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Вивчено процеси застосування композитних адсорбційних матеріалів «силікагель – натрій сульфат» та «силікагель – натрій ацетат», отриманих золь – гель методом. За допомогою диференційно-термічного аналізу виявлено якісну відмінність адсорбиійних властивостей синтезованих композитів та механічної суміші сіль – силікагель, сорбиійна ємність якої постипається їм в середньому на 30 %. Встановлено, що теплоти адсорбції водяної пари композитними адсорбентами матеріалів «силікагель – натрій сульфат» та «силікагель – натрій ацетат» близько на 30 % більше, ніж лінійна суперпозиція солі та силікагелю

Ключьові слова: теплоакумулюючі матеріали, композитні сорбенти, золь – гель синтез, теплота адсорбції, густина запасання енергії, кинетика гідратації

Изучены процессы применения композитных адсорбционных материалов «силикагель – сульфат натрия» и «силикагель – ацетат натрия», полученных золь – гель методом. С помощью дифференциально-термического анализа выявлено качественное отличие адсорбиионных свойств синтезированных композитов и механической смеси соль – силикагель, адсорбционная емкость которой уступает им в среднем на 30 %. Установлено, что теплоты адсорбции водяного пара композитными адсорбентами материалов «силикагель – натрий сульфат» и «силикагель – натрий ацетат» примерно на 30 % больше, чем линейная суперпозиция соли и силикагеля

Ключевые слова: теплоаккумулирующие материалы, композитные сорбенты, золь – гель синтез, теплота адсорбции, плотность запасания энергии, кинетика гидратации

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# 1. Introduction

Adsorption conversion of heat energy based on the thermal effects of adsorption on solid sorbents is one of the

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# THE STUDY OF PROPERTIES OF COMPOSITE ADSORPTIVE MATERIALS "SILICA GEL – CRYSTALLINE HYDRATE" FOR HEAT STORAGE DEVICES

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promising technical solutions that allow optimizing the operation of renewable energy sources, as well as absorption, accumulation and transformation of low-potential thermal energy. Nevertheless, the use of adsorption converters of thermal energy as heat accumulators and heat pumps in heat supply systems, in refrigeration solar plants is significantly limited by the low level of operating characteristics of the adsorbents used.

According to [1], the working pairs  $CaCl_2-H_2O$ ,  $SrBr_2-H_2O$ ,  $Na_2S-H_2O$ ,  $MgCl_2-H_2O$  could be promising for the accumulation of thermal energy. They allow realizing the energy storage density of 1.9–2.7 GJ/m<sup>3</sup> of crystalline hydrate. However, their application is limited by physical and chemical instability along with the corrosive activity of these salts at high temperatures, instability in repeated cycling, degradation in time, and also an underdeveloped heat exchange surface. The energy storage density of magnesium sulfate heptahydrate is 1 GJ/m<sup>3</sup>, but the dehydration rate of MgSO<sub>4</sub>·7H<sub>2</sub>O at low pressures occur to be low [2]. Apparently, similar problems are typical for any massive salt.

Thus, it was proposed to apply a working pair of  $MgCl_2-H_2O$  in an open-type thermal energy accumulator [3]. However, the irreversible hydrolysis of magnesium chloride at an elevated temperature required its replacement by 13X zeolite [4]. In the Netherlands, a solar installation for the heat supply of residential buildings, including an adsorption module has been developed [1]. As a heat-accumulating material along with massive salts, zeolite and silica gel were tested.

However, the wide introduction of systems based on traditional adsorbents is restricted by low sorption capacity and high regeneration temperature. Therefore, the task-oriented development of heat-storage devices based on adsorption heat-accumulating materials becomes the task of current interest.

### 2. Literature review and problem statement

The efficiency of devices for absorption, storage and transformation of heat energy is determined primarily by the characteristics of heat-storage media. In these conditions, the task-oriented synthesis of heat-accumulating materials, taking into account the features of the operation of devices based on them is the most promising.

