FACTORIAL DESIGN ANALYSIS OF HYDRATION OF ANHYDRITE CEMENT

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A full factorial design was employed to evaluate the hydration of anhydrite cement produced from flue gas desulfurization gypsum (FGD gypsum) using three activators ($KAl(SO_4)_2 \cdot 12H_2O$, Na_2SO_4, $FeSO_4 \cdot 7H_2O$). The effect of three independent variables such as the calcination temperature of FGD gypsum (500-800°C), the hydration time (3-28 days) and the amount of activator (0-1%) on the hydration of anhydrite cement were studied. The experimental results and statistical analysis showed that the hydration time and the amount of activator had a positive effect on the hydration of anhydrite cement, while the temperature had a negative effect on this process. The multiple linear regression models were developed to correlate the significant variables to the chemically combined water content in hydrated anhydrite cement. The mean absolute percentage error between experimental and calculated values of the chemically combined water content in hydrated anhydrite cement was less than 2%.

Keywords: *factorial design, anhydrite cement, hydration, activators*

1. Introduction

Anhydrite cement is widely used in the construction industry. It can be produced from natural anhydrite, natural gypsum or industrial gypsum such as phosphogypsum, FGD gypsum, nitrogypsum, etc. In order to produce anhydrite cement, natural gypsum or industrial gypsum must be calcined at high temperature (500-1180°C) [1]. Anhydrite sets, hydrates and hardens very slowly, then various chemical activators (such as Na_2SO_4, K_2SO_4, $KAl(SO_4)_2 \cdot 12H_2O$, $FeSO_4 \cdot 7H_2O$, etc.) are used to activate these processes [2-4].

Different authors suggest to calcine natural gypsum, phosphogypsum or FGD gypsum at different temperature and add some activators (such as Na_2SO_4, K_2SO_4, $FeSO_4 \cdot 7H_2O$, etc.) in order to produce anhydrite cement with improved physical and mechanical properties. Singh and Garg [5] calcined phosphogypsum at temperatures of 500, 600, 700, 800, 900 and 1000°C. They established that a stable anhydrite can be produced by heating phosphogypsum at 1000°C. The best physical-mechanical properties were obtained when 1.5% $Na_2SO_4 \cdot 10H_2O$ and 0.5% $FeSO_4 \cdot 7H_2O$ had been used together. Cesniene [6] burnt neutralized phosphogypsum at temperatures of 400, 600 and 800°C. She was able to produce anhydrite cement with good physical-mechanical properties burning it at 800°C and using 2% K_2SO_4 or 2% Na_2SO_4. Leskeviciene and Nizeviciene [7] estimated that increasing neutralized phosphogypsum calcination temperature from 800°C to 900°C and specific surface area to 600 m^2/kg and using 2% K_2SO_4 or 2% Na_2SO_4, the properties of anhydrite cement were improved: the setting time shortened and the compressive strength increased. Fridrichova et al. [8] heated FGD gypsum at temperatures of 500, 600 and 700°C. Liudwig et al. [9] calcined FGD gypsum at temperatures of 525, 600, 675 and 750°C. It was established that increasing calcination temperature the setting time of anhydrite cement increased, the degree of hydration was lowered, but the compressive strength increased when using 1% K_2SO_4.

The paper analyses the influence of the calcination temperature of FGD gypsum (500-800°C) and the activators ($KAl(SO_4)_2 \cdot 12H_2O$, Na_2SO_4, $Fe_2SO_4 \cdot 7H_2O$) on the hydration of anhydrite cement produced from FGD gypsum. The significance of the independent variables such as the calcination temperature, the hydration time, the amount of activator, and the significance interaction between variables to the hydration of anhydrite cement is analyzed using the statistical modeling, based on the 2^3 full factorial design. Linear mathematical model, which describes the relation between significant variables and the chemically combined water content in hydrated anhydrite cement, is created. The main objective of this paper is to forecast the hydration of anhydrite cement within limits (constraints on temperature, time and amount of activator).

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2. Experimental

2.1. Materials

The chemical composition of FGD gypsum is given in Table 1. FGD gypsum consists of 97.32% $CaSO_4{\cdot}2H_2O$ and 2.05% $CaCO_3$. The pH is 6.33. The specific surface area S_{spec} of ground FGD gypsum is 300 m^2/kg.

