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Deposition of Transition Metal onto Carbonate Materials Surface: Theoretical Evaluation of Optimal Parameters

Deposition probabilities of transition metal ions on carbonate materials have been discussed in this paper. The deterministic and probabilistic design of the experiment has been used to obtain the optimal deposition parameters. The special features of deposition of copper, nickel, cobalt and zinc cations on surface of marble have been analyzed. Based on this research, the authors proposed the generalized multiple factor equations to predict the behavior of the selected metals on a marble surface. It was demonstrated that copper deposition is affected only by concentration of copper sulfate solution. For nickel, the strength of a complex with transition metal ion affects the deposition of an insoluble compound on carbonate surface. Deposition of cobalt under the specified conditions is very weak and an impact is exerted by the basicity and concentration of cobalt sulfate. For zinc, deposition under specified conditions has a strong dependence on the influencing factors, and the amount of deposited zinc varies within a wide range. The obtained results permit to use the application method of the protective and decorative coatings on products made of the natural minerals and inorganic materials such as marble, concrete, dolomite, limestone, gypsum, etc.

Keywords: transition metals, carbonate materials, deposition, marble surface, hardly soluble compounds, complexing agents, deterministic and probabilistic design of the experiment, optimal parameters.

Introduction

Marble is one of the frequently used natural materials in construction [1–11]. It has been used as a building cladding material in construction of monuments, various types of works of art, cultural heritage sites, etc. [10, 12, 13]. However, marble is a fragile and heterogeneous material and its composition depends on its deposit [4, 8, 12]. During the operation, marble is exposed to various natural water phenomena, temperature changes, weathering, etc. Therefore, the protection of such material from the external influences is relevant and of interest from beginning of its use [10, 13]. The authors [2, 14] developed methods for obtaining of coatings from various organic substances based on the density functional theory. Various types of complexing agents are also applied and they slow down the deposition rate and improve the quality of the marble coating [15–17]. Processes of the chemical deposition of transition metal ions on carbonate materials have been studied in some papers [18–20]. This is primarily related to water treatment and recovery of trace metals. Mechanism of a chemical deposition of copper on calcite has been described in [21]. We have showed before the deposition probability of malachite and azurite minerals from the organic complex copper compounds on carbonate materials [22, 23]. Moreover, the paper described the stabilization of the unstable polymorphic forms of minerals under copper ion influence [24]. An approach closest to this project is described in [25], where the electrokinetic methods have been applied for deposition of calcium oxalate on the marble surface. This paper focuses on substitution of cations (instead of anions) on a surface of the treated materials.

The research purpose is to find the optimal conditions of deposition processes of the selected transition metals (copper, nickel, cobalt and zinc) as applied to carbonate inorganic construction material.

A series of experiments using the deterministic and probabilistic design of the experiment have been carried out to study the deposition methods of the insoluble transition metal compounds on the surface of a carbonate reservoir [26, 27].

Experimental

In order to select *d*-elements, the main criteria were availability and price of salts of these metals, and also stability of an element in the valence state of 2+. Cu, Ni, Co and Zn compiled with the relevant criteria and they were selected for the research.

Marble was chosen as a carbonate reservoir. The experiments used the cubic samples of the cubic polycrystalline marble with a side of 2.5 cm and a polished surface. This was done to exclude a factor of the difference in the specific area of the rough cube surface for deposition intensity of the main carbonate transition metal on it.

For all experiments, a five-factor experiment matrix has been developed with four levels for each factor. The factors influencing on deposition intensity have been selected as below:

– concentration of transition metal salt;

– concentration of a strong electrolyte salt with an anion similar to transition metal salt to study an effect of an ionic strength of solution;

– amount of *KOH* in solution to study an effect of basicity of medium;

– holding time of cube in solution;

– vacancy factor required for calculations.

The amount of transition metal deposited on surface of a marble sample has been taken as the result of the experiment. For this purpose, a surface layer of the extracted sample has been dissolved in a 1:100 sulfuric acid solution. Then the obtained solution has been brought to 50 ml. Concentration of transition metal has been measured by the photometric methods.

