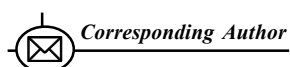




### Change In The Adsorption Activity Of Silicagel Under The Influence Of Magnetic Field

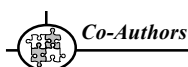

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#### ABSTRACT

Theoretical structures of the silicon acid oligomers most probable for an aqueous medium were obtained. Silica gel oligomer structures are considered as a self-similar system of "pacemakers" capable of restructuring under magnetic field. Increase of the sorption capability of gel after magnetic field exposure is determined. Spiral polymer chain of silicon acid unwind under the external field and rehabilitate itself after elimination of the external field. The change in the gel structure leads to the destruction-polymerization processes of the silica gel matrix, which cause a change in the number of active sorption centers. The medium returns in a certain period of time and silica gel sorption decrease to initial values. This paper contributes to the theory of gel sorbing agents, which in future will enable us to predict their properties to increase sorption activity.

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#### KEYWORDS

Silicon acid;  
Magnetic field;  
Silica gel;  
Self-similar system;  
Destruction-polymerization  
processes;  
Sorption activity;  
Computer modeling.

#### INTRODUCTION

It was established<sup>[1]</sup> that silicate dispersion structures are wave-like in their formation, although classical theories give no clear explanation for the phenomenon. It is known<sup>[2]</sup>, that electric and magnetic fields influence the structure of the mesophases of

organic liquid crystals and the optical, sorption and rheological properties of heavy metal gels<sup>[3]</sup>.

The morphogenetic processes that take place in the air-dried patterns of silicon acid gels are the subject of the investigation covered by this paper. The influence of pulsed magnetic field on the sorption properties of xerogels is shown and an attempt is

made to explain the periodic mechanism of the structuring of these patterns. The results are matched with data obtained from the quantum-mechanic calculations of the probable structures of silicon acid oligomers. Assumptions are made about the reasons for the change of the sorption capacity of the patterns.

## EXPERIMENTAL

Computer modeling, based on a combined technique, was used to investigate the structural variety of the oligomers. This technique includes probabilistic structure modeling, using the original genetic algorithm MOPS<sup>[4]</sup>, which is the developed version of MECH<sup>[5]</sup>, and which was first used for the non-organic system. Then the obtained aggregate was optimized ab initio in the GAMESS environment.

To prepare the gel-forming mixtures, a solution of sodium metasilicate, preliminarily filtered and diluted with distilled water to the required density, was added dropwise to the solution of nitric acid. The mixture was mixed continuously until the required pH value in the 5 liter reactor was achieved. The pH was measured by an I-120.2 ion-meter. The synthesis time was 4 hours. The concentration of the initial solution of sodium metasilicate changed from 0.1 to 0.5 mol/l in increments of 0.1 mol/l with pH values of ranging from 5.0 to 6.0. The obtained mixtures were covered and kept in darkness until the "quasi-crystallization" of gel. Then, the gel was dried at ambient temperature over 3-6 months. The resulting patterns were granulated with a 0.3-1.25mm fraction.

This paper investigates the isothermal concentration equilibrium of silica gel patterns in calcium chloride solutions under pH equal to 5.5 to 6.5, as the function  $\Gamma = f(C_p)$  (where  $\Gamma$  is the specific sorption of  $\text{Ca}^{2+}$  ions, and  $C_p$  their equilibrium density in the system).