Table 1

Chemical composition of FGD gypsum.

Constituents, wt. %				
CaO	SO_3	R_2O_3	SiO_2	Ignition loss
32.82	45.30	0.10	0.50	21.27

The X-ray diffraction analysis (Fig. 1) confirms that gypsum $CaSO_4{\cdot}2H_2O$ and unreacted limestone $CaCO_3$ (aragonite $CaCO_3$ and calcite $CaCO_3$) dominate in FGD gypsum. This corresponds with the results of simultaneous thermal analysis STA (Fig. 2). Gypsum dehydrated and water evaporated in temperature range of 105-190°C. Soluble anhydrite was formed. It became insoluble anhydrite in temperature range of 340-370°C. Limestone decomposed into CaO and CO_2 at temperatures between 600°C to 700°C.

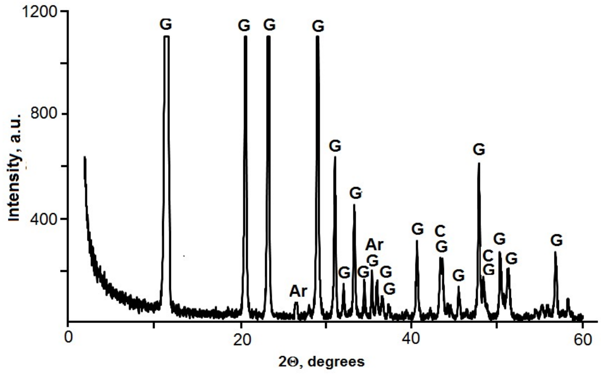

Fig. 1 - X-ray diffraction pattern of FGD gypsum. *Indexes: G – gypsum, C – calcite, Ar – aragonite.*

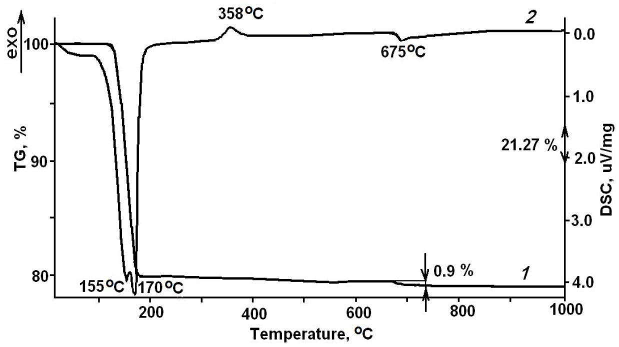

Fig. 2 - STA curves of FGD gypsum. 1 – TG, 2 – DSC.

$KAl(SO_4)_2{\cdot}12H_2O$, Na_2SO_4 and $FeSO_4{\cdot}7H_2O$ are used as activators.

2.2. Methods

Chemical composition was determined according to the European Standard EN 196-2-2005.

X-ray diffraction analysis (XRD) were carried out with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating at 30 kV voltage and 20 mA emission current. The step-scan covered the angular range 5-60° (2θ) in steps of 2θ=0.02°.

Simultaneous thermal analysis (STA: differential scanning calorimetry, DSC, and thermogravimetry, TG) was carried out on a Netzsch 409 PC Luxx simultaneous thermal analysis instrument with ceramic sample handlers and crucibles of Pt-Rh. At a heating rate of 15°C/min, the temperature ranged from 30°C up to 1000°C under a nitrogen atmosphere.

FGD gypsum was ground for 10 min in a Fritsch vibrating disc mill "Pulverisette 9" (speed: 800 rpm).

Specific surface area S_{spec} was determined by the Blaine method according to the European Standard EN 196-6-2005.

pH was measured by pH-meter 673 M, when the ratio of water (W) and gypsum (G) W/G – 10.

FGD gypsum was burnt at temperature range of 500-900°C for 1 hour in a muffle furnace.

The chemically combined water of hydrated anhydrite cement was calculated after heating the material at 400°C. The hydration of anhydrite cement was impeded at different intervals of time (after 1, 3, 7 and 28 days). The hydration was impeded by grinding the substance in a porcelain mortar, adding acetone, by filtration and drying at 50°C.