The experiment matrix for deposition of copper, nickel, cobalt and zinc as their basic carbonates has been generally described. Table 1 summarizes the selected factors and levels. In this case, differences for four metals are the first and second factors.

The factor designations are as follows:

factor 1 — $CuSO_4$ concentration (mol/l) for Cu; $Ni(NO_3)_2$ concentration for Ni; $CoSO_4$ concentration for Co and $ZnSO_4$ concentration for Zn;

factor 2 — Na_2SO_4 concentration (mol/l) for Cu, Co and Zn; Na_2NO_3 concentration for Ni.

factor 3 — the amount of 0.1 M KOH solution (ml);

factor 4 — the holding time of the marble sample in solution (a week);

factor 5 — vacant.

The volume of solution was 300 ml.

Table 1

Factors and levels

Factor No.	Factor	Designation	Level 1	Level 2	Level 3	Level 4
1	Factor 1	X1	0.01	0.02	0.03	0.04
2	Factor 2	X2	0	0.1	0.15	0.2
3	Factor 3	X3	4.2	8.4	12.5	16.8
4	Factor 4	X4	1	2	3	4
5	Factor 5	X5	1	2	3	4

The volume of solution was 300 ml.

In order to exclude deposition of $Cu(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$ and $Zn(OH)_2$ with increasing basicity of a solution and possible increase in activity of ions of Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}, a complexing agents have been added to the solution, i.e. Na-EDTA for copper, sodium acetate for nickel, sodium citrate for cobalt and lactate ion for zinc. All substances have been added in concentrations equivalent to the concentrations of Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} ions.

Analysis of the solutions obtained by the above approach has been performed photometrically according to the method of analysis of Cu^{2+} ions with Na-DDTC (sodium diethyldithiocarbamate); Ni^{2+} with dimethylglyoxime and Co^{2+} with nitroso-r-salt. The content of Zn^{2+} ions has been analyzed by the atomic absorption spectroscopy.

For copper, the obtained optical density of the analyzed samples relative to a pure solvent has been taken as the result. For nickel and cobalt, the result contained the received optical density of the analyzed samples relative to a blank sample. For zinc, the result included the obtained values of zinc content in the analyzed samples.

The amount of deposited metal has been used as a comparative measure of *Y*.

MS Excel program has been applied for calculations and graphs. Table 2 summarizes the design of the experiment for all explored metals.

Table 2

The design of the experiment by factors

No.	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
1	0.01	0	4.2	1	1
2	0.01	0.1	8.4	2	2
3	0.01	0.15	12.5	3	3
4	0.01	0.2	16.6	4	4
5	0.02	0	8.4	3	4
6	0.02	0.1	4.2	4	3
7	0.02	0.15	16.6	1	2
8	0.02	0.2	12.5	2	1
9	0.03	0	12.5	4	2
10	0.03	0.1	16.6	3	1
11	0.03	0.15	4.2	2	4
12	0.03	0.2	8.4	1	3
13	0.04	0	16.6	2	3
14	0.04	0.1	12.5	1	4
15	0.04	0.15	8.4	4	1
16	0.04	0.2	4.2	3	2

Results and Discussion

Table 3 demonstrates the obtained results of factors for the studied transition metals.

Table 3

The results of calculations for Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}

No	Calculation results, kg/m^2			
	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}
1	0.107	0.189	0.04	33.141
2	0.469	0.487	0.06	339.9
3	0.047	0.56	0.023	1084.4
4	0.081	0.489	0.06	1427.7
5	0.16	0.339	0.027	63.7
6	0.065	0.402	0.047	2.1
7	0.156	0.212	0.047	123
8	0.284	0.39	0.081	359.4
9	0.090	0.449	0.097	38.2
10	0.086	0.132	0.022	30.1
11	0.567	0.300	0.088	0.2
12	0.180	0.322	0.079	0.6
13	0.590	0.181	0.089	28.5
14	0.223	0.174	0.042	1.8
15	0.249	0.844	0.121	4.5
16	0.153	1.153	0.034	1.5

Results of the computational calculations are shown by the partial dependencies. The graphical data are also presented for them.

