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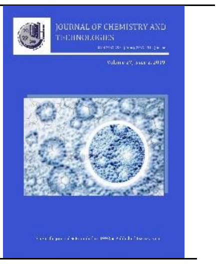

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TECHNOLOGY OF OBTAINING NEW MATERIALS FOR ADSORPTIVE HEAT ENERGY TRANSFORMATION TYPE OF «SILICA GEL – CRYSTALLINE HYDRATE»

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Abstract

This article is focused on sol-gel technology of industrial production of composite sorbents «silica gel – sodium sulphate» and «silica gel – sodium acetate», which includes the next stages: preparation of aqueous solution of silicate glass and polymer quaternary ammonium salt (PQAS), formation of nuclei of the silicate phase, formation of silicon-oxygen matrix, drying and fractionation of sorbent. According to the developed technology, sorbents were prepared with a granula size of 3 – 5 mm. Bulk density is stated to be of 0.72 g/cm^3 and 0.65 g/cm^3 for composites «silica gel – sodium sulphate» and 'silica gel – sodium acetate'. It is shown that composite sorbents are characterized by high water adsorption at the level of 0.42 – 0.66 g/g. Temperatures of regeneration of composites «silica gel – sodium sulphate» and 'silica gel – sodium acetate' are stated to be of 90 °C and 60 °C. Heats of adsorption of composites «silica gel – sodium sulphate» and «silica gel – sodium acetate» are 2200 kJ/kg and 1400 kJ / kg, respectively.

Keywords: heat storage; adsorptive heat energy transformation; composite adsorbent, sol – gel technology.

ТЕХНОЛОГІЯ ОТРИМАННЯ НОВИХ МАТЕРІАЛІВ ДЛЯ АДСОРБЦІЙНОГО ПЕРЕТВОРЕННЯ ТЕПЛОВОЇ ЕНЕРГІЇ ТИПУ «СИЛІКАГЕЛЬ – КРИСТАЛОГІДРАТ»

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Анотація

Стаття присвячена золь-гель технології промислового виробництва композиційних сорбентів «силікагель – Na$_2$SO$_4$» і «силікагель – CH$_3$COONa», що включає наступні стадії: підготовка водного розчину силікатного скла і полімерної солі четвертинного амонію (ПЧАС), формування ядер силікатної фази, утворення кремній-кисневої матриці, сушіння та фракціонування сорбенту. За розробленою технологією сорбенти готувалися з розміром гранул 3 – 5 мм. Насипна густина складає 0,72 г/см^3 та 0,65 г/см^3 для композитів «силікагель – натрій сульфат» та «силікагель – натрій ацетат». Показано, що композиційні сорбенти характеризуються високою адсорбційною ємністю на рівні 0,42 – 0,66 г води/г адсорбенту. Температура регенерації композитів «силікагель - натрій сульфат» і «силікагель - натрій ацетат» становить 90 °С і 60 °С. Теплота адсорбції композитів «силікагель – натрій сульфат» і «силікагель – натрій ацетат» дорівнює 2200 кДж/кг і 1400 кДж/кг.

Ключові слова: акумулювання теплової енергії; адсорбційне перетворення теплової енергії; композитні адсорбенти; золь-гель технологія**.**

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ТЕХНОЛОГИЯ ПОЛУЧЕНИЯ НОВЫХ МАТЕРИАЛОВ ДЛЯ АДСОРБЦИОННОГО ПРЕОБРАЗОВАНИЯ ТЕПЛОВОЙ ЭНЕРГИИ ТИПА «СИЛИКАГЕЛЬ – КРИСТАЛЛОГИДРАТ»

