

**ПОЛУЧЕНИЕ СИЛИКАТА НАТРИЯ ИЗ МОДИФИЦИРОВАННОГО СИЛИКАГЕЛЯ,
ПОБОЧНОГО ПРОДУКТА ФТОРИДА АЛЮМИНИЯ****Е.А. Мамченков, В.Ю. Прокофьев**

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В статье рассматривается процесс производства силиката натрия из модифицированного микрокремнезема, побочного продукта производства фтористых солей. Предлагаемый метод соответствует принципам ресурсо- и энергосбережения. Получение растворимого силиката натрия осуществляется из техногенного сырья при атмосферном давлении исключая использования сложных в обслуживании аппаратов. Микрокремнезем представляет собой аморфный диоксид кремния с примесями фторида алюминия и, в некоторых случаях, кремнефтористоводородной кислоты. Используемый в работе микрокремнезем является побочным продуктом производства фторида алюминия предприятия «Фосагро» Череповец. Целью данного исследования является изучение возможностей использования предельно модифицированного микрокремнезема для производства силиката натрия. Исследования показывают, что гидроксид натрия значительно эффективнее, по сравнению с минеральными кислотами, с целью химической модификации поверхностного слоя микрокремнезема при 20 °С. Модифицирующий раствор с концентрацией щелочи 25% и более может использоваться многократно в процессе обработки диоксида кремния. Определена оптимальная концентрация щелочи и время модификации микрокремнезема. В исследовании были проанализированы следующие параметры обработки микрокремнезема: время реакции (от 0 до 90 мин), молярное отношение SiO_2/NaOH (1, 2, 3), массовое отношение воды и диоксида кремния (1; 2,5; 5) и температура (60, 80, 95 и 105 °С). Установлено, что соотношение диоксида кремния и гидроксида натрия достигает 2,8 при 95 °С в течение 12-15 мин. В процессе растворения модифицированного микрокремнезема удалось достигнуть перехода в растворимый силикат натрия около 92% диоксида кремния.

Ключевые слова: модифицированный силикагель; AlF_3 отходы производства; силикат натрия

**SODIUM SILICATE MANUFACTURING FROM MODIFIED SILICA GEL AS BY-PRODUCT
OF ALUMINUM FLUORIDE****E.A. Mamchenkov, V.Yu. Prokof'ev**

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The article considers the waste-free production of sodium silicate from modified silica gel. The proposed method corresponds the principles of green chemistry. Synthesis is carried out from

industrial raw materials at atmospheric pressure without the formation of unrecyclable by-products. Silica gel is an amorphous silica with impurities of aluminum fluoride and fluorosilicic acid, which is obtained as a by-product of aluminum fluoride production from Cherepovets "Phosagro". The goal of this study is to investigate the possibilities of using modified silica gel, for manufacture of sodium silicate with minimum waste production. Studies show, that sodium hydroxide can be used for chemical modification of the surface of silica gel at 20 °C. Optimal alkali concentration and time of silica modification was determined. Alkaline solution with concentration 25% or more could be used multiple times in a process of silica modification. The following variables in this work had been analyzed: time of reaction (varying of 0 to 90 min), molar ratio SiO₂/NaOH (1, 2, 3), mass ratio H₂O/SiO₂ (1; 2.5; 5) and reaction temperature (60, 80, 95, and 105 °C). It is observed that the SiO₂/NaOH ratio reaching 2.8 at 95 °C, in 12-15 min of reaction. In the process of dissolving the modified microsilica, it was possible to achieve a transition to soluble sodium silicate about 92% of silicon dioxide.

Key words: modified silica gel; AlF₃ production waste; sodium silicate; green technology

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INTRODUCTION

"Phosagro" Chemical Plant (Cherepovets) producing aluminum fluoride from fluorosilicic acid. The reaction between fluosilicic acid and aluminum hydroxide, apart from the main product, i.e. aluminum fluoride, results the by-product silica gel SiO₂·nH₂O (1).



