coatings

Supplementary Materials: Evaluating the Protective Effects of Calcium Carbonate Coating on Sandstone Cultural Heritage

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Determination of the Experimental Plan

In the preliminary experiment, we studied four influencing factors, namely the type of surfactant (Ts), the time of action of the surfactant (T), the titration rate (R) and surfactant concentration (C). The influence of the combination of different factors on the crystal form of calcium carbonate does not consider the interaction between the factors. We need to deposit aragonite crystal type and vaterite crystal type calcium carbonate on the surface of sandstone. Therefore, the evaluation index is the mole ratio of mixed crystal calcium carbonate crystal aragonite crystal form and vaterite crystal form. Three different types of surfactant Ts are selected, respectively: PVA、PVP、SDS. Similarly, the time of action of the surfactant T (h) is divided in three levels are: 6, 12, 24. The number of the levels for the titration rate R (mL/min) are 10, 5, 1. The three levels of surfactant concentration C (g/L) are divided into 1, 2, 4. The factor levels of the orthogonal tests are shown in Table S1. (All tests are carried out at room temperature, all surfactants are added to calcium chloride, and the action time is the action time of the surfactant and calcium chloride).

Table S1. Orthogonal factor and level table.

Level	Factors			
	Ts	**T/h**	**R/mL·min^{-1}**	**C/g·L**
1	PVA	6	10	1
2	PVP	12	5	2
3	SDS	24	1	4

The core of orthogonal experiment design is orthogonal experiment a series of various factors and levels. In this article, four study free parameters, each parameter has three levels, determine the design accuracy. In order to reduce the workload simulation and test combination obtained by L9 (3^4) Orthogonal table [1]. Orthogonal table is a set of rules for designing tables. For L9 (3^4), L represents the name of the orthogonal table, and the number 9 represents a 9-row table, indicating that there are 9 cases in the research program of the orthogonal table design. The number 3 means that each factor has 3 levels, and 4 means that there are 4 factors. As shown in Table S2, the number is from 1 to 9 in the first column that is represented 9 cases. Second to fifth columns is denoted different factors, namely Ts, T, R, C. The row in the table is corresponded to an instance. The number of "1, 2, 3" is indicated different levels of factors. The factors are shown in Table S2. For example, the third case is corresponded to the first level of Ts, third level of T, third level of R, and third level of C.

Table S2. L9 (3^4) Orthogonal array.

Level	Factors			
	Ts	**T/h**	**R/mL·min⁻¹**	**C/g·L**
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	2
5	2	2	3	3
6	2	3	1	1
7	3	1	3	3
8	3	2	1	1
9	3	3	2	2

Observing the orthogonal table above, we can find that the frequency of occurrence of all three levels is equal. Between the two columns, including any possible combination of levels, their appearance is equal. In other words, each level of a factor is equal to other factors. Based on orthogonality, the orthogonal experimental design is more typical, and it can be uniformly and formally distributed on the full-scale experimental site.

Figure S1 shows the XRD test results of calcium carbonate samples obtained by orthogonal experiments. The X-ray diffraction data acquired for samples prepared at orthogonal experiment and the fraction of vaterite and aragonite were analyzed using the equations suggested by Kontoyannis et al [2]. Assuming that the sum of the mole ratio of calcite, aragonite, and vaterite is 1, the mole fractions in a calcium carbonate specimen may be determined from the following relationships [3]:

$$X_A = \frac{1.395 \times I_A^{221}}{I_c^{104} + 3.157 \times I_A^{221} + 7.691 \times I_V^{110}} \quad (1)$$

$$X_c = \frac{I_c^{104} \times X_A}{3.157 \times I_A^{221}} \quad (2)$$

$$X_V = 1 - X_C - X_A \quad (3)$$

Here, X_C, X_A, and X_v are the mole ratio of calcite, aragonite, and vaterite in the precipitated calcium carbonate mixture; I_C and I_A are the intensity of the calcite peaks at 2θ = 29.4° and of aragonite at 2θ = 45.6°. The mole fraction results we get are shown in the Table S3.

