

ISTC Project No. A-2133p

**“New Technology of Obtaining of Thermoregulating Coatings for
Space Vehicles”**

**Annual Project Technical Report
on the work performed from 01.02.2015 to 31.01.2016**

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Title of the Project: New Technology of Obtaining of Thermoregulating Coatings for Space Vehicles

Contracting Institute: Institute of General and Inorganic Chemistry of the National Academy of Sciences of the Republic of Armenia

Participating Institutes: A.Alikhanyan National Laboratory (Yerevan Physics Institute)

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1. Brief description of the work plan: objective, expected results, technical approach

The purposes of the Project are

- Study of regularities and determination of optimal conditions for the production of solutions of silicates ($\text{Na}_2\text{O}\cdot n\text{SiO}_2$, $\text{K}_2\text{O}\cdot n\text{SiO}_2$) of controlled compositions from siliceous rocks by hydrothermal-microwave (HTMW) processing.
- Research aimed at the development of a method of cleaning of silicate solutions from coloring impurities by a combination of electromagnetic and microwave activation of silicate solutions.
- Research aimed at the development of a HTMW method of obtaining zinc and zirconium silicates using yttrium and cerium modified oxides. Study of physical, chemical properties and radiation resistance of crystalline and amorphous zinc and zirconium silicates.
- Research aimed at the development of compositions for thermoregulating coatings of "solar reflectors" type. Study of radiation-stimulated processes in irradiated silicate pigments.
- Development of a technology for thermoregulating coatings from siliceous rocks, meeting the parameters necessary for long-term operation of space vehicles under the impact of space environment.

Expected results

- Development of a HTMW method of obtaining solutions of silicates ($\text{Na}_2\text{O}\cdot n\text{SiO}_2$, $\text{K}_2\text{O}\cdot n\text{SiO}_2$) with predetermined properties on the basis on siliceous rocks.
- Development of a method of deep cleaning of silicate solutions from coloring impurities by a combination of electromagnetic and microwave activation of silicate solutions.
- Development a HTMW method of obtaining zinc and zirconium silicates and investigation of their physical, chemical and radiological properties.
- Development of compositions for thermoregulating coatings of "solar reflectors" type.
- Development of a HTMW technology for thermoregulating coatings.

Technical Approach and Methodology

The main novelties of the work carried out are the development of the hydrothermal-microwave (HTMW) method of processing of rocks to produce silicate solutions, the synthesis of pigment silicates using microwave chemistry, as well as the development of new compositions for thermoregulating coatings on the basis of the synthesized pigments.

To solve the problem of obtaining high-purity silicate solutions on the basis of siliceous rocks and silicates doped with different components, several detailed theoretical and experimental investigation of silicate formation processes were carried out. Sodium and potassium silicates were obtained from siliceous rocks (diatomite, perlite, quartz) on the basis of detailed theoretical and experimental studies of the interaction of rocks with alkaline solutions during the HTMW processing of the rocks within the temperature range of 100-240°C and the pressure range of $1\cdot 10^5$ - $20\cdot 10^5$ Pa. Physical, chemical and radiation characteristics of the rocks and the influence of various factors (the processing time, concentration of the initial solutions, degree of particle fineness, ratio of liquid and solid phases) on the kinetics of silicate formation processes were studied. Based on these studies, silicate solutions with predetermined characteristics were obtained by a single-stage method. During the experiments, a variety of physical and chemical methods of analysis were used to determine the composition and structure of several intermediate and final products.

The problem of cleaning of silicate solutions from coloring impurities was solved by combination of electromagnetic treatment and microwave heating with the deposition of the impurities in the form of complex salts using a collector. The structure and composition of the coloring impurities in the silicate solutions were determined by IR spectroscopy, X-ray diffraction, which allowed revealing the mechanism of formation of the coloring impurities compounds and selecting the optimum treatment conditions to obtain high-purity silicate solutions. The content of the coloring impurities in the silicate

solutions before and after the treatment was determined by atomic absorption spectroscopy, fluorometry, and polarography.

Using the HTMW method, $ZnO \cdot SiO_2 \cdot mH_2O$, $ZrO_2 \cdot SiO_2 \cdot mH_2O$ hydrosilicates were obtained from the purified silicate solutions and corresponding soluble zinc and zirconium salts on the basis of theoretical calculations and elemental analysis.

A method of doping of $ZnO \cdot SiO_2 \cdot mH_2O$, $ZrO_2 \cdot SiO_2 \cdot mH_2O$ hydrosilicates with rare earth elements directly during synthesis was developed. The structure, properties, composition and surface characteristics of the doped nanocrystalline silicates (pigments) were determined by BET, electron microscopy, IR spectroscopy, thermography, X-ray diffraction and elemental analysis. Electron microscopy study were carried out using FE - SEM, LEO1530 electron microscope. The characteristics of optical absorption spectra of silicate in the near infrared region of the spectrum were studied. The irradiation was carried out using ELU-5 linear electron accelerator at 90K, X-ray fluorescence analysis of the samples was performed using Thermo Scientific ARL QUANT'X Energy-Dispersive X-Ray Fluorescence (EDXRF) Spectrometer. All measurements were carried out in vacuum. Each sample was measured under eight different excitation conditions, which involve different X-ray tube voltage in the range from 4 to 50kV and corresponding primary beam filters. The problem of obtaining compositions for thermoregulating coating was solved by a detailed study of the radiation resistance, reflectivity, structural modifications of pigments, binder and coatings under the conditions of UV, vacuum UV and X-ray irradiation. It is proposed to obtain and test several samples of different compositions and to select optimum compositions of thermoregulating coatings. The developed new thermoregulating coatings will be tested at the Alikhanyan National Science Laboratory (ANSL) using a special facility for study of the effect of space environment factors (separately and combined) on the properties of the coatings. on the influence of space factors (individually and collectively) on the properties of the coatings. On the basis of the results to be obtained, a new siliceous rocks based technology of thermoregulating coatings using the hydrothermal microwave method should be developed for space vehicles.