The interval of sorbate concentration change was 0.05 to 0.5 mol/l in increments of 0.05 mol/l. The ionic strength in sorbate solutions of various concentrations was maintained by adding base electrolyte (1.5M of potassium chloride). Portions of the air-dried silica gel equal to  $5 \times 10^{-4} \pm 1 \times 10^{-7}$  kg were

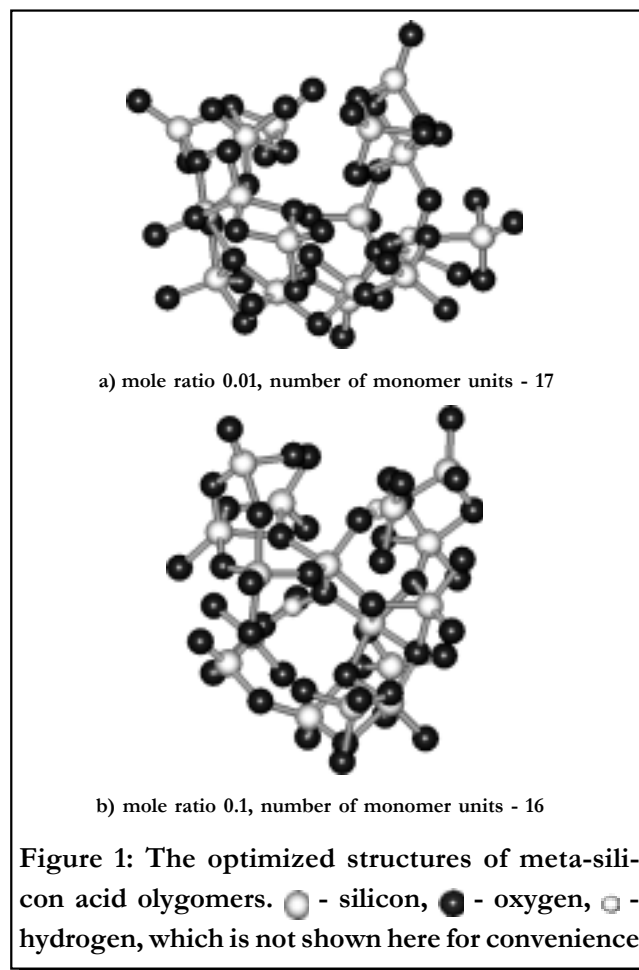
placed in an agitator and mixed with 25ml of sorbate. The contact time was 24 hours. The concentration of  $\text{Ca}^{2+}$  ions was determined by titration using EDTA.

The pulsed magnetic field was created by a specially designed device, consisting of a current generator and magnetic coil. The frequency of magnetic field pulses was equal to 3 Hz and the voltage of the coil was 80 V. The air-dried pattern was exposed to the pulsed magnetic field for 3 hours.

## RESULTS AND DISCUSSION

As a result of quantum-chemical calculations, the theoretical structures of the silicon acid oligomers, most probable for an aqueous medium, were obtained. The calculations were made through the stepwise addition of silicon acid and water to the monomer aggregate.

