Հայաստանի Գիտությունների Ազգային Ակադեմիա
Национальная Академия Наук Армении
National Academy of Sciences of Armenia

Հայաստանի Կենսաբանական Հանդես
Биологический Журнал Армении
Biological Journal of Armenia

• ***Փորձարարական և տեսական հոդվածներ*** •***Экспериментальные и теоретические статьи***•
•***Experimental and theoretical articles***•

Biolog. Journal of Armenia, 1 (68), 2016

SYNTHESIS SODIUM, POTASSIUM SILICATES FOR THERMOREGULATING COATINGS SPACE VEHICLES BY MICROWAVE METHOD

V.V. BAGHRAMYAN[1], A.A. SARGSYAN[2], V.V. HARUTYUNYAN[3]

[1,2] Institute of General and Inorganic Chemistry of NAS of RA,
[3] A.Alikhanyan National Laboratory (YerPhI)
v_bagramyan@mail.ru

Systematic investigation of the possibility of using microwave (MW) energy for obtaining of silicates as pigments for the thermoregulating coating for the first time has been carried. Were obtained sodium and potassium silicate solutions different composition by hydrothermal microwave (HTN MW) treatment diatomite. Kinetic regularities were studied and were revealed the conditions obtaining of sodium and potassium silicates solutions using MW heating. The effect of various factors on the degree of SiO_2 recovery and the reaction rate was studied. The optimal conditions of HTMW processing of diatomite to produce silicate solutions with maximum reaction yield were determined. The behavior of sodium and potassium silicates after UV irradiation was investigated. The studies demonstrate the efficiency of microwave heating for obtaining of silicate solutions from silica-containing rocks. It has been established that microwave heating leads to an acceleration of the process and energy savings.

Diatomite – sodium and potassium silicates – hydrothermal microwave (HTN MW) treatment

Առաջին անգամ ուսումնասիրվել է միկրոալիքային (ՄԱ) էներգիայի օգտագործման հնարավորությունը ջերմակարգավորիչ ծածկույթների համար սիլիկատային պիգմենտներ ստանալու նպատակով: Ստացվել են տարբեր բաղադրության նատրիումի և կալիումի սիլիկատային լուծույթներ դիատոմիտների հիդրոջերմային միկրոալիքային (ՀՋՄԱ) մշակման միջոցով: Ուսումնասիրվել են ՄԱ տաքացմամբ նատրիումի և կալիումի սիլիկատային լուծույթների ստացման կինետիկական օրինաչափությունները և որոշվել օպտիմալ պայմանները: Ուսումնասիրվել են տարբեր գործոնների ազդեցությունը SiO_2-ի կորզման աստիճանի և ռեակցիաների արագության վրա: Որոշվել են դիատոմիտի ՀՋՄԱ մշակման լավագույն պայմանները առավելագույն ելքով սիլիկատային լուծույթների ստացման համար: Հետազոտվել են նատրիումի և կալիումի սիլիկատների հատկու-թյունները ՈւՄ ճառագայթումից հետո: Ուսումնասիրությունները ցույց են տվել միկրոալիքային տաքացմամբ սիլիկատային ապարներից սիլիկատային լուծույթների ստացման արդյունավետու-թյունը: Հաստատվել է, որ միկրոալիքային տաքացումը հանգեցնում է պրոցեսների արագացմանը և էներգիայի խնայողությանը:

Դիատոմիտ – նատրիումի և կալիումի սիլիկատներ –
հիդրոջերմային միկրոալիքային (ՀՋՄԱ) մշակում

Впервые исследована возможность использования микроволновой (МВ) энергии с целью получения силикатных пигментов для терморегулирующих покрытий. Получены растворы силикатов натрия и калия различного состава гидротермально микроволновой (ГТМВ) обработкой диатомита.

Изучены кинетические закономерности и определены условия получения растворов силикатов натрия и калия с использованием МВ нагрева. Исследовано влияние различных факторов на степень извлечения SiO_2 и скорость реакции.

Определены оптимальные условия ГТМВ обработки диатомита для получения силикатных растворов с максимальным выходом. Изучены свойства силикатов натрия и калия после УФ облучения. Исследования показали эффективность микроволнового нагрева для получения силикатных растворов из кремнеземсодержащих пород. Установлено, что микроволновый нагрев приводит к ускорению и энергосбережению процессов .