2. Technical progress during the first year

Task Subtask	Start (quarter)	End (quarter)	Current Technical Status / Comments
Task 1	1	4	Work finished
Subtask 1.1	1	3	Work finished
Subtask 1.2	1	3	Work finished
Subtask 1.3	3	4	Work finished
Task 2	3	8	Be continued
Subtask 2.4	3	6	Work proceeds according to WP
Subtask 2.5	3	7	Work proceeds according to WP
Task 3	4	8	Work proceeds according to WP
Subtask 3.7	4	8	Work proceeds according to WP
Subtask 3.8	4	8	Work proceeds according to WP

3. Technical progress during the year of reference

Task 1. Development of the hydrothermal-microwave method for obtaining and clearing of silicate solutions ($Na_2O \cdot nSiO_2$, $K_2O \cdot nSiO_2$, $n=1-3,8$) on the basis of silica containing rocks. Study of physical, chemical and radiation properties of silicate materials for TRC over a wide range of parameters.

Stage A1. Study of conditions and investigation of chemical regularities of the hydrothermal-microwave method when obtaining sodium, potassium silicates solutions from silica containing rocks (perlite, diatomite, etc.). The hydrothermal microwave treatment will be conducted at the conditions that ensure obtaining of silicate solutions with predetermined characteristics.

X-ray fluorescence analysis of chemical composition of sodium, potassium silicates and silica containing rocks.

The impact of UV radiation on physical characteristics of silicate materials in extreme conditions (high vacuum and temperature interval from -110 to +200°C).

Thermoregulating Coatings (TRC) are used in various areas, particularly in aerospace engineering to protect space vehicles (SV) from aggressive radiation and control the SV surface thermal regime. The TRC materials for SV should have low absorption coefficient (α_s) high reflection coefficient (ϵ) in a wide radiation range, as well as high radiation resistance.

Ionizing radiations: In space, there are only two kinds of radiation: electromagnetic and corpuscular. The main sources of these emissions are the sun and the galaxy. In this connection, in all directions, including toward the earth, the following types of ionizing radiation are propagated:

- galactic cosmic rays;
- electromagnetic solar radiation;
- solar wind;
- solar cosmic rays.

Galactic cosmic rays: As galactic cosmic rays have relatively low flow intensity, they are practically not dangerous to reflective coatings within a lifetime of less than 10 years, so they will not be considered.

Electromagnetic Radiation: Electromagnetic solar radiation (ESR) is a quantum flux with energy from X-ray to the near infrared region.

The energy of ESR quanta is determined from the following relationship:

$$E = 1240/\lambda,$$

where the energy is in eV, λ is the wavelength in nanometers.

From the above formula it is seen that the major part of ESR quanta has energy less than 5-6 eV.

Solar wind: Solar wind is a flow of plasma propagating from the Sun in all directions, including toward the Earth, at a speed of 400 km/s. Its traveling time from the Sun to the Earth is about 4 days. The positive component of the plasma are protons (about 96%) and α - particles (about 4%), its negative component are electrons. The energy of protons is up to 3 keV, the energy of electrons makes 10-20 eV. The proton flow density reaches a few protons per $10^8 \text{ cm}^{-2}\cdot\text{s}^{-1}$.

Solar cosmic rays: Chromospheric Sun flares may be accompanied by emission of high-energy particles, solar cosmic rays (SCR) into interplanetary space. Solar cosmic rays consist mainly of protons, owing to this the flares generating them are called proton flares. The nucleonic component of the SCR includes nuclei of helium and heavier elements up to iron. They also include electrons. Proton flares create a powerful X-ray and radiofrequency emission. The content of α -particles in corpuscular flows emitted by flares, is not constant and varies from 10 to 0.3%. Usually, the share of α -particles makes 0.8 - 2.5%. During the increase of the flow to maximum the share of α -particles reduces to approximately 0.7%. The flows of heavier nuclei are ten times less than α -particle flows.

Charged particles trapped by the Earth's magnetic field: A special factor of cosmic space are Van Allen radiation belts (RB) originated from the capture of charged particles by the Earth's magnetic field. As a result, the Earth's magnetosphere is filled with electrons, protons and ions of various energie.

Figure 1 shows the structure of the Earth's magnetosphere and RBs. When contacting the solar wind with the geomagnetic field, a shock wave is generated followed by a transition region, and then – magnetopause, a boundary of the geomagnetic field. The night side of the Earth's magnetic field is essentially stretched, forming the so-called magnetospheric tail with a plasma layer. The radiation trapped by the geomagnetic field fills the zones of stable capture and quasi-capture. Just these areas are of the most interest in view of the impact of charged particles of Van Allen radiation belts on SV coatings.

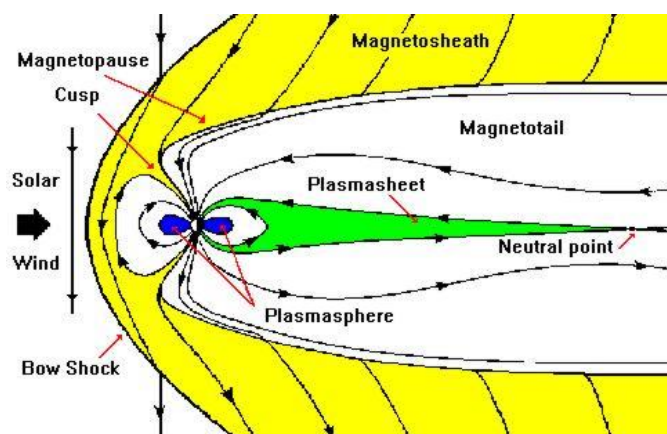


Fig.1 Scheme of radiation fields in the Earth's magnetosphere

There are two belts in the trapped radiation: internal and external ones (Fig. 1). The division into two belts is rather arbitrary and is related to the spatial distribution of electron flows with two expressed maxima of intensity. The sources of the internal belt electrons are cosmic rays and particles injected during strong magnetic storms. The energy of the particles reaches hundreds keV. The sources of the external belt electrons are the solar wind electrons. The spatial distribution of intensity of electron flows are subject to significant variations that are determined by the phase of solar activity, magnetic disturbances, the 27-day solar cycle period and the time of day.