Then, agitating the solution at 100 °C for 4 h produces the trihydrate aluminum fluoride crystals. The trihydrate crystals are converted to anhydrous form after calcination in a rotary kiln or a fluidized bed calcinatory. Silica precipitates should be filtered from the aqueous solution immediately and before the onset of crystallization of aluminum fluoride. However, impossible to obtain the silica gel without any admixture of aluminum fluoride, which reduces the scope of application of silica gel.

Producing 1 t of aluminum fluoride generally formed about 0.5 t of silica gel waste. However, different chemical plants produce silica gel waste with different impurity composition and particle size. This makes problems for realization silica gel recycle technology. That is why most of silica gel stored in a landfill site [1-3].

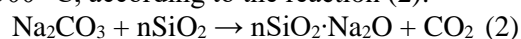
The presence amorphous silica in composition of silica gel can be used in various industries. One of the most common methods of disposal of the silica gel is obtain construction materials. Silica gel can be used as an additive in hardened cement paste [4-7]. Thermal activation of Silica gel improves its pozzolanic activity [1, 3, 9-11]. The other way, to recycle silica gel is production of silica-based pigments [12] and zeolites [13, 14].

The investigation comprises a process for the manufacture of a sodium silicate solution from by-product AlF₃ production – silica gel. Sodium silicate is used as raw material for several purposes: preparation of catalysts, inks, and load for medicines, concrete hardening accelerator, component of detergents and soaps, refractory constituent and deflocculant in clay slurries.

The existing processes for the industrial production of sodium silicate generally comprise 2 stages:

1. Calcination;

Sodium carbonate, mixed with raw silica material (diatomite, quartz, cristobalite, ect.), in furnaces at 1400-1500 °C, according to the reaction (2):



2. Dissolution in water;

The product obtained in the previous stage, in an autoclave, under pressure 2-5 bars at temperature 120-150 °C. Sodium silicates are produced in this stage.

Described technology has several disadvantages. Both stages are very energy intensive. Raw materials with impurities are not allowed.

Another way for sodium silicate manufacturing is a dissolution various by-products with high (50-90%) content of SiO₂ [15-19]. However, this method requires preliminary purification of silica raw material. This leads to the formation of by products and/or large volume of wastewater.

This paper describes a method of sodium silicate manufacture, with allows sodium silicate solution to be synthesized from a variety of materials including recycled resources and mineral wastes such as SiO₂

with impurities of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ [20]. It's reduces the energy demands during production. A procedure for utilizing silica gel, by-product from aluminum fluoride production, was developed in this research.

MATERIALS AND METHODS

As silica source used silica gel from a local industry (Cherepovets, Vologodskaya region, Russia). The reaction between silica gel and sodium hydroxide solution was carried out under atmospheric pressure. The system consisted of a glass reaction vessel, heating source, temperature measuring device and reflux condenser, to keep constant volume of the reaction mixture.

The conversion silicate to sodium silicate, expressed in weight percentage, was determined by mass balance, as described in next procedure. The solid residues obtained in the stage of filtration had been washed with distilled water and later dried at 105 °C, for constant mass. The conversion was determined from of known silica mass in the silica gel and from the residue content gotten in the filtration.

The following variables in this work had been analyzed: time of reaction (varying of 0 to 90 min), molar ratio SiO_2/NaOH (1, 2, 3), mass ratio $\text{H}_2\text{O}/\text{SiO}_2$ (1; 2,5; 5) and reaction temperature (60, 80, 95, and 105 °C). The time of "0 min" corresponds to the time necessary for reaction system to reach the desired temperature.

RESULTS AND DISCUSSION

The composition of silica gel produced by the chemical plant "Phosagro" was the following one (% by weight): 88.3 (SiO_2); 5 (Al_2O_3); 0.59 (MnO); 0.3 (CaO); 0.001 (MgO); 0.015 (Fe_2O_3); 5.01 (F^-); 0.05 (SO_4); 0.002 (ZnO); 0.001 (CuO). The water content in silica gel is 42.8%.