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Аннотация

Статья посвящена золь-гель технологии промышленного производства композиционных сорбентов «силикагель – Na_2SO_4» и «силикагель – CH_3COONa», включающий следующие стадии: подготовка водного раствора силикатного стекла и полимерной соли четвертичного аммония (ПЧАС), формирование ядер силикатной фазы, образование кремний-кислородной матрицы, сушку и фракционирование сорбента. По разработанной технологии сорбенты готовились с размером гранул 3 - 5 мм. Насыпная плотность составляет 0,72 г/см^3 и 0,65 г/см^3 для композитов «силикагель – сульфат натрия» та «силикагель – ацетат натрия». Показано, что композиционные сорбенты характеризуются высокой адсорбционной емкостью на уровне 0,42 - 0,66 г воды/г адсорбента. Температура регенерации композитов «силикагель – сульфат натрия» и «силикагель – ацетат натрия» составляет 90°C и 60°C. Теплота адсорбции композитов «силикагель – сульфат натрия» и «силикагель – ацетат натрия» равна 2200 кДж/кг и 1400 кДж/кг.

Ключевые слова: аккумулирование тепловой энергии; адсорбционное преобразование тепловой энергии; композитные адсорбенты; золь - гель технология.

Introduction

Urgency of thermal energy storage and transformation systems based on the sorption phenomena results from their high density of heat energy storage, low heat losses and repeated accumulation operations. Moreover, working fluids used for adsorptive heat energy transformation (AHET) are environmentally safe. AHET exhibits high potential for saving fossil fuels. However, recent developments in the AHET industry cannot be considered as satisfactory not least because of the insufficient properties of adsorbents. Recent studies are focused on the selection among the existing sorbents or the synthesis and study of new materials. Further progress in AHET can be achieved only through the use of innovative adsorbents with enhanced properties. The composites “salt inside of the porous matrix» (SIPM) composites are recognized as promising materials for AHET due to their high sorption capacity for conventional working liquids (water, methanol and ammonia). Despite the large number of publications describing SIPM and their applications, the data are contradictory, often inconsistent, and sometimes conflicting. Energy saving and reduction of pollutants emission into the environment are two crucial problems for energy companies [1; 2]. Adsorption technology for heat energy storage and conversion is one of the engineering solutions for this problem. However, the current state of the art in this field cannot be considered to be quite satisfactory due to the insufficient properties of the adsorbing materials. Recently, attempts to improve them have been focused on the existing sorbents, as well as on the synthesis and study of composites SIPM due to the increased sorptive capacity to conventional working fluids [3; 4]. Silica gel, aluminum oxide, γ-Al_2O_3, vermiculite, activated carbon, attapulgite, burnt clay are used as porous matrix, and salts are lithium bromide and magnesium chloride, calcium chloride, barium chloride, lithium chloride, lithium nitrate and LiBr, $BaCl_2$ and $BaBr_2$, $CaCl_2$ and $CaBr_2$ [5–7]. Adsorbates are water vapor, ammonia, and methanol. It is obvious that the heat energy storage is based on three different mechanisms based on the heat capacity of the solid medium, phase transition, and adsorption [17]. Salt reacts with water vapor, a complex crystalline hydrate of salt being formed. Subsequent adsorption leads to complex dissolution and conversion into a salt - sorbate solution [8]. Composite sorbents SIPM can become widespread in low heat storage devices, adsorptive chillers, heat and moisture regenerators in ventilation and air conditioning systems, gas drying and drinking water extraction from the atmosphere [13]. The main advantages of composite sorbents are not only the possibility of control modification of their sorption properties, but also the low driving temperature and high heat storage capacity [18 – 20]. However, their commercialization in energy storage strongly inhibited by their production techniques associated with the quite complex and quite expensive technologies of dry and wet impregnation of porous media with crystalline hydrated solutions [9]. As efficient adsorbents for heat storage porous materials with high sorption capacity, high specific surface area, chemically inert, non-toxic, available in large quantities and not requiring too high temperature for regeneration can be used [14–16]. Such adsorbents include silica gel, zeolites, aluminum oxide and activated carbon. The open adsorptive system based on synthetic zeolite 13X was used to equalize loads in the district heating network. Efficiency factors are of 0.9 and 0.86 for cooling and heating, respectively. However, performance of this system is rather energy-consuming, because regeneration of zeolite 13X occurs at a temperature of about 180°C. Austrian scientists in a number of studies used silica gel in closed cycles and experimentally reached a heat storage density of about 50 kWh/m^3, which is 4 – 6 times smaller as compared with theoretically expected values. Activated carbon appears to be a good compromise between high adsorption and desorption capacity. Natural zeolites ought to be used in large quantities, beacause only a small amount of adsorbate is desorbed with increasing temperature. However, the adsorption isotherms of zeolites show a very nonlinear dependence on pressure related to solar cooling systems. On the contrary, for activated carbon and silica gel a linear dependence of isotherms on pressure is observed. Silica gel corresponds to most of the criteria for adsorbents, but it is expensive and may not be available in most countries. Additionally, another problem is the decreasing of adsorption potential and the aging of silica gel [10].