The proton component of RBs is very stable over time (especially at high energies). There are also internal and external proton belts, but the spatial distribution of proton flow does not coincide with that of electron flow; in particular, the intensity of proton flow reaches its maximum in the gap between the internal and external electron belts. The internal zone encloses high-energy protons. Their source are albedo neutrons of cosmic rays, i.e. the interaction of protons and ions of cosmic origin with atmosphere generates neutrons that secondary interact with gases and form high-energy protons ($E > 30 \text{ MeV}$). The external radiation belt is filled with protons of lower energies ($E < 30 \text{ MeV}$), their sources are solar wind protons.

Along with protons and electrons, the Earth's magnetosphere captures α -particles and heavier ions, but their content in the radiation belts is small.

Table 1. Parameters of galactic and solar cosmic rays, Van Allen radiation belts and hot magnetospheric plasma

Type of corpuscular cosmic radiation	Structure	Energy of the particles, MeV	Flow density, $\text{m}^{-2}\cdot\text{s}^{-1}$
Galactic cosmic rays	Protons (p) He (α) nuclei Hevier nuclei	$10^2 - 10^{15}$	$1,5 \cdot 10^4$ 10^3 $1,2 \cdot 10^4$
Solar cosmic rays	Protons (p)	$1 - 10^4$	$10^7 - 10^8$
The Earth's radiation belts	Protons (p) Electrons (e)	1-30 > 30 0.1-1.0 > 1.0	$3 \cdot 10^{11}$ $2 \cdot 10^8$ $1 \cdot 10^{12}$ $1 \cdot 10^{10}$
Hot magnetospheric plasma	Protons (p) Electrons (e)	$10^{-3} - 10^{-1}$	$10^{11} - 10^{14}$

Cosmic radiation makes about 16% of the total natural background radiation on the Earth's surface, and almost half of external radiation received by the population from natural sources of radiation: the average dose of external radiation from earth sources is 0.35 mSv, while cosmic rays give external dose of 0.3 mSv. Here, the dose of internal exposure from earth sources is more than 1.3 mSv, and from cosmic rays less than 0.02 mSv. The CI flows irradiate the entire Earth, but uneven: for example, the

North and South poles receive more radiation than equatorial regions because Earth's magnetic field deflects the charged particles that constitute the major part of cosmic rays. The composition, flow density and energy spectra of particles in natural earth radiation belts depend on the time of variations, mainly related to the processes occurring in the Sun (Fig.2). Here, the inner radiation belt is not practically subject to time variations and the external natural earth radiation belt varies greatly in time. Therefore, the radiation belts are a serious danger during long flights in near-Earth space. The flows of low-energy protons can damage the solar cells and cause turbidity of thin optical thermal coatings.

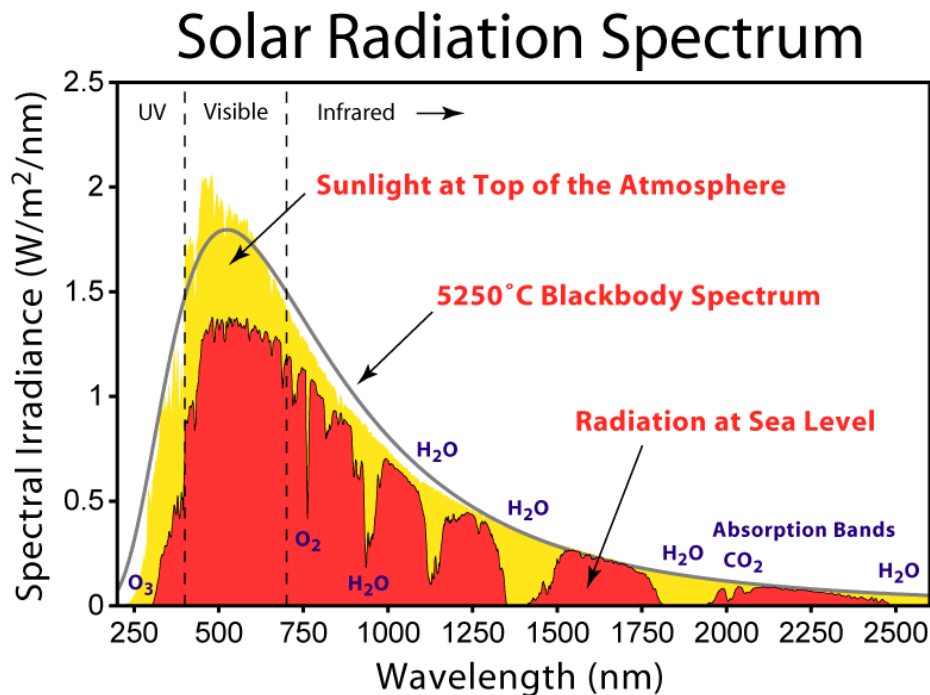


Fig. 2. Solar radiation spectrum

Physical characteristics of SV thermomaterials, interaction of particles with thermoregulating coatings (TRC). Despite the fact that by now considerable experience is gained regarding the behavior of materials and the individual structure units during cosmic flight, continuous complication of flight programs and update of the element base of cosmic facilities require the development of persistent, reliable products of space technology.

The basic trend of modern cosmic instrumentation engineering is increase of SV active over 10 years.

Therefore, it is advisable to use the methods of physical modeling to study thoroughly the behavior of SV materials in conditions of ground forced impact of main cosmic space factors (CSF): deep vacuum, flows of charged high-energy particles, electromagnetic solar radiation, thermal cycling, etc.