Studies show, that sodium hydroxide can be used for chemical modification of the surface of silica gel at 20 °C. This increases the solubility of silica gel in an alkali. Synthesis of sodium silicate from modified silica gel was performed in 2 stages. Stage 1: silica gel mixed with NaOH at 20 °C and time 10-30 min. After dividing solid and liquid phases, the liquid phase is subjected to regeneration. Modified the silica gel is heated with water at temperatures up to 60-105 °C. As a result, series of experiments were performed to determine the optimal concentration of NaOH and time of alkali treatment of silica gel.

Fig. 1 shows, that concentration of aluminum impurities reached acceptable value for sodium silicate synthesis after 10 min treatment by 10% NaOH. Data on the effect of impurities on the solution of silica gel activation is shown in Fig. 2.

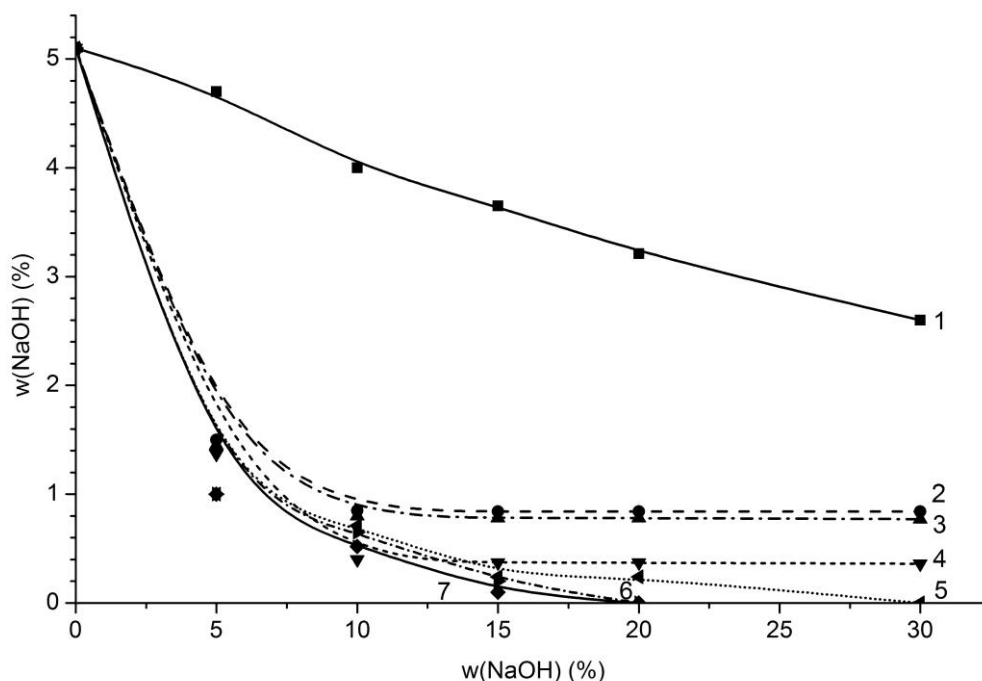


Fig. 1. Change in content of aluminum fluoride impurities in terms of aluminum oxide in the silica gel sample depending on the concentration of the alkali $\omega(\text{NaOH})$, %: 5 (1), 10 (2), 15 (3), 20 (4), 25 (5), 30 (6), 35 (7)

Рис. 1. Изменения содержания примесей фторида алюминия в пересчете на оксид алюминия в зависимости от концентрации применяемой щелочи $\omega(\text{NaOH})$, %: 5 (1), 10 (2), 15 (3), 20 (4), 25 (5), 30 (6), 35 (7)