Attempts to improve adsorption heat-accumulating materials are mainly focused on the choice among existing adsorbents [1] or synthesis and investigation of the composite sorbents "porous matrix – salt" due to increased sorption capacity to ordinary working fluids [5]. Additionally, the distribution in the porous matrix allows stabilizing the salt during repeated hydration-dehydration cycles [1]. Silica gel [6], zeolites [7], vermiculite [8], graphite [9], and salts, i. e. magnesium chloride and lithium bromide [10], lithium chloride [8], magnesium oxide [9], calcium chloride [11] are used as a matrix. The adsorbed substance is water vapor [8, 9], ammonia [7, 11, 12] and methanol [13].

Obviously, the accumulation of thermal energy by the composite sorbents is based on three mechanisms: capacitive, phase-transitional and adsorptive. The salt reacts with water vapor, which leads to the formation of crystalline hydrate, further adsorption leads to complex dissolution and transformation into a "salt – sorbate" solution. Nevertheless, the presence of a crystalline salt in the matrix contributes not only to the growth of the adsorption capacity, but also to a qualitative change in the sorption kinetics. Composite water sorbents such as "salt in a porous matrix" in thermal energy storage devices, adsorption refrigeration plants and air conditioning devices are known to be widely spread. However, manufacturing is associated with the use of rather complex impregnation technologies with solutions of crystalline hydrates of porous media, often expensive, which impedes commercialization in energy storage devices [5, 7].

This problem can be solved by synthesizing composites such as silica gel – crystalline hydrate by the sol-gel method [14–16]. However, the correlation of the properties of heat-accumulating media (composition, structure, kinetics of adsorption of water vapor) of the composite sorbents "silica gel – salt" synthesized by the sol-gel method and the performance characteristics of heat storage devices have not been studied enough. Therefore, it may be promising to use thermal energy accumulators based on the "salt in a porous silica gel" composites and to investigate the correlation of properties and performance characteristics.

#### 3. The aim and objectives of the study

The aim of the work was to study the properties (composition, structure, kinetics of adsorption of water vapor) of the composite sorbent "silica gel – sodium sulfate" synthesized by the sol-gel method and its performance characteristics as a heat-storage material.

To achieve the aim, the following objectives were set:

 to synthesize samples of the composites "salt in a porous matrix of silica gel" by the sol-gel method;

 to study the adsorption properties of samples of composite materials;

 to conduct a comparative analysis of the characteristics of composite materials and thermal energy accumulators based on them.

# 4. Materials and methods of obtaining of samples of the composite heat storage materials and study of characteristics

# 4. 1. Sol-gel synthesis technique of composite heat storage material

Porous composite materials were prepared by deposition of liquid sodium silicate glasses with various acids, i. e. sulphuric and acetic. Composite materials are obtained in a three-dimensional silicate matrix, which contain 20-40 wt. % of sodium sulfate or acetate. The composite material "silica gel – Na<sub>2</sub>SO<sub>4</sub>" was obtained by the neutralization reaction of sulfuric acid H<sub>2</sub>SO<sub>4</sub>:

$$Na_2Si_3O_7 + H_2SO_4 = Na_2SO_4 + (SiO_2)_n + H_2O.$$
 (1)

To synthesize the composite material "silica gel –  $Na_2SO_4$ ", it is necessary to take the components (98 % sulfuric acid and 54 % liquid sodium silicate glass) in such a ratio (mass %): the solution of liquid sodium silicate glass is 81.76 and sulfuric acid – 18.24.

The neutralization reaction of 98 % acetic acid solution with a 54 % solution of liquid sodium silicate glass is described by the following reaction:

$$Na_2Si_3O_7 + 2CH_3COOH =$$
  
=2CH\_3COONa+(SiO\_2)\_n+H\_2O. (2)

At such concentrations of the reagents, for the synthesis of the silica gel - CH<sub>3</sub>COONa composite material, the fol-

lowing ratio of components (mass. %) was used: a liquid sodium silicate glass solution of 78.54 and acetic acid of 21.46.