Диатомит – силикаты натрия и калия – гидротермально микроволновая (ГТМВ) обработка

Thermoregulating coatings are used in space vehicles (SV) for the purpose of maintenance of their thermal regime. Nowadays it is provided with enamel and ceramic thermoregulating coverings of “solar reflectors” type on the basis of oxide pigments. Our analysis of scientific and technical information, experience and investigations in the field of synthesis of high-purity materials have shown that nanopowders of silicates of zirconium and zinc, doped with atoms of rare earth elements (REE) – yttrium, cerium, etc. – can be successfully used as pigments for solar reflectors [2-5, 10]. Preliminary studies indicated TRC on the basis of these materials will ensure their long-term operation in space. The use of silicate pigments for TRC is limited due to complicated technology of their obtaining. The stated materials are obtained on the basis of expensive high-purity chemical substances modified by nanopowders of definite compositions at high temperatures. The process of obtaining of nanocrystalline powders, as well as highpurity silicates of zirconium, zinc, etc. is multi-stage and prolonged, carried out at high temperatures. We have developed a hydrothermal-microwave (HTMW) method for the synthesis of nanocrystalline silicates that is more effective compared to solid phase or sol-gel methods. The aim of work is development of new compositions of thermoregulating coatings for space vehicles (SV) and new technology of their obtaining by original and perspective method – method of hydrothermal-microwave synthesis. Microwave heating provide contactless delivery of energy to the reacting fluids, high energy density possible, and short heating times in the range of minutes instead of hours. Microwave chemistry of obtaining silicate scarcely been studied. Developed method of obtaining of silicate by hydrothermal-microwave treatment is an effective method in comparison with the solid phase or zol-gel methods.

The first step is to develop a method of obtaining precursors from rocks for TRC. The essence of the method is the HTMW treatment of siliceous rocks by alkali solution to obtain sodium and potassium silicates. The developed method makes it possible to use siliceous rocks as a raw material for obtaining solutions of sodium and potassium silicates at low-temperature (90-200^{0}C) for synthesis of silicates zinc and zirconium. In the mass industry traditional methods for production of sodium and potassium silicate solutions include a two step process: a) melting of silica rock and sodium/ potassium carbonate mixture at 1450-14700C in the glass furnace to obtain “silicate blocks”; b) dissolution in water of “silicate blocks” in rotating autoclaves at high pressure and temperature of 170-1800C for 5-6 hours [1, 6-9, 11]. Disadvantages of traditional methods of the production of alkaline silicate solutions are: high energy requirements, expensive and multistage production process and release of carbon dioxide and sulphuric anhydride to the atmosphere. One of the directions of intensification and improvement of ecological cleanness of the production of alkaline silicate solutions is the development of efficient methods for their production. This goal could be reached using a hydrothermal microwave approach which excludes high-temperature melting.

As a raw material were used diatomites from Armenian deposites. The sodium silicate solutions (with silica module 1) will be used to obtain silicates of zirconium, zinc and pigments on their basis. Potassium silicate solution (with silica module 3-4) will be used as a binder when forming TR coatings. There is not any information about rock use in production of silicate pigment. The analysis of references has shown that for production of pure silicates the use of rock is consider impossible because of the high content of coloring impurities. The patent-literary analysis shows that known methods of clearing silicates and their solutions from coloring impurities do not ensure necessary minimum content of iron compound, as these systems are difficult to clear. The obtaining of pure silicate materials by HT MW method synthesis of silicate pigments for TRC on the basis of rocks has not been described in the scientific literature. Meanwhile, our study on obtaining high-purity silicates testify to possibility of expansion of a raw-material base for production of pure silicates from natural siliceous rocks. Diatomite is chosen for obtaining different silicates.

Materials and methods. As a raw material for the production of solutions of alkali silicates some diatomites from Armenian deposites were used with the following content of basic components (in *wt.%):* SiO_2 – 84.24; Al_2O_3 – 3.65; TiO_2 – 0.31; CaO – 1.80; MgO–1.05; Na_2O +K_2O – 0.36; Fe_2O_3 – 1.75; loss at calcinations and moisture – 6.84 (moisture – 3.30). Externally, diatomites are loose or lightly compacted deposits of white, light gray, yellowish or pinkish floury and easily pulverized porous material. Diatomites are easy sedimentary rocks consisting mostly of amorphous silica in the form of microscopic (0.002-0.3 mm) frustules of diatomic algae. Bulk density of diatomites is 300-800 kg/m^3, specific surface is 5-6 m^2/g. X-ray analysis has shown that diatomites are mainly amorphous substances. To heat diatomites by microwave radiation, its dielectric properties should be determined. Dielectric parameters of diatomite (dielectric permeability ε` = 7.42, tgδ = 0.525) allow performing MW heating for chemical reactions. High silica content in diatomites and its amorphous structure enable to use diatomite for obtaining silicate solutions.

Synthesis of sodium and potassium silicates from ground diatomite (particle size < 1.0 mm) was performed in "Samsung" CE1073AR microwave oven in an open glass. Synthesis was carried out at a frequency of 2.45 GHz and microwave power of 900 W. In parallel, synthesis at similar ratios of the initial components was carried out in a thermostat at the boiling point of the solution and mechanical stirring. Heating time of the reaction mixture to boiling point at microwave treatment was 3-4 minutes at a power of 900 W.