Versions of the aggregation of meta-silicon acid



## Full Paper

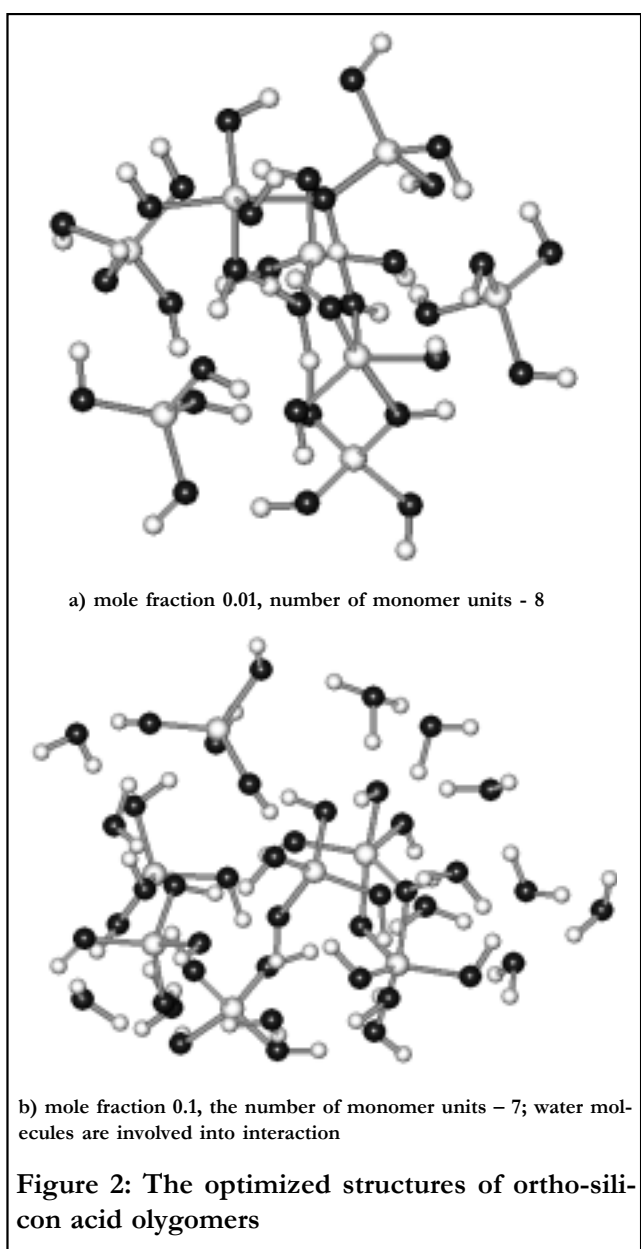
particles with the following parameters were considered. The number of monomer molecules ranges from 2 to 20; mol fractions of acid in the solution are 0.1 and 0.01 to one monomer (which corresponds to a sufficiently concentrated 43% gel and a gel experimentally obtained with gelling agent concentration equal to 0.4M); the 'water-monomer' mole ratio in structures is 1:2. Examples of the calculated structures are shown in figure 1.

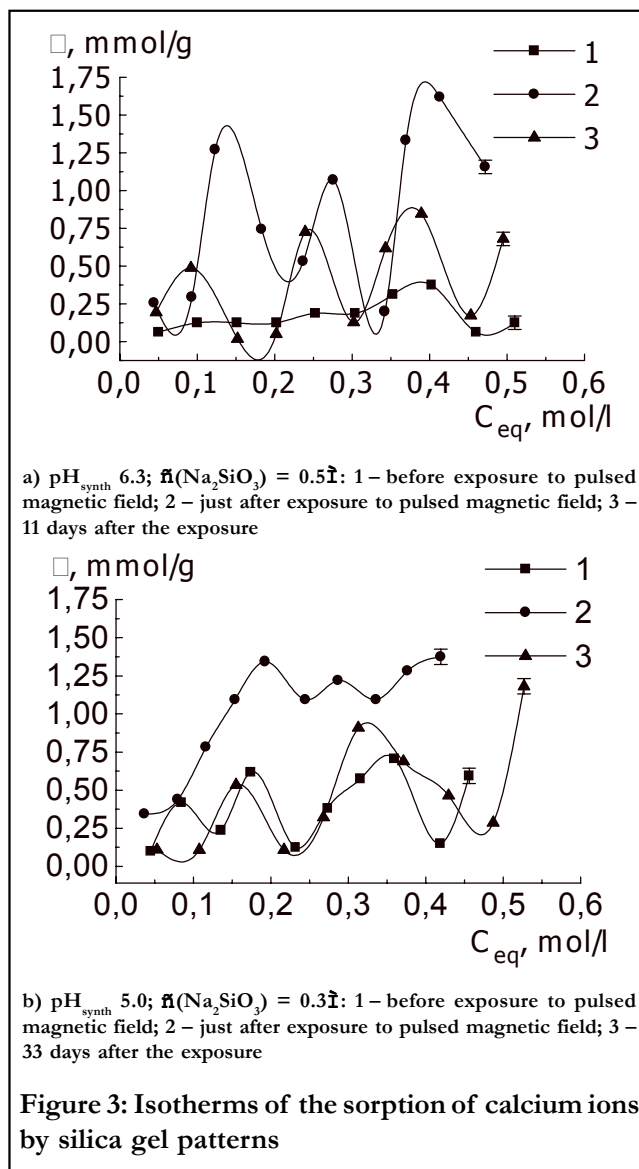
In addition, the oligomeric silica gel aggregates were calculated, where the ortho-silicon acid was used as the monomer (Figure 2). The mole fraction of acids in the solutions, in terms of the monomer

in the three sets of calculations, were 0.001, 0.01 and 0.1 and the number of monomer molecules in the aggregate ranges from 2 to 9.