The consistency and setting time of anhydrite cement was determined according to the European Standard EN 196-3-2005.

Statistical method. Factorial design is tool that is used to examine different problems. This method enable not only to save the time of researcher but also materials and energy, not only to greatly reduce the number of experiments but to get maximum information about the process.

Factorial designs are widely used in experiments involving several factors, where it is necessary to study the join effect of the factors on a response. The most important of these cases is that of k factors, each at only two levels. The level of each factor is coded as low (-1) and high (+1). A complete replicate of such a design requires 2^k observations and is called a 2^k factorial design. The 2^k design provides the smallest number of runs with which k factors can be studied in a complete factorial design. Because there are only two levels for each factor, it is assumed that the response is approximately linear over the range of the factor levels chosen. In a 2^k factorial design, it is easy to express the results of the experiment in term of a regression model [10]. A multiple linear regression model (in code form) is defined as follows:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{\substack{i,j=1 \\ i \neq j}}^{k} b_{ij} x_i x_j + \sum_{\substack{i,j,u=1 \\ i \neq j \neq u}}^{k} b_{iju} x_i x_j x_u \quad (1)$$

where Y is a response, i.e. a dependent variable; x – an independent variable that represents factor; b_0 – an intercept term, b_i – a regression coefficient for the linear terms, b_{ij} – a regression coefficient for the binary-interaction terms, b_{iju} – a regression coefficient for the triple-interaction terms. A regression coefficient, $b<0$ indicates that an independent variable has a negative effect on a dependent variable (it means that when an independent variable increase, a dependent variable decrease), while regression coefficient, $b>0$ indicates a positive effect of an independent variable on a response (it means that when an independent variable increase, a dependent variable also increase [11].

3. Results and discussion

3.1. Calcination temperature

Temperature is one of the important factors, which influences a production and quality of anhydrite cement. FGD gypsum was calcined at temperatures between 500°C to 900°C. The setting and hydration of anhydrite cement was investigated.

The results (Fig. 3) indicated that anhydrite cement produced by calcining FGD gypsum at 500°C and 600°C bound the best. The anhydrite cement produced at 500°C started to bind in 2 min. and ended to bind in 3 min., the product calcined at 600°C started to bind in 3 min. and finished in 5 minutes. The anhydrite cement produced at 900°C bound the slowest.

According to the results (Fig. 3), anhydrite cement produced at 500°C hydrated the fastest. After 28 days the chemically combined water content in hydrated anhydrite cement is 20.0%.

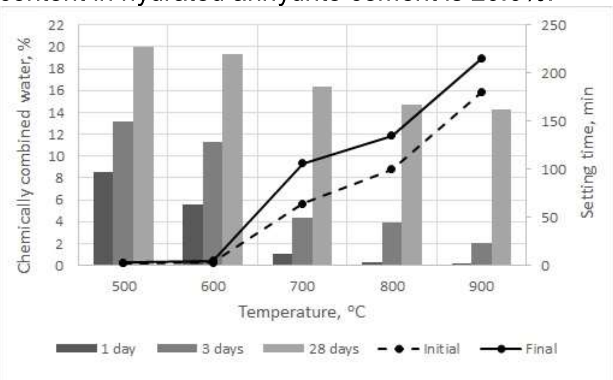

Fig. 3 - Setting time and chemically combined water content of hydrated anhydrite cement produced at different calcination temperatures.

Meanwhile anhydrite cement produced at 900°C hydrated the slowest. The chemically combined water content after 28 days was only 14.2%. Theoretically the chemically combined water content in gypsum is 20.92% [1].

Thus it is possible to state that increasing calcination temperature of FGD gypsum forces the anhydrite cement to set and hydrate slower. These results are in accordance with the results of Ludwig et al. [9].

3.2. Activators

The hydration of anhydrite decreases with increasing production temperature. The crystal structure of anhydrite could have influence on the hydration process. When gypsum is dehydrated to anhydrite at temperature between 500 and 700 °C, wide channels in the $CaSO_4$ chain are formed. Anhydrite reacts with water very fast. Anhydrite produced at higher temperature (700-900 °C) has narrow channels, the closest packing of ions, which makes anhydrite the densest. Lacking empty channels, anhydrite reacts very slowly with water [1]. However, it can set and hydrate more quickly when suitable activators are used.