Several options for improving the properties of the adsorbent should be noted. The conventional adsorbents can be doped to provide better properties when used in adsorption cooling systems. At the end of the XXth century, activated carbon fiber was developed to use in adsorptive refrigerators. An example was described by Vasilyev et al. who reported on the development of a prototype solar refrigerator based on working pairs 'activated carbon fiber - ethanol' and «activated carbon - methanol» [21]. Wang et al. studied specially treated fiber of activated carbon. This adsorbent exhibits two to three times greater adsorption capacity to methanol and a shorter adsorption cycle as compared with standard activated carbon [22–25]. Modification of conventional adsorbents with salt was proposed in the early XXth century to increase their sorption capacity. The authors believe that further progress in AHET is possible only through the use of innovative adsorbents with additional properties - composites SIPM. They are a two-component system: one component is a matrix and the other is an inorganic salt located inside the pores of the matrix.

Sorbent S reacts with sorbate V (water, methanol, ethanol or ammonia) which results in formation of the complex of the molecules of salt and sorbate $S \cdot NV$ (hydrate, methanolate etc) according to the reaction: $S + NV = S \cdot NV$ [11].

Further sorption results in a complex process of dissolution and transformation of the salt-sorbate system. The equilibrium «sorbent-sorbate» is strongly affected by the salt content in the pores of the matrix. In particular, the bivariate sorption equilibrium which is typical for conventional adsorbents is changed into the mono-variant equilibrium between salt and vapor. The porous matrix is also important. It is conductive not only to dispersion of the salt particles, but to the phase composition and sorption properties of the salt which affects heat and mass transfer to the salt particles located inside the matrix. The adsorptive capacity of the composites for the main working liquids (water, methanol, ethanol and ammonia) exceeds the conventional adsorbents [12]. Aristov et al. revealed that the adsorptive capacity of the composite «$CaCl_2$ – silica gel» for water is 0.6 g/g, which is 5 – 6 times silica gel's. A similar effect was stated for composites «LiBr – silica gel» [23–26].

So, the aim of present work is to develop a technology for obtaining a new class of composite sorbents «silica gel – Na_2SO_4» and «silica gel – CH_3COONa» with heat energy storage density of 0.30 – 0.36 kWh/kg.

Experimental

Porous composite materials were obtained by deposition of sodium silicate solution with sulphuric or acetic acid. In porous silicate matrix 40 wt. % of sodium sulphate or sodium acetate were distributed.

Composite material «silica gel - Na_2SO_4» was obtained neutralization reaction with sulphuric acid H_2SO_4:

$$Na_2Si_3O_7 + H_2SO_4 = Na_2SO_4 + (SiO_2)_3 + H_2O$$

So, when for synthesis of composite «silica gel – Na_2SO_4» solutions of 98 wt. % sulphuric acid and 54 wt. % of sodium silicate used, the components are required in the following ratio, wt. %: solution of sodium silicate – 81.76 and solution of the sulphuric acid – 18.24.