Earlier<sup>[6]</sup>, suppositions were made that silicon acid gel can be formed primarily by cyclic oligomers, which can be explained by the density of active Si-OH terminal groups in trimers and tetramers. Calculations including the solvating effects and conformational variety of the poly-silicon acid have shown the probabilistic nature of these suppositions. It is theoretically proved that ring-shaped aggregates can only be formed in highly concentrated gel with the help of hydrogen-bonds and ol-bonds. However, it has been determined that mainly open circuits, with a form of three-dimensional spirals and circuits with various forking are present in gel. (Figure 1) The most widespread types of bonds between monomers are two oxo-bonds, oxo- and ol- bond, two ol-bonds. The aggregate is an oligomer in the form of a "coil" which is more compact and bound in the concentrated gel. The silicon coordinate number of the central aggregate items rises to 5, and in some cases to 6, which proves the statement that five-coordinated silicon is the necessary intermediate state in the formation of air-dried silica gel from hydro gel<sup>[7]</sup>. The calculations of monomer interactions taking place in the presence of water point to the fact that in more concentrated gels water plays an active role in the oligomer chain formation, making open-work structures and increasing the incidence of forking. The polymer chains in water-diluted gels are flatter; the water is either on the periphery of the aggregate or it fills the interlayer space. This is the reason why a more accurate mesophase-like aggregate system is formed in such gels and they have higher sorption ability. Estimation of the un-optimized structural energy using the MOPS algorithm has shown that a symbate change of the obtained aggregate permanence is observed, depending upon the number of monomers.

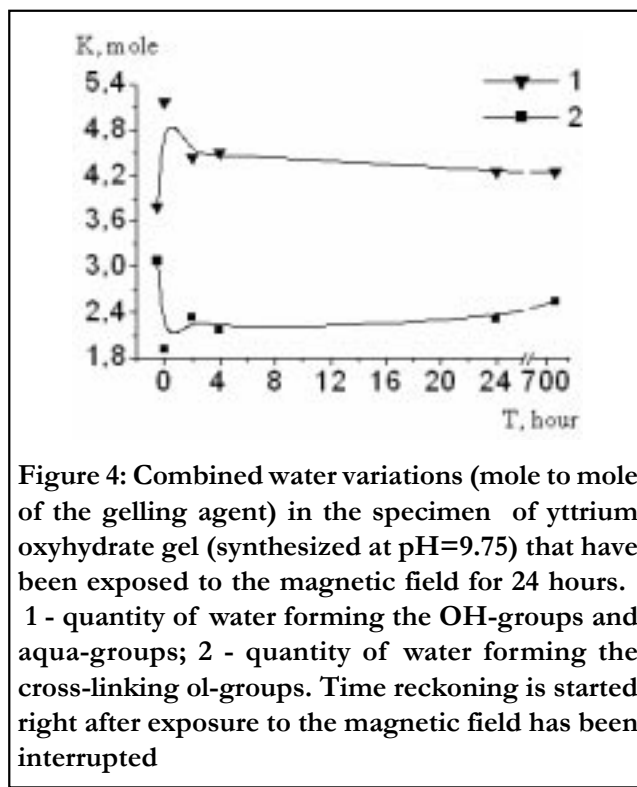
It has been experimentally determined that exposure to electromagnetic field influences the adsorption properties of silicon acid gel. The unexposed patterns show minimal sorption properties compared with calcium ions with a pH equal to 9.0. Exposure to magnetic field causes a sharp increase in the sorption property of silica gel, which reaches 1.5 mmol/





g (Figure 3). To track the change in silica gel activity over time, isotherms of pattern sorption, taken after 5 to 30 days of exposure to pulsed magnetic field were obtained. It is noted that the gel's capacity to sorb the calcium ions from the solution decreases with time, that is, the isotherms return to the initial values of sorption.