Various chemical activators are used to accelerate the hydration of anhydrite cement. In this case three activators such as $KAl(SO_4)_2 \cdot 12H_2O$, Na_2SO_4 and $FeSO_4 \cdot 7H_2O$ were used. The influence of the activators on the hydration of anhydrite cement produced at 700°C was examined. 2% of activator by the weight of anhydrite was added together with the gauging water.

The results (Fig. 4) indicated that the influence of $KAl(SO_4)_2 \cdot 12H_2O$ or Na_2SO_4 on the hydration is similar and larger than the impact of $FeSO_4 \cdot 7H_2O$.

3.3. Amount of activator

The amount of activator has influence on the hydration of anhydrite cement. The impact of the amount of $KAl(SO_4)_2 \cdot 12H_2O$ on the hydration of anhydrite cement produced at 700°C was examined. 1% and 2% of activator were added.

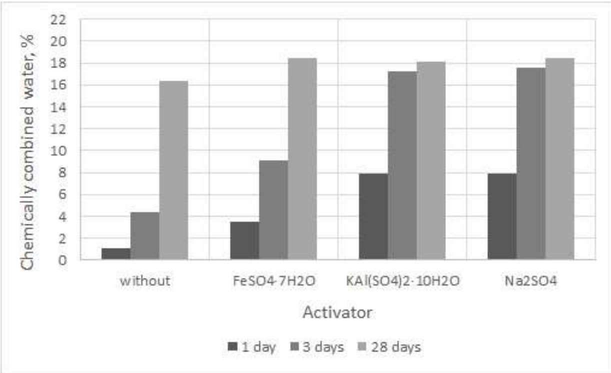

Fig. 4. - Effect of the activators on the chemically combined water content in hydrated anhydrite cement.

According to the results (Fig. 5) it is possible to state that the amount of activator makes a large impact on the hydration of anhydrite cement at its early age (up to 3 day). After 28 days almost no influence on the hydration process was noticed. Thus the further research was proceeded using only 1% of activator in the mixture.

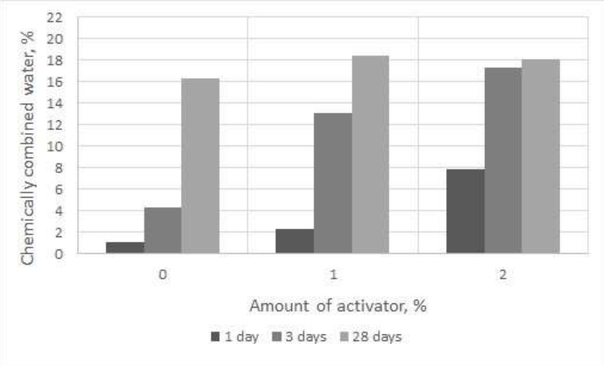

Fig. 5 - Effect of the amount of $KAl(SO_4)_2 \cdot 12H_2O$ on the chemically combined water content in hydrated anhydrite cement.

In summary, the calcination temperature, the activators and the amount of its influence the hydration of anhydrite cement.

3.4. Statistical analysis

Calcination temperature of FGD gypsum, amount of activator and hydration time were chosen as independent variables and chemically combined water content of hydrated anhydrite cement was chosen as dependent variable (response). Since the factorial design involves three independent variables at two levels, 2^3 full factorial design was applied. The range and levels of the three independent variables studied in terms of coded and actual values are shown in Table 2.

2^3 full factorial design was used to investigate the effect of each independent variable and interaction between variables on the hydration process of anhydrite cement. With three independent variables, 2^3 full factorial design required 8 runs for three activators. The complete design matrix and the experimental results are shown in Table 3.

Table 2

Range and levels of the independent variables

Independent variable	Coding	Range and levels	
		+1	-1
Temperature (°C)	x_1	800	500
Hydration time (days)	x_2	28	3
Amount of activator (%)	x_3	1	0

The data of the 2^3 full factorial design was fitted to a multiple linear regression model as in Eq. 2:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_{12} + b_{13}x_{13} + b_{23}x_{23} + b_{123}x_{123} \quad (2)$$

where Y is the response, i.e., the measured chemically combined water content in hydrated anhydrite cement, %; x_1, x_2, x_3 are the independent variables that represent the factors such as calcination temperature, hydration time and amount of activator (in coded form), respectively; x_{12}, x_{13}, x_{23}, x_{123} – represent the interaction between factors such as between x_1 and x_2, the interaction between x_1 and x_3, the interaction between x_2 and x_3, the interaction between x_1, x_2 and x_3, respectively; b_0 – is the intercept term; b_1, b_2, b_3 – the regression coefficients for the linear terms; b_{12}, b_{13}, b_{23} – the regression coefficients for the binary-interaction terms; b_{123} – the regression coefficient for the triple-interaction terms.

Regression analysis was used to estimate the regression coefficients b_0-b_{123} in Eq. 2. The significance of the coefficients was tested using the Student‘s *t*-test [11]. The coefficients that were not significant were dropped from the Eq. 2 leaving only the significant terms. The final regression equations, which correlate the significant variables to the chemically combined water content in hydrated anhydrite cement using different activators such as $KAl(SO_4)_2 \cdot 12H_2O$, Na_2SO_4 and $FeSO_4 \cdot 7H_2O$, are given in Eq. 3-5, respectively.

Table 3

Experimental design matrix and results

Run	Independent variable			Coded experiment matrix			Chemically combined water*, %		
	Temperature, °C	Hydration time, days	Amount of activator, %	x_1	x_2	x_3	$KAl(SO_4)_2 \cdot 12H_2O$	Na_2SO_4	$FeSO_4 \cdot 7H_2O$
1	800	28	1	1	1	1	17.56	18.02	17.36
2	500	28	1	-1	1	1	19.73	19.74	20.39
3	800	3	1	1	-1	1	6.23	16.26	1.50
4	500	3	1	-1	-1	1	19.62	19.53	16.54
5	800	28	0	1	1	-1	14.70	14.70	14.70
6	500	28	0	-1	1	-1	19.99	19.99	19.99
7	800	3	0	1	-1	-1	3.88	3.88	3.88
8	500	3	0	-1	-1	-1	13.20	13.20	13.20

*-the average of chemically combined water was calculated from six measurements for each run

$KAl(SO_4)_2\cdot 12H_2O$ $\hat{Y_1} = 14.36 - 3.77x_1 + 3.63x_2 + 1.42x_3 + 1.91x_{12} - 0.77x_{23} + 0.90x_{123}$ (3)

Na_2SO_4 $\hat{Y_2} = 15.67 - 2.45x_1 + 2.45x_2 + 2.72x_3 + 0.70x_{12} + 1.20x_{13} - 1.96x_{23}$ (4)

$FeSO_4\cdot 7H_2O$ $\hat{Y_3} = 13.45 - 4.09x_1 + 4.67x_2 + 0.50x_3 + 2.01x_{12} - 0.43x_{13} + 1.00x_{123}$ (5)

where $\hat{Y}$ is the response, i.e., the calculated chemically combined water content in hydrated anhydrite cement, %;

The adequacy of the models was evaluated using the Fisher criterion [11]. In all cases adequate model was gotten. Thus it is possible to state that 3-5 equations correspond to the experimental results.

Regression Eq. 3-5 show that the hydration time (x_2), the amount of activator (x_3) and the interaction between temperature and hydration time (x_{12}) has a positive effect on the hydration process of anhydrite cement when different activators are used. The coefficient for hydration time (b_2) is the highest of all coefficients in Eq. 3 and 5. So the effect of hydration time on the chemically combined water content is the strongest. The coefficient for hydration time (b_2) and the coefficient for amount of activator (b_3) are very similar in Eq. 4. It means that the influence of hydration time and the amount of activator to the chemically combined water content using Na_2SO_4 is similar. The coefficient for amount of activator (b_3) in Eq. 5 and the coefficient for interaction between temperature and hydration time (b_{12}) in Eq. 4 are also positive but low magnitude suggesting low effect on the response.