The synthesis of the composite sorbents "silica gel – crystalline hydrate" involves two stages. In the first stage, a polymeric quaternary ammonium salt (PQAS)



was added to the 50 % aqueous solution of silicate glass (with a silicate module of 3.2) at a rate of 1 g per 100 g of a dry residue of SiO<sub>2</sub> and heated to 35 °C with stirring, after which the appropriate acid (sulfuric or acetic) was added dropwise to the desired pH. Then, the resulting solution was heated for an hour to a temperature of 95 °C. At this stage, the silicon phase nuclei were formed, which was stated by the turbidity of the reaction medium. In the second stage, with intensive stirring, solutions of the corresponding acid and silicate glass of a certain concentration were simultaneously added dropwise. At the same time, the particles coarsened and the highly porous silica gel, in the pores of which the corresponding crystalline hydrates (sodium sulfate in the case of sulfuric acid and sodium acetate when using acetic acid) were introduced, was formed. The composite sorbents were precipitated as a fine precipitate, filtered from the liquid phase and dried to a constant weight at a temperature of 40-50 °C.

A technology for the synthesis of composite sorbents such as "salt in a porous matrix" has been developed. In the first stage, 7 g of liquid glass (2.39 %  $SiO_2 - 100$  ml), 93 ml H<sub>2</sub>O and 0.07 g PQAS were charged into a flask with a capacity of 250 ml. This mixture was heated to 35 °C and stirred vigorously with the addition of 1 g of  $H_2SO_4$  and 39 ml of  $H_2O$  (2.4 % solution) for 30 minutes. At the same time, about 80 % of the alkali is neutralized and the pH value is reduced to 9. After the addition of the acid, a significant turbidity of the solution was observed. Such a transparent sol was heated to 95 °C for 15 minutes to increase the particle size. The alkali that was released due to the reduction of the silica surface causes an increase in pH to about 10. In the second stage, 7.25 g of liquid glass and 13 ml of H2O (13.22 % SiO<sub>2</sub> – 100 ml) were charged into one dropping funnel, and 1 g of H<sub>2</sub>SO<sub>4</sub> (or CH<sub>3</sub>COOH) and 20 ml of H<sub>2</sub>O (4.65 % solution) - into the second one. Simultaneously, with vigorous stirring, the mixture was added dropwise to the basic solution at 95 °C for 2 hours.

These proportions allow maintaining the pH at the level of 10. At this stage, the composite sorbent was precipitated from the solution. After that, a 4.65 % solution of  $H_2SO_4$  (or CH<sub>3</sub>COOH) was added dropwise within 20 minutes to reduce the pH to 5 and the reaction mixture was held at 90 °C for 4 hours to completely hydrolyze the functional OH-groups, which eliminated the coalescence of particles during filtration.

At the end of the synthesis, the composite sorbent in the form of a fine precipitate (200–500  $\mu$ m) was filtered from the aqueous phase and dried at a temperature of 60 °C to a constant weight.

The bulk density for the composite sorbents "silica gel – sodium sulfate" was  $0.72 \text{ g/cm}^3$ , and for the composite sorbents "silica gel – sodium acetate" –  $0.65 \text{ g/cm}^3$ .

### 4. 2. Study of the phase composition of composites

The study of the phase composition of the composites and its change in the heat treatment process, mass change during sorption-desorption was carried out by differential thermal analysis on the Q-1500D derivatograph of R. Paulik, I. Paulik, L. Erdei in the air environment in a dynamic mode in the temperatures range of 20–1000 °C with a heating rate of 5 °C/min. An inert substance is corundum. The mass of the samples was 200 mg.

4.3. Investigation of adsorption equilibrium in the "composite sorbent – water" system

The sorption equilibrium between water vapor and dry sorbent was studied by the weight method. Chemical balance "AXIS-ANG200C", class II of accuracy was used at temperatures of 20, 40 and 60 °C and pressures of 20 and 760 mm Hg. Prior to the tests, the test substances were kept in a thermal cabinet at a temperature of 140 °C for 4-6 hours. After drying, the samples (in an amount of 1-2 g) were placed in a desiccator, at the bottom of which distilled water was contained.

Filled desiccators were loaded into the thermal cabinets with a predetermined temperature. The temperature in the thermal cabinets was maintained with an accuracy of  $\pm 0.1$  °C. The necessary pressure was maintained by means of a vacuum pump, which was attached to the desiccator. The pressure was recorded with a sensor "MKS Baratron type 626A". Every 20 minutes, the test samples were removed and weighed on analytical scales. The samples were held at predetermined temperatures until equilibrium was established, until the sorbent absorbed the theoretically required amount of water.

