [14], can be found in reference literature. However, publications on the methods of mathematical statistics for optimizing of the composition and strength properties of composite concrete with additives of carbonate raw products are rather scarce in reference literature.

The present paper shows the results from the investigated quantitative influence of important formulation parameters, including of the new active additive (BCA), on the mechanical properties of the high-strength concrete in the course of one-year hardening. The method of the planned experiment has been applied and regression equations have been obtained for these effects for different ages of hardening.

2. MATERIALS AND METHODS

2.1 Initial materials

Bulgarian cement brand PC 42.5 (“Devnya” SA) was used, which meets the requirements of the Bulgarian State Standard BDS EN 196-1. The mineral composition is: $\text{C}_3\text{S} = 59.0\%$, $\text{C}_2\text{S} = 19.5\%$, $\text{C}_3\text{A} = 7.2\%$ and $\text{C}_4\text{AF} = 13.0\%$. The fineness of grinding determined according to the Bulgarian State Standard BDS EN 196-6 is 4.5% . The specific density is 3.16 g/cm^3 , respectively. The normal consistency is 21.0% , the beginning of setting – 2 hours and 5 minutes and the end of setting – 8 hours and 50 minutes.

Composite concretes were prepared with cement/aggregate ratio 1:3 and different water/cement ratio. The artificial medium-grained sand is a good balanced combination of ecological neat granulated slag from non-ferrous metallurgy. It replaces entirely the natural sand in the concrete.

The natural carbonates with blended composition are used as a natural mineral additive by the present experimental investigation. They are found as non-ore raw material or as a component of the host rocks surrounding ore beds, forming own mineral associations in the Kremikovtsi deposit, [15]. The bulk density is 2.88 g/cm^3 , the specific density is 3.44 g/cm^3 and the dispersity is $7.1 \mu\text{m}$. The following mineral phases have been identified: calcite, siderite, haematite and impurities. Calcite represents a polymorphic modification of CaCO_3 with bulk density of 2.87 g/cm^3 .

The ecological neat acid slag has graphite-black color and porous structure. The chemical composition is: $\text{CaO} = 23.0\%$, $\text{SiO}_2 = 24.0\%$, $\text{Al}_2\text{O}_3 = 5.0\%$, $\text{MgO} = 1.5\%$, $\text{Fe}_2\text{O}_3 = 36.0\%$, $\text{CuO} = 0.5\%$, $\text{ZnO} = 2.0\%$, $\text{MnO} = 0.9\%$, $\text{Na}_2\text{O} = 1.0\%$, $\text{K}_2\text{O} = 1.0\%$ and $M_0 = 0.84$. The basic mineral phases have been recorded in it [16]. The presence of melilite (solid solution of gehlenite and okermanite), monticellite, CaO , wuestite and Fe_3O_4 has been proved. Melilite glass represents the basic component in composition of the slag. The specific density of the granulated slag is 3.73 g/cm^3 and the dispersity determined by the Blaine specific surface is $3800 \text{ cm}^2/\text{g}$. The slag is produced according to a wet method of granulation. Its basic physico-mechanical parameters are measured using the standard test methods, its chemical activity – by measuring the swelling when treated in alkaline solutions and the released heat of hydration – by differential calorimetric method [17, 18].

2.2. Two-stage technology for the activating of natural blended carbonates

To increase of the reactive activity of the natural carbonates, a separate-stage technology has been applied. Preliminary technological stages are: grinding to a powder with high dispersity, optimizing of the quantity and its mechanical-chemical activation. The fine grinding contributes to significant increase of the specific surface, the surface energy activity of the minerals and their capability of

transformation into other phases. In the course of activation, due to the high velocity of mixing the dispersity is an additionally increased and the crystalline-chemical surface features of the carbonate particles are further improved. New surfaces are formed for chemical interactions. At the same time, the chemical bonds in the crystal lattices of calcite and siderite are disturbed. Groups of free radicals and free ions are formed. Adsorption centers are originated. Enhanced physico-chemical processes are passed place of phase boundaries as surface wetting, adsorption and dissolution. Hence, the choice of this technological stage successfully ensures the preliminary intensification of hydration process. During the subsequent homogenization of blended carbonate powder with Portland cement chemically active products are additionally introduced. They improve the microstructure and physico-mechanical properties of the whole composite cement system.