Neutralization reaction of 98% solution of the acetic acid with 54% solution of sodium silicate is described by the next reaction:

$Na_2Si_3O_7 + 2CH_3COOH = 2CH_3COONa + (SiO_2)_3 + H_2O$

When composite «silica gel – CH_3COONa» synthesized, the next ratio of the components were used, wt. %: solution of sodium silicate is 78.54, and acetic acid is 21.46. Polymeric quaternary ammonia salts (polyionenes) were used to decrease the surface tension in the diluted solutions due to the adsorption and molecular orientation on the phase interface.

Obtaining of the composite sorbents «silica gel – crystalline» hydrate involves two stages. On the first stage 1 % of polymeric quaternary ammonium salt (PQAS) per the dry residue of SiO_2 was added to the solution of sodium silicate (silica ratio of 3.2) and heated to 35 °C with stirring, and then the corresponding acid (sulfuric acid or acetic acid) was added upto the desired pH. Then the resulting solution was heated to a temperature of 95 °C during one hour, allowing formation the particles with size of 5–7 nm. On the second stage acid and silicate glass solutions were added gradually, simultaneously and dropwise to this solutions upto a certain concentration with vigorous stirring, which allowed maintaining the pH in a certain range. At that, a highly porous silica gel was formed. Appropriate crystalline hydrates (sodium sulfate in the case of sulphuric acid and sodium acetate when acetic acid used) were introduced into its pores. The obtained composite sorbents were converted into a finely dispersed precipitate, which was filtered and dried to constant weight.

As the developed technology of production of composite sorbents «silica gel – crystalline hydrate» involves the use of sulfuric and acetic acids of the same concentration in solution, its description is demonstrated with the example of sulphuric acid. Sodium silicate solution (silica ratio of 3.2) and a SiO_2 concentration of 45% was used for the experiments. Upon completion of the synthesis, the precipitate of the composite sorbent was filtered and dried at a temperature of 60 °C to constant weight. The bulk densities for composite sorbents «silica gel – sodium sulphate» and «silica gel – sodium acetate» were 0.72 g/cm^3 and 0.65 g/cm^3, respectively. During the synthesis of composite sorbents «silica gel - crystalline hydrate» without the addition of PQAS, a white gelled precipitate is formed in the interaction of sodium silicate solution with H_2SO_4 and CH_3COOH. In the presence of PQAS a fine precipitate of composite sorbents «silica gel-crystalline hydrate» is formed and settled out almost completely in about 3-7 minutes. This results from that fact in the hot suspension at pH 9–10 the silica particles begin to coagulate as soon as the concentration of sodium ions exceeds approximately 0.3 n. In a solution of sodium silicate with the usual ratio of $SiO_2 : Na_2O = 3.2 : 1$ the concentration of sodium ions occurs to be 0.1·C, where C is the concentration of silica, expressed in gram-equivalent/1000 ml of solution. Many silica deposition processes are based on these simple facts. They involve the neutralization of the sodium silicate solution with acid so the colloidal particles of silica are grown in a light alkaline solution and can be flocculated under the influence of ammonium ions from the polymeric quaternary ammonium salts. To determine the effect of temperature on the dispersion of composite sorbents «silica gel – crystalline hydrate» synthesis was carried out at ambient and elevated temperatures. During the synthesis of the composite sorbents «silica gel crystalline hydrate» at ambient temperature, gel formation was observed on the first stage of synthesis, and the gradual transition of the gel in the second stage into separate jelles, which are difficult to disperse into noticeably large particles when dried.

Deposition of silica at a temperature of more than 50°C is significantly different from the above mentioned. At elevated temperatures, jelles formed at the end of the first stage and passed into the precipitate after the second. Thus, increasing the synthesis temperature promotes the formation of dispersed particles of composite sorbents «silica gel – crystalline hydrate».