The active thermoregulating systems are special shutters connected by a piping system filled with circulating working medium, liquified gas. Depending on the thermal load, opening angle of the shutters varies to control the amount of removed heat into space. These systems are bulky, heavy and require special operation control. Therefore, along with them it is necessary to use some passive thermoregulating systems that do not require operation control. There is a number of compositions for thermoregulating coatings of "solar reflectors" type, which include enamel and ceramic coating based on pigments with organic and inorganic binders that are deposited on SV external surfaces. The temperature of SV at passive thermoregulating is determined by the amount of absorbed solar energy, which depends on integral coefficient of absorption of solar radiation and the amount of heat generated by onboard equipment and radiated into space. In SVs the largest covered areas are just stable thermoregulating coating of "solar reflectors" type, which are designed to reflect electromagnetic solar radiation and re-emit into space the heat generated by onboard equipment.

Therefore, knowledge of the physico-chemical characteristics, their sensitivity to prolonged impact of exposure of CSF allows selecting the most stable and predictable material of thermoregulating coating to develop passive thermoregulating systems for long-lived SVs.

One of the main objectives of the project is the application of methods of physical modeling for a comprehensive study of the behavior of SV materials in conditions of ground forced impact of main cosmic space factors (CSF): deep vacuum, flows of charged high-energy particles, electromagnetic solar radiation, thermal cycling, etc.

Interaction of particles with thermoregulating coatings (TRC): A review of the literature on the effect of high-energy particles on physical properties of different kinds of thermoregulating particles was carried out. The use of electrostatic accelerators and burst-type generators in laboratory experiments to create particle flows on the basis of condensed explosives allowed investigating the effects of particles interaction with thermoregulating coatings (TRC) of different types at the impact velocity of 0.5^{10} km/s. As particles, powders of various metals and metal compounds sized from 1 to 50 microns were used. The studies were conducted in vacuum chambers at residual pressures of 10^{-2} , 10^{-4} and 10^{-5} (in the case of electrostatic acceleration) mm Hg. As TRC, some samples currently employed in SV were used. The main objectives of the experiments was to determine the character of interaction between TRC and particles and to evaluate the As changes depending on the particles flow characteristics and materials, as well as degradation parameters.

The results of these experiments allow predicting the state of TRP exposed to radiation in space environment for a long time. Here, it is necessary to use experimental data on the parameters of craters at high-speed interaction (size dependence on the particle speed and mass), and the distribution of micrometeoroid and technogenic particle flows in near-Earth space. Thus, it is possible to obtain an approximate picture of the evolution of TRC coefficients (As and e) in SV working conditions. The degree of change in TRC parameters can be considered directly proportional to the fraction of the surface area occupied by the defects formed as a result of interaction with the particle flow. Accordingly, the change in optical properties of the surface is not linear, is most remarkable at low levels of surface damage, and has the character of a saturating process. The observed changes in optical characteristics due to the physics of the particles interaction with TRC of various types allow specifying the initial data on As and e degradation as well as SV thermal regime. According to, for one year of SV operation the particle flow of $\sim (0.05 - 0.25)10^6 \text{ m}^{-2}\times\text{s}^{-1}$ can affect on 1 m^2 of its outer surface depending on the orbit parameters, time of year, and etc. Here, As increases by a factor of $\sim 1.5 - 2$. The results of such research can be used in mathematical modeling of the functioning of thermoregulating systems to solve the problems related to the analysis of the effect of micrometeoroid and technogenic particles in the near-Earth space on violations of the SV thermal regime.

So, in radiation resistance (resistance to UV radiation, flows of electrons, protons, γ - radiation, etc.) and optical properties of TRC materials affect the surface TRC structure, particle size of TRC pigment powders, quality and quantity of the elements modifying their properties. When working in extreme outer-space conditions, their physico-mechanical and chemical characteristics change and reduce their lifespan.

The problem of increasing the radiation resistance of pigments for TRC in extreme conditions can be addressed in different ways: the development of new compositions, modification methods, production of pigments with appropriate structure and particle size.

It is known from the analysis of the scientific and technical literature that SV materials are obtained on the basis of white oxide pigments. These materials are prepared from expensive high-purity chemical substances by modifying certain compositions of their nanopowders at high temperatures. The process of their manufacture is multi-stage, long-term and inefficient. So, to manufacture TRC, there is a need to develop new compositions and innovative methods for their preparation using cheap materials. Our previous work in the area of obtaining high-purity silicates from rocks, development of hydrothermal microwave (HTMW) methods for the synthesis of pigments has shown that nanopowders of zirconium, zinc, etc. silicates may be used as pigments for solar reflectors. Preliminary studies indicated TRC on the basis of these materials will ensure their long-term operation in space.

In recent years, promising opportunities opened the application of microwave (MW) heating for chemical processes. MW radiation provides a contactless and rapid heating of reaction media in the entire volume. Microwave chemistry for obtaining silicates is insufficiently studied. 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 developed method makes it possible to use siliceous rocks as a raw material.

Objective: 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.

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 initial rocks by alkali solution to obtain sodium and potassium silicates.

There is no information on using rocks in the production of silicate pigments. Our analysis of publications has shown that in production of pure silicates the use of rocks is considered as impossible because of high content of impurities. The analysis of patent information shows that known methods of cleaning silicates solutions from impurities do not ensure necessary minimum content of iron compound, as it is difficult to clean these systems. The obtaining of pure silicate materials by a new HTMW method synthesis of silicate pigments on the basis of rocks for TRC has not been described in the scientific literature. Meanwhile, our study on obtaining high-purity silicates testifies to the possibility of expansion of a raw-material base for production of pure silicates from natural siliceous rocks. Perlite, quartzite, diatomite are chosen for obtaining different silicates.

Obtaining of sodium/potassium silicates from natural rocks: diatomite, perlite, quartzite: Hydrothermal microwave treatment of diatomite, perlite and quartzite has been carried out under various conditions with the purpose of obtaining sodium and potassium silicates.