### 5. Results of the study of sorption properties and heatstorage capacity of composite materials

The composite sorbents "silica gel – crystalline hydrate" were synthesized without and with the addition of polymeric quaternary ammonium salt (PQAS). Without the addition of PQAS, the liquid silicate glass reacted with  $H_2SO_4$  and  $CH_3COOH$  for a few seconds to form a gel in the entire reaction volume, which was not readily mechanically dispersed after drying. In the presence of the PQAS, according to the described technology, a fine (200–500 µm) precipitate of the composite sorbents "silica gel – crystal hydrate" was formed.

The differences in the formation of the silicone phase in the presence of the PQAS are explained as follows. When silica particles are present in the hot suspension and the pH reduced to 7 (with the addition of acid), they begin to coagulate. When the solution of sodium silicate is neutralized with acid in the presence of strongly basic cation-active PQAS, the colloidal silica particles grow in a weakly alkaline solution and flocculate in the micellar solution of cationic PQAS. These simple facts underlie many processes of precipitation of silica.

The temperature conditions for the synthesis of the composite sorbents "silica gel –crystalline hydrate" were optimized. In the synthesis of the "silica gel – crystalline composite sorbents at room temperature, gel formation in the first stage of synthesis and a gradual transition of the gel in the second stage into separate jellies, which, when dried, are poorly amenable to mechanical dispersion were observed.

The deposition of silica, which occurred at a temperature of more than 50 °C, differs significantly from the described. At elevated temperatures, the jelly formed at the end of the first stage and passed into a precipitate at the end of the second stage. Thus, an increase in the synthesis temperature promotes the formation of dispersed particles with a size of 200–500  $\mu$ m of the composite sorbents "silica gel – crystal-line hydrate".

The sequence of introduction of components significantly affects the result of synthesis. In all cases, the acid was added dropwise to a solution of silicate glass. When a silicate glass was added dropwise to the acid solution in the first stage, a gel formation was observed, both with sulfuric and acetic acids. This occurs because of polymerization of silicic acid, formed by the interaction of liquid glass with the acid introduced into it, in an excessively acid solution into extremely small particles. These particles are collected as chains and form a grid of gel, which permeates the aqueous phase throughout the entire volume.

When the mass loss curves of the "silica gel – sodium sulfate" composite (Fig. 1, *a*) are analyzed, it can be noted that the composite after desorption, when heated to 1000 °C, loses only 2 % of the mass (curve 2). The mass loss for the composite after adsorption of air moisture is 46 %. For the composite "silica gel – sodium acetate" in a fully hydrated state, the mass loss is 42 % (Fig. 1, *b*). To determine the differences in the thermophysical properties of the investigated composite sorbents from the properties of massive crystalline hydrates, a differential thermal analysis was carried out for 10-aqueous (Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O) and anhydrous sodium sulfate, as well as for dried KCM branded silica gel at 100 °C. Silica gel can be considered as an analogue of the silicon-oxygen matrix of the investigated composites (Fig. 2).

The sorption properties of the composite "silica gel – sodium sulfate" differ somewhat from the properties of the bulk salt and silica gel because of the characteristics of this disperse system. This can be illustrated by comparing the sorption capacities of these substances. As resulted from the studies conducted, the sorption capacity of "pure" silica gel is 0.18 g/g, bulk sodium sulfate is 1.27 g/g and bulk sodium acetate is 0.65 g/g. The sorption capacities of the "slica gel – sodium sulfate" and "silica gel – sodium acetate" composites are 0.85 g/g and 0.42 g/g, respectively. The stoichiometric composition of the composite sorbent, according to the synthesis conditions, is Na<sub>2</sub>SO<sub>4</sub>:SiO<sub>2</sub>=1:1.27. The linear superposition of the sorption abilities of "pure" silica gel and sodium sulfate was calculated by the following formula:

$$m_{\Sigma} = a \cdot m_{\text{Na}_2\text{SO}_4} + (1-a) \cdot m_{\text{SiO}_2},\tag{1}$$

where *a* is the mass content of sodium sulfate in the composite a=0.44;  $m_{\text{Na}_2\text{SO}_4}$ ,  $m_{\text{SiO}_2}$  is the mass of water (g), adsorbed by 1 g of massive salts Na<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COONa and 1 g of silica gel, respectively,  $m_{\text{Na}_2\text{SO}_4} = 1,27$ ,  $m_{\text{CH3COONa}} = 0.65$  and  $m_{\text{SiO}_2} = 0,18$ .







Fig. 2. Mass loss curves of massive salts and silica gel: a - silica gel - sodium sulfate; b - silica gel - sodium acetate; 1 - salts after adsorption; 2 - silica gel KCM; 3 - salts after desorption

By substituting the corresponding data into equation (1), a linear superposition of the sorption capacity of mechanical mixtures of silica gel and sodium sulfate (Table 1) and also silica gel and sodium acetate was calculated (Table 2). The actual values of the sorption capacities of the studied composites exceed by approximately 30 % the linear superposition of the sorption capacities of mechanical mixtures of silica gel and salts. As a result, the heat of adsorption increases by 30 %.

Adsorptive properties of the composite sorbent "silica gel – Na<sub>2</sub>SO<sub>4</sub>"

Content of silica gel, %	Content of Na <sub>2</sub> SO <sub>4</sub> , %	Results of DTA analysis Mass loss, %	Limiting adsorp- tion, kg/kg		Heat of adsorp- tion, kJ/kg	
			Calculated by linear superposi- tion	Ac- tual value	Calcu- lated by linear superpo- sition	Actual value
20	80	57.4	1.046	1.349	3486.67	4497.81
40	60	51.4	0.822	1.060	2740.00	3534.60
60	40	43.5	0.598	0.771	1993.33	2571.40
80	20	32.5	0.374	0.482	1246.70	1608.24

Table 2

Table 1

Adsorptive properties of the composite sorbent "silica gel – CH<sub>3</sub>COONa"

Content of silica gel, %	Contract (	Results of DTA analysis Mass loss, %	Limiting adsorption, kg/kg		Heat of adsorp- tion, kJ/kg	
	CH <sub>3</sub> COONa, %		Calcu- lated by linear super- position	Ac- tual value	Calcu- lated by linear superpo- sition	Actual value
20	80	43.1	0.557	0.756	1856.10	2431.49
40	60	37.3	0.455	0.596	1517.07	1987.36
60	40	31.6	0.353	0.462	1178.05	1543.25
80	20	24.8	0.252	0.330	1099.11	1608.24

The kinetic curves of water sorption by the substances under study in comparison with massive salts are shown in Fig. 3. The kinetics of equilibration in the composite sorbent – water system provides important information about the mechanism of sorption and the time characteristics of this process. In order to determine these parameters, the sorption of water by the "silica gel – sodium sulfate" and "silica gel – sodium acetate" composites was studied at temperatures of 20, 40 and 60 °C and a pressure of 1010.8 mbar (atmospheric pressure).

The kinetic curves of sorption clearly demonstrate that the mechanism of sorption of water vapor for the composite sorbents "silica gel – crystalline hydrate" differs significantly from sorption by massive salts.



6. Discussion of the results of the study of the correlation of sorption properties and heat-storage capacity of

2 - 40; 3 - 60

composite materials

The introduction of crystals of sodium sulfate or sodium acetate salts into the porous silicon dioxide matrix obviously results in an increase in the sorption capacity of the composite sorbents. As a consequence, the heat of adsorption and the density of energy storage increase, which is confirmed by the results of calculating the linear superposition of the sorption capacity of silica gel and acetate or sodium sulfate (Tables 1, 2). Sol-gel synthesis technology allows obtaining crystals of salts distributed in the silicon-oxygen matrix of silica gel at the molecular level. Thus, the sorption properties of the synthesized composite sorbents "silica gel - crystalline hydrate" are not a linear combination of properties of silica gel and massive salt. The synthesized composite sorbents possess a unique structure that increases the rate of reactions between salt crystals and water vapor in the developed pores of the silicon-oxygen matrix, which is confirmed by the kinetic curves of sorption (Fig. 3).

So, for massive salts, hydration proceeds in a kinetic regime, as evidenced by the S-shaped form of the kinetic curve (Fig. 3, *a*, *b*). For the composite sorbents, the initial section of the kinetic curve is practically linear in the coordinates  $A - \tau^{0.5}$  (Fig. 3, *c*, *d*). This indicates the diffusion character of the process, i.e. the sorption of water by the crystalline hydrate proceeds rapidly, and the limiting factor is the transport of water through the silica gel pore system. Kinetic equilibrium for massive salts is reached much slower than for the composites. The increase in temperature obviously results in the growth of the rate both of diffusion and of the chemical reaction. There is a faster achievement of kinetic equilibrium with increasing temperature in the range of

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20–60 °C. As temperature increases, the initial section of the kinetic curve of the adsorption of water by massive salts is straightened (Fig. 3, *a*, *b*), being probably a consequence of a change in the limiting stage. At 60 °C, the shape of the kinetic curves for sodium sulfate and sodium acetate is similar to that for the composite sorbents (curve 3).

The diffusion coefficient of water vapor in the pores of the composites "silica gel sodium sulfate" and "silica gel – sodium acetate" was calculated by the formula [17]:

$$D_n = 0.308 \cdot \frac{R^2}{\pi^2 \cdot \tau_{0.5}},\tag{1}$$

where  $\tau_{0.5}$  is the time to reach maximum concentration, sec; *R* is the radius of the composite granula, m.

Values of  $\tau_{0.5}$  were determined by the curves given in Fig. 3, c, d.

The water vapor diffusion coefficient in the pore system as a function of temperature is stated to be linear in semilog coordinates for both composite sorbents. For the sorbents "silica gel – sodium sulfate" and "silica gel – sodium acetate":

$$\ln D_n = -2,95 - 6282,02 \cdot \frac{1}{T},\tag{2}$$

$$\ln D_n = 2,52 - 7733,59 \cdot \frac{1}{T}.$$
(3)

The activation energy of this process is determined from the slope of the dependences (2) and (3) to be about 52 kJ/mole for the "silica gel – sodium sulfate" composite, and 64 kJ/mole for the "silica gel – sodium acetate" composite.

Therefore, the synthesized composite sorbents can be called a highly porous three-dimensional silicon-oxygen matrix, in the pores of which molecules of crystalline hydrate are located.

The sorption of water with massive crystalline hydrates is complicated by kinetic limitations, and water transport through the pore system of the composite sorbents is much easier. It should be noted that negative changes in the appearance, granulometric composition and sorption properties of the composite sorbent were not observed during 2-3 cycles per day for 4-6 months.

### 7. Conclusions

1. The technology of sol-gel synthesis of composite sorbents such as "salt in a porous matrix" has been developed. The composite sorbents "silica gel – sodium sulfate" and "silica gel – sodium acetate" synthesized by the sol-gel method were studied. It is shown that the sorption properties are not a linear combination of properties of silica gel and salt. This indicates the formation of an unique structure that promotes an increase in the rate of reaction between crystalline hydrates and water vapor in the developed pores of the silicon-oxygen matrix.

2. Qualitative differences in the kinetics of hydration of the composite sorbents and massive salts are shown. The temperature dependence of the coefficient of water vapor diffusion in the sorbent pore system has been stated to be described by the equations for the sorbents "silica gel – so-dium sulfate" and "silica gel – sodium acetate", respectively:  $\ln D_n = -2.95 - 6282.02 \cdot T^1$  and  $\ln D_n = 2.52 - 7733.59 \cdot T^1$ . The activation energy of diffusion of water vapor for the adsorbent "silica gel – sodium sulfate" is determined to be about 52 kJ/mole, and for "silica gel – sodium acetate – 64 kJ/mole.

3. A correlation between the composition of the studied composites and the limiting adsorption of water vapor by the composite sorbents "silica gel – sodium sulfate" and "silica gel – sodium acetate" was revealed. This value is stated to increase from 1608.24 kJ/kg to at least 2431.49 kJ/kg with an increase in the content of crystalline hydrate in the composite from 20 to 80 wt. %. The heat of adsorption, and, consequently, the energy storage density of the composite sorbents are shown to exceed by 30 % the value calculated from the linear superposition of the sorption capacities of the sorbent and massive salt.

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