It is shown<sup>[8]</sup> that the majority of gels have a self-similar periodic structure made of polymer aggregates of different sizes. Such particles are mostly formed by spiral-shaped oligomer chains, which are proved by the theoretical calculations of probable structures. The higher the concentration of the gel-forming substance, the higher the cross-linking between the chains. Since the mole fraction of the sili-



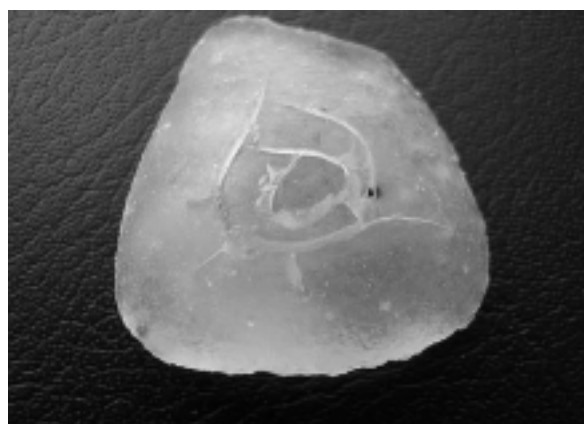
con acid in the pattern increases under drying, the theoretical conclusions about the aggregate properties in the concentrated gel may be deemed correct for the air-dried gel. In such aggregates, the cross-linking bonds are mostly formed by hydrogen and ol-bonds, which are capable of breaking under weak electromagnetic field. Under a certain threshold value of the magnetic field voltage, the spiral pitch begins to change, which is proved by the change in the optical gel properties. Meanwhile, the electric axes of 'spiral' aggregates level out in the direction towards the field, they 'unwind', and breakdown. Many new active sorption centers, earlier situated in the microstructure of the particle and which have moved to the periphery, now appear. The results of thermogravimetric research of oxyhydrate yttrium gels<sup>[3]</sup> enable us to predict that under electromagnetic field, the spiral will 'unwind' and the polymer chains will breakdown. Here, the quantity of water connected by ol-bonds decreases and the quantity of water connected by the terminal hydroxo- and aqua-groups increases (Figure 4). The cross-linking bonds break and become terminal OH-groups. These are terminal groups that become adsorption centers in the polymer gel matrix. The sorption of calcium ions

## Full Paper

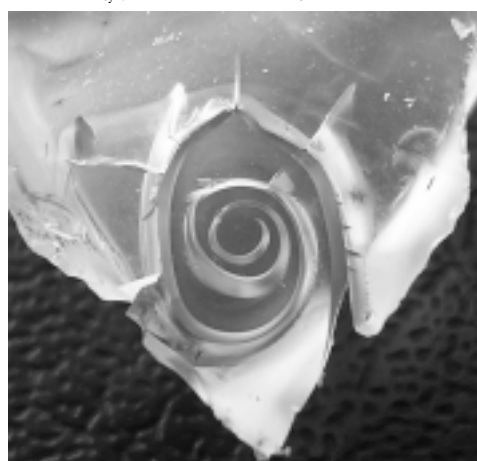
increases sharply and they are involved in the formation of a new 'quasi-equilibrium' structure of gel aggregates. The structural transformation of polymer gel is another reason for the periodic character that is detected in the sorption isotherms of calcium ions. Some time after the patterns have been exposed to the magnetic field, the reverse process commences; the phenomenon of relaxation is observed. Part of the coordinated water (aqua-groups) transforms into the OH-groups, which then passes into the cross-linking ol-groups as a result of macromolecular convergence and transformation.