Obtaining of sodium/potassium silicates. In recent years interest in the solutions of alkaline silicate has significantly increased, mainly due to their valuable properties, ecological cleanness of their production, non-flammability, cheapness and availability of raw materials. In the mass industry traditional methods for production of sodium and potassium silicate solutions include a two step process: a) melting of quartz sand and sodium/potassium carbonate mixture at 1450-1470°C in the glass furnace to obtain "silicate blocks"; b) dissolution in water of "silicate blocks" in rotating autoclaves at high pressure and temperature of 170-180 °C for 5-6 hours. 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. Some possibilities of obtaining silicate solutions from silica rock by hydrothermal-microwave (HTMW) method were studied and conditions of their production were developed.

As a raw material for the production of solutions of alkali silicates, some diatomite, perlite, quartzite from Armenian deposits were used.

Diatomite are loose or lightly compacted deposits of white, light gray, yellowish or pinkish floury and easily pulverized porous material. Diatomites are easy organic, sedimentary rocks consisting mostly of amorphous silica in the form of microscopic (0.002- 0.3 mm) frustules of diatomic algae. The frustules have the form of hollow bivalve double-leaf cups with different patterns. Bulk density of diatomites is 300-800 kg/m³, specific surface is 5-6 m²/g. with the following content of basic components (in wt.%): SiO₂ – 84.24; Al₂O₃ – 3.65; TiO₂ – 0.31; CaO – 1.80; MgO–1.05; Na₂O +K₂O – 0.36; Fe₂O₃ – 1.75; loss at calcinations and moisture - 6.84 (moisture - 3.30).

X-ray analysis has shown that diatomite are mainly amorphous substances.

High silica content in diatomites and its amorphous structure enable to use diatomite for obtaining silicate solutions. Fig.3 and Fig.4 presents some samples of diatomite, - electron microscopic photo of diatomite.



Fig.3. Samples of diatomites of the Jradzor deposit in Armenia

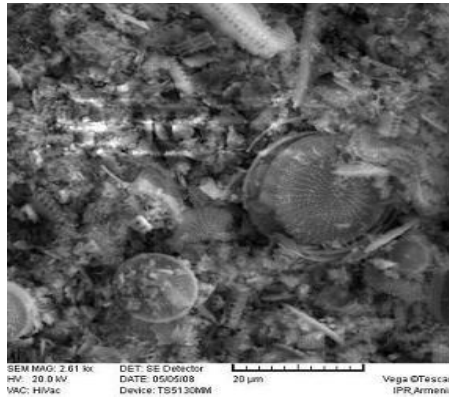


Fig.4. Electron microscopic photo of diatomite of the Jradzor deposit in Armenia

Perlite is an acidic volcanic glass-rich rock. Physical and mechanical characteristics of perlite rocks are determined by their origin (genesis). Formation of perlite rocks in Armenia is related to young volcanism). The Petrographic characteristics are as follows: perlites of the Armenian deposits are fine-pored, glassy rocks; they are grey, light grey, whitish, grey-brown, brown in color, and characterized by perlitic or other structure and fluidal texture. It is significant that there is extremely slight amount of crystalline phase (0-4%) in it. Principal components of perlite are silica, alumina and alkaline metals' oxides, and the content of the main coloring components, iron oxides is rather high. Perlite rocks do not contain any organic matters. As raw material for the production of the alkali silicate solutions, perlites of the Aragats deposit were used. Their content of main components in (wt.%) is: SiO_2 - 73.7, Al_2O_3 - 13.58, Na_2O - 3.85, K_2O - 4.14, Fe_2O_3 - 0.82, MgO - 0.4, CaO - 0.8, , ignition losses (removal of combined water) - 2.7, average particle size after grinding – below $250 \mu\text{m}$. Bulk density of perlites in a piece is from 750 to 2200 kg/m^3 . According to the data of physico-chemical analysis, the chemical composition of perlites may be presented by an empirical formula: $\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$. Fig. 5 and 6 show the Aragats deposit perlite samples and their electron microscopic photo.



Fig. 5. Samples of perlite of the Aragats deposit

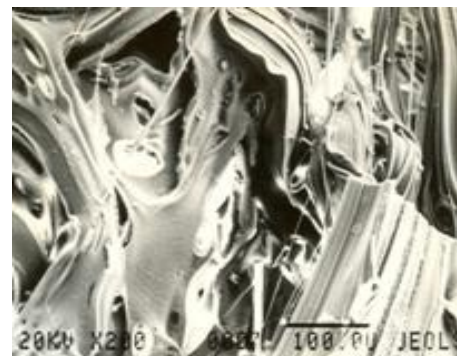


Fig.6. The electronic-microscopic photo of perlite of the Aragats deposit.

Quartzites are natural siliceous rocks with a high content of silica. Quartzites belong to the metamorphic rocks formed from quartz sandstones under the influence of high temperature and pressure. They are massive, in some cases laminated, fine- and medium-grained rock consisting of quartz grains cemented by silica. Quartzites are hard materials (Mohs hardness: 7) with a high fire resistance. Soft quartzites form in the course of tectonic movements followed by leaching of readily soluble materials. Natural cleavages of bluish and white quartzite rocks differ from each other in sizes of quartz crystals. Most often quartzites are formed during sandstone recrystallization. As the rock

name implies, quartzites are represented mainly by quartzes (80%). Quartzites also include mica, feldspar, talc, and some other minerals. In accordance with other minerals contained in quartzites, we distinguish mica, garnet, corniferous and other quartzites. Ferrous (or chemogenic) quartzites are formed from siliceous gels of chemogenic origin. They have high silica content that contributes to their high mechanical strength and fire resistance.

Quartzite is very strong rock, various examples of which may have relatively monotonous color from white to gray and reddish-brown. Sometimes appearance of quartzite fracture presents a mesh formed by solidified quartz crystals that fill the cracks in the rock mass. The structure is granular (often granoblastic), aphanic. The texture is massive, foliaceous, spotty. The electron microscopic investigations of quartzites using Vega-Tescan gear were carried out. Natural chips of quartzite rock of bluish and white colors differ from each other in sizes of small quartz crystals. Their sizes make from 5 up to 20 micron. Fig.7 presents a photo and microstructure of quartzites.

