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The dependence of the gathering characteristics of nanocarbon cement on the parameters of its production process

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Abstract. The article covers issues connected to the justification of the relationship between gathering characteristics of structure-modified materials and parameters of technological processes connected to the materials' production. On the basis of preliminary analysis of experimental data, the procedure has been proposed for formation of analytical dependence of weight gain values for carbon nanotubes and nanofibres on cement particles (with the use of gas-phase synthesis applied to carbon nanostructures) on time parameters of reduction of iron oxide and synthesis of nanostructures directly on the matrix surface. As a base of the mentioned-above dependence, it has been proposed to use a superposition of two components: the linear component defined by the reduction parameter and a logistic component defined by the synthesis parameter. It has been proposed to use optimization modeling tools for the determination of parameters of analytical dependence. On the basis of the results of the procedure, the conclusion has been made about the adequacy of the obtained results and, as a sequence, high practical importance of the proposed analytical dependence. As part of the further stage of the research, it is planned to carry out laboratory experiments and form the corresponding analytical dependences to assess the effect of synthesis modes on the characteristics of the resulting product for alternative matrix cement materials, such as sulfate-resistant cement, magnesia, slag Portland cement, alumina, pozzolanic.

1. Introduction

Modern conditions for the development of the construction industry define the need for the development and application of innovative technologies for obtaining of more efficient construction materials in terms of their operational characteristics [1–3], as well as the cost of manufacturing and installation [4, 5]. At the same time, one of the most promising directions of operational properties improvement for the materials of building structures is modification of cement structure by means of carbon nanostructures integration [6, 7] into it to increase radar absorption capacity and strength of building material [6–8]. In this regard, one of the most important tasks is to determine the relationship between the operational characteristics of structurally modified nanocarbon cement and the parameters of the creation process for the specified construction material. At the same time, the results of scientific works analysis in the corresponding research field showed the limitations of existing tools used for the determination of adequate forecast values of material's operational characteristics on the basis of regulated values of the technological parameters for the material's creation process [9–11, 14–17].

That circumstance determined the feasibility of the research, which aim is to develop tools for determination of the operating characteristics for structurally modified cement on the basis of the

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technological parameters of the material's creation. To achieve the specified aim, the following tasks have been formulated:

1. Carry out the analysis of the scientific works related to the justification of the relationship between obtained characteristics of structure-modified materials and parameters of technological processes connected to the materials' production.

2. Conduct a series of laboratory experiments to obtain structurally modified cement M500D0 (CEM I 42.5 N) with different characteristics of the technological process connected to the material's creation.

3. Propose an analytical dependence of the acquired characteristics values of the structurally modified material on the values of the technological process parameters connected to the material's production.

4. Propose and implement on the basis of conducted experiments results a procedure for formation of the analytical dependence of acquired characteristics values of the structurally modified material on the values of the parameters for the technological process connected to the material's production.

In this case the research object is the process of creation of the structurally-modified cement (by integration of carbon nanostructures on its particles) as the building material's element providing the improvement of corresponding physical and mechanical properties (in comparison with materials without nanocarbon cement). The research subject is the relationship between the values of the acquired characteristics of the structurally-modified cement and parameters of technological process connected to the material's creation.

The scientific novelty of the research is determined by the composition of considered parameters of the material and technological process for its creation, and also by specific structure of the proposed analytical dependence based on the superposition of linear and non-linear components.

At the initial stages of the research the analysis of the scientific works connected to the research field has been carried out. Detailed description of the main scientific developments is presented in Table 1.

Table 1. The results of the review of scientific papers on the research topic

№	The name of development	The content and features of development
1	Determination of the characteristics of the thermal catalytic steam decomposition (CVD) system for the growth of carbon nanotubes [14]	description of the process of synthesis of carbon nanofibers growth using the Taguchi matrix design using nitrogen as a transport gas; analysis of factors that have the influence on the growth of nanostructures; identification of the factor that has the greatest influence on the growth of nanostructures on the basis of the experiments' results; synthesis with medium temperature
2	Determination of characteristics for the carrier gas to ensure the maximum yield of carbon nanotubes during synthesis with the use of CVD method [15]	analysis of the influence of the flow rate, the composition of the carrier gas (H_2, N_2, and Ar), and the amount of benzene on the quality and yield of carbon nanotubes created by catalytic vapor decomposition; identification of the carrier gas variant that provides the maximal (most preferred) values of the yield characteristics and the best qualities of carbon nanotubes on the basis of the results obtained during conducted experiments
3	Analysis of the effect of ferrocene on the structure of carbon nanotubes synthesized on the basis of Si / SiO2 / Al2O3 [16]	analysis of the growth process for multilayer carbon nanotubes under the following conditions: silicon aluminum substrate is used as the matrix base; ethylene is selected as the gas used for nucleation of nanostructures. identification of ferrocene as a catalyst that provides high purity characteristics of carbon structures on the basis of the experiments' results.
4	Direct synthesis of carbon nanofibers on cement particles [17]	analysis of processes connected to the direct synthesis of carbon nanotubes and nanofibers on cement particles; C_2H_2, CO_2, and CO are used as carbon carrier gases; the method of low-temperature and high- performance synthesis that provides a significant increase (in comparison with previously proposed methods) of the characteristics of compressive strength and electrical conductivity for the created structurally modified material.

On the basis of the information presented in Table 1, it has been concluded that scientific works do not include mathematical description (approximation dependence, tendency, extrapolation formula, etc.) of the patterns revealed within conduction of laboratory experiments. Therefore corresponding scientific results cannot be directly used for more complex tasks connected to prediction and optimization. That circumstance confirmed the necessity for the research being conducted.

At the further stages of the research, a series of laboratory experiments assuming the analysis of the operational properties of structurally modified cement of grade M500D0 (CEM I 42.5 N) (by integration of carbon nanostructures on its particles) in conditions of different values of parameters of the technological process connected to the material's creation – growth of carbon nanostructures on the surface of cement powder with the use of the gas-phase synthesis method [9, 14] – has been conducted. The mentioned-above technological process included the following main steps:

1. Preliminary heating of a certain volume of pure cement powder in the furnace in the atmosphere of argon at the temperature of 650 °C.

2. Reduction of iron oxide in cement structure by addition of hydrogen [15] in the argon atmosphere for a certain time – controlled value, hereinafter referred to as reduction parameter.

3. Synthesis of carbon nanostructures on the surface of cement powder by replacement of argon-hydrogen atmosphere with acetylene-hydrogen mixture with ratio of hydrogen to acetylene 8.3:1 within a certain time period [16] – controlled value, hereinafter referred to as synthesis parameter.

4. Creation of fine-grained concrete on the basis of pure cement in combination with nanocarbon cement by mixing with fine aggregate and water.

5. Creation of prototype samples by the placement of produced concrete into mold with subsequent holding of material for several days till its complete hardening and carrying out of physical and mechanical tests with subsequent analysis [7, 13].

It's necessary to note that during the described-above technological process the initial material's weight increase or IMWI (%), caused by the growth of carbon nanotubes and nanofibers, has been considered as one of the key operational characteristics. The corresponding calculation formula is the following:

$$y = \frac{M_1 - M_0}{M_0}, \tag{1}$$

where M_0, M_1 are the masses of the sample obtained on the basis of pure and modified cement, respectively (g).

The results of the experiments in the form of a three-dimensional plot (surface) of the IMWI value dependence on the reduction and synthesis parameters' values is shown in Table 2 and Fig. 1. It's also necessary to note that the mentioned surface is based on the results of 25 experiments performed with various combinations of values for the reduction and synthesis parameters.

2. Methods

During the next stage of the research the procedure has been proposed for the formation of analytical dependence [14–16] of the IMWI value on the reduction and synthesis parameters' values. The main provisions for the implementation of the procedure are the following:

1. The parameters of reduction and synthesis are considered as the most significant factors determining the IMWI (the influence of the other parameters of the technological process connected to the material's creation on the specified increase value is either absent or negligible).

2. The two-dimensional dependence of IMWI value on the reduction and synthesis parameters' values is monotonically increasing (confirmed by the data presented in Table 2 and Fig. 1).

3. The IMWI value is linearly depends on the reduction parameter value and nonlinearly depends on the synthesis parameter value (confirmed by the data presented in Table 2 and Fig. 1); in the latter case, the corresponding relationship in the Cartesian coordinate system "IMWI – synthesis parameter" is described by an s-shaped curve containing an inflection point (argument values, that are smaller and larger than the abscissa of the inflection point, indicate concavity and convexity, respectively).

Table 2. The results of experiment, shown in analytical form

Experiment number	Value of parameter of the process connected to the creation of the structurally modified material		Initial material's weight increase (IMWI)
	reduction parameter	synthesis parameter	
1	5	5	0.87
2	10	5	0.88
3	15	5	1.04
4	20	5	1.03
5	25	5	1.08
6	5	10	1.05
7	10	10	1.12
8	15	10	1.37
9	20	10	1.55
10	25	10	1.64
11	5	15	1.68
12	10	15	1.79
13	15	15	2.11
14	20	15	2.42
15	25	15	2.62
16	5	20	2.51
17	10	20	2.73
18	15	20	3.28
19	20	20	3.60
20	25	20	3.74
21	5	25	2.78
22	10	25	3.02
23	15	25	3.50
24	20	25	3.85
25	25	25	4.03

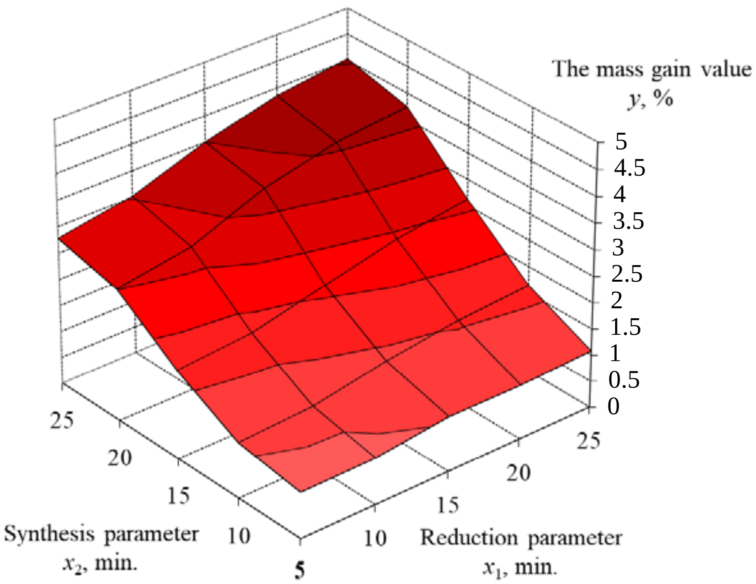


Figure 1. The results of experiments (shown in graphic form).

4. The analytical dependence of the IMWI value on the reduction and synthesis parameters' values is proposed to be described in the form of a superposition of two components: linear, determined by the value of the reduction parameter, and so-called logistic, determined by the value of the synthesis parameter; the corresponding formula is the following:

$$\tilde{y}(x_1, x_2) = \tilde{y}_1(x_1) + \tilde{y}_2(x_2) = a_0 + a_1 \cdot x_1 + \frac{a_2}{1 + b_2 \cdot e^{-c_2 \cdot x_2}}, , \qquad (2)$$

where x_1 is the value of reduction parameter (min);

x_2 is the value of synthesis parameter (min);

$\tilde{y}$ is the theoretical IMWI value determined by the reduction and synthesis parameters' values (%);

$\tilde{y}_1$ is the value of the linear component of the analytical dependence of the IMWI value on the reduction and synthesis parameters' values (%); the component value is determined only by the reduction parameter value;

$\tilde{y}_2$ is the value of the logistic component of the analytical dependence of the IMWI value on the reduction and synthesis parameters' values (%); the component is determined only by the value of the synthesis parameter;

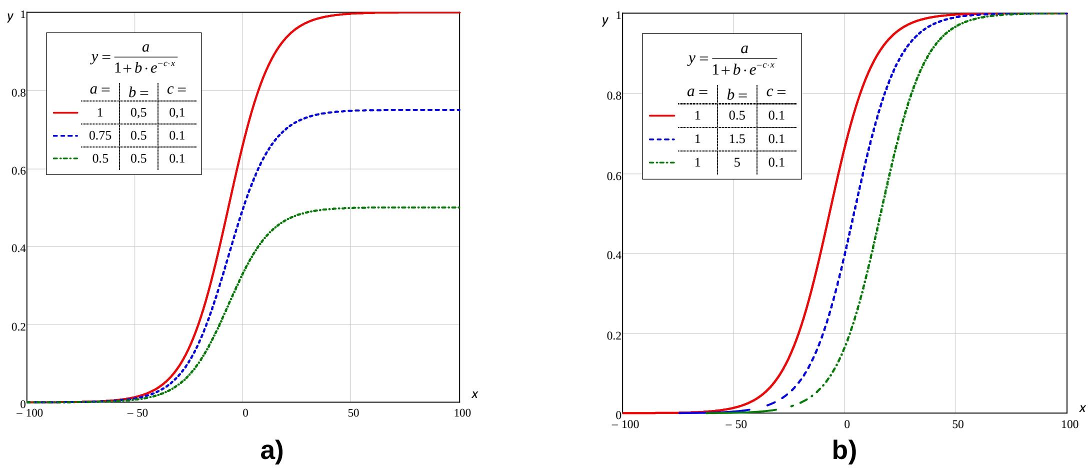
Description of other elements of the formula is given in Table 2 (lines 2.1–2.5); the purpose of parameters a_2, b_2, c_2 of the logistics component of the analytical dependence is illustrated in Fig. 2.

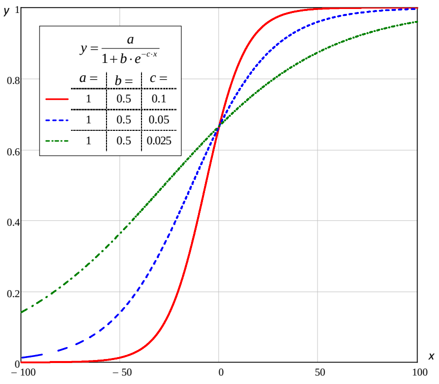
5. The analytical dependence formation of the IMWI value on the reduction and synthesis parameters' values is based on the determination of values for parameters a_0, a_1, a_2, b_2, c_2 of linear and logistical components (see formula (2)) as part of the nonlinear approximation procedure and is performed by building and implementation of the optimization model based on minimization of the sum of squares for deviations of the calculated (theoretical) IMWI values from the respective actual (experimental) values.

6. In order to evaluate the adequacy of the formed analytical dependence, i.e. the degree of compliance of calculated (theoretical) IMWI values obtained on the basis of the specified dependence with the actual values obtained by experiments, it is proposed to use the determination index R; formed analytical dependence will be able to be used for the calculation of predicted IMWI values on the basis of known values of reduction and synthesis parameters in case of fulfillment of the following condition [21]

$$R \geq 0.9. \qquad (3)$$

The description of the source data for the implementation of the proposed procedure, as well as unknown variables of the corresponding optimization model (see paragraph 5 of the main provisions), is given in Table 2. The description of the calculated characteristics enumerated during the procedure's implementation is given in Table 3.





c)

Figure 2. Main parameters of the logistic function and their purposes:
a) – scale parameter; b) – offset parameter; c) – form parameter

Table 3. Source data required for the implementation of the procedure and unknown variables of the corresponding optimization model

№	Name of the initial data element / of the unknown variable	Measure unit	Designation / formula
1	Initial data (input parameters)		
1.1	Basic initial data		
1.1.1	Number of measurements	units	m
1.1.2	The share of the actual IMWI value determined by value of reduction parameter*	-	Δ_1
1.1.3	The share of the actual IMWI value determined by value of synthesis parameter*	-	Δ_2
1.2	Indexes		
1.2.1	Index of experiment	-	$i = 1, 2, ..., m$
1.3	Characteristics of each experiment i $(i = 1, 2, \ldots, m)$		
1.3.1	Reduction parameter value	min.	x_{1i}
1.3.2	Synthesis parameter value	min.	x_{2i}
1.3.3	IMWI value	%	y_i
1.4	Initial values of unknown variables		
1.4.1	Value of the form parameter for the logistic component of the formed analytical dependence**	min^{-1}	c_2^0
2	Unknown variables*** (output parameters)		
2.1	Value of the offset parameter for the linear component of the formed analytical dependence	%	a_0
2.2	Value of the scale parameter for the linear component of the formed analytical dependence	$\frac{\%}{\text{min.}}$	a_1
2.3	Value of the scale parameter for the logistic component of the formed analytical dependence	%	a_2
2.4	Value of the offset parameter for the logistic component of the formed analytical dependence	-	b_2
2.5	Value of the form parameter for the logistic component of the formed analytical dependence	min^{-1}	b_2

Note: * – the values of the source data elements must meet the following conditions: $\Delta_1, \Delta_2 \geq 0$; $\Delta_1 + \Delta_2 = 1$; ** – the value of the source data element is determined by the actual IMWI values depending on the values of the reduction and synthesis parameters; *** – in the names of variables, the formed analytical dependence means the dependence of the IMWI value on the reduction and synthesis parameters' values.

Table 4. Calculated characteristics enumerated during the proposed procedure's implementation

№	Name of calculated characteristic	Measure unit	Formula
1	Calculated characteristics for each experiment i ($i = 1, 2, ..., m$)		
1.1	Actual IMWI value determined by the reduction parameter value	%	$y_{1i} = y_i \cdot \Delta_1$
1.2	Actual IMWI value determined by the synthesis parameter value	%	$y_{2i} = y_i \cdot \Delta_2$
1.3	Theoretical IMWI value determined by the reduction parameter value	%	$\tilde{y}_{1i} = a_0 + a_1 \cdot x_{1i}$
1.4	Theoretical IMWI value determined by the synthesis parameter value	%	$\tilde{y}_{2i} = \frac{a_2}{1 + b_2 \cdot e^{-c_2 \cdot x_{2i}}}$
1.5	The total theoretical IMWI value	%	$\tilde{y}_i = \tilde{y}_{1i} + \tilde{y}_{2i}$
1.6	The share of the calculated IMWI value (in total theoretical value), determined by the value of the reduction parameter*	-	$\tilde{\Delta}_{1i} = \frac{\tilde{y}_{1i}}{\tilde{y}_i}$
1.7	The share of the calculated IMWI value (in total theoretical value), determined by the value of the synthesis parameter*	-	$\tilde{\Delta}_{2i} = \frac{\tilde{y}_{2i}}{\tilde{y}_i}$
2	Generalized calculated characteristics for the entire set of experiments		
2.1	Minimal reduction parameter value	min.	$x_1^{\min} = \min_i \{x_{1i}\}$
2.2	Maximal reduction parameter value	min.	$x_1^{\max} = \max_i \{x_{1i}\}$
2.3	Minimal synthesis parameter value	min.	$x_2^{\min} = \min_i \{x_{2i}\}$
2.4	Maximal synthesis parameter value	min.	$x_2^{\max} = \max_i \{x_{2i}\}$
2.5	Minimal actual IMWI value determined by the reduction parameter value	%	$y_1^{\min} = \min_i \{y_{1i}\}$
2.6	Maximal actual IMWI value determined by the reduction parameter value	%	$y_1^{\max} = \max_i \{y_{1i}\}$
2.7	Minimal actual IMWI value determined by the synthesis parameter value	%	$y_2^{\min} = \min_i \{y_{2i}\}$
2.8	Maximal actual IMWI value determined by the synthesis parameter value	%	$y_2^{\max} = \max_i \{y_{2i}\}$
2.9	The average (among the experiments) share of the calculated IMWI value determined by the reduction parameter value*	–	$\tilde{\Delta}_1 = \frac{\sum_{i=1}^{m} \tilde{\Delta}_{1i}}{m}$
2.10	The average (among the experiments) share of the calculated IMWI value determined by the synthesis parameter value*	–	$\tilde{\Delta}_2 = \frac{\sum_{i=1}^{m} \tilde{\Delta}_{2i}}{m}$
3	Initial values of unknown variables		
3.1	Value of the offset parameter for the linear component of the formed analytical dependence**	%	$a_0^0 = y_1^{\min} - a_1^0 \cdot x_1^{\min} = y_1^{\max} - a_1^0 \cdot x_1^{\max}$
3.2	Value of the scale parameter for the linear component of the formed analytical dependence	$\frac{\%}{\text{min.}}$	$a_1^0 = \frac{y_1^{\max} - y_1^{\min}}{x_1^{\max} - x_1^{\min}}$

№	Name of calculated characteristic	Measure unit	Formula
3.3	Value of the scale parameter for the logistic component of the formed analytical dependence***	%	$a_2^0 = y_2^{\min} \cdot \left(1 + b_2^0 \cdot e^{-c_2^0 \cdot x_2^{\min}}\right) = = y_2^{\max} \cdot \left(1 + b_2^0 \cdot e^{-c_2^0 \cdot x_2^{\max}}\right)$
3.4	Value of the offset parameter for the logistic component of the formed analytical dependence	–	$b_2^0 = -\frac{y_2^{\min} - y_2^{\max}}{e^{-c_2^0 \cdot x_2^{\min}} \cdot y_2^{\min} - e^{-c_2^0 \cdot x_2^{\max}} \cdot y_2^{\max}}$
4	The adequacy indicators for the formed analytical dependence of the IMWI value on the reduction and synthesis parameters' values		
4.1	The sum of squared values of deviations of the theoretical IMWI values from the actual IMWI values	–	$\Delta^{\Sigma} = \sum_{i=1}^{m} \left(\tilde{y}_i - y_i\right)^2$
4.2	Determination index****	–	$R = \sqrt{1 - \frac{\Delta^{\Sigma}}{\sum_{i=1}^{m} \left(y_i - \frac{\sum_{i=1}^{m} y_i}{m}\right)^2}}$

Note: * – the calculated characteristic is used to assess the deviations of the final share characteristics $\tilde{\Delta}_1$ и $\tilde{\Delta}_2$ (lines 2.9 and 2.10 of Table 3, respectively) for the theoretical IMWI values with the corresponding share characteristics Δ_1 и Δ_2 (lines 1.1.2 and 1.1.3 of Table 2, respectively) for the actual IMWI values; ** – enumeration of the calculated characteristic is based on the results of the calculation of the characteristic described in the line 3.2 of Table 3;*** – enumeration of the calculated characteristic is based on the results of the calculation of the characteristic described in the line 3.4 of Table 3; **** – the calculated characteristic takes values in the interval $[0;1]$ and is used to assess the adequacy of the formed analytical dependence of the IMWI value on the reduction and synthesis parameters' values: the closer the value of the characteristic to the value 1, the greater is the degree of compliance for the actual and theoretical IMWI values.

The structure of the proposed procedure is described by the block-scheme shown in Fig. 3 and has the following distinctive features:

- on the basis of the prepared source data (stage 1) and the generated characteristics (stage 2), the optimization model is constructed and implemented (stage 4), which provides approximation of experimental data (growth rates for carbon nanotubes / nanofibers by the weight of the initial material for different combinations of the values of the reduction and synthesis parameters) on the basis of component analytical dependence (expression (2)); since the mentioned-above optimization model is nonlinear, its implementation with application of standard software (such as "Microsoft Excel", "Mathcad", "Matlab", etc.) assumes the use of the generalized reduced gradient (GRG) method, which requires preliminary setting of the correct initial values for unknown variables of the model – the corresponding operation is performed as part of stage 3 of the procedure;
- based on the results of the optimization model's implementation, the degree of compliance of the theoretical IMWI values with the actual IMWI values is verified (stage 5) in accordance with the condition (3). In case the calculated values are not adequate, the initial data are adjusted in terms of the number of experiments and the corresponding results – the actual IMWI values.

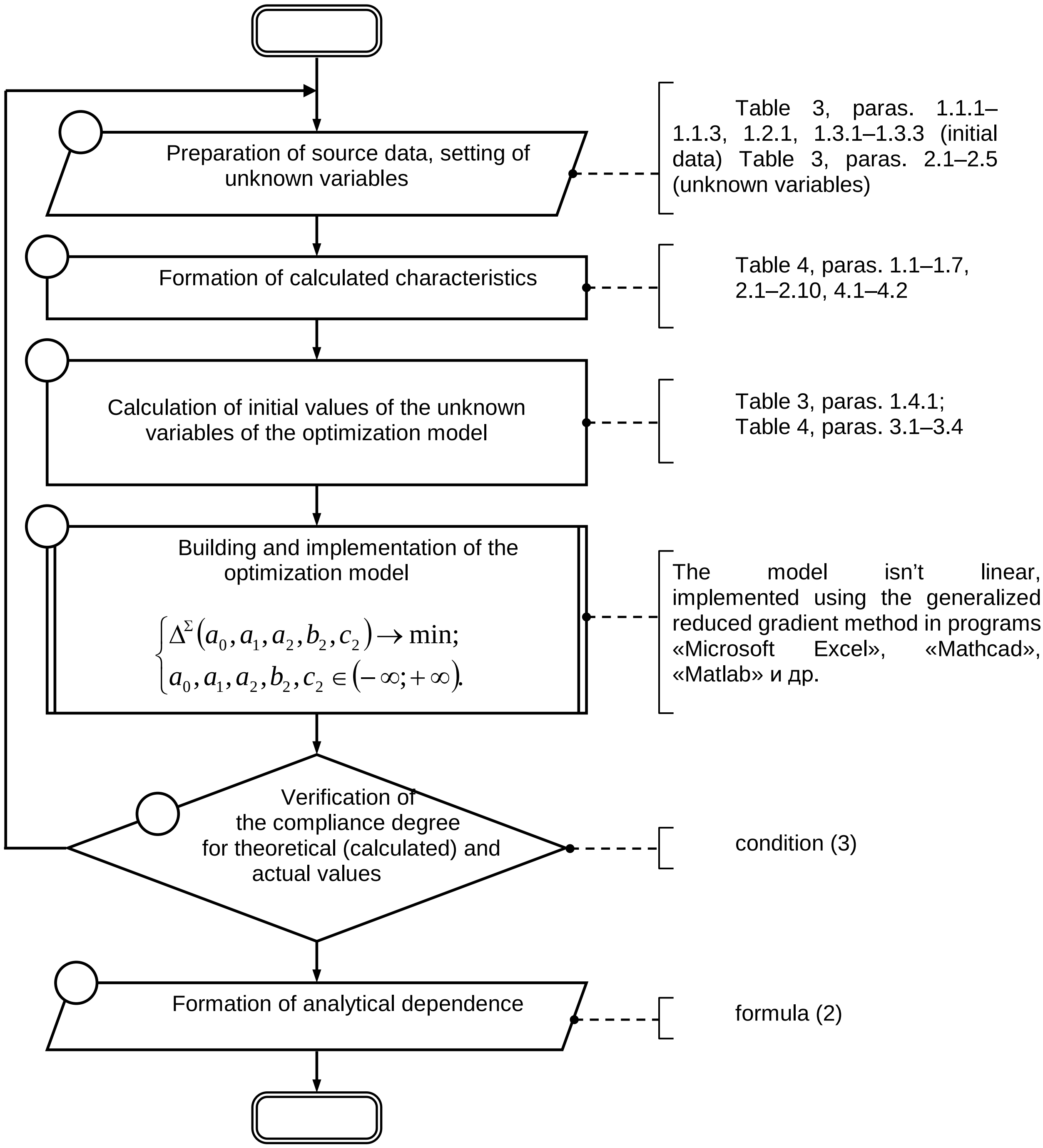


Figure 3. The block-scheme of the proposed procedure for the formation of the analytical dependence of the value of initial material's weight increase (IMWI) on the values of the reduction and synthesis parameters.

3. Results and Discussion

During the final stage of the research, the proposed procedure has been implemented on the basis of the experimental data obtained at the initial stage (see Table 1, Fig. 1). Corresponding process assumed the use of the software "Microsoft Excel" (a workbook has been created, within which one worksheet has been used) and the add-in "Solver" [24] for the direct implementation of the optimization model in accordance with step 4 of the procedure (see the block-sheme in the Fig. 3). The general view of the "Microsoft Excel" worksheet, as well as the principles for filling in the corresponding cells are presented in Fig. 4 and Table 5, respectively. Values of "Solver" add-in parameters used for the implementation of the optimization model are shown in Table 6. The resulting analytical dependence of the IMWI value on the values of the reduction and synthesis parameters' values is determined by the following expression:

$$\tilde{y}\left(x_1, x_2\right) = 0.265 + 0.0454 \cdot x_1 + \frac{2.5493}{1 + 222.5493 \cdot e^{-0.3525 \cdot x_2}}. \quad (4)$$

A graphical description of the dependence (for the experiments' characteristics in terms of the values of the reduction and synthesis parameters indicated in Table 1) is presented in Fig. 5.

The calculated value of the determination index is $R \approx 0.987$, which satisfies the condition (3) and indicates a high degree of the theoretical IMWI values compliance with the corresponding actual values, and, therefore, the high practical significance of the formed dependence as a tool.

Table 1. Initial data connected to the components of the formed analytical dependence

Parameter name	Value for the parameter: reduction parameter	Value for the parameter: synthesis parameter
-	Δ_{1i}	Δ_{2i}
-	-	-
The share of the actual value of gain of UT/UV on the mass of initial cement determined by value of the parameter	0.5	0.5

Table 2. Initial data and calculated characteristics describing the measurement results

Index of measurement	Value of the parameter connected to the process of the creation of structurally modified material: reduction parameter	synthesis parameter	Value for the growth of UT/UV on the mass of initial material: actual: total	actual: component, determined by the value of the parameter: reduction parameter	synthesis parameter	theoretical: total	theoretical: component, determined by the value of the parameter: reduction parameter	synthesis parameter	The share of the actusl value o the growth of UT/UV on the ma of initial material, determined b the parameter: reduction parameter	synthesis parameter
i	x_{1i}	x_{2i}	y_i	y_{1i}	y_{2i}	$\tilde{y}_i$	$\tilde{y}_{1i}$	$\tilde{y}_{2i}$	$\tilde{\Delta}_{1i}$	$\tilde{\Delta}_{2i}$
-	мин.	мин.	%	%	%	%	%	%	-	-
1	5	5	0.87	0.435	0.435	0.558	0.492	0.066	0.8812	0.1188
2	10	5	0.88	0.44	0.44	0.785	0.719	0.066	0.9156	0.0844
3	15	5	1.04	0.52	0.52	1.012	0.946	0.066	0.9345	0.0655
4	20	5	1.03	0.515	0.515	1.239	1.173	0.066	0.9465	0.0535
5	25	5	1.08	0.54	0.54	1.466	1.400	0.066	0.9548	0.0452
6	5	10	1.05	0.525	0.525	0.836	0.492	0.344	0.5885	0.4115
7	10	10	1.12	0.56	0.56	1.063	0.719	0.344	0.6764	0.3236
8	15	10	1.37	0.685	0.685	1.290	0.946	0.344	0.7333	0.2667
9	20	10	1.55	0.775	0.775	1.517	1.173	0.344	0.7732	0.2268
10	25	10	1.64	0.82	0.82	1.744	1.400	0.344	0.8027	0.1973
11	5	15	1.68	0.84	0.84	1.715	0.492	1.223	0.2869	0.7131
12	10	15	1.79	0.895	0.895	1.942	0.719	1.223	0.3702	0.6298
13	15	15	2.11	1.055	1.055	2.169	0.946	1.223	0.4361	0.5639
14	20	15	2.42	1.21	1.21	2.396	1.173	1.223	0.4895	0.5105
15	25	15	2.62	1.31	1.31	2.623	1.400	1.223	0.5337	0.4663
16	5	20	2.51	1.255	1.255	2.671	0.492	2.179	0.1842	0.8158
17	10	20	2.73	1.365	1.365	2.898	0.719	2.179	0.2481	0.7519
18	15	20	3.28	1.64	1.64	3.125	0.946	2.179	0.3028	0.6972
19	20	20	3.6	1.8	1.8	3.352	1.173	2.179	0.3500	0.6500
20	25	20	3.74	1.87	1.87	3.579	1.400	2.179	0.3912	0.6088
21	5	25	2.78	1.39	1.39	3.008	0.492	2.516	0.1636	0.8364
22	10	25	3.02	1.51	1.51	3.235	0.719	2.516	0.2223	0.7777
23	15	25	3.5	1.75	1.75	3.462	0.946	2.516	0.2733	0.7267
24	20	25	3.85	1.925	1.925	3.689	1.173	2.516	0.3180	0.6820
25	25	25	4.03	2.015	2.015	3.916	1.400	2.516	0.3575	0.6425
Minimum value	5	5	0.87	0.435	0.435	0.558	0.492	0.066	0.164	0.045
Maximum value	25	25	4.03	2.015	2.015	3.916	1.400	2.516	0.955	0.836
Average value	-	-	-	-	-	-	-	-	0.53	0.47

Table 3. Parameters of the formed analytical dependence

Name of the component for the analytical dependence	Vame of the parameter	Designation	Measure units	Value: initial	Value: optimal
Linear component	offset parameter	a_0	%	0.04	0.2650
	scale parameter	a_1	%/мин.	0.079	0.0454
Logistic component	scale parameter	a_2	-	4.6698	2.5993
	offset parameter	b_2	-	16.0505	222.5493
	form parameter	c_2	-	0.1	0.3525

Table 4. Characteristics of the adequacy for the formed analytical dependence

Name of the characteristic	designation	Measure units	Value
The total difference of the squared deviations of the theoretical values of the growth of UT/UV on the mass of initial material from the actual	Δ^{Σ}	-	0.700051135
Index of determination	R	-	0.986807002

Figure 4. General view of the worksheet of the "Microsoft Excel" workbook during the implementation of the proposed procedure.

Table 5. The principles of filling of the cells for the worksheet of the "Microsoft Excel" workbook during the implementation of the proposed procedure

Worksheet cell addresses	Formula / comment	Element of procedure
Table 1		
E8;F8	Cells with the initial data values	Table 2, para 1.1.2, 1.1.3
Table 2		
A21:A45 B21:B45 C21:C45 D21:D45	Cells with the initial data values	Table 2, paras. 1.2.1 Table 2, paras. 1.3.1 Table 2, paras. 1.3.2 Table 2, paras. 1.3.3
E21(:F45)	=$D21*E$8	Table 3, paras. 1.1–1.2
G21(:G45)	=H21+I21	Table 3, para. 1.5
H21(:H45)	=$H$53+$H$54*B21	Table 3, para. 1.3
I21(:I45)	=$H$55/(1+$H$56*EXP(-$H$57*C21))	Table 3, para. 1.4
J21(K45)	=H21/$G21	Table 3, paras. 1.6, 1.7
B46[;C46;E46;F46]	=MIN(B21:B45)	Table 3, paras. 2.1, 2.3, 2.5, 2.7
D46	=MIN(D21:D45)	-
G46(:K46)	=MIN(G21:G45)	-
B47[;C47;E47;F47]	=MAX(B21:B45)	Table 3, paras. 2.2, 2.4, 2.6, 2.8
D47	=MAX(D21:D45)	-
G47(:K47)	=MAX(G21:G45)	-
J48(:K48)	=AVERAGE(J21:J45)	Table 3, paras. 2.9, 2.10
Table 3		
G53	=E46-G54*B46	Table 3, para. 3.1
G54	=(E47-E46)/(B47-B46)	Table 3, para. 3.2
G55	=F46*(1+G56*EXP(-G57*C46))	Table 3, para. 3.3
G56	=-(F46-F47)/(EXP(-G57*C46)*F46-EXP(-G57*C47)*F47)	Table 3, para. 3.4
G57	the cell with the initial data values	Table 2, para. 1.4.1
H53:H57	cells with the values of variables into which the calculated values from cells G53:G57 are copied before launching the "Solver" add-in	–
Table 4		
G61	=SUMXMY2(D21:D45;G21:G45)	Table 3, para. 4.1
G64	=SQRT(1-G61/(VAR.P(D21:D45)*ROWS(A21:A45)))	Table 3, para. 4.2

Note: the designation with abstract addresses of cells X1 (:Y10) means that in the cell X1 it is necessary to enter the formula indicated in the corresponding column of table 5, after which the result "stretch" to cell Y10; the designation with abstract addresses of cells X1 [; Y2; Z3] means that in the cell X1 you need to enter the formula indicated in the corresponding column of table 5, then copy the contents of cell X1 and paste it into cells Y2 and Z3 one by one.

Table 6. Parameters of the "Solver" add-in of the "Microsoft Excel" software for the implementation of the optimization model assumed by the proposed procedure for the formation of analytical dependence

No.	Parameter name	Parameter value
1	General parameters	
1.1	Set Objective	$G$61
1.2	To:	Min
1.3	By Changing Variable Cells:	$H$53:$H$57
1.4	Make Unconstrained Variables Non-Negative	[disabled]
1.5	Select a Solving Method	GRG Nonlinear
2	Solving method options	
2.1	Convergence	0,0001
2.2	Derivatives	Forward
2.3	Multi-start Options for Global Optimization	
2.3.1	Use Multi-start	[disabled]
2.3.2	Population Size	100
2.3.3	Random Seed	0
2.3.4	Require Bounds on Variables	[enabled]

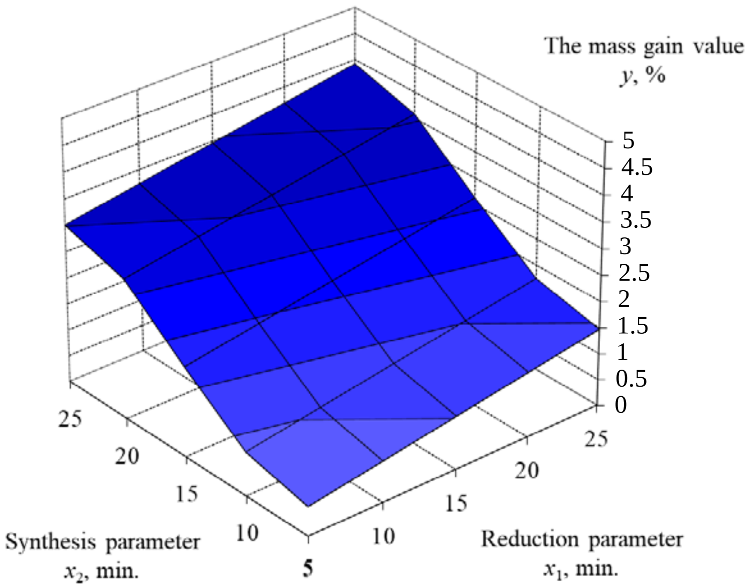


Figure 5. Graphic description of the formed analytical dependence

However, it should be noted that the share indicators $\{\tilde{\Delta}_{1i}\}$ for the calculated IMWI, determined by the reduction parameter value (Table 3, line 1.6), in comparison with the similar rate Δ_1 but for the actual IMWI value, differ from each other by experiments and vary in a relatively wide range – from 0.164 to 0.955 (see Fig. 4). A similar statement (with a slight difference at the borders of the range) is true for share indicators $\{\tilde{\Delta}_{2i}\}$ and Δ_2, which are related to the synthesis parameter (Table 3 line 1.7 and Table 2 line 1.1.3, respectively). That circumstance is connected to the nonlinear nature of the analytical dependence (Expression (2)) with respect to the synthesis parameter and does not negatively affect the adequacy of the results of the proposed procedure, since the values of fractional indicators Δ_1 and Δ_2, fixed by measurements, are used only to calculate the initial values of unknown variables of the optimization model with a relatively simple structure of the objective function.

It's also important to note that as there is no description of scientific developments (in published literature related to the research topic) in the field of nonlinear two-dimensional approximation of the experimental results on structurally modified cement in terms of the dependence of IMWI value on the reduction and synthesis parameters' values, the results of the study cannot be compared with the results of other studies in the field of structurally modified building materials.

4. Conclusions

During the performed research the following results have been obtained:

1. Laboratory experiments have been carried out to create structurally modified cement of the initial grade M500D0 (CEM I 42.5 N) with the measurement of the operational characteristics of the final material for various values of characteristics for the technological process of the material's creation.

2. The analytical dependence of the value of weight increase of the initial material from the values of the time parameters connected to the reduction of iron oxide and synthesis of carbon nanostructures has been formed; the dependence includes two components – linear, defined by the time parameter connected to the reduction of iron oxide and logistic, defined by the time parameter connected to the synthesis of carbon nanostructures;.

3. Based on the results of the experiments, the procedure for formation of analytical dependence of the value of weight increase of the initial material from the values of the time parameters connected to the reduction of iron oxide and synthesis of carbon nanostructures has been proposed and implemented on a practical case. The obtained results of the procedure's implementation indicate the high adequacy of the formed analytical dependence, and, as a result, the high practical significance of the developed tool.

However, it is important to note that the formation of this dependence has been made on the basis of initial data, which includes a relatively small number of weight increase measurements with unique combinations of the controlled parameters' values (m = 25 units) due to the difficulty of conduction of the corresponding experiments. The specified amount of initial data was sufficient to assess the nature of the dependence and correctly select the structure of the approximating function (Expression (2)). However, the statement that the dependence obtained at the current stage of research (Expression (4)) is a reference for all, without exception, brands of cement obtained by modification of the pure cement on the basis of carbon nanostructures is incorrect due to the insufficient number of experiments.

At the further stages of the research the following measures are planned to be implemented:

- carrying out of additional experiments to increase the number of corresponding measurements and possible clarification of the values of the parameters of the final analytical dependence (formula (4)) based on the results of repeated execution of the proposed procedure for formation of the dependence (block-scheme in Fig. 3).
- analysis of changes in the adequacy of the formed analytical dependence when its structure becomes more complex by adding an additional linear component determined by the value of the synthesis parameter;
- carrying out of laboratory experiments and formation of the corresponding analytical dependences to assess the effect of synthesis modes on the characteristics of the resulting product for alternative matrix cement materials, such as sulfate-resistant cement, magnesia, slag portland cement, alumina, pozzolanic.