2.3. Mechanical testing

The compressive strength is determined by means of prismatic test specimens with dimensions 4x4x16 cm. After removing the moulds at the 24th hour the specimens are cured under standard conditions – temperature $T = 20 \pm 3^{\circ}\text{C}$ and humidity of the air $W = 70\%$ till the corresponding age of testing: 1, 7, 28, 180 and 365 days. The results are obtained as the mean arithmetic value from the single data of three prisms (6 half prisms).

2.4. Experimental plan

The variable parameters are:

X_1 – Portland cement, % of the total dry mass;

X_2 – active blended carbonate additive, % of the total dry mass;

X_3 – water /cement ratio;

The boundaries of the variation of these three factors in natural coordinates were determined on the basis of preliminary experimental results:

X_1 – varies from 20 to 25 %. The choice is made with the aim of achieving high compressive strength.

X_2 – varies from 5 to 15 %, with consideration of the action mechanism of the new admixture and the realization of the preliminary mechanical-chemical activation of the selfsame.

X_3 – varies from 0.45 to 0.55.

The variation levels in natural coordinates are shown in Table 1. The selected values allow the accurate study of the relationship between the three formulation parameters and the compressive strength for a long period of hardening.

Table 1 Experimental Plan

	Variation levels in natural coordinates			Interval of variation ΔX_i
	$X_{i, \min}$	$X_{i, o}$	$X_{i, \max}$	
Cement (X_1), %	20	22.5	25	2.5
BCA (X_2), %	5	10	15	5
W/C (X_3), -	0.45	0.50	0.55	0.05

The plan of the experiment contains 27 compositions (test points) for five ages of investigation - 1, 7, 28, 180, 365 days.

2.5. Mathematical method

The coefficients of regression equations were calculated by means of MS Excel program and included in the program function of multiple linear regression LINEST. Some description of this function can be found in MS Excel Help, as well as in literature [19, 20].

The unknown target function $R_c(X_1, X_2, X_3)$ is searched as a polynomial for each of the selected ages:

$$R_c = b + a_1.X_1 + a_2.X_2 + a_3.X_3 + a_{11}.X_1^2 + a_{22}.X_2^2 + a_{33}.X_3^2 + a_{12}.X_1.X_2 + a_{23}.X_2.X_3 + a_{31}.X_3.X_1 + a_{123}.X_1.X_2.X_3 \quad (1)$$

The function LINEST returns correct regression coefficients regardless of the fact whether the variables are standardized (with uniform distribution around the zero point) or not.

3. RESULTS AND DISCUSSION

The experimental results are shown in Table 2. In regression analysis by equation (1) is found that values of the coefficients a_{12} , a_{23} , a_{31} and a_{123} are smaller than their standard errors. This means that they can be neglected. On this reason is accepted model (2):

$$R_c = b + a_1.X_1 + a_2.X_2 + a_3.X_3 + a_{11}.X_1^2 + a_{22}.X_2^2 + a_{33}.X_3^2 \quad (2)$$

The polynomial models of the compressive strength of the composite concrete for the above mentioned ages are shown in Table 3.

Table 2 Experimental plan and corresponding compressive strength for different ages

Sample No	Plan of experiment			Compressive strength R_c , MPa for different ages, days				
	X_1 , %	X_2 , %	X_3	1	7	28	180	365
1	20	5	0.45	5	14	22	25	27
2	20	5	0.50	6	17	23	26	29
3	20	5	0.55	4	13	19	22	25
4	20	10	0.45	7	20	30	35	39
5	20	10	0.50	8	25	33	38	40
6	20	10	0.55	6	18	28	32	36
7	20	15	0.45	7	19	27	31	34
8	20	15	0.50	7	22	31	32	35
9	20	15	0.55	5	16	24	26	31

10	22.5	5	0.45	8	22	33	38	41
11	22.5	5	0.50	8	25	36	40	44
12	22.5	5	0.55	7	20	30	34	38
13	22.5	10	0.45	11	31	46	53	58
14	22.5	10	0.50	12	37	51	57	62
15	22.5	10	0.55	10	28	42	48	54
16	22.5	15	0.45	9	29	41	48	52
17	22.5	15	0.50	11	33	47	50	54
18	22.5	15	0.55	8	24	38	43	48
19	25	5	0.45	7	20	29	34	37
20	25	5	0.50	8	23	33	36	40
21	25	5	0.55	6	18	27	31	33
22	25	10	0.45	10	28	42	48	53
23	25	10	0.50	11	34	46	52	56
24	25	10	0.55	8	25	38	44	49
25	25	15	0.45	9	26	36	43	47
26	25	15	0.50	10	30	42	45	48
27	25	15	0.55	7	22	34	39	44