For factors of 1-4, the results for Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} are illustrated in Figures of 1-4. It should be stated that the graphical data are presented only for the significant factors.

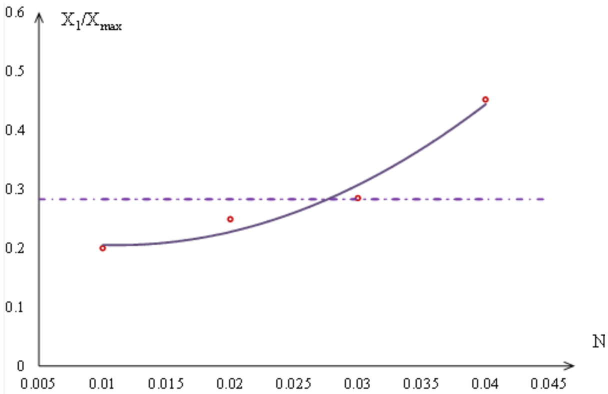
Correlation coefficients of all factors for all metals are shown in Table 4. Table 4 demonstrates that only factor 1 was significant for copper, i.e., the amount of copper deposited on marble surface is affected only by concentration of copper sulfate solution.

For nickel and zinc, all factors are significant. For cobalt, factors of 1 and 3 are relevant.

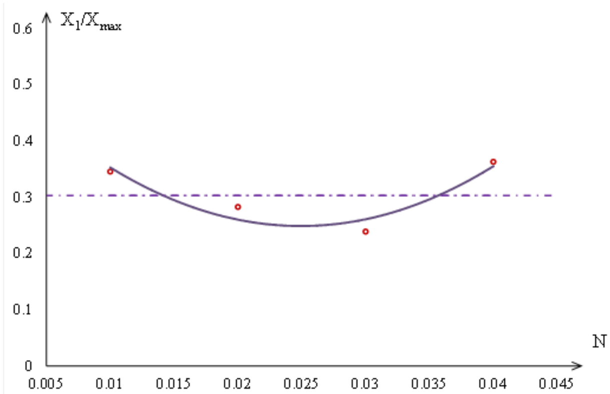
Table 4

Correlation coefficients by factors 1-5 for Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} metals

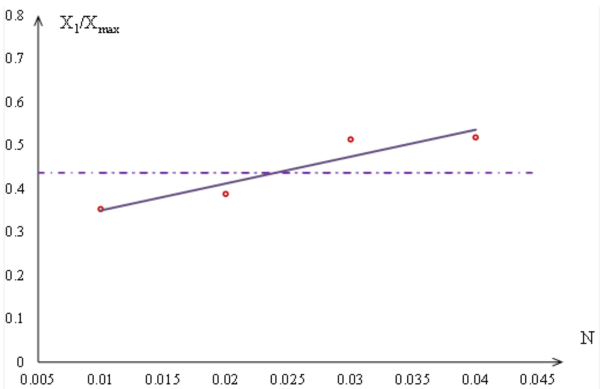
Factor	Correlation coefficients			
	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}
X1	R = 0.9766	R = 0.8001	R = 0.9104	R = 0.9968
X2	R = 0.5211	R = 0.9632	R = 0.6704	R = 0.9879
X3	R = 0.5683	R = 0.9834	R = 0.8617	R = 0.9788
X4	R = 0.6380	R = 0.9998	R = 0.6606	R = 0.9712
X5	R = 0.5376	R = 0.8087	R = 0.9959	R = 0.8427



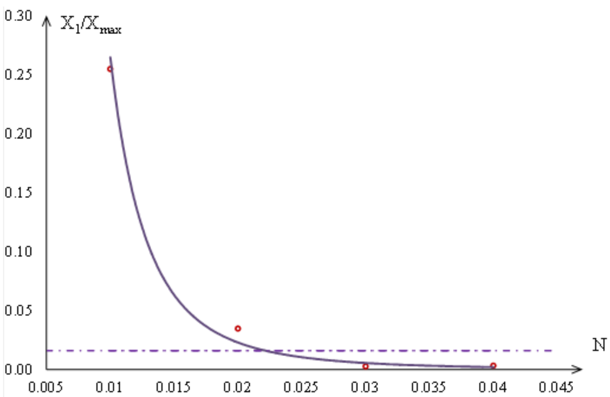
a) for copper (II)



b) for nickel (II)



c) for cobalt (II)



d) for zinc (II)