The sorption equilibrium between water vapor and dry sorbent was studied by weight method. After drying, the samples (1 or 2 g) were placed in polymer flasks, and their weight was determined. Then they were kept on a grate in desiccators, on the bottom of which distilled water was poured. Before the experiment, the studied substances were maintained in a drying box at 140 °C for 4–6 hours.

Mass of the samples was determined with analytic balance AXIS-ANG200C (measurement accuracy II) at the temperatures of 20, 40 and 60 °C and pressure 20 and 760 mm Hg.

Results and discussion

The technological process for the production of composite sorbents consists of the following stages: preparation of an aqueous solution of sodium silicate and PQAS, the formation of nuclei of the silicate phase, the formation of silicon-oxygen matrix, drying and fractionation of the sorbent.

Stage 1. 100 parts by wt. of 20% aqueous solution of sodium silicate (silica ratio 2,9 – 3,3) from the vessel 1, through the measuring tank 3, is fed to the reactor-mixer 7 with a volume of 1000 l, where the thermocouple 6 and the heating element 8 are set up to control the temperature of the solution. Then 2 parts by wt. of 5% PQAS aqueous solution is added in the mixer reactor 5 from the vessel 2 through the measuring tank 4 with constant stirring. The mixture was stirred thoroughly for 15 minutes. Using the heating element 8, the mixture is heated up to 35°C for 20 minutes.

Stage 2. From the drip feed meter 5 40 parts by wt. of 2.4 % solution of sulphuric or acetic acid is added up to a neutral pH for 15 min with stirring. The mixture is heated to a temperature of 90°C and maintained at this temperature and stirring for one hour. At this stage, the formation of the nuclei of silicon matrix occurs.

Stage 3. 20 parts by wt. of 4.65 % acid solution and 15 - 20 wt. parts 50% solution of silicate glass are added simultaneously to obtained mixture through the measuring tank 13 and from the vessel 14, through the measuring tank of with constant stirring for two hours at a constant temperature of 95°C. The pH is maintained to be 10. At this stage, the formed sorbent is precipitated from the solution.

Stage 4. 4.65% acid solution is added to reduce the pH to 5 within 20 minutes from the drip feed meter 13. The obtained gel is exposure at 90°C for one hour. The precipitated sorbent is filtered off, the liquid is poured into a vessel 10, and the sorbent is sent to fluidized-bed dryer 11, where it is dried to constant mass at a temperature of 60°C. The dried composite is fed to a vibratory sieve 12, where it is fractionated by the size of the granules. After leaving the dryer, saturated air (exhaust) is dehydrated in the dehumidifier 16, heated in the heat exchanger 17 and returned to the dryer again.

Table 1

Sequence of the synthesis components introduction

Stage	Component	Consumption, parts by wt.
1	20 wt. %solution of sodium silicate	100
	5 wt. % solution PQAS	2
2	2.4 wt.% acid solution	40
3	4.65 wt.% acid solution	20
	50% wt. %solution of sodium silicate	20
4	4.65 wt.% acid solution	10-20
	Yield of the composite	14

Table 2

Properties of the composite synthesized according to technology

	Silica gel – sodium sulphate	Silica gel – sodium acetate
Bulk density, g/cm^3	0.72	0.65
Sorption capacity, g/g	0.66	0.42
Regeneration temperature, °C	90	60
Diameter of granules, mm	3-5	3-5
Heat of adsorption, kJ/kg	2200	1400

As a comparison, the properties of composites obtained by impregnation are given in the Table 3.

Table 3

Basic properties of some composite adsorbents

Material	Sorption capacity, g/g	Regeneration temperature, °C	Heat storage density, kJ/kg
20 wt. % $MgSO_4$ та 80 wt. % $MgCl_2$		130	1590
$CaCl_2$ – silica gel	0.73	90	950
$CaCl_2$ - $FeKIL_2$	0.63	150	920
$LiNO_3$ – vermiculite	0.4	62-65	900
$Ca(NO_3)_2$ – silica gel	0.2-0.3		890
LiCl – silica gel LiBr – silica gel	0.8		1000

The prepared composite have to be stored in a tightly closed and sealed package or container to avoid sorption of moisture from the environment. The commercial process flowsheet of the production of composite sorbents «silica gel –

crystalline hydrate» which involves all of the above stages is given in Fig.