The concentration of initial solutions of sodium hydroxide in terms of Na_2O made 40-150 g/l of Na_2O, and the ratio of moles of sodium oxide solution and silicon dioxide was 0.1-1.0. The weight ratio of the liquid (alkaline solution) and solid (rock) phases (L:S) was 4.0 to 6: 1.

Potassium silicate solution will be used as a binder when forming TR coatings. For this purpose it is necessary to have the potassium silicate solutions with silica module 3-4.

The concentration of initial potassium hydroxide solutions was 40-50 g/l of K_2O, and the ratio of moles of potassium oxide solution and silicon dioxide in the rock was 0.1-1.0; L: S = 4.0 - 6.5: 1. Heating time of the reaction mixture to boiling point at microwave treatment was 3-4 minutes at a power of 900 watts.

The process kinetics was controlled by changing the silicon dioxide concentration in the solution and precipitation depending on time, the initial amount of alkali and microwave power. The quantity of SiO_2 in the sodium/potassium silicate was determined by gravimetric method.

X-ray analysis the solid phase (after filtration and grinding below 20 μm) were registered using diffractometer "DRON-2" (CuKα radiation).

Figs. 1-4 show the kinetic curves of diatomite interaction with sodium/potassium hydroxide at hydrothermal and hydrothermal-microwave treatment when obtaining sodium/ potassium silicates. As it is seen from fig. 1, 2 when preparing sodium/potassium silicate solutions under identical conditions, the rate of MW processing of diatomite using alkali solutions is higher by a factor of 2 - 3 as compared with the conventional method of heating, where as the reaction yield is practically the same.

When preparing solutions of sodium metasilicate, SiO_2 yield is 90%, and when preparing potassium tetrasilicate – 80% of the rock silicon oxide.

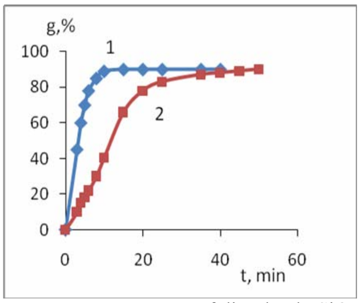

Fig.1. Degree of dissolved SiO_2 diatomite in obtaining $Na_2O{\cdot}SiO_2$ vs. the treatment time for: 1–MW-heating; 2– conventional heating.

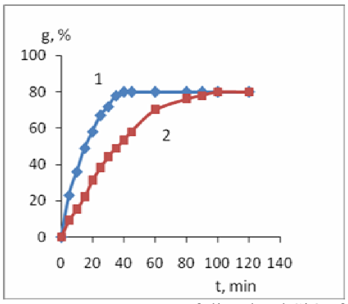

Fig.2. Degree of dissolved SiO_2 from diatomite in obtaining $K_2O{\cdot}\ 4SiO_2$ vs.the treatment time for: 1– MW-heating; 2 – conventional heating.

An important determinant of the properties and functional activity of a particular type of sodium/ potassium silicate is Silica Modulus, M, which indicates the ratio of SiO_2 and Na_2O/K_2O moles. Maximum silica modulus of the potassium silicate reaches 4.0 and that of sodium silicate – 3.3.

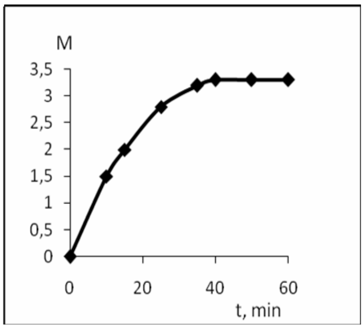

Fig.3. Silica Modulus, M (SiO_2/Na_2O) vs. the treatment time (t).

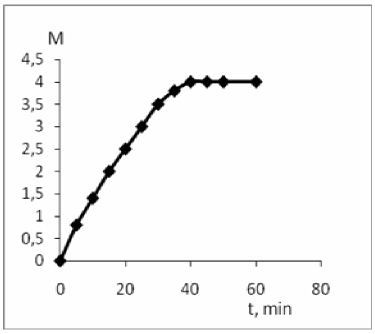

Fig.4. Silica Modulus M (SiO_2/K_2O) vs. treatment time (t)

The rate of the reactions producing silicate solutions depends on the type of alkali: treatment of rock by NaOH solution is faster than by KOH solution. On the basis of the obtained results, the following optimal conditions of HTMW processing of diatomite were determined to produce silicate solutions with maximum reaction yield. For obtaining sodium metasilicate: Na_2O concentration of 130 – 150 g/l, the ratio of liquid and solid phases (L:S) of 5.5 – 6.0, microwave oven power 900 W, T-100^oC, reaction time 15 min diatomite particle size less then 1 mm, reaction yield 90%.

When obtaining potassium liquid glass with modulus 4: K_2O concentration of 50 g/l, the ratio of liquid and solid phases (L:S) of 5.0, microwave power 900 W, T-100^oC, treatment time 40 min, diatomite particle size less then 1 mm, the reaction yield 80%.

The behavior of sodium and potassium silicates after UV irradiation was investigated: Some transmission spectra were measured in the wavelength range from 1 to 2.2 mkm for the samples subjected to UV radiation. Before the irradiation, the potassium and sodium silicates obtained by HTMV treatment of diatomite were dried. UV irradiation was carried out using various exposures UV radiation cycles: 30 to 150 min. After UV radiation the measurements of transmission/absorption spectra were carried out. The sample, powdered test substance was mixed with KBr in the ratio of 30 to 130 mg. Then the mixture was milled and pressed in tablets 20 mm in diameter using a special molding tool. The measurements of transmission/absorption spectra were carried out at regular intervals after UV radiation.

Results and Discussion. Thus, for the first time systematic investigation of the possibility of using microwave energy to produce silicate solutions from diatomite was carried out. Kinetic regularities were studied and the conditions for obtaining solutions of sodium and potassium silicates using MW heating were revealed. The rate of the reactions producing silicate solutions depends on the type of alkali: treatment of rock by NaOH solution is faster than by KOH solution. This is due to the fact that sodium ion (ion radius Na^+ is 0.102 nm), in aqueous solutions is more active than potassium ion (ion radius. K^+ is 0.138 nm). The ionic strengths of solutions of these cations are different because of different ionic radii at the same charges. Experimentally, the rate of heating of the reaction mixture and the exposure time for obtaining silicate solutions of given compositions were determined. The optimum parameters of HTMW processing of diatomite were identified. It was found that the compositions of intermediate and target products of synthesis of sodium/potassium silicate solutions are identical regardless of the heating method – microwave or convective. It was revealed that the use of microwave energy can significantly intensify the process of hydrothermal treatment of diatomite compared with conventional heating methods.

The carried out experiments have shown the effectiveness of the microwave heating in the preparation of silicate solutions from silica-containing rocks – diatomite.

The transmission (absorption) spectra of sodium and potassium liquid glass obtained from diatomite show that the UV radiation contributes to a defect formation in the crystal lattice and, thus contributes to an increase of the resistance of materials with respect to radiation sources.

Acknowledgment. *The work was supported by in frame of the ISTC Project A 2133.*

REFERENCES

1. *Ayler R.* Chemistry of silica. Transl. from English, in 2 vol., M., Mir, 1106 pp., 1982.
2. *Baghramyan V.V., Haroutunyan R.V., Sargsyan A.A., Meliksetyan A. M., Ghazaryan A.A., Petrosyan G.Kh, Leonelli C.* Microwave synthesis of vanadium – zircon pigments. Armenian chemical bulletin, Yerevan, *66*, 4, p. 578-587, 2013.
3. *Baghramyan V.V., Sargsyan A.A., Ghazaryan A.A., Haroutunyan R.V., Petrosyan G.Kh. Meliksetyan A.M.* Microwave synthesis and drying of zircon pigments' charges. Armenian chemical bulletin, Yerevan, *66*, 2, p.244-251, 2013.
4. *Baghramyan V.V., Sargsyan A.A., M.Meliksetyan A., Ghazaryan A.A., Leonelli, C.* Microwave synthesis alkaline metalls silicate solution. Armenian chemical bulletin, Yerevan, *66*, 1, p.49-56, 2013.
5. *Baghramyan V.V., Sargsyan A.A., Meliksetyan A. M., Ghazaryan A.A, Leonelli C.* The influence of microwave treatment on the formation kinetics of alkalinesilicate solutions. 2nd Global Congress on Microwave Energy Applications, Kalifornia, Book of Abstracts, p. 98, 2012.
6. *Joseph Pierr, Huhert Theunissen*. Preparation of sodium silicate, Patent EP 0363197 A2, registered on 5th Oct. 1989.
7. *John A., Kostinko*. Preparation of sodium silicate solutions, Patent, US 4539191A, Registered 3rdSept. 1985.
8. *Kitaygorodsky I. I.* The technology of glass. Moscow, 621 pp., 1961.
9. *Korneev V.I., Danilov V.V.* Production and use of soluble glass. Liquid glass. L. Stroyizdat, LO, 176 pp., 1991.
10. *Sargsyan A.A., Baghramyan V.V., Haroutunyan R.V., Leonelli C.*, "Hydrothermal-microwave synthesis of zircon". International Conference "Current problems of chemical physics", Ереван, 298 p., 2012.
11. *Wells A.F.* Structural Inorganic Chemistry 5th edition Oxford Science Publications ISBN 0- 9-855370-6. 1984.

Received on 18.01.2016