Table 3 Regression equations and coefficients

$R_C = b + a_1.X_1 + a_2.X_2 + a_3.X_3 + a_{11}.X_1^2 + a_{22}.X_2^2 + a_{33}.X_3^2$, MPa								Coefficient of determination	Standard error
Age, days	b	a_1	a_2	a_3	a_{11}	a_{22}	a_{33}	R^2	MPa
1	-323.4	15.3	1.67	609	-0.329	-0.0756	-622	0.96	0.46
7	-1046	44.6	4.94	2172	-0.960	-0.220	-2200	0.97	1.2
28	-1302	67.6	6.98	2149	-1.458	-0.311	-2178	0.98	1.3
180	-1280	75.5	8.39	1693	-1.627	-0.380	-1733	0.98	1.3
365	-1314	82.1	9.19	1522	-1.769	-0.416	-1556	0.98	1.4

The changes in the compressive strength depending on two factors simultaneously are illustrated in Figures 1, 2, 3 by the isolines for the 28-day strength and Fig. 4 by the isolines for 365 day strength. The two-factor graphs are plotted by varying two of the factors within the accepted range and fixing the third one at selected level.

The influence of the quantitative participation of the Portland cement and the blended carbonate additive on the strength is shown in Fig. 1. The water/cement ratio is constant ($W/C=0.50$). As can be seen in Fig. 1 a sufficiently broad range of the BCA variation exists, in which the achievement of the necessary design strength is guaranteed. For example, the strength of 45 MPa can be achieved for two different mass combinations of the blended carbonate additive – $BCA = 7.3\%$ or $BCA = 15.4\%$ for almost one and the same cement amount of 23.0% . At the same time, an optimal amount of the active BCA exists, which ensures the high 28-day strength for fixed constant Portland cement amount and W/C ratio. The increase or decrease of the BCA quantity with respect to this optimal amount leads to strength diminution. The same relationship can be observed for the changes in the other formulation components $PC - W/C$ and $BCA - W/C$ within the shown ranges of variation in Fig. 2 and Fig. 3.

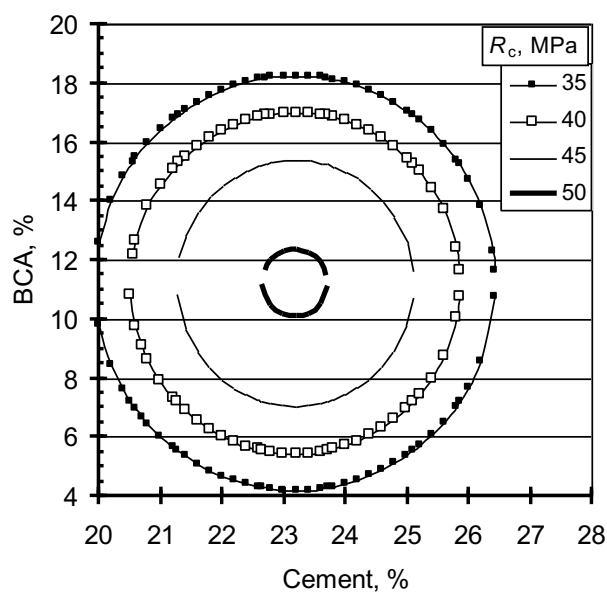


Fig. 1 Isolines of the compressive strength R_{28} depending on the amount of the formulation components BCA and PC for constant $W/C = 0.50$