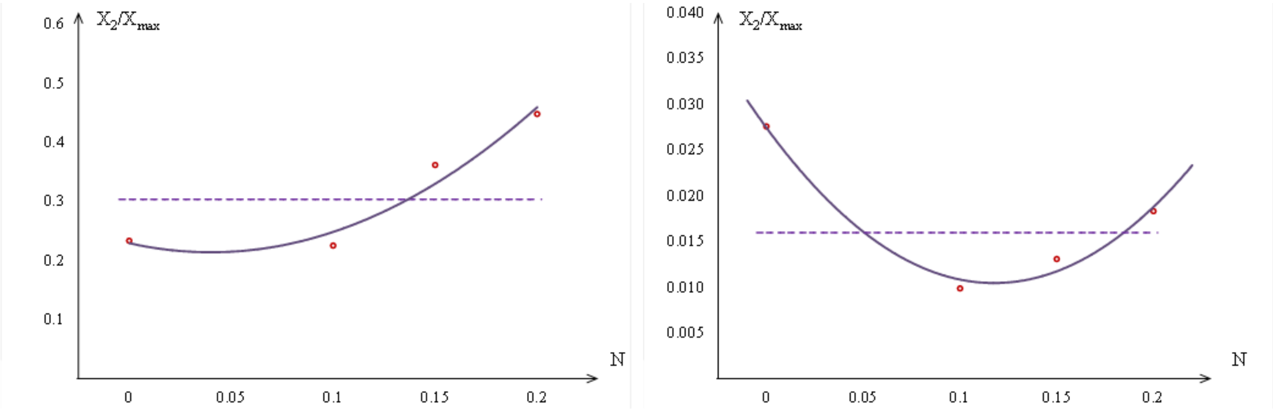
Figure1. Dependence of factor 1 on the amount of deposited metal

The equations for all studied metals are described. For copper, the significant factor is 1, thus, the equation is showed only for it:

$$Y_1 = 0.00751 e^{48.45 X_1} X_1^{-0.4953}, \text{ kg/m}^2 \quad (1)$$

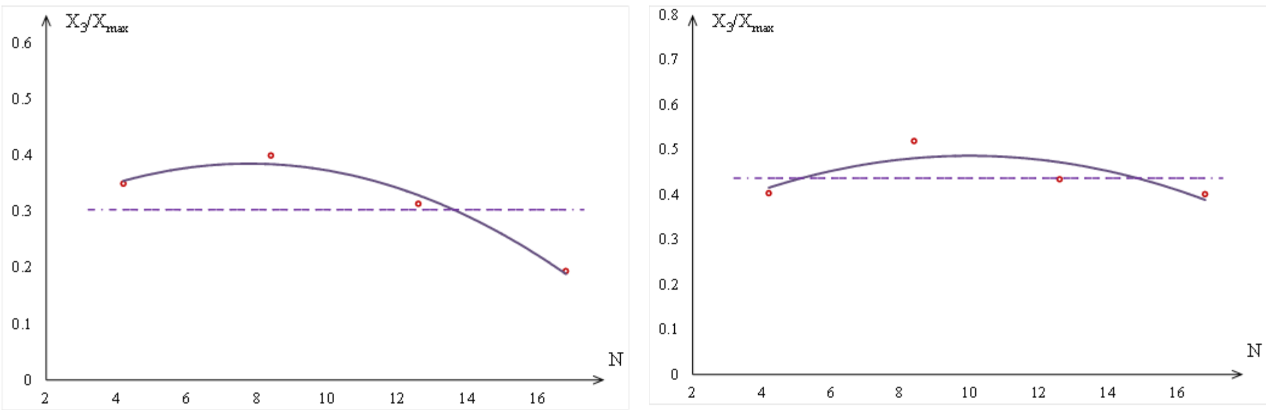
For nickel, all factors were relevant, so the overall multiple factor equation is as follows:

$$Y = Y_{av}^{-3} \cdot \left(0.0004032e^{62.19X_1} X_1^{-1.367}\right)\left(11.05X_2^2 - 0.8843X_2 + 0.2641\right)\times$$
$$\times\left(-0.04898X_3^2 + 0.0832X_3 + 0.4084\right)\left(0.19e^{0.1219X_4} X_4^{0.3646}\right), \text{ kg/m}^2 \qquad (2)$$