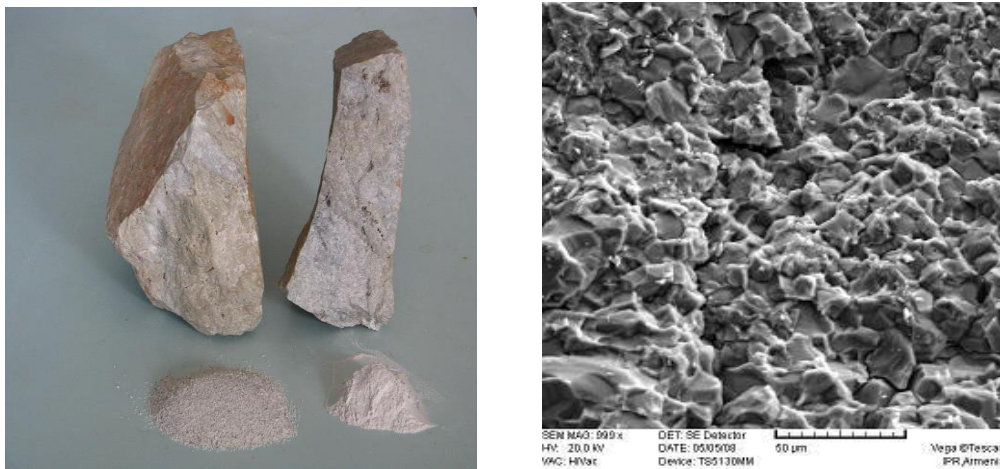


Fig.7. Samples and electron microscopic photo of quartzite of the Shakhnazar deposit (Armenia).

In the present study we used quartzite from Shahnazars deposit (Armenia) with the following average chemical composition (weight. %): SiO_2 : 94.13; Al_2O_3 : 3.12; $\text{Na}_2\text{O} + \text{K}_2\text{O}$: 0.17; Fe_2O_3 : 0.80, MgO : 0.08; CaO : 0.45; TiO_2 : 0.20. The physical properties of quartzite are as follows: the average density makes 2.68 g/cm^3 , compressive strength is 100-450 MPa, resistance to fire reaches 1770°C .

Fluorescent element analysis was carried out using X-ray radiation for chemical compounds of diatomoite, perlite, quartzite. X-ray fluorescence analysis of the samples was performed using Thermo Scientific ARL QUANT'X Energy-Dispersive X-Ray Fluorescence (EDXRF) Spectrometer. All measurements were carried out in vacuum. Each sample was measured under eight different excitation conditions, which involve different X-ray tube voltage in the range from 4 to 50kV and corresponding primary beam filters. Acquired eight spectra were analysed using UniQuant standardless analysis software.

The chemical composition of rocks measured by XRF analysis shows in the Fig. 8-10.

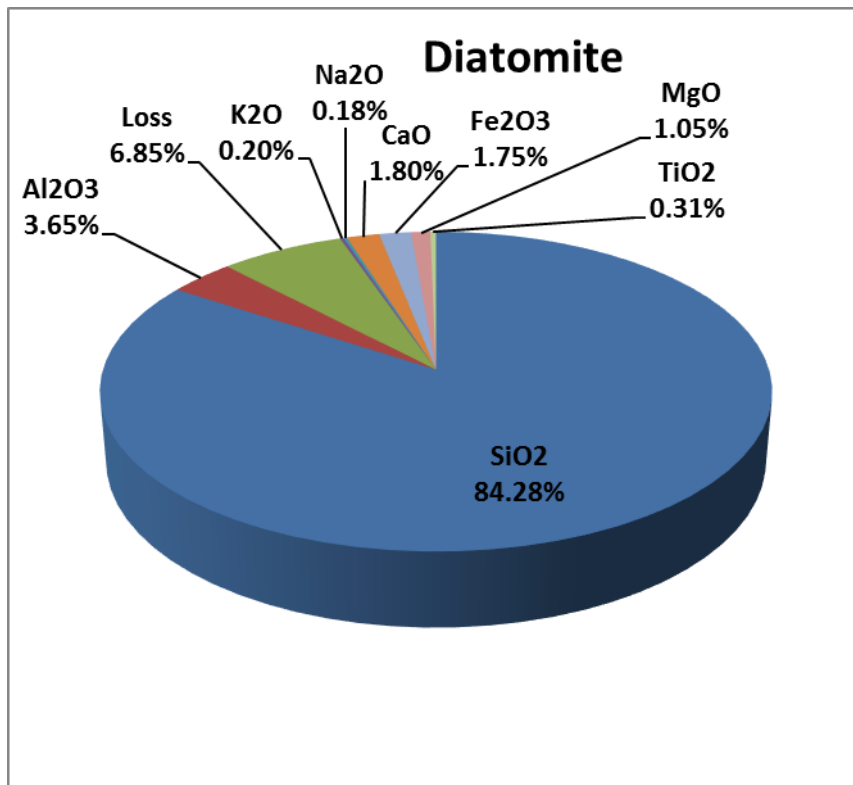


Fig. 8. Chemical composition of diatomite measured by XRF analysis.