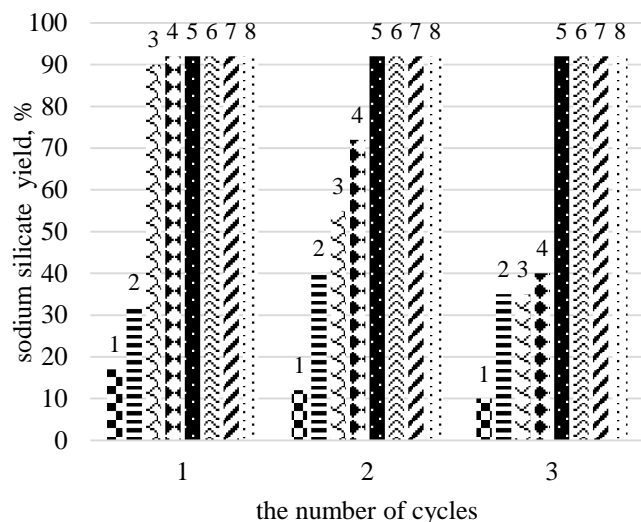


Fig. 2. The effect of impurities in modifying solution on yield of sodium silicate as function of the number of cycles, C(NaOH), %: (1), 10 (2), 15 (3), 20 (4), 25 (5), 30 (6), 35 (7), 40 (8)
 Рис. 2. Влияние примесей в модифицирующем растворе на выход жидкого стекла в зависимости от количества циклов C(NaOH), %: 5 (1), 10 (2), 15 (3), 20 (4), 25 (5), 30 (6), 35 (7), 40 (8)

To reduce the cost of produced sodium silicate, sodium hydroxide after activation of silica gel was returned to the cycle. After each treatment of silica gel, the concentration of sodium hydroxide solution was restored to the original concentration. Fig. 2 shows that sodium hydroxide solution concentration less than 25% is not effective for activation of silica gel in a cycle. This effect is caused by the accumulation of the impurities of aluminum fluoride in sodium hydroxide solution. The increase of the alkali concentration to 25% or more makes possible to use sodium hydroxide solution repeatedly without significant reduction SiO₂/Na₂O ratio in sodium silicate solution.

Fig. 3 presents the influence of reaction temperature on NaOH/SiO₂ ratio. It is observed that the NaOH/SiO₂ ratio increases with the temperature rise, reaching 2.8 at 95 °C, in 12-15 min of reaction. Further increase in temperature is impractical because SiO₂/NaOH ratio does not exceed the value of 2.8. Decreasing the temperature to 80 °C leads to a significant reduction SiO₂/NaOH ratio. Temperature of 60 °C does not allow synthesizing sodium silicate solution. Particle size of silica gel is too high for the synthesis at temperature 60 °C. Additional refinement of silica gel is not economically profitable. Increasing the duration of the process does not significantly affect the value of SiO₂/NaOH ratio.

Fig. 4 shows that the silica conversion into sodium silicate solution that the conversion increases with the temperature rise, reaching 90% at 95 °C, in

12-15 min of reaction. It is observed that the increase of the H₂O/SiO₂ ratio from 1 to 5 practically does not modify the values of the conversion, for the different assayed NaOH/SiO₂ ratios. It is observed that the conversion increases with the temperature rise, reaching 1.45 at 95 °C, in 12-15 min of reaction.

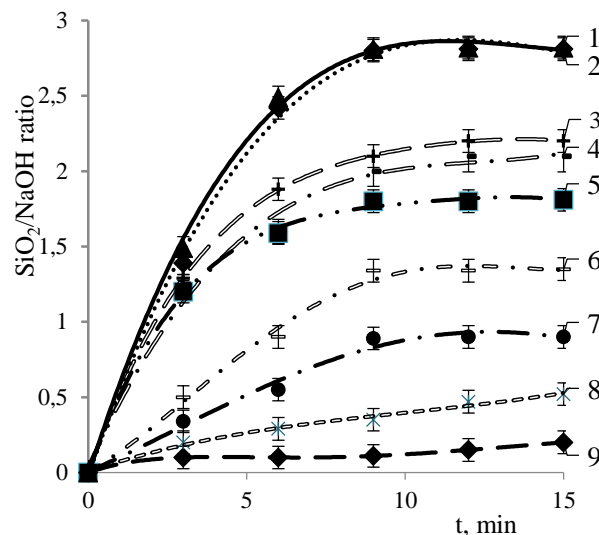


Fig. 3. SiO₂/NaOH ratio as a function of reaction time for different temperatures, °C: 105 (1), 95 (2), 90 (3), 85 (4), 80 (5), 75 (6), 70 (7), 65 (8), 60 (9)
 Рис. 3. Зависимость величины силикатного модуля жидкого стекла от температуры и времени процесса °C: 105 (1), 95 (2), 90 (3), 85 (4), 80 (5), 75 (6), 70 (7), 65 (8), 60 (9)