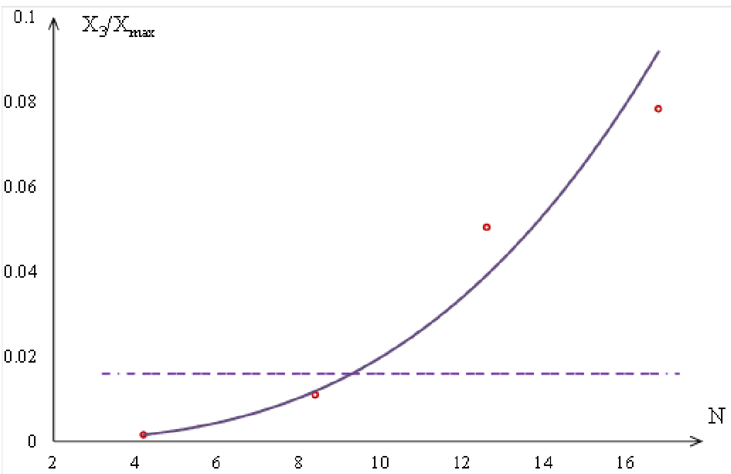


a) for nickel (II) b) for zinc (II)

Figure 2. Dependence of factor 2 on the amount of deposited metal

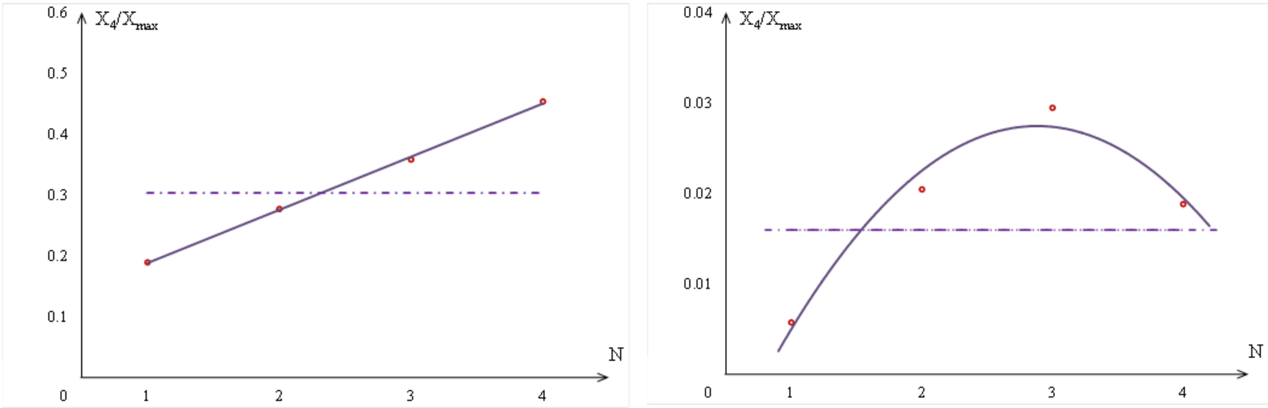


a) for nickel (II) b) for cobalt (II)



c) for zinc (II)

Figure 3. Dependence of factor 3 on the amount of deposited metal



a) for nickel (II)　　　　b) for zinc (II)

Figure 4. Dependence of factor 4 on the amount of deposited metal

For cobalt, we describe a generalized multiple factor equation for factors of 1 and 3:

$$Y = Y_{av}^{-1} \cdot \left(0.03485 + 0.749 X_1\right)\left(0.02087 e^{-0.102 X_3} X_3^{0.8965}\right), \text{ kg/m}^2. \quad (3)$$