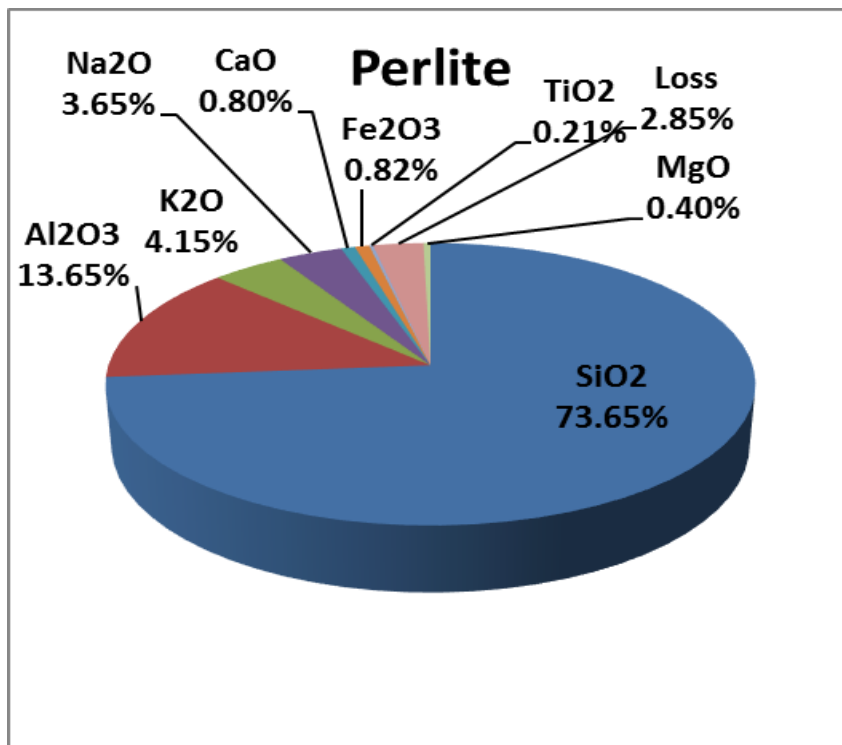


Fig. 9. Chemical composition of perlite measured by XRF analysis.

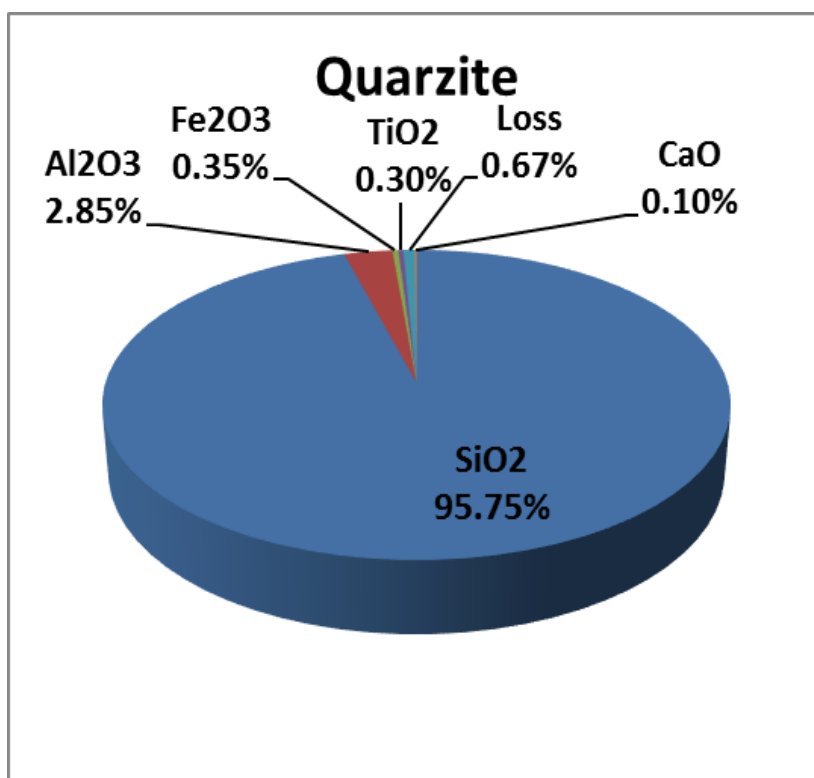


Fig. 10. Chemical composition of quartzite, measured by XRF analysis.

To heat samples of diatomites, perlite, quartzite by microwave radiation, its dielectric properties determined. Dielectric parameters of diatomite -dielectric permeability $\epsilon' = 7.42$, $\text{tg}\delta = 0.525$; of perlite $\epsilon' = 7.354$, $\text{tg}\delta = 0.2585$; of quartzite $\epsilon' = 6.03$, $\text{tg}\delta = 0.0194$.

Dielectric parameters of diatomite, perlite, quartzite allow performing MW heating for chemical reactions.

Radiation resistance of rocks. It is known that natural rocks have a certain petrochemical composition formed in certain geological conditions and characterized by various radioactivity. The basic factor of radioactivity of rocks is their content of uranium, thorium, their decay products, potassium and rubidium. Availability of radioactive elements such as uranium and thorium and their families in perlites has resulted in the need to study the radioactive properties of rocks to develop recommendations for their use as raw materials for silicate solutions for TRC. The object of research were perlites of different density: porous (1400 kg/m^3), low-porous (1600 kg/m^3), compact (1900 kg/m^3) varieties. Comparative data on abundance ratio of radioactive elements in acidic crustal rocks with their content in perlites of the Aragats deposit are shown in Table 2.

Table 2

The amount of radionuclides in perlites

Characteristics of the rock	U, wt.%	Th, wt.%	K, wt.%	Rb, wt.%
Abundance ratio of acidic rocks	$3.5 \cdot 10^{-4}$	$18.0 \cdot 10^{-4}$	3.34	-
Perlite : 1400 kg/m^3	$2.9 \cdot 10^{-4}$	$22.0 \cdot 10^{-5}$	3.8	$3 \cdot 10^{-3}$
1600 kg/m^3	$3.8 \cdot 10^{-5}$	$25.0 \cdot 10^{-5}$	3.0	$3.0 \cdot 10^{-3}$
1900 kg/m^3	$2.4 \cdot 10^{-4}$	$22.0 \cdot 10^{-5}$	4.0	$5.0 \cdot 10^{-3}$

The sample radiometry was carried out jointly using UMF-3 type device with low background (“ditch” method) and UMF-1500M (thick layer of the sample). As detectors, SI-16 and SBT-13 -counters were used, respectively.

Table 3 shows the specific and effective specific activities of perlites, as well as the content of radionuclides in their samples.