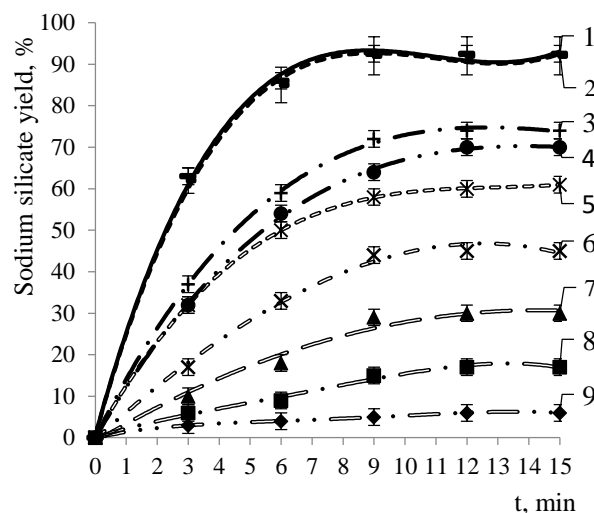


Fig. 4. Yield of sodium silicate as function of reaction time for different temperatures, °C: 105 (1), 95 (2), 90 (3), 85 (4), 80 (5), 75 (6), 70 (7), 65 (8), 60 (9)
 Рис. 4. Зависимость выхода жидкого стекла от температуры и времени процесса, °C: 105 (1), 95 (2), 90 (3), 85 (4), 80 (5), 75 (6), 70 (7), 65 (8), 60 (9)

CONCLUSION

The results of experiments confirm the possibility of utilizing modified silica gel, waste products of

production aluminum fluoride, for the manufacturing of sodium silicate solution. Developed technology providing sodium silicate production without wastewaters. The optimum concentration of alkali solution for modification of silica gel is 25% and reaction time 10 min at 20 °C. It is possible to dissolve 90 % of the contained silica in modified silica gel by the reaction with aqueous solution of NaOH, at 95 °C. The dissolved silica percentage increases with the increase of the temperature to 95 °C. A further increase in temperature doesn't influence the dissolution of modified silica gel. The molar ratio H₂O/SiO₂ practically does not influence in the silica dissolution. The optimal time for silica dissolution in alkali is 12-15 min. The method provides a production of sodium silicate with SiO₂/Na₂O ratio 2.8 and density of 1.40 g/cm³.