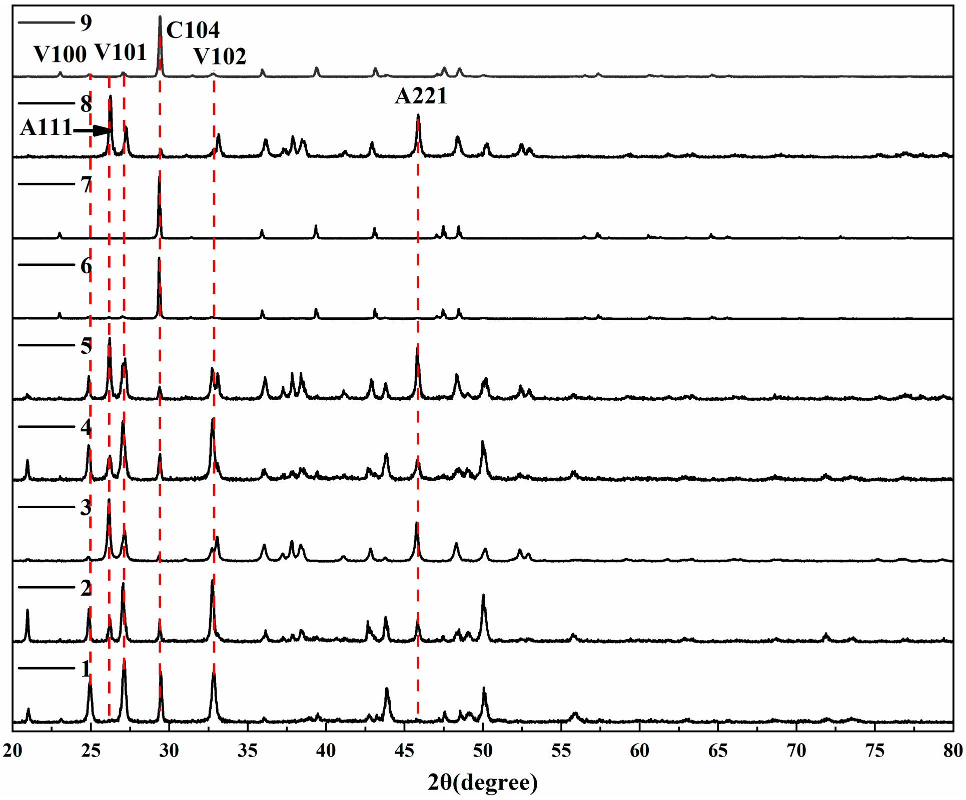

Figure S1. XRD diffraction pattern of orthogonal experiment sample.

Table S3 shows the results of the orthogonal experiment. We analyzed the XRD diffraction pattern of the calcium carbonate powder sample obtained in the orthogonal experiment. According to the characteristic peaks of different crystal types in the diffraction pattern, the mole fractions of different crystal types are calculated, and the aragonite crystal type and vaterite crystal type are selected as inspection indicators.

Table S3. L9 (3^4) Orthogonal designed table and its results.

Test No.	Factors				Evaluation Index	
	Ts	T/h	R/mL·min^{-1}	C/g·L	A/%	V/%
1	PVA	6	10	1	0	90.3
2	PVA	12	5	2	17.5	80
3	PVA	24	1	4	91.2	8.8
4	PVP	6	5	2	60.5	34
5	PVP	12	1	4	80.3	19.7
6	PVP	24	10	1	0	19.8
7	SDS	6	1	4	51.5	46
8	SDS	12	10	1	0	0
9	SDS	24	5	2	0	28

In this work, through the range analysis of Table S4 data, Tables S4 and S5 are obtained. Tables S4 and S5 are the range analysis of two evaluation indexes. X_{ct} and Y_{dt} in Tables S4 and S5 represent the sum of the mole fractions of calcium carbonate and vaterite calcium carbonate at different levels in the orthogonal test. $X_{ct}/3$ and $Y_{dt}/3$ represent the average value of X_{ct} and Y_{dt}.

Table S4. Range analysis of the evaluation indexes Aragonite mole fractions.

Evaluation Indexes	Factors			
	Ts	**T/h**	**R/mL·min⁻¹**	**C/g·L**
X_{c1}	108.7	112	0	0
X_{c2}	140.8	97.8	78	129.5
X_{c3}	51.5	91.2	222.9	223
$X_{c1}/3$	36.3	37.3	0	0
$X_{c2}/3$	46.9	32.6	26	43.2
$X_{c3}/3$	17.2	30.4	74.3	74.3
R_c	29.7	6.9	74.3	74.3
Optimization Level	A2	B1	C3	D3

Table S5. Range analysis of the evaluation indexes Vaterite mole fractions.