Table 3

Effective specific activity of perlites from the Aragats deposit

Perlite rock characteristics	Specific activity, curie/g			
	²²⁸ Th	²²⁶ Ra	⁴⁰ K	C eff
1400 kg/m ³	1,9	3,0	26	7,7
1600 kg/m ³	1,6	2,2	30,0	6,8
1900 kg/m ³	1,6	2,0	31,0	6,8
Heat-treated perlite	2.5	2.8	31.0	8.7

From our experimental results, we conclude that perlite with such radioactive properties is a successful raw materials for silicates.

Experiments. Synthesis of sodium and potassium silicates from ground diatomite, perlite, quartzite (particle size < 1.0 mm) was performed in microwave oven. Synthesis was carried out at a frequency of 2.45 GHz and microwave power of 900 watts. The synthesis was carried out with exposure times of 3 minutes to 4 hours. The resulting solution of sodium/potassium silicate was separated from the precipitate by filtration. Determination of SiO₂ in the solution of sodium/potassium silicate was performed gravimetrically by dissolving the solution of sodium/potassium silicate in hot water, double dehydration of silicic acid in hydrochloric acid medium, separation and calcination of the precipitate, distilling off the silicic acid as silicon tetrafluoride. Determination of Na₂O/K₂O was performed by acidimetric method: acidimetric titration of sodium silicate solution using methyl orange.

X-ray analysis the solid phase (after filtration and grinding below 20 μm) were registered using diffractometer "DRON-2" (CuKα radiation) and Differential thermal and thermal gravimetric analysis up to 1500 °C were performed using MOM Derivatograph (Hungary).

Obtaining of sodium and potassium silicate solutions from rocks. Sodium /potassium silicates are obtained using HTMW processing of diatomites diatomites, perlite, quartzite by sodium / potassium hydroxide solution . The sodium silicate solutions will be used to obtain metasilicates of zirconium, zinc and pigments on their basis. 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.

Obtaining of silicate solutions from diatomite. Synthesis of sodium and potassium silicates from ground diatomite (particle size < 1.0 mm) was performed in "Samsung" CE1073AR microwave oven destined for chemical processes in an open glass flask equipped with a backflow condenser and teflon mixer (Fig. 11). Synthesis was carried out at a frequency of 2.45 GHz and microwave power of 900 watts. 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. The synthesis was carried out with exposure times of 3 minutes to 3 hours .

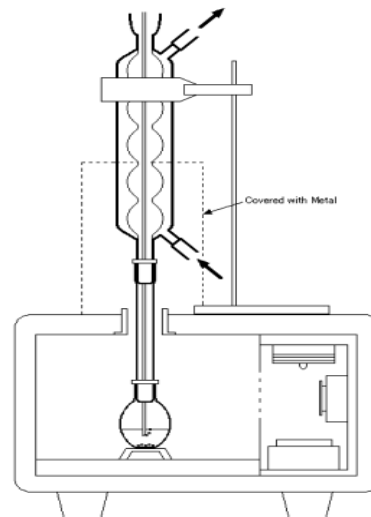


Fig.11.The microwave oven SAMSUNG“CE1073AR”.

Obtaining of sodium silicate solutions. Sodium silicates are obtained using HTMW processing of diatomites by sodium hydroxide. Since the diatomite contains organic substances, annealing was conducted at 600°C to remove organic components (about 2-2.5%). The experiments were performed with source and heat-treated diatomite samples. 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. Heating time of the reaction mixture to boiling point ($T= 100^{\circ}\text{C}$) at microwave treatment was 3-4 minutes at a power of 900 watts.

Obtaining of potassium silicate solutions. Potassium silicates were prepared by HTMW treatment of diatomite with potassium hydroxide solution. 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.

Obtaining of silicate solutions from perlite. Hydrothermal microwave (HTMW) treatment of perlite was carried out under different conditions with the purpose of obtaining sodium and potassium silicates. The perlites contain silica in an alkali-aluminosilicate frame and unlike diatomite, higher temperatures are required to extract it from the perlites. At 100°C the rate of reaction of perlite interaction with alkali solutions is quite low, so the HTMW treatment was carried out at higher temperatures and pressures than the when processing diatomite. The HTMW treatment was performed in an ETHOS TC (Milestone, Torre Boldone, Bergamo, Italy) multimode microwaves applicator, operating at the frequency of 2.45 GHz and output power of 500 Watts(Fig.12). Initial concentration of sodium hydroxide solutions in terms of Na_2O was 60-200 g/l Na_2O , which of potassium hydroxide solutions in terms of K_2O was 80-120 g/l K_2O . The mole ratio of sodium/potassium oxide solution and the SiO_2 -containing perlite (indicated as C) varied between 0.1 and 1.0. The total amount of the solution used was 4-12 ml, the perlite weight was fixed to 1- 6 grams. The weight ratio of the liquid (alkaline solution) and solid (rock) phases (L: S) was 1.5 to 7. The HTMV treatment was conducted at $100 - 200^{\circ}\text{C}$. Reaction temperature and pressure were automatically monitored during each dissolution cycle by temperature and pressure monitoring devices. Several sodium/potassium silicate solutions were obtained from perlites with various silicate modules. For comparison, hydrothermal treatment of perlites was carried out in conditions of conventional heating in an electric furnace using stainless steel autoclaves. After the hydrothermal treatment the solution was separated by filtering from the undissolved rock, precipitate. The obtained silicate solutions and precipitate were subjected to physical and chemical analysis. The filtration processes were studied when separating the sodium/potassium silicate solutions from precipitate. The filtering period was time required to filter 300 ml of pulp through a filter cloth (at a filter pressure of $8.1 \cdot 10^4$ Pa). The dependence of the filtration time on

the solution temperature at the initial solution density $\rho = 1.3 \text{ g/cm}^3$ (at 20°C) as well as the dependence of the filtration time on the solution density at 90°C were studied. The filtration time decreased with increasing temperature, as expected, as well as with decreasing density and viscosity of the pulp. The filtration time at 90°C made one-third of the filtration time at room temperature testifying to the necessity of "hot" filtration in case of large volumes.



Figs.12. «ETHOS" microwave oven

Obtaining of silicate solutions from quartzite. