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Statistical approach to the production of cement composites doped with ZnO and ZnO-based materials

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Abstract: In this study, physical and functional properties of the cement composites containing ZnO, ZnO/lignin and lignin admixtures were investigated using Response Surface Methodology (RSM). The *I*-optimal design based on RSM was used to assess the influence of ZnO-based doping agent, of either commercial or synthetic origin, on cement composite production in the function of average compressive strength and cost. Polynomial mathematical models were developed by RSM confronting results from the experimental design. The accuracy and precision of the utilized models established by *I*-optimal design were tested using Analysis of Variance (ANOVA). The first stage of formulation optimization revealed that the use of commercially available ZnO-based admixture no. 4 (ZnO-SA, supplied by Sigma Aldrich) allowed to achieve the desired results, passing all the requirements, i.e., the best microbial purity combined with reasonable cost, followed by satisfactory physical properties. In the second stage of formulation optimization, the influence of implementing the hybrid materials, i.e., ZnO-SA mixed in different proportions with lignin was evaluated. RSM revealed that doping admixture no. 3, i.e., ZnO-SA/lignin (5:1), is the best candidate, which comprised augmented functional and physical properties of the fabricated cement composite. This component exhibited the best microbial purity as well as the lowest total pore volume, followed by satisfactory physical properties. Verification of the model findings indicated considerable agreement between the predicted and experimental values. From the findings, it was confirmed that a reasonable cost-performance balance for cement composites can be achieved using ZnO-SA and ZnO-SA/lignin (5:1).

Keywords: cement composites, zinc oxide, hybrid materials, design of experiments

1. Introductions

The systematic and organized design of experiments (the Design of Experiments, DoE) is the most efficient method for developing solutions because it ~~which~~ allows us to understand the cause-and-effect connection in processes. Through strategic planning and deliberation, a chemical engineer may utilize the DoE technique to effectively gather data and then apply it to the development of novel and high-quality products. It is perfect for establishing how to make the best possible commercial products out of a wide range of ingredients (Bartman et al., 2023; Jędrzejczak et al., 2023; Balicki, 2021; Bartman et al., 2021). Such a technique has a strong connection to Quality-by-Design (QbD). Manufacturers of new formulations in the areas of building materials, cosmetics, or various Fine Chemicals (e.g., specialized surfactants, nanocarriers for drug delivery systems, bioactive compounds, etc.) are primarily responsible for delivering products of outstanding quality to clients. According to the Quality-by-Design concept, this task must be done by understanding all aspects and phases of the planned product's development. The idea behind quality via design is that quality considerations should be built

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into every step of production, not only the last stage (quality control), so that outputs are consistently high in quality. The tools suitable for applying this concept into reality may be found in statistical data analyses and planning and design of experiments ~~techniques~~ (Bartman et al., 2023; Jędrzejczak et al., 2023; Balicki, 2021; Bartman et al., 2021).

Models for optimizing independent parameters in the processes of production or formulation development may be easily constructed using the response surface methodology~~,~~ since it employs effective theoretical, statistical, and numerical approaches (da Silva et al., 2023; Elevado et al., 2019). This approach permits several variables to impact a single or multiple response factors (da Silva et al., 2023; Elevado et al., 2019). More specifically, RSM aims to propose sequential procedures for performing experiments and validating the compatibility of experimental data with built models (Sinkhonde et al., 2021). Numerous derivatives of RSM approaches, based on different computational and statistical models, have been utilized to determine the compromise between a wide range of possible best solutions to the studied problem. It is believed that RSM has the ability to determine the optimal proportions of doping agents (TiO_2- or ZnO-based materials) in cement composites, thereby maximizing the compressive strength at a cheaper cost, as well as augmenting the resulting formulation with functional properties~~,~~ such as photocatalytic or antimicrobial activity (Jędrzejczak et al., 2023; Klapiszewska et al., 2023).

When new materials are introduced into ~~the~~ cement composites, it is necessary to consider whether the strength and other physical parameters of the resulting concrete can meet the requirements. The best proportioning scheme is closely connected to the compressive strength and economic value of cementitious admixtures, both of which are essential considerations for the production and application of novel materials. Therefore, the RSM (Box and Wilson, 1951) is a widely used experimental design method to optimize ~~the~~ composite formulations and production processes. This approach reduces the planned experiment number~~,~~ and fits the relationship between independent input factors within the range and response results (Wu et al., 2020; Zhou et al., 2019; Daud et al., 2018) according to ~~upon~~ desired requirements. Thus, under the conditions of average compressive strength, plasticity, and porosity, the proportion of admixture materials in the composite formulation can be optimized by using the multi-objective function method to obtain the best economic and functional benefit (Uche et al., 2022). To summarize, it is possible to conclude that RSM utilization results in significant savings in terms of effort, length of time, and expense; hence, in this work, this technique was used in detail and adopted for research on functional cement composites.

The primary goal of the research conducted in the first stage of optimization was to study the admixture type's (independent variable) impact on the response factors (the dependent variables). It was examined using a statistical approach employing the RSM. Therefore, the essential quality and economic indicators of cement composites—namely, compressive strength, microbiological purity, initial setting time, plasticity, and cost—served as response variables. Thereafter, a second round of optimization was conducted based on the results of the first stage, which determined the optimal ZnO-based admixture type. The secondary goal of the research in the consecutive step of optimization was to find the best doping agent based on ZnO-lingin hybrids. The statistical analysis, i.e., RSM combined with multivariate ANOVA, allowed once again examination of the effect of the doping agent types on the functional and quality properties of the resulting cement composites. The performed investigation revealed the composite, which gave the desired results, passing all the requirements, i.e., the best microbial purity together with the smallest total pore volume, followed by satisfactory physical properties.

2. Materials and methods

2.1. Materials

Commercial zinc oxides from the following companies were used in the research: (*i*) Chemat, Gdańsk, Poland (ZnO-CH), (*ii*) Alfa-Aesar, Ward Hill, Massachusetts, USA (ZnO-AA) and (*iii*) Sigma-Aldrich, Saint Louis, Missouri, USA (ZnO-SA). In addition, zinc oxides synthesized by hydrothermal (ZnO-H) and microwave (ZnO-M) methods were used. A detailed synthesis of these materials was included in our earlier article (Klapiszewska et al., 2022a). Kraft lignin – alkali lignin from Merck (Darmstadt, Germany) was also used to obtain the hybrid materials.

In addition, the following compounds were used to obtain cement composites: (*i*) cement containing Portland clinker (95%) as the main component and a setting time regulator (up to 5%) (Portland CEM I 42.5R cement; standard requirements according to PN-EN 197-1) from Górażdże Cement SA, Górażdże, Poland, and (*ii*) standard quartz sand (standard requirements according to PN-EN 196-1) from Kwarcmix, Tomaszów Mazowiecki, Poland.

2.2. Preparation of ZnO/lignin hybrid materials

The inorganic–organic materials were obtained using a mechanical method. This method is environmentally friendly and it is also relatively cheap, which is important for potential use in the construction industry. The detailed process of preparation of ZnO/lignin hybrid materials was described by us in an earlier study (Klapiszewska et al., 2021).

2.3. Characteristics of admixtures

The dispersive properties of admixtures were characterized by particle size measurements using a Zetasizer Nano ZS (0.6–6000 nm) instrument (Malvern Instruments Ltd., Malvern, UK), operating based on the non-invasive backscattering (NIBS) technique.

The parameters of the porous structure were assessed using an ASAP 2020 apparatus from Micromeritics Instrument Co. (Norcross, Georgia, USA). The aim of the experiments was to determine nitrogen adsorption–desorption isotherms of the analyzed samples. The following values were determined: (*i*) BET surface area using the Brunauer–Emmett–Teller method; and (*ii*) pore volume and pore size according to the BJH (Barret–Joyner–Halenda) model. The parameters were measured with the use of low-temperature nitrogen adsorption (–196 ºC).

2.4. Preparation of cement composites

Experimental studies were carried out in two stages – in the first stage, various zinc oxides were taken into account, which were used as admixtures for cement composites and compared in order to select the cement composite with the best desired properties. In the second stage, ZnO/lignin hybrid materials were produced with the best zinc oxide in weight ratios of 5:1, 1:1 and 1:5, which were also used as admixtures for cement mortars. To compare the effect of hybrid materials, the cement composite was also doped with pristine ingredients, i.e. ZnO and lignin. All the admixtures used, in the amount of 0.1 wt.%, were distributed in 225 mL of mixing water using a magnetic stirrer before being placed in the mixing bowl. After the water dispersion was formed, it was poured into the mixing bowl, then 450 g of cement were added and the standard mixing process was started in accordance with PN-EN 196-1, which is schematically described in Fig. 1. After the mixing program was completed, the fresh mortar was placed in two layers in form, compacting each layer with 60 strokes of the compactor. Beams with dimensions of 40 x 40 x 160 mm were demolded after 24 h and stored in water until strength testing.

2.5. Characteristics of cement composites

Determination of both the standard consistency and setting time of the cement paste was carried out in accordance with the EN 196-3 standard using a Vicat apparatus.

The consistency of the fresh cement mortar was determined in accordance with the EN 1015-3 standard. Two orthogonal diameters of sample flows were measured, and the results were averaged.

The heat of hydration test was performed using a semi-adiabatic calorimeter (Testing, Berlin, Germany) according to the procedure described in EN 196-9. The test consisted of recording temperature changes inside the calorimeter (reference calorimeter) produced by the thermal effect. Recording of thermal parameters took place at preset time intervals, not shorter than 41 h.

The compressive strength tests were carried out using a Servo-Plus Evolution testing machine (Matest S.p.A., Treviolo BG, Italy), based on the procedure described in the EN 196-1 standard. The samples were placed between two square compression plates and the load was increased in steps of 2.4 ± 0.2 kN/s until the sample was crushed.

The contact method on agar plates was applied to determine the microbial purity of cement composites. Evaluation of microbial purity by contact method was performed according to the

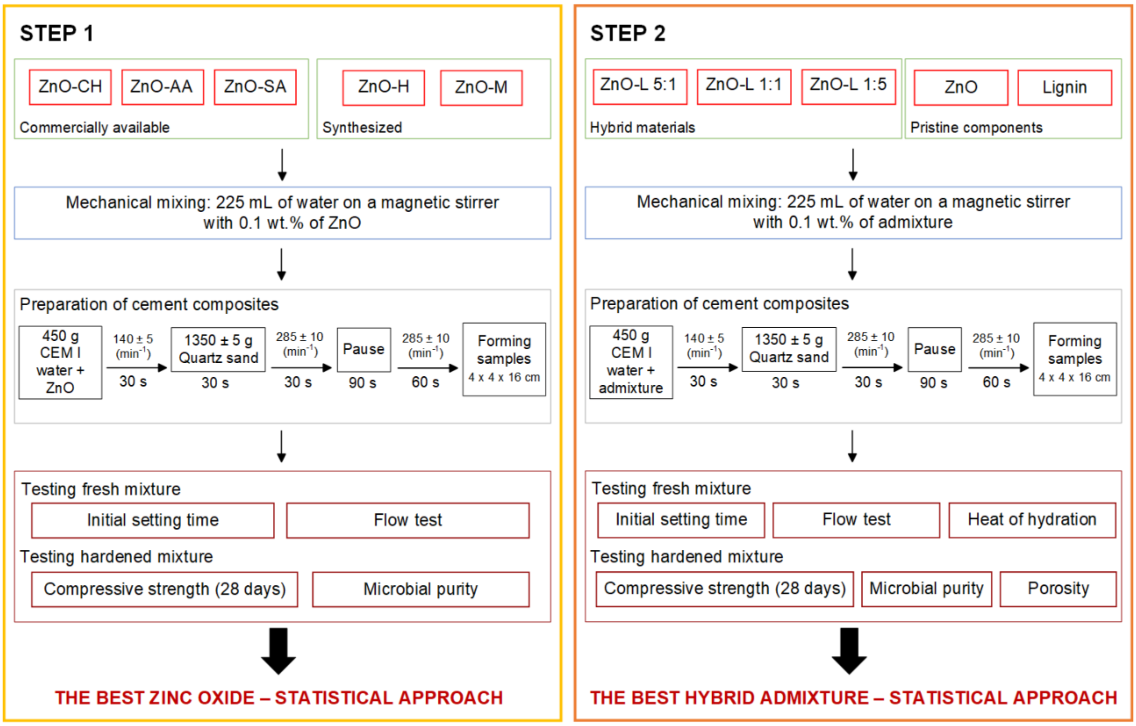

Fig. 1. Schematic presentation of the most important research and manufacturing processes of cement composites

procedure described in earlier studies (Klapiszewska et al., 2021; Klapiszewska et al., 2022a). Antimicrobial activity and microbial purity data are represented as a mean of three identical experiments undertaken as three replicates.

Mercury porosimetry (MIP) tests were carried out using a PoreMaster 33 mercury porosimeter (Quantachrome Instruments, Boynton Beach, Florida, USA) on matured samples of cement mortar with dimensions of 4 x 4 x 20 mm. In the initial stage of the measurement, a sample was degassed at ambient temperature until a vacuum of 10 mmHg was reached. The pressure range for the low-pressure measurement was 3–50 PSI, and the high-pressure range was 20–33000 PSI, equivalent to the pore size distribution in the range from 7 nm to 1 mm.

2.6. Design of experiments – selection of the optimal zinc oxide and hybrid admixture

determine the best doping admixtures from ZnO and ZnO-based materials, the Design of Experiments (DoE) and Response Surface Methodology (RSM) were both used. The selection of the best doping agent for the cement composites was divided into two stages. In the first step of statistical calculations, a randomized quadratic *I*-optimal model in coordinate exchange mode, with no blocks (a subtype of an RSM technique), was studied by Design Expert Software (ver. 13.05.0, State-Ease, Inc., Minneapolis, USA (Balicki, 2021; Balicki et al., 2020). An altered 6^1 full factorial *I*-optimal (shown in Table 3) was used to explore the reduced response surface and optimize the decisive component of the cementitious composites, i.e., the admixture type (A1) at 6 discrete levels (1 – pure cement CEM, 2 – ZnO-CH, 3 – ZnO-AA, 4 – ZnO-SA, 5 – ZnO-H, 6 – ZnO-M). In the current contribution, in the first stage, a 16-run *I*-optimal experimental matrix was generated from six ~~6~~ candidate experiments (based on Tables 1 and 2), representing the ideal approach for using the minimization criterion of the ensuing response factors. The RSM was used to analyze how the response factors (the dependent variables) were affected by the independent variable A1. Therefore, the principal quality and economic measures of cement composites served as response factors, i.e., $1Y_1$ (compressive strength), $1Y_2$ (microbial purity), $1Y_3$ (initial setting time), $1Y_4$ (plasticity), and $1Y_5$ (cost).

Furthermore, the correlation between the dependent and independent variables is shown by the following reduced second-order polynomial regression equation, which is based on the optimization design model (equation 1):

$$1Y_1 \text{ to } 1Y_5 = \beta_0 + \beta_1 A1 + \beta_{1,1} A1^2 \quad (1)$$

where: $1Y_1$ to $1Y_5$ are the dependent variables; A1 is the independent variable; β_0 is an intercept term; β_1 is the linear coefficient, while $\beta_{1,1}$ is the quadratic coefficient.

Based on the findings of the first stage, which identified the optimal ZnO-based admixture type, a second round of optimization was carried out. Briefly, another modified 6^1 complete factorial *I*-optimal design (coordinate exchange type) (see Table 12) was utilized to investigate the response surfaces and optimize the significance of the admixture component, i.e., ZnO-based hybrid materials with lignin, of the cement composites, i.e., the admixture type (A2) at 6 levels (1 – pure cement, CEM, 2 – ZnO, 3 – ZnO/lignin (5:1), 4 – ZnO/lignin (1:1), 5 – ZnO/lignin (1:5), 6 – pristine lignin). The RSM was used once more in order to investigate the impact of the explanatory variable on the dependent variables. Key functional features of concrete composites were taken into account as response factors ($2Y_1$ – $2Y_5$) - they included compressive strength, microbiological purity, porosity, plasticity, and ~~as well as~~ heat of hydration.

The following second-order polynomial regression equation (Balicki et al., 2020), which comes from the optimal design model (equation 2), represents the relationship between the dependent and independent variables

$$2Y_1 - 2Y_5 = \beta_0 + \beta_1 A2 + \beta_{1,1} A2^2 \tag{2}$$

where: $2Y_1$ – $2Y_5$ are the dependent variables; 2A is an independent variable; β_0 is an intercept term; β_1 is the linear coefficient, while $\beta_{1,1}$ is the quadratic coefficient.

Analysis of variance (ANOVA) and related statistical parameters, i.e., p-values and F-values, were used to assess the aforementioned regression models' efficacy. The accuracy of the optimization design models in predicting the experimental outcomes was evaluated using the R^2 coefficients (actual, adjusted, and predicted). Finally, 2D response surfaces (Balicki, 2021; Balicki et al., 2020) were prepared using the obtained polynomial equations for $1Y_1$ - $1Y_5$ and $2Y_1$ - $2Y_5$ response factors to determine the optimal ZnO-based admixture type as well as the best ZnO/lignin-based hybrid material admixture type and to explain the correlation between the factors.

3. Results and discussion

3.1. Characteristics of the zinc oxides used in the study

Dispersion characteristics and assessment of porous structure parameters for all zinc oxides used in the tests are presented in Table 1. The determined dispersion properties allowed to indicate oxides with relatively smallest particles – ZnO-SA and ZnO-M, of which ZnO-SA is additionally characterized by the lowest polydispersity index of 0.052. In the case of porous structure analysis, synthesized zinc oxides are characterized by a higher average pore size compared to commercial oxides. ZnO-AA is the oxide with the most developed BET surface area, while the ZnO-M oxide is characterized by the largest total pore volume. Depending on the method of synthesis, zinc oxides may be characterized by various parameters, both of porous structure and particle size (Kołodziejczak-Radzimska and Jesionowski, 2014).

Table 1. Dispersion and porous structure properties of zinc oxides used in this study

Sample	Dispersion properties		Porous structure properties		
	Particle size range (nm)	Polydispersity index (-)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
ZnO-CH	255-825	0.054	4.8	0.002	2.2
ZnO-AA	142-6439	0.446	17.5	0.006	2.2
ZnO-SA	142-531	0.052	12.5	0.005	2.2
ZnO-H	955-4800	0.743	2.3	0.005	12.1
ZnO-M	220-531	0.245	8.3	0.020	24.2

3.2. Optimization of the process of obtaining cement composites with the participation of zinc oxides along with their characteristics

Cement composites doped with various zinc oxides were tested for the most important properties of the fresh and hardened mix, the results of which are presented in Table 2. For a better comparison of the effect of ZnO on the cement matrix, a reference sample of pure cement mortar (CEM) was also prepared. By analyzing the results of the initial setting time, the retarding effect of zinc oxide on the hydration process of the cement mortar was confirmed. The oxides obtained by hydrothermal (ZnO-H) and microwave (ZnO-M) methods were characterized by the most extended setting time. The retarding effect of zinc oxide has been previously reported by other researchers (Klapiszewska et al., 2021; Thangapandi et al., 2020; Liu et al., 2019; Bordoloi et al., 1998). The plasticity test of the fresh mortar was performed using a flow table. For the cement composite without admixture, the result was 17.0 cm. Cement composites containing commercial zinc oxides were characterized by flows that were similar (ZnO-CH) or slightly lower (ZnO-SA – 16.5 cm; ZnO-AA – 16.0 cm) compared to the reference sample. The mortars containing synthesized zinc oxides were characterized by flows slightly larger than the reference sample, by 1.0 and 1.5 cm for ZnO-H and ZnO-M oxides, respectively. In their work, Liu and co-workers (Liu et al., 2019) confirmed that the addition of zinc oxide may slightly impair the plasticity of the mixture.

In the case of the properties of hardened cement composites, Table 2 presents the results of compressive strength after 28 days and microbiological purity determined by the contact method after 24 h of exposure to microorganisms. By analyzing the influence of zinc oxide on the mechanical properties, a beneficial effect of the admixture was observed. All of the introduced zinc oxides allowed to obtain more favorable parameters of mechanical strength, which is consistent with literature reports in this area (Kumar et al., 2021; Nochaiya et al., 2015). The contact method used to assess microbiological purity allowed to obtain appropriate differences between composites containing the ZnO admixture. The composites with the best antibacterial properties are the ZnO-SA and ZnO-M composites, because only in the case of these two admixtures no growth of microorganisms was observed. The largest increase, apart from the CEM reference sample, was recorded for the ZnO-CH composite. In the literature, zinc oxide is known for its antimicrobial properties, which is evidenced by numerous scientific articles (Ijaz et al., 2020; Kumar et al., 2017; Sirelkatim et al., 2015), and is also used as an admixture giving antibacterial properties to cement composites (Augustyniak et al., 2022; Klapiszewska et al., 2022b; Lázaro-Mass et al., 2022; Voicu et al., 2022; Klapiszewska et al., 2021).

The cost of the admixture is important from the point of view of the cost of manufacturing cement composites with an admixture of zinc oxide. Although the commercial zinc oxides used in the research represent a similar cost, the materials synthesized by the hydrothermal or microwave method are definitely more expensive in application. The ongoing optimization in order to select the best zinc oxide is also supplemented by the criterion of the production/obtaining price of this admixture.

Table 2. List of test results of cement composites doped with zinc oxides

Sample	Initial setting time (min)	Plasticity (cm)	Compressive strength after 28 days (MPa)	Microbial purity (contact method) after 24 h
CEM	170	17.0	63.1	+++ (extensive growth)
ZnO-CH	410	17.0	65.2	+++ (extensive growth)
ZnO-AA	385	16.0	65.9	+ (little growth)
ZnO-SA	460	16.5	63.5	− (lack of growth)
ZnO-H	600	18.0	71.3	++ (high growth)
ZnO-M	550	18.5	71.5	− (lack of growth)

The RSM is commonly applied in assessment studies and the optimization of various processes. It can provide a useful solution to a problem in which the direct effect of the independent variables (process parameters) on the dependent variables (response factors) must be established, especially in complex systems that ~~which~~ may include various correlations between the variables in question. Numerous restrictions may impede the correct fitting of an optimization model to experimental findings. By using multiple linear regression or polynomial analyses of interactions between optimized process variables, RSM can ~~allows~~ to overcome this disadvantage (Bartman et al. 2021; Myers et al., 2016). In the presented studies, the influence of the ZnO-based doping agents (described previously in this section) on the functional and physical properties of the resulting cement composites was studied by statistical evaluation with the randomized quadratic *I*-optimal design in the coordinate exchange mode. The direct impact of the ZnO-based type doping agent (A1) on the quality and economy measures of the optimized cement composite formulation, i.e., compressive strength ($1Y_1$), microbial purity ($1Y_2$), initial setting time ($1Y_3$), plasticity ($1Y_4$), and cost ($1Y_5$), was tested for statistical significance. Table 3 displays the experimental design matrix for a randomized *I*-optimal experiment with 16 replicates, all of which have the same levels of independent variables and the same experimental values for response factors.

Table 3. A randomized quadratic *I*-optimal design's experimental matrix of independent variable (A1) with its corresponding levels and analyzed response factors 1Y1 – 1Y5: compressive strength, microbial purity, initial setting time, plasticity, and cost, respectively

Run	Factor A1: admixture type*	Response $1Y_1$: Compressive strength (MPa)	Response $1Y_2$: Microbial purity	Response $1Y_3$: Initial setting time (min)	Response $1Y_4$: Plasticity (cm)	Response $1Y_5$: Cost
1	4	63.5	0	460	16.5	1
2	6	71.5	0	550	18.5	3
3	4	63.5	0	460	16.5	1
4	1	63.1	3	170	17	0
5	3	65.9	1	385	16	1
6	5	71.3	2	600	18	2
7	1	63.1	3	170	17	0
8	1	63.1	3	170	17	0
9	3	65.9	1	385	16	1
10	1	63.1	3	170	17	0
11	3	65.9	1	385	16	1
12	2	65.2	3	410	17	1
13	6	71.5	0	550	18.5	3
14	4	63.5	0	460	16.5	1
15	1	63.1	3	170	17	0
16	6	71.5	0	550	18.5	3

* 1 – CEM, 2 – ZnO-CH, 3 – ZnO-AA, 4 – ZnO-SA, 5 – ZnO-H, 6 – ZnO-M

The 2D response surfaces in this study serve to visually represent the multiple linear regression model equations derived from the quadratic *I*-optimal design (see Fig. 2). By navigating the response surfaces, we were able to evaluate the potential associations between the independent and dependent factors of cement composite~~s~~ formulations. The main purpose of the first stage of optimization was to determine the best ZnO-based doping agent as an admixture for cement composites. The key factors~~,~~ that should exist ~~in~~ to the highest extent~~,~~ were the best, i.e., compressive strength ($1Y_1$), high microbial purity ($1Y_2$), and finally the cost of ZnO doping agent (depending either on the commercial market price or the cost of the synthesis). As can be seen from the 2D response surfaces, the cement composites containing the commercially available zinc oxides, i.e., ZnO-SA and ZnO-AA (factors A1: 3 and 4 respectively), allowed to achieve the optimal functional and physical properties of the resulting cementitious composites, i.e., good compressive strength and microbial purity, satisfactory setting time and plasticity, as well as the lowest cost of implementation, which was the most crucial factor.

The mathematical and statistical modeling-based response surface approach and design of experiments (DoE) assessment method are used to successfully anticipate and confirm the functional qualities of chemical formulations and end products of optimized manufacturing processes. Analyses of variance (ANOVA) performed on the response surfaces derived from the randomized *I*-optimal design for dependent factors $1Y_1$ – $1Y_5$ revealed that the quadratic and quartic multiple linear regression model provided the best fit in all instances, which is a common solution in optimization by RSM and DoE, as provided by the literature (Klapiszewska et al., 2023; Balicki, 2021, Bartman et al., 2021; Sinkhonde et al., 2021; Hou et al., 2020; Meyers et al., 2016). The mentioned best-fit model included very appropriate statistical measures, i.e., a negligible lack of fit with a suitable number of degrees of freedom, followed by experimental, adjusted, and predicted R^2 coefficients that matched exceptionally well. For all five predicted response factors, the resulting *p*-values of model fitting were lower than 0.05, indicating that the *I*-optimal design chosen for optimization was statistically significant. The actual results of the ANOVA analysis are described in Tables 4 through 8. In the case of $1Y_1$ (compressive strength), the type of ZnO-based admixture had a quadratic effect on its values, while for the remaining ones, i.e., $1Y_2$ – $1Y_5$, the effect of admixture type gave a quartic relationship. The following is a summary of the ANOVA analyses that were conducted, including the multiple linear regression formulae that were obtained based on the *I*-optimal model that was fitted to the observed values of the response factors:

$$\text{Compressive strength} = +65.12 + 4.03A + 2.33A^2$$

$$\text{Microbial Purity} = +0.1329 - 1.36A + 9.50A^2 - 0.1244A^3 - 8.13A^4$$

$$\text{Setting Time} = +404.92 + 160.75A + 495.70A^2 + 28.84A^3 - 504.72A^4$$

$$\text{Plasticity} = +16.04 + 1.05A + 5.37A^2 - 0.3022A^3 - 3.66A^4$$

$$\text{Cost} = +0.9141 + 0.2336A + 2.21A^2 + 1.27A^3 - 1.63A^4$$

Table 4. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $1Y_1$ (compressive strength)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	142.67	2	71.33	24.71	< 0.0001
A-Admixture	137.66	1	137.66	47.68	< 0.0001
A^2	17.20	1	17.20	5.96	0.0297
Residual	37.54	13	2.89		
Cor Total	180.20	15			
R^2 = 0.7917, Adjusted R^2 = 0.7597, Predicted R^2 = 0.7165					

Table 5. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $1Y_2$ (microbial purity)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	27.39	4	6.85	137.94	< 0.0001
A-Admixture	0.9434	1	0.9434	19.00	0.0011
A^2	5.57	1	5.57	112.16	< 0.0001
A^3	0.0071	1	0.0071	0.1434	0.7122
A^4	4.71	1	4.71	94.85	< 0.0001
Residual	0.5461	11	0.0496		
Cor Total	27.94	15			
R^2 = 0.9805, Adjusted R^2 = 0.9733, Predicted R^2 = 0.7974					

These formulae support the investigated relationships between response factors and independent variables of the cementitious composites formulations, resulting in the production of cements with the required microbiological purity and adequate physical qualities. To conclude, after statistical evaluation and interpretation of the response surfaces (see Fig. 2) during the RSM optimization process, also taking into account the desirability function, we were able to present the best candidate profile (see Table 9) and therefore select the best solution. It turned out, that ZnO-based admixture no. 4 (ZnO-SA) allowed to achieve the desired results, passing all the requirements, i.e., the best microbial purity together with reasonable cost, followed by satisfactory physical properties.

Table 6. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $1Y_3$ (initial setting time)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	3.754E+05	4	93855.50	3734.52	< 0.0001
A-Admixture	13231.72	1	13231.72	526.49	< 0.0001
A^2	13031.39	1	13031.39	518.52	< 0.0001
A^3	382.33	1	382.33	15.21	0.0025
A^4	18144.18	1	18144.18	721.96	< 0.0001
Residual	276.45	11	25.13		
Cor Total	3.757E+05	15			
R^2 = 0.9993, Adjusted R^2 = 0.9990, Predicted R^2 = 0.9924					

Table 7. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $1Y_4$ (plasticity)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	11.42	4	2.85	1635.61	< 0.0001
A-Admixture	0.5632	1	0.5632	322.72	< 0.0001
A^2	1.78	1	1.78	1019.51	< 0.0001
A^3	0.0420	1	0.0420	24.05	0.0005
A^4	0.9559	1	0.9559	547.72	< 0.0001
Residual	0.0192	11	0.0017		
Cor Total	11.44	15			
R^2 = 0.9983, Adjusted R^2 = 0.9977, Predicted R^2 = 0.9826					

Table 8. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $1Y_5$ (cost)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	17.72	4	4.43	1427.46	< 0.0001
A-Admixture	0.0279	1	0.0279	9.00	0.0121
A^2	0.3019	1	0.3019	97.32	< 0.0001
A^3	0.7425	1	0.7425	239.30	< 0.0001
A^4	0.1883	1	0.1883	60.67	< 0.0001
Residual	0.0341	11	0.0031		
Cor Total	17.75	15			
R^2 = 0.9981, Adjusted R^2 = 0.9974, Predicted R^2 = 0.9801					

Table 9. Selected candidate for the optimal fabrication of the cementitious composites proposed by *I*-Optimal model optimization, based on desirability function, comparison of predicted and actual values, as well as compromise between microbial purity, cost, and physical properties

Solution	Admixture type	Compressive strength		Microbial purity		Setting time		Plasticity		Cost		Desirability
		P[1]	A[2]	P	A	P	A	P	A	P	A	-
1	4 – ZnO-SA	66.0	63.5	0.228	0.000	454.9	460.0	16.46	16.50	1.057	1.000	0.493

[1] values predicted by the *I*-optimal model

[2] actual experimental values

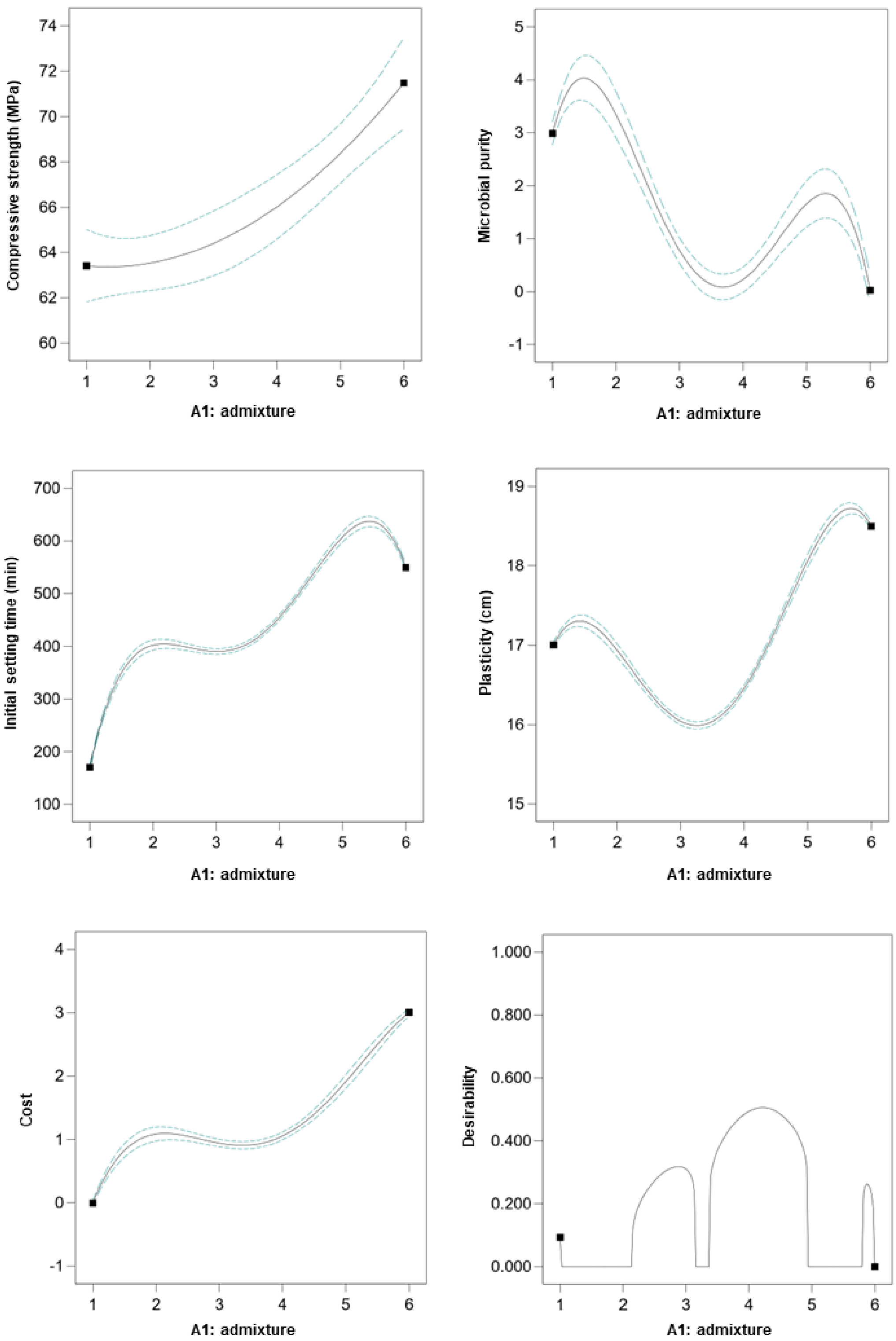

Fig. 2. A graphical representation of the response surfaces, is based on a randomized quadratic *I*-optimal model for the dependent factors $1Y_1$ (compressive strength), $1Y_2$ (microbial purity), $1Y_3$ (initial setting time), $1Y_4$ (plasticity), and $1Y_5$ (cost) vs. the independent variable: type of ZnO-based admixture type (A1), followed by desirability function measure

3.3. Characteristics of the ZnO/lignin materials and pristine kraft lignin

Zinc oxide ZnO-SA was used in the second stage of the research, on the basis of which hybrid systems with lignin were produced. The results of the dispersion properties and porous structure tests for the produced hybrid materials and lignin are presented in Table 10. The particle size determined for the hybrid materials indicates that the particle size distribution increases with the increase in lignin content in the sample. The particles with the smallest dispersion are observed in case of the ZnO/lignin (5:1) system, for which the polydispersity index is also the lowest (PdI=0.208). The increase in the particle size of hybrid materials is closely related to the increasing amount of introduced lignin, which is characterized by relatively large particles (255-955 nm) and a high polydispersity index (PdI=0.738).

In the case of the analysis of the results of the study of the properties of the porous structure, it was observed that with the increase in lignin content, the BET surface area decreases, which is equal to 5.4 m^2/g for the ZnO/lignin (5:1) material, while for the ZnO/lignin (1:5) system it is already at 3.6 m^2/g. Pristine lignin is characterized by the value of this parameter at the level of 1.4 m^2/g. The opposite situation occurs in the case of medium pore size – the ZnO/lignin (5:1) hybrid material is characterized by the smallest dimension – 2.1 nm, while the ZnO/lignin (1:5) system – 2.3 nm. For pristine lignin, the measured average pore size is 9.5 nm. The determined parameters of the porous structure for lignin are consistent with previous studies (Wysokowski et al., 2014).

Table 10. Dispersion and porous structure properties of ZnO/lignin materials and pristine kraft lignin

Sample	Dispersion properties		Porous structure properties		
	Particle size range (nm)	Polydispersity index (-)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
ZnO/lignin (5:1)	295-825	0.208	5.4	0.001	2.1
ZnO/lignin (1:1)	531-1106	0.237	4.1	0.001	2.3
ZnO/lignin (1:5)	190-1106	0.418	3.6	0.001	2.3
Lignin	255-955	0.738	1.4	0.001	9.5

3.4. Optimization of the process of obtaining cement composites with the participation of ZnO, lignin or ZnO/lignin materials along with their characteristics

In order to characterize cement composites doped with hybrid systems and pristine precursors, tests of plasticity, heat of hydration, compressive strength after 28 days, porosity and microbiological purity using the contact method after 24 h of exposure were carried out, the results of which are summarized in Table 11. The data obtained through plasticity tests allowed to note that the introduction of lignin into the cement matrix results in an increase in the plasticity of the composites, as evidenced by the flow rates for ZnO (16.4 cm), ZnO/lignin hybrid systems: 5:1 – flow 16.4 cm; 1:1 – 17.3 cm; 1:5 – 17.7 cm, as well as pristine lignin (17.8 cm). The plasticizing effect of lignin has already been confirmed by researchers in other reports (Huang et al., 2018; Gupta et al., 2017; Kalliola et al., 2015), in which lignin was used as a plasticizer or superplasticizer to reduce the amount of mixing water. The addition of lignin also changes the heat of hydration of cement composites, as the value of 300.1 J/g of released heat was determined for the reference sample, for the composite with an admixture of ZnO it is equal to 310.5 J/g, while the admixture of pristine lignin reduced the heat of hydration to 290.2 J/g, which is the lowest recorded result. The assessment of the impact of lignin on the heat of hydration was carried out by Darweesh (Darweesh, 2021), who confirmed that the admixture of lignin up to 0.3 wt.% has a positive effect on this parameter. The mechanical properties determined on the basis of compressive strength tests after 28 days of seasoning confirmed the beneficial effect of zinc oxide (64.5 MPa) on the strength of cement composites in relation to the reference sample (55.5 MPa). The admixture of lignin reduces this parameter, resulting in a strength value of 44.5 MPa. In the case of hybrid materials, a slight deterioration of mechanical properties is visible, the highest value was achieved by the composite with the admixture of ZnO/lignin (5:1), amounting to 60.7 MPa. The decrease in mechanical properties may be related to the slight aeration of the composite structure, which is also confirmed by the porosity results presented as the total pore volume, which for the composite with lignin admixture was 2.50 cm^3/g. A similar behavior of a cement composite with an admixture of lignin was demonstrated in the work of Klapiszewski et al. (Klapiszewski et al., 2019). The cement composite with the lowest total pore volume is ZnO/lignin (5:1), in case of which a value of 1.20 cm^3/g was achieved. Liu with co-workers confirmed the densification of the structure of the cement composite with an admixture of ZnO (Liu et al., 2019). The final stage of the research was the assessment of microbiological purity determined by the contact method after 24 h of exposure. The observations show that both the admixture of zinc oxide and lignin have a positive effect on antimicrobial properties. The highest number of bacterial colonies was observed in the reference sample, small amounts of microorganisms were also found for the ZnO/lignin (1:5) composite. Both zinc oxide (Khezerlou et al., 2018) and lignin (Gala Morena and Tzanov, 2022; Gala Morena et al., 2022) are known in the literature for their antimicrobial properties.

In the second stage of the presented research, similarly to those described in previous sections, the influence of the ZnO, lignin, and ZnO/lignin doping agents (described above) on the functional and physical properties of the resulting cement composites was studied by statistical evaluation with the randomized quadratic *I*-optimal design in the coordinate exchange mode. The direct impacts of the type of doping agent (A2) on the quality and physical characteristic measures of the optimized cement composite formulation, i.e., compressive strength ($2Y_1$), microbial purity ($2Y_2$), total pore volume ($1Y_3$), plasticity ($1Y_4$), and heat of hydration ($2Y_5$), were tested for statistical significance. Table 12 displays the experimental design matrix for a randomized *I*-optimal experiment with 16 replicates, all of which have the same levels of independent variables and the same experimental values for response factors.

able 11. List of test results of cement composites doped with ZnO, lignin and ZnO/lignin materials

Sample	Plasticity (cm)	Heat of hydration (J/g)	Compressive strength after 28 days (MPa)	Total pore volume (cm^3/g)	Microbial purity (contact method) after 24 h
CEM	17.2	300.1 (0)	55.5	1.39	++ (high growth) (2)
ZnO	16.4	310.5 (1)	64.5	1.26	− (lack of growth) (0)
ZnO/lignin (5:1)	16.4	294.3 (-1)	60.7	1.20	− (lack of growth) (0)
ZnO/lignin (1:1)	17.3	292.1 (-1)	55.1	1.90	− (lack of growth) (0)
ZnO/lignin (1:5)	17.7	294.6 (-1)	48.5	1.83	+ (little growth) (1)
Lignin	17.8	290.2 (-1)	44.5	2.50	− (lack of growth) (0)

Table 12. A randomized quadratic *I*-optimal design's experimental matrix of independent variable (A2) with its corresponding levels and analyzed response factors $1Y_1$ – $1Y_5$: compressive strength, microbial purity, total pore volume, plasticity, and heat of hydration, respectively

Run	Factor A2: admixture type*	Response $2Y_1$: Compressive strength (MPa)	Response $2Y_2$: Microbial purity	Response $2Y_3$: Total pore volume (cm^3/g)	Response $2Y_4$: Plasticity (cm)	Response $2Y_5$: Heat of hydration (J/g)
1	3	60.7	0	1.20	16.4	1
2	4	55.1	0	1.90	17.3	-1
3	1	55.5	2	1.39	17.2	0
4	1	55.5	2	1.39	17.2	0
5	4	55.1	0	1.90	17.3	-1
6	6	44.5	0	2.50	17.8	-1
7	3	60.7	0	1.20	16.4	1
8	2	64.5	0	1.26	16.4	1
9	4	55.1	0	1.90	17.3	-1
10	5	48.5	1	1.83	17.7	-1
11	2	64.5	0	1.26	16.4	1
12	4	55.1	0	1.90	17.3	-1
13	1	55.5	2	1.39	17.2	0
14	6	44.5	0	2.50	17.8	-1
15	6	44.5	0	2.50	17.8	-1
16	1	55.5	2	1.39	17.2	0

* 1 – CEM, 2 – ZnO, 3 – ZnO/lignin (5:1), 4 – ZnO/lignin (1:1), 5 – ZnO/lignin (1:5), 6 – lignin

The 2D response surfaces (see Fig. 3) once more visually represent the multiple linear regression model equations derived from the quadratic *I*-optimal design. By navigating the response surfaces, we were able to evaluate the potential associations between the independent and dependent factors of cement composites ~~s~~ formulations. The main purpose of the second stage of optimization was to determine the best ZnO, lignin, or ZnO/lignin doping agent as an admixture for cement composites. The key factors, that should exist ~~in~~ to the highest extent~~,~~ were the best, i.e., compressive strength ($2Y_1$), high microbial purity ($2Y_2$), and finally satisfactory total pore volume ($2Y_3$). As it can be seen from the 2D response surfaces, the cement composites containing the commercially available zinc oxides, i.e., ZnO-SA and ZnO/lignin hybrid material with the lowest ratio of lignin to zinc oxide (factors A2: 2 and 3 respectively), allowed to achieve the optimal functional and physical properties of the resulting cementitious composites, i.e., good compressive strength and microbial purity, satisfactory total pore volume, plasticity, as well as visibly lowered heat of hydration.

Analyses of variance (ANOVA) performed on the response surfaces derived from the randomized *I*-optimal design for dependent factors $2Y_1 – 2Y_5$ revealed that the quadratic, cubic, and quartic multiple linear regression models provided the best-fit in all instances, which is a common solution in optimization by RSM and DoE, as provided by the literature (Klapiszewska et al., 2023; Balicki, 2021; Bartman et al., 2021; Sinkhonde et al., 2021; Hou et al., 2020; Meyers et al., 2016). The mentioned best fit model included very appropriate statistical measures, i.e., a negligible lack of fit with a suitable number of degrees of freedom, followed by experimental, adjusted, and predicted R^2 coefficients that matched exceptionally well. For all five predicted response factors, the resulting *p*-values of model fitting were lower than 0.05, indicating that the *I*-optimal design chosen for optimization was statistically significant. The actual results of the ANOVA analysis are described in Tables 13 through 17. In the case of $2Y_1$ (compressive strength), the type of admixture had a quadratic effect on its values, while for the remaining ones, the relationships of the interaction were as follows: $2Y_2$ cubic effect, $2Y_3$ quadratic effect, $2Y_4$ cubic effect, and finally $2Y_5$ also cubic effect. The following is a summary of the ANOVA analyses that were conducted, including the multiple linear regression formulae that were obtained based on the *I*-optimal model that was fitted to the observed values of the response factors:

$$\text{Compressive strength} = +58.13 -16.60A -1.87A^2 +11.06A^3 -6.26A^4$$

$$\text{Microbial Purity} = -0.0830 +1.16A +1.10A^2 -2.14A^3$$

$$\text{Total pore volume} = +1.57 +0.5869A +0.3616A^2$$

$$\text{Plasticity} = +16.86 +1.80A +0.6411A^2 -1.51A^3$$

$$\text{Heat of hydration} = -0.0709 -3.37A -0.4123A^2 +2.90A^3$$

These formulae support the investigated relationships between response factors and independent variables of the cementitious composites ~~s~~ formulations, resulting in the production of cements with the required microbiological purity and adequate physical qualities. To conclude, after statistical evaluation and interpretation of the response surfaces (see Fig. 3) during the RSM optimization process, also taking into account the desirability function, we were able to present the best candidate profile (see Table 18)

Table 13. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $2Y_1$ (compressive strength)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	616.34	4	154.08	1134.13	< 0.0001
A-Admixture	160.42	1	160.42	1180.75	< 0.0001
A^2	0.2608	1	0.2608	1.92	0.1933
A^3	61.98	1	61.98	456.19	< 0.0001
A^4	3.48	1	3.48	25.61	0.0004
Residual	1.49	11	0.1359		
Cor Total	617.83	15			
R^2 = 0.9976, Adjusted R^2 = 0.9967, Predicted R^2 = 0.9853					

Table 14. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $2Y_2$ (microbial purity)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	11.46	3	3.82	96.58	< 0.0001
A-Admixture	0.8806	1	0.8806	22.26	0.0005
A^2	3.66	1	3.66	92.51	< 0.0001
A^3	2.57	1	2.57	64.96	< 0.0001
Residual	0.4748	12	0.0396		
Cor Total	11.94	15			
R^2 = 0.9602, Adjusted R^2 = 0.9503, Predicted R^2 = 0.9304					

Table 15. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $2Y_3$ (total pore volume)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	2.99	2	1.50	52.01	<0.0001
A-Admixture	2.80	1	2.80	97.27	<0.0001
A^2	0.3964	1	0.3964	13.78	0.0026
Residual	0.3739	13	0.0288		
Cor Total	3.37	15			
R^2 = 0.8889, Adjusted R^2 = 0.8718, Predicted R^2 = 0.8494					

Table 16. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $2Y_4$ (plasticity)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	3.83	3	1.28	180.14	< 0.0001
A-Admixture	2.11	1	2.11	297.11	< 0.0001
A^2	1.24	1	1.24	175.48	< 0.0001
A^3	1.27	1	1.27	179.28	< 0.0001
Residual	0.0850	12	0.0071		
Cor Total	3.91	15			
R^2 = 0.9783, Adjusted R^2 = 0.9728, Predicted R^2 = 0.9628					

Table 17. ANOVA results for the randomized quadratic *I*-optimal optimization model for dependent variable $2Y_5$ (heat of hydration)

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value
Model	9.90	3	3.30	35.89	< 0.0001
A-Admixture	7.37	1	7.37	80.16	< 0.0001
A^2	0.5143	1	0.5143	5.60	0.0357
A^3	4.69	1	4.69	51.02	< 0.0001
Residual	1.10	12	0.0919		
Cor Total	11.00	15			
R^2 = 0.8997, Adjusted R^2 = 0.8747, Predicted R^2 = 0.8266					

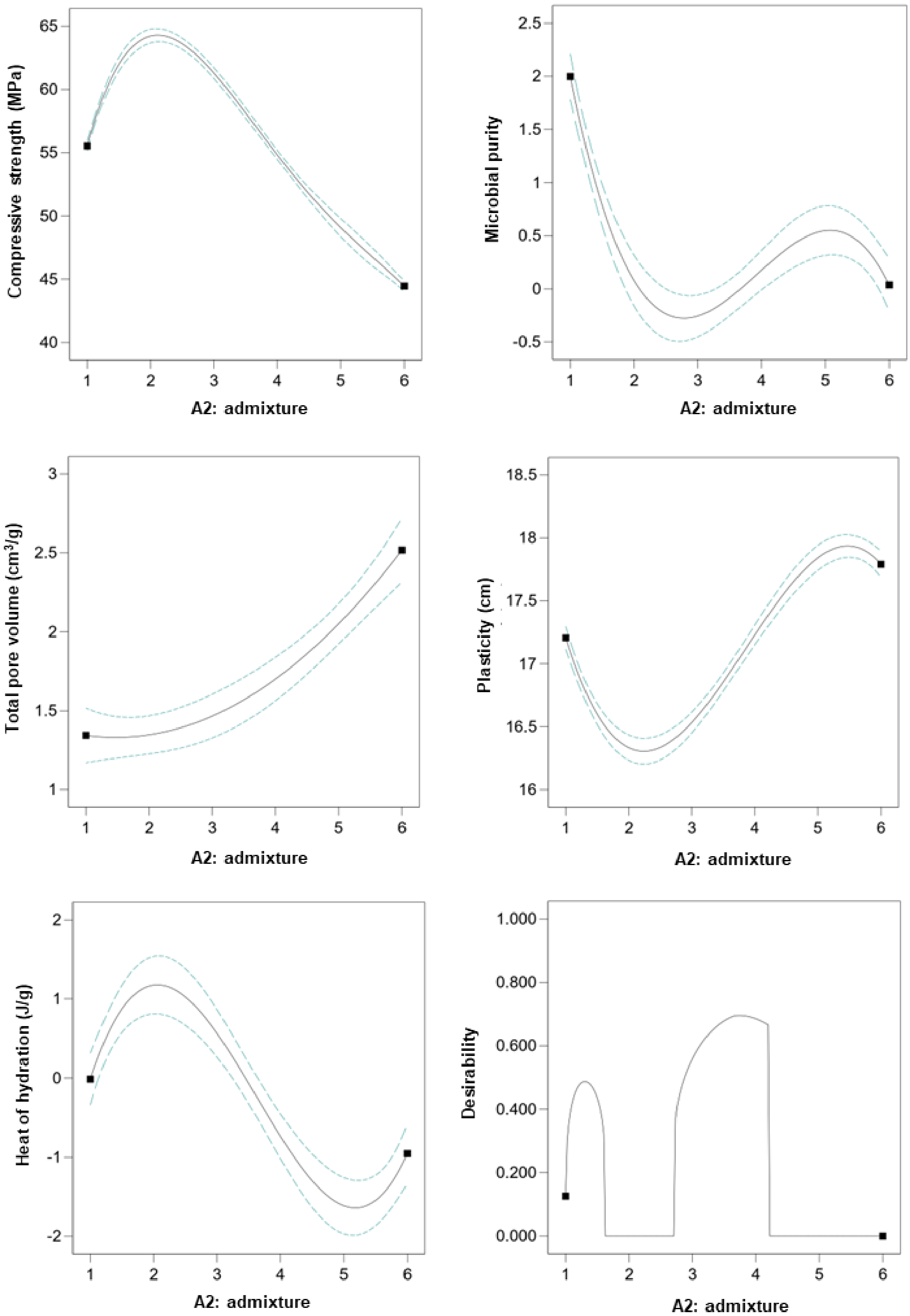

Fig. 3. A graphical representation of the response surfaces, is based on a randomized quadratic *I*-optimal model for the dependent factors $2Y_1$ (compressive strength), $2Y_2$ (microbial purity), $2Y_3$ (total pore volume), $1Y_4$ (plasticity), and $1Y_5$ (heat of hydration), vs. the independent variable: type of ZnO, lignin, and ZnO/lignin admixture (A2), followed by desirability function measure

and therefore select the best solution. It turned out, that ZnO/lignin admixture no. 3 (ZnO/lignin (5:1)) gave the desired results, passing all the requirements, i.e., the best microbial purity together with the smallest total pore volume, followed by satisfactory physical properties.

Table 18. Selected candidate for the optimal fabrication of the cementitious composites proposed by *I*-Optimal model optimization, based on desirability function, comparison of predicted and actual values, as well as compromise between microbial purity, cost, and physical properties

Solution	Admixture type	Compressive strength		Microbial purity		Total pore volume		Plasticity		Heat of hydration		Desirability
		P[1]	A[2]	P	A	P	A	P	A	P	A	-
1	3 – ZnO/lignin (5:1)	61.3	60.7	0.255	0.000	1.466	1.200	16.54	16.40	0.563	-1.000	0.560

[1] values predicted by the *I*-optimal model
[2] actual experimental values

4. Conclusions

In the first stage of the statistical evaluation, optimization through the response surface methodology~~,~~ by means of a quadratic randomized *I*-optimal model ~~has~~ revealed that the commercially available ZnO-SA doping agent was the most cost-effective and suitable from the point of view of the physical and functional properties of the fabricated cement composites. Moreover, the second stage of the statistical analysis has proved that doping agent in ~~a~~ the form of a hybrid material, i.e., ZnO-SA/lignin (5:1), allowed for the production of ~~the~~ highly desirable cementitious composites~~,~~ with the required microbial purity, followed by satisfactory compressive strength and total pore volume – ~~a~~ crucial factors in such formulation types. The cement composite formulations were optimized in both stages of statistical analysis using an *I*-optimal model, response surface methodology (RSM), and multivariate analysis of variance (ANOVA). Such an approach allowed us to explain the influence of the doping agent types on the functional and quality properties of the resulting composites. The statistical measures have shown a very high match between predicted and actual experimental data. Moreover, by studying the 2D response surfaces, the RSM proved the non-linear relationship between independent and dependent variables in the optimized formulations. Therefore, statistical analysis during the production of cement composites doped with different materials can feasibly allow for quick determination of the effects on the physical and quality properties of the final professional product, with a relatively low number of experiments required to be performed.

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