REFERENCES

ЛИТЕРАТУРА

1. **Vaičiukynienė D., Kantautas A., Vaitkevičius V., Sasnauskas V.** Using of modified AlF₃ production waste in cement-based materials. *Mater. Sci.* 2009. V. 15. N 3. P. 255-261. DOI: 10.5755/j01.ms.18.2.1925.
2. **Mahmoud B., Abbas T.** Investigation of different stages of aluminum fluoride crystal growth. *Chem. Chem. Eng.* 2005. V. 24. N 1. P. 27-32.
3. **Kubiliūtė R., Kaminskas R.** The pozzolanic activity of calcined clay – silica gel composites. *Mater. Sci.* 2013. V. 19. P. 453-460. DOI: 10.5755/j01.ms.19.4.2300.
4. **Vaičiukynienė D., Kantautas A., Vaitkevičius V., Sasnauskas V.** Effect of AlF₃ production waste on the properties of hardened cement Paste. *Mater. Sci.* 2012. V. 18. P. 187-191. DOI: 10.5755/j01.ms.18.2.1925.
5. **Vaičiukynienė D., Vaitkevičius V., Kantautas A.** Mechanochemical treated technogenic silica gel additive in Portland cement based materials Conference. 18 Internationale Baustofftagung IBAUSIL 12-15 September 2012. Weimar, Germany. 2011. V. 1. P. 0929-0934. DOI: 10.1016/j.cemconcomp.2011.08.009.
6. **Vaičiukynienė D., Borg R., Kielė A., Kantautas A.** Alkali-activated blends of calcined AlF₃ production waste and clay. *Ceram. Inter.* 2018. V. 44. P. 7-10. DOI: 10.1016/j.ceramint.2018.04.054.
7. **Kawai K., Osako M.** Reduction of natural resource consumption in cement production in Japan by waste utilization. *J. Mater. Cycles Waste Manag.* 2012. V. 14. N 2. P. 94-101. DOI: 10.1007/s10163-012-0042-4.
8. **Vaitkevičius V., Vaiciukyniene D., Kantautas A., Kartovickis A., Rudžionis Ž.** Blended cements produced with synthetic zeolite made from industrial by-product. *Mater. Sci.* 2015. V. 21. P. 136-143. DOI: 10.5755/j01.ms.21.1.5635.
9. **Vaičiukynienė D., Vaitkevičius V., Kantautas A., Sasnauskas V.** Utilization of by-product waste silica in concrete-based materials. *Mater. Res.* 2012. V. 15. N 4. P. 561-567. DOI: 10.1590/S1516-14392012005000082.
10. **Bocullo V., Vaičiukynienė D., Vaitkevičius V.** The influence of the silica/sodium ratio on the fly ash geopolymer binder. *Cheminė Technologija.* 2017. V. 1. P. 23-28. DOI: 10.1016/j.ceramint.2018.04.054.
11. **Bocullo V., Vaičiukynienė D., Kantautas A., Borg R., Briguglio C.** Alkaline activation of hybrid cements binders based on industrial by-products. *J. Sust. Arch. Civil En.* 2017. V. 19. P. 65-73. DOI: 10.5755/j01.sace.19.2.17836.
12. **Pishch I.V., Maslennikova G.N., Podbolotov K.B., Karizna Yu.A., Belyakovich I.V.** Silica based pigments. *Glass Ceram.* 2011. V. 68. N 3-4. P. 71-75. DOI: 10.1007/s10717-011-9324-x.
13. **Doneliene J., Vančukiniene D., Kantautas A.** The influence of aluminosilicate gel aging on the synthesis of NaX zeolite scientific. *J. Riga Technical University.* 2010. V. 22. P. 30-34.
14. **Vaičiukynienė D., Kantautas A., Vaitkevičius V., Jakevičius L., Rudžionis Ž., Paškevičius M.** Effects of ultrasonic treatment on zeolite NaA synthesized from by-product silica. *Ultrason. Sonochem.* 2015. V. 27. P. 515-521. DOI: 10.1016/j.ultsonch.2015.06.001.
15. **Fadi M., Trabzuni S.** US Patent N 8734750. Sodium silicate solutions. Publ. 2014-05-27.
16. **Fadi M., Trabzuni S.** US Patent N 8512664. Sodium silicate solutions. Publ. 2013-08-20.
17. **Fadi M., Trabzuni S.** US Patent N 8287833. Sodium silicate solutions. Publ. 2012-10-16.
18. **Fadi M., Trabzuni S.** US Patent N 8057770. Process for hydrothermal production of sodium silicate solutions and precipitated silicas. Publ. 2011-11-15.
19. **Fadi M., Trabzuni S.** US Patent N 7622097. Process for hydrothermal production of sodium silicate solutions and precipitated silicas. Publ. Nov 24, 2009.
20. **Estruga M., Meng F., Li L., Chen L., Li X., Jin S.** Large-scale solution synthesis of α-AlF₃·3H₂O nanorods under low supersaturation conditions and their conversion to porous β-AlF₃ nanorods. *J. Mater. Chem.* 2012. V. 22. P. 20991-20997. DOI: 10.1039/C2JM33782G.

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