For zinc, generalized multiple factor equation for all studied factors:

$$Y = Y_{av}^{-3} \cdot \left(3.194 \cdot 10^{-5} X_1^{-3.536}\right)\left(1748 X_2^2 - 410.9 X_2 + 39.04\right) \times$$
$$\times \left(0.01672 e^{-0.06677 X_3} X_3^{3.55}\right)\left(35{,}5 e^{-1.49 X_4} X_4^{4.127}\right), \text{ kg/m}^2. \quad (4)$$

After obtaining of the multiple factor equations, the additional experiments have been performed. Results of the experimental data are summarized in Table 5. A correlation coefficient compared to the experimental data is present in a bottom line of Table 5. This table includes the results for cobalt which are not significant.

Table 5

Obtained experimental data for Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}

No	Calculation results, kg/m^2			
	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}
1	0.1439	0.2007	0.03948	21.6699
2	0.2129	0.4629	0.03951	250.8943
3	0.1323	0.6166	0.0386	1071.8711
4	0.05735	0.4599	0.03678	2637.4584
5	0.1589	0.2743	0.0478	73.0732
6	0.06992	0.4667	0.03525	2.7565
7	0.1539	0.1558	0.04178	49.6374
8	0.237	0.3926	0.05878	138.4649
9	0.09267	0.4719	0.05615	40.839
10	0.2045	0.1722	0.04058	46.3329
11	0.3302	0.2998	0.04467	0.7753
12	0.2056	0.4229	0.07192	2.7098
13	0.4639	0.1844	0.05382	34.7992
14	0.2931	0.1822	0.05179	1.8646
15	0.1265	0.7322	0.06328	2.0041
16	0.2905	1.038	0.06751	0.5478
R	**0.6718**	**0.9636**	**0.4764**	**0.6117**

Conclusions

Thus, matrix experiments have been performed for each type of the inorganic transition metal salt using the mathematical design of the experiment.

The amount of copper deposited on a marble surface has been established to be affected only by the concentration of copper sulfate solution. The other factors are not significant. Hypothetically, the weak deposition of basic copper carbonate has been particularly influenced by the presence of Trilon B in solution, binding copper ions in a sufficiently strong complex.

For nickel, the obtained results can be used to predetermine the effect of strength of the complex with a transition metal ion on deposition of an insoluble compound on the carbonate surface.

Acetate forms a less strong complex with nickel and prevents its deposition in the form of hydroxide in the presence of KOH. Thus, acetate does not prevent the Ni^{2+} ion to react with calcium carbonate in the basic medium. This feature is confirmed by the fact that nickel hydroxide deposits with increasing KOH concentration. In addition, the complex of copper with Trilon B does not deposit at a high KOH content in solution. The solution concentration has the least effect on the amount of the deposited basic nickel carbonate. Thus, it indicates a low reaction rate, which is limited by the specific surface of calcium carbonate.

Deposition of cobalt under the specific conditions is very weak, i.e., it is confirmed by very low concentration of cobalt in all analyzed solutions. The cobalt citrate complex has the sufficient strength to prevent the formation of cobalt hydroxide deposit at the high concentrations of KOH in the solution. The strong complex is also thought to slow down the reaction of cobalt with calcium carbonate. However, in model solutions, cobalt without the extraneous ions showed a much lower deposition rate on the $CaCO_3$ surface than ions of nickel or copper. Therefore, the influence of a complexing agent is not significant. The conducted research described that the significant factors are the basicity of solution and concentration of cobalt sulfate.

For zinc, deposition under the specific conditions is highly dependent on the influencing factors. The amount of the deposited zinc varies within a wide range. Zinc deposition elevates with increasing concentration of the complexing agent. However, zinc deposition is maximized in the absence of a complexing agent. Thus, it indicates that the strength of zinc complexes is high to slow down the reaction of zinc with calcium carbonate. All studied factors are significant. The most significant factors are the basicity of solution and concentration of zinc sulfate. However, the basicity of solution has a positive correlation with the amount of the deposited zinc, but the concentration of zinc sulfate has a negative correlation.

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