The coefficient for temperature (b_1) is negative in Eq. 3-5. It suggests that the temperature has a negative effect on the chemically combined water content in hydrated anhydrite cement using above-mentioned activators. The negative coefficient of binary interaction effect (b_{23}) suggests antagonistic effect on the response when $KAl(SO_4)_2\cdot 12H_2O$ (in Eq. 3) and Na_2SO_4 (in Eq. 4) are used, while for $FeSO_4\cdot 7H_2O$ this coefficient of binary interaction effect (b_{23}) is not significant (in Eq. 5).

The coefficient of triple interaction effect (b_{123}) is positive in Eq. 3 and 5. So it has positive effect on the chemically combined water content in hydrated anhydrite cement and the magnitude is similar when $KAl(SO_4)_2\cdot 12H_2O$ (in Eq. 3) and $FeSO_4\cdot 7H_2O$ (in Eq. 5) are used.

The coefficients of determination (R^2) for Eq. 3-5 were calculated as 0.9996, 0.9962 and 0.9984, respectively, and the mean absolute percentage error (MAPE) between experimental and calculated values of the chemically combined water content were found to be 0.83%, 1.98% and 1.95%, respectively. The values of the coefficient of determination for three regression equations are almost equal to one and the values of the mean absolute percentage error are less than 2% indicate that the equations are reliable predicting the chemically combined water content in hydrated anhydrite cement.

Thus it is possible to state that 3-5 regression equations reliably forecasted the relation between the significant variables and the chemically combined water content in hydrated anhydrite cement.

In order to forecast how at a certain time (from 3 to 28 days of hydration) anhydrite cement produced at a certain temperature (between 500°C to 800°C) will hydrate, 3-5 equations were used, and the experiments were provided to check their reliability. The calcination temperature of 700°C was chosen to produce anhydrite. 1% of activator was added. The chemically combined water content in hydrated anhydrite cement was calculated and measured after 3, 7 and 28 days. The mean absolute percentage error between experimental and calculated values of the chemically combined water content was found. The results are presented in Table 4. The MAPE is less than 10%.

Thus it is possible to forecast the hydration of anhydrite cement at a certain time (from 3 to 28 days) if FGD gypsum is calcined at 500-800°C and up to 1% of activator ($KAl(SO_4)_2\cdot 12H_2O$, Na_2SO_4 or $FeSO_4\cdot 7H_2O$) is used.

4. Conclusions

The hydration of anhydrite cement produced from FGD gypsum was explored by applying the 2^3 full factorial design. The effect of three independent variables such as the calcination

Table 4

Experimental and calculated values of the chemically combined water in hydrated anhydrite cement using various activators.

Curing period, days	Activator					
	$KAl(SO_4)_2\cdot 12H_2O$		Na_2SO_4		$FeSO_4\cdot 7H_2O$	
	Chemically combined water, %					
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
3	10.73	13.04	17.25	17.58	6.78	5.93
7	11.95	13.17	17.48	17.60	8.59	7.98
28	18.32	18.42	18.70	18.38	18.11	17.78
MAPE, %	8.13		1.44		5.62	

temperature of FGD gypsum (500-800^oC), the hydration time (3-28 days) and the amount of activator (0-1%) on the hydration of anhydrite cement was studied. Three activators ($KAl(SO_4)_2 \cdot 12H_2O$, Na_2SO_4 and $FeSO_4 \cdot 7H_2O$) were used. The results of the experiments and statistical analysis showed that the chemically combined water content in hydrated anhydrite cement increased with the increase in hydration time and the use of activators. But when the calcination temperature was increased from 500^oC to 800^oC the chemically combined water content in hydrated anhydrite cement decreased. Thus it is possible to state that the hydration time and the amount of activator had a positive effect, therefore the temperature had a negative effect on the hydration of anhydrite cement. The results of modeling indicated that the individual variables had a larger effect on the chemically combined water content in hydrated anhydrite cement than their interaction. The multiple linear regression models were developed to correlate the significant variables to the chemically combined water content in hydrated anhydrite cement. The mean absolute percentage error between experimental and calculated values of the chemically combined water content was less than 2%. It is possible to forecast the hydration of anhydrite cement produced from FGD gypsum if the calcination temperature, the activators and the amount of its will be within the defined limits.

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