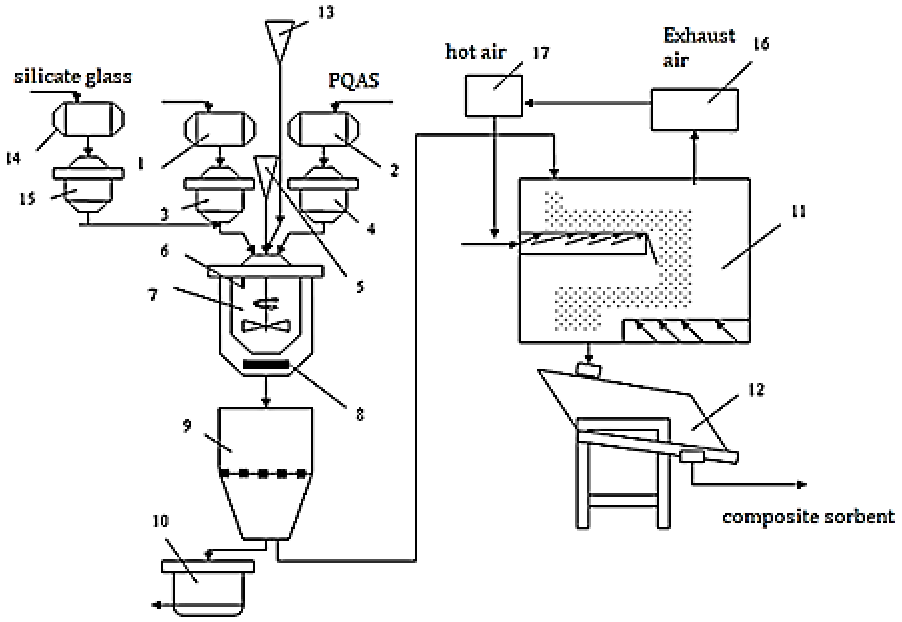

Fig. Process flowsheet of the commercial production of composite sorbents «silica gel –crystalline hydrate» 1, 14 – vessels with sodium silicate solution; 2 – vessel with PQAS solution; 3, 4, 15 – measuring tanks; 5, 13 – drip feed meter for acid; 6 – thermocouple; 7 – mixing reactor; 8 – heating unit; 9 – filter; 10 – vessel for liquid drain; 11 – fluidized-bed dryer; 12 – vibratory sieve; 16 – air dehumidifier; 17 – heat exchanger.

The sorption properties of the synthesized composite sorbents «silica gel – crystalline hydrate» are not a linear combination of the properties of silica gel and a massive salt, the rate of sorption of water being three times higher. The process of hydration proceeds from the kinetic regime, which is typical for the massive salt, to the diffusion mode, i.e. the limiting step becomes the transport of water to the salt through the system of pores of the silicon-oxygen matrix.

Conclusion

The technology of commercial production of the composite sorbents «silica gel – Na_2SO_4» and «silica gel – CH_3COONa» sol-gel method is developed. It includes the following steps: preparation of aqueous solutions of silicate glass and polymeric quaternary ammonium salt (PQAS), formation of nuclei of silica gel phase, formation of the silicon-oxygen matrix, drying and fractionation of the sorbent.

New composite sorbents «silica gel – crystalline hydrate» were obtained and their sorption properties were studied. These composite sorbents are shown to be characterized by high values of water absorption at the level of 0.42 – 0.66 g/g.

It was found that the sorption properties of such composite sorbents are significantly different from the properties of the massive salts.

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