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References

1. Yusuf, M.O. Synergistic-effect of iron-filing and silica-fume on the absorption and shrinkage of cement paste. Magazine of Civil Engineering. 2019. 91(7). Pp. 16–26. DOI: 10.18720/MCE.91.2.
2. Shakhov, S.A., Rogova, E.V. Factors affecting the ultrasonic disaggregation of powders. Magazine of Civil Engineering. 2019. 88(4). Pp. 14–24. DOI: 10.18720/MCE.88.2
3. Rassokhin, A.S., Ponomarev, A.N., Figovsky, O.L. Silica fumes of different types for high-performance fine-grained concrete. Magazine of Civil Engineering. 2018. 78 (2). Pp. 151–160. DOI: 10.18720/MCE.78.12
4. Frolov, A.V., Chumadova, L.I., Cherkashin, A.V., A.L.I. Ekonomichnost ispolzovaniya i vliyaniye nanorazmernykh chastits na svoystva legkikh vysokoprochnykh betonov. Stroitelstvo unikalnykh zdaniy i sooruzheniy. 2014. 4 (19). Pp. 51–61. URL: http://unistroy.spbstu.ru/index_2014_19/5_frolov_19.pdf
5. Mastalygina, E.E., Ovchinnikov, V.A., Chukhlanov, V.Y. Light heat-resistant polymer concretes based on oligooxyhy-dridesilmethylensiloxysilane and hollow spherical fillers. Magazine of Civil Engineering. 2019. 90 (6). Pp. 37–46. DOI: 10.18720/MCE.90.4
6. Zhdanok, S.A., Polonina, E.N., Leonovich, S.N., Khroustalev, B.M., Koleda, E.A. Influence of the Nanostructured-Carbon-Based Plasticizing Admixture in a Self-Compacting Concrete Mix on Its Technological Properties. Journal of Engineering Physics and Thermophysics. 2019. 92 (2). Pp. 376–382. DOI: 10.1007/s10891-019-01941-7
7. Ponomarev, A.N., Guskov, V.D., Vorontsov, V.V., Ageyev, I.V., Kemenov, L.A., Romanov, A.V., Shegelman, I.R. A new high performance neutron-absorbing materials based on the mineral binder and polymer components. Magazine of Civil Engineering. 2012. (9). Pp. 9–13. DOI: 10.5862/MCE.35.1.
8. Lesovik, R.V., Klyuyev, S.V., Klyuyev, A.V., Netrebenko, A.V., Durachenko, A.V. High-strength fiber-reinforced concrete containing technogenic raw materials and composite binders with use of nanodispersed powder. Research Journal of Applied Sciences. 2014. 9. Pp. 1153–1157. DOI: 10.3923/rjasci.2014.1153.1157. URL: http://docsdrive.com/pdfs/medwelljournals/rjasci/2014/1153-1157.pdf
9. Cherkashin, A.V., Pykhtin, K.A., Begich, Y.E., Sherstobitova, P.A., Koltsova, T.S. Mechanical properties of nanocarbon modified cement. Magazine of Civil Engineering. 2017. 72(4). DOI: 10.18720/MCE.72.7
10. Cherkashin, A.V., Golubkov, A.G., Firsenkov, A.A., Koltsova, T.S. Radar-absorbent composite material for construction applications and method for production thereof. RU2655187C1. 2017.
11. Ziari, H., Amini, A., Goli, A., Mirzaeiyan, D. Predicting rutting performance of carbon nano tube (CNT) asphalt binders using regression models and neural networks. Construction and Building Materials. 2018. 160. Pp. 415–426. DOI: 10.1016/j.conbuildmat.2017.11.071
12. Sun, X., Zhao, W. Prediction of stiffness and strength of single-walled carbon nanotubes by molecular-mechanics based finite element approach. Materials Science and Engineering A. 2005. 390(1–2). Pp. 366–371. DOI: 10.1016/j.msea.2004.08.020
13. Tang, X., Yan, X. Acoustic energy absorption properties of fibrous materials: A review. Composites Part A: Applied Science and Manufacturing. 2017. 101. Pp. 360–380. DOI: 10.1016/j.compositesa.2017.07.002.
14. Nasibulin, A.G., Koltsova, T., Nasibulina, L.I., Anoshkin, I. V., Semencha, A., Tolochko, O. V., Kauppinen, E.I. A novel approach to composite preparation by direct synthesis of carbon nanomaterial on matrix or filler particles. Acta Materialia. 2013. 61(6). Pp. 1862–1871. DOI: 10.1016/j.actamat.2012.12.007.

15. Barde, A.A., Klausner, J.F., Mei, R. Solid state reaction kinetics of iron oxide reduction using hydrogen as a reducing agent. International Journal of Hydrogen Energy. 2016. 41(24). Pp. 10103–10119. DOI: 10.1016/j.ijhydene.2015.12.129.
16. Kraynova, K.A., Yeroshkina, N.A., Korovkin, M.O. Issledovaniye vozmozhnosti primeneniya syrya otechestvennykh proizvoditeley v tekhnologii sukhikh stroitelnykh smesey dlya nalivnogo pola [Investigation of the possibility of using raw materials from domestic manufacturers in the technology of dry building mixtures for self-leveling floors]. Mezhdunarodnyy nauchno-tekhnicheskiy zhurnal «TEORIYa. PRAKTIKA. INNOVATsII». 2017. 5 (17). Pp. 100–105. (rus)
17. Cherkashin, A., Begich, Y., Sherstobitova, P., Semencha, A., Doroshin, I. Heat-resistant properties of construction composites based on nanocarbon cement (nCMC). E3S Web of Conferences. 2019. 91. Pp. 3–8. DOI: 10.1051/e3sconf/20199102029
18. Levensov, V., Radaev, A., Salkutsan, S. Mathematic model of production technology transformation. SHS Web of Conf. 2018. 00054(44 (2018)). Pp. 1–8.
19. Malyuk, V.I., Radaev, A.E., Silkina, G.Y. Procedure for determining the characteristics for development of industrial enterprises using optimization modeling tools. St. Petersburg State Polytechnical University Journal. Economics. 2018. 11 (6). Pp. 195–211. DOI: 10.18721/JE.11617
20. Leventsov, V.A., Radaev, A.E., Nikolaevskiy, N.N. The aspects of the «industry 4.0» concept within production process design. St. Petersburg State Polytechnical University Journal. Economics. 2017. 1. Pp. 19–31. DOI: 10.18721/JE.10102
21. Porro, S., Musso, S., Giorcelli, M., Chiodoni, A., Tagliaferro, A. Optimization of a thermal-CVD system for carbon nanotube growth. Physica E: Low-Dimensional Systems and Nanostructures. 37(1–2). Pp. 16–20. DOI: 10.1016/j.physe.2006.07.010. (2007)
22. Samant, K.M., Haram, S.K., Kapoor, S. Synthesis of carbon nanotubes by catalytic vapor decomposition (CVD) method: Optimization of various parameters for the maximum yield. Pramana - Journal of Physics. 68(1). Pp. 51–60. DOI: 10.1007/s12043-007-0005-9. (2007)
23. Khan, Y., Shukrullah, S., Naz, M.Y., Ghaffar, A., Ahmad, I., Alsuhaibani, S. Ferrocene weight optimization for CVD growth of carbon nanotubes over Si/SiO2/Al2O3. Digest Journal of Nanomaterials and Biostructures. 12 (4). Pp. 957–963. (2017)
24. Excel Solver – Define and solve a problem / Frontline Systems.Inc. URL: https://www.solver.com/excel-solver-define-and-solve-problem

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