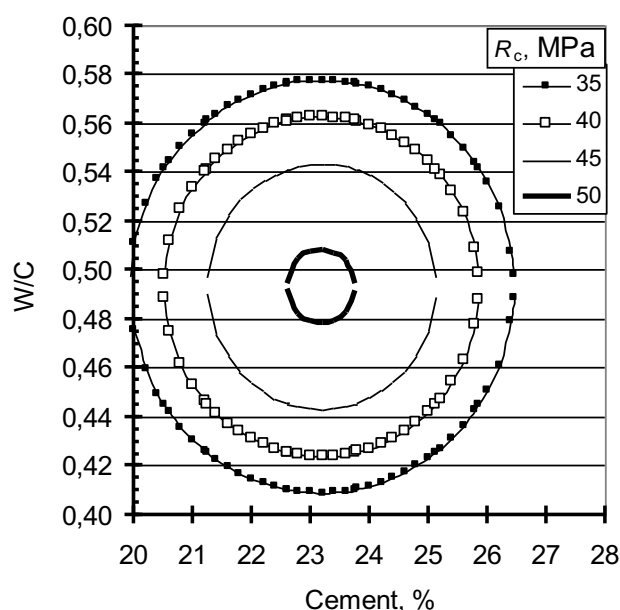


Fig. 2 Isolines of the compressive strength R_{28} depending on the amount of the formulation components PC and W/C for constant BCA = 11 %

It is seen in Fig. 2 that the contribution of the Portland cement to obtaining the compressive strength of 45 MPa is observed for the amount PC = 23.2 % and BCA = 11 %, while the participation of the water/cement varies from 0.445 to 0.545 %.

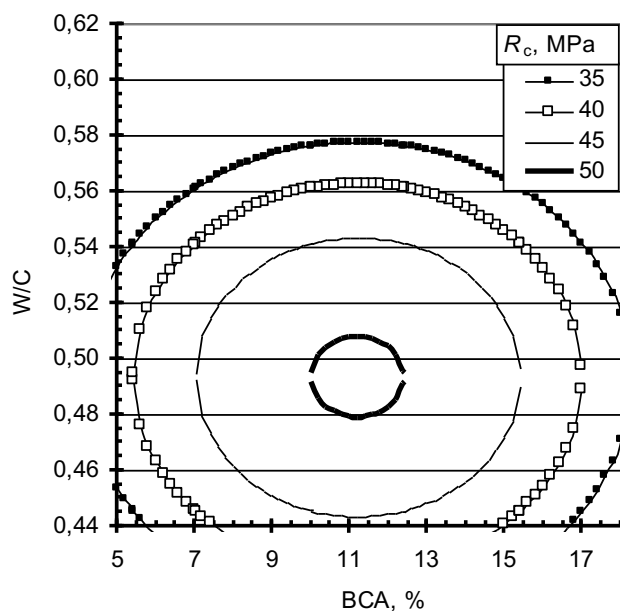


Fig. 3 Isolines of the compressive strength R_{28} depending on the amount of the formulation components BCA and W/C for constant cement = 23 %

The regression model for a normative age of 28 days shows that the maximum strength is obtained for a composition with the following values of the investigated parameters: $X_1=23.2\%$; $X_2=11.2\%$ and $X_3=0.49$. The coordinates of the optimal composition for the rest four ages do not differ substantially from the above mentioned values.

The data in Fig. 4 exhibit the same character of changes in the compressive strength due to the variation of the active additive and the quantity of cement but increase in the strength value R_{365} to 61 MPa is observed.

The investigation carried out proves that depending on the preliminary set design compressive strength, a broad range of combinations exists for optimizing the quantitative participation of the main formulation components of the high-strength composite concrete for all ages.

The maximum compressive strength of this composition varies from 11.9 MPa for the first day to 61.1 MPa for the age of 365 days, Fig.5 and Table 4.

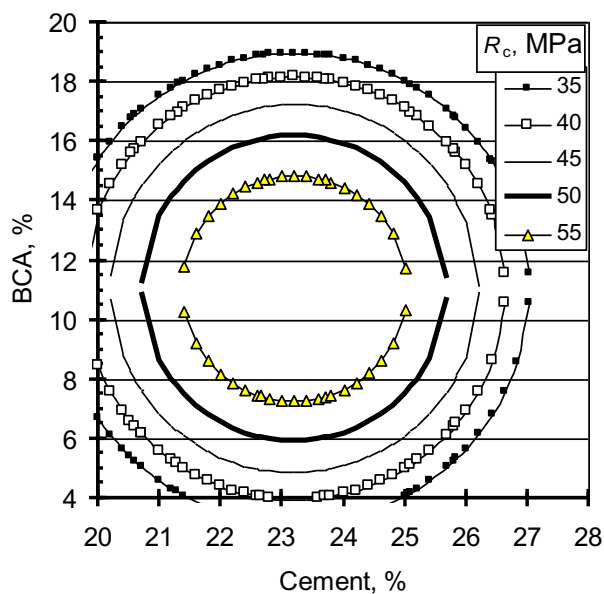


Fig. 4 Isolines of the compressive strength R_{365} depending on the amount of the formulation components BCA and PC for constant $W/C = 0.50$