Evaluation Indexes	Factors			
	Ts	**T/h**	**R/mL·min⁻¹**	**C/g·L**
Y_{d1}	179.1	170.4	110.1	110.1
Y_{d2}	73.5	99.6	141.9	142
Y_{d3}	74.1	113.7	74.4	145.7
$Y_{d1}/3$	59.7	56.8	36.7	36.7
$Y_{d2}/3$	24.5	33.2	47.3	47.3
$Y_{d3}/3$	24.7	18.9	24.8	48.6
R_d	35.2	37.9	22.5	11.9
Optimization Level	A1	B1	C2	D3

When the factor is certain, the difference in these average values of X_{ct} and Y_{dt} is indicated influence degree of the levels for factor c (c = 1, 2, 3; t = 1, 2, 3) on the mole fraction of aragonite and vaterite difference of all orthogonal structures. Through range analysis of Equations (7) and (8), the range value R_c (or R_d) of X_{ct} (or Y_{dt}) is obtained as follows:

$$R_c = \mathrm{Max}_{\left(\frac{Xc_t}{3}\right)} - \mathrm{Min}_{\left(\frac{Xc_t}{3}\right)},\ c = (Ts, T, R; t = 1, 2, 3) \quad (4)$$

$$R_d = \mathrm{Max}_{\left(\frac{Yd_t}{3}\right)} - \mathrm{Min}_{\left(\frac{Yd_t}{3}\right)},\ c = (Ts, T, R; t = 1, 2, 3) \quad (5)$$

The influence of the four factors of Ts, T, R and C based on the range analysis on the difference in the mole fraction of aragonite crystals and vaterite crystals is shown in Figure S2a,b. Figure S2a shows that among the four factors, the titration rate and the concentration of the surfactant have the greatest influence, followed by the type of surfactant, and finally the action time. Therefore, according to the range analysis, the optimal preparation plan is selected to obtain a higher mole fraction of aragonite crystalline calcium carbonate, PVP is selected as the surfactant, the surfactant concentration is 4 g/L, the action time is 6 h, and the titration rate is 1 mL/min. Figure S2b shows that the action time of the surfactant has the greatest influence, followed by the type of surfactant, then the titration rate, and finally the concentration of the surfactant. Therefore, in order to obtain a higher mole fraction of vaterite crystalline calcium carbonate, the best dosage is to choose PVA as the surfactant, the concentration of the surfactant is 4 g/L, the action time is 6 h, and the titration rate is 5 mL/min. The verification of the best scheme of orthogonal experiment has been verified and explained in Section 3.2. Characterization and analysis of powder samples in the article.

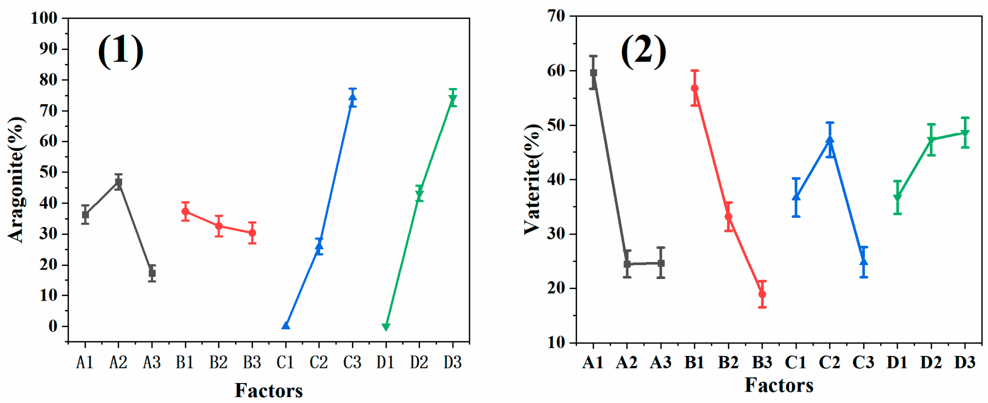

Figure S2. Effect of factors in different levels on difference crystal form, (1) is aragonite, and (2) is vaterite.

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