Thus, the degree of gel polymerization increases. On average the processes of relaxation complete within 30 days. The gel transfers into a state with lower sorption activity compared with the initial state of gel obtained just after the pulsed magnetic field exposure (Figure 3). The gel probably has the same structure but one that is slightly different from the initial one. It is known<sup>[2]</sup> that even under high values of intensity, liquid crystal spiral order does not experience complete breakdown. The swirls remain owing to the constant reverse rotation of the direct (topological barrier). When the influence of the magnetic field decreases or it disappears, the zones of the periodic surface elongation, swerving and zones, filling the space, increase. This process is analogous to the forming of cholesteric phase in liquid crystals.

The fracturing of gel following lines similar to spirals or torn circles occurs mostly when drying the gel at ambient temperature (Figure 5). Analogous super-molecular forms were fixed in gels of certain heavy metal oxyhydrates (niobium, yttrium and gadolinium)<sup>[8]</sup>, which is evidence of the mesophase-like character of a wide range of gel matrices. It is probable that in air-dried gel media these spiral phenomena have attained their form owing to the diffuse movement and subsequent water evaporation on the boundary areas of spiral growth in the thickness of the gel. This fact testifies favorably to the hypotheses that gels are self-similar reproducible systems of 'pacemakers'. The basis of such a system is the polymer chains of silicon acid, swirled in the form of spirals, which is the most energetically favorable conformation in the solution medium. On a large



Fragment of air-dried silica gel,  
 $\text{pH}_{\text{synth}} = 5.25$ ;  $c(\text{Na}_2\text{SiO}_3) = 0.2 \text{ mol/l}$



Fragment of air-dried silica gel with a spiral-shaped crack,  
 $\text{pH}_{\text{synth}} = 5.0$ ;  $c(\text{Na}_2\text{SiO}_3) = 0.3 \text{ mol/l}$

**Figure 5: Pictures of the spirals of air-dried silica gel patterns**

scale the structure reproduces itself on a level of micro gel, forming 'pacemakers', and on a level of gel as a whole, manifesting itself in spiral cavities, impoverished by gelling agent and non-visible in hydrogel. However, these spiral cavities become weak places under gel drying and contraction. Due to the concentration gradient, crystallites, experimentally found in the zirconium oxyhydrate gel, can be formed there.

The change of silica gel structure can be presented as the periodic unwinding and the subsequent restoration of spiral conformations over time, according to the deviation of the axis of spiral swirls from the direction of magnetic field of gel exposition in the magnetic field. This property of the liq-

uid-crystal phase can be explained by the so-called Frederics Transfer, which means the deformation of the director in the liquid crystal layer with homogeneous orientation under the external field. Such structural transformations, leading to a change in the microscopic orientation structure and which take place at a certain threshold value of the external field, are physically equivalent to phase transition of the second type and are convertible. Given the elimination of the external field influence, the medium returns to its initial state in a certain period of time.

### CONCLUSION

Comparison of experimentally obtained data with theoretical computations of silica gel oligomer structures has shown the applicability of the model for the gel forming as a self-similar system of 'pacemakers', capable of restructuring under magnetic field. The influence of pulsed magnetic field on the sorption gel properties, which manifests itself in an increase of the sorption capability of gel patterns after magnetic field exposure, is determined. The increase in calcium ion sorption by the gel can be explained by the 'unwinding' effect of the spiral polymer chain of silicon acid under the external field and its 'restoration' after elimination of the external field. In this case the change in the gel structure leads to the destruction-polymerization processes of the silica gel matrix, which, in their turn, cause a change in the number of active sorption centers. Such behavior of the gel phase is convertible; given the elimination of the influence of the external field, the medium returns in a certain period of time, which leads to a decrease in silica gel sorption activity to initial values. This paper contributes to the theory of gel sorbing agents, which in future will enable us to predict their properties to increase sorption activity.

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