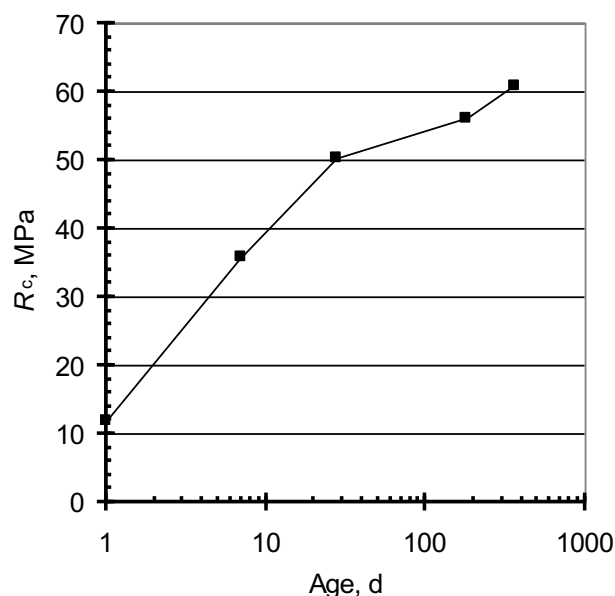


Fig. 5 Increment of the compressive strength for a composite concrete by cement = 23.3 %, BCA = 11.2 %, W/C = 0.49

Table 4 Relative alteration of the compressive strength at different ages

Age, days	1	7	28	180	365
Relative compression strength	$R_1 / R_{365} = 0.19$	$R_7 / R_{365} = 0.55$	$R_{28} / R_{365} = 0.80$	$R_{180} / R_{365} = 0.91$	1

At the same time, the experimental data and model data show that for each ratio of binder substance to water/cement ratio, there is a corresponding optimal amount of the active blended carbonate additive. Increasing or decreasing the BCA amount above or below this optimal quantity leads to strength drop. This dependence obviously results from the interaction of BCA with clinker minerals. The positive role of the introduced BCA is due to proved physical and chemical effects of the fine carbonate particles. The significant role of natural blended carbonates on structure formation and hydration hardening has been shown in [8]. It should be taken into account that during the mechanical processing of the BCA, surface decomposition takes place, which contributes to increasing of the hydration and hardening. The found optimal amount of the active additive is sufficient for obtaining hydrate products formed by a dissolution and reaction, as well as for the later stage when this process continues according to a solid state mechanism. With these optimal quantities of BCA is formed hydrate product of calcium monohydrocarboaluminate which are typical for blended carbonate composites. It improves the microstructure and increases the mechanical properties of this cement

system [8]. If the amount of the active additive (BCA) is less than the established optimal one, then the reactions mentioned above do not proceed in the entire volume and hence lower strength of the concrete is recorded. The understanding of the character of the reactions and hydration products for quantities of the active additive (BCA) higher than the optimal ones will obviously need further investigations.

4. CONCLUSIONS

A planned experiment is made for determination of compressive strength on similar silicate compositions, as dependent from the content of cement, blended carbonate additive and W/C ratio. The following conclusions are made:

1. Three-parameter models have been used for description of the influence of the main components on the compressive strength of the composite, hardening for up to 365 days. The influence of the studied parameters on the compressive strength is analyzed on the basis of these models. It is shown that an optimal quantity of the new active admixture exists, depending on the composition of the other two components. For specific values of the Portland cement and granulated slag amounts, any increase or decrease of the active additive (AA) amount with respect to its optimal values is accompanied by the compressive strength drop for the two investigated ages – 28 and 365 days.
2. The obtained results confirm the established positive effect of the preliminary joint mechanical-chemical activation of the new active additive (BCA) on the strength properties of the high-strength composite concrete. The relative quantity of BCA is up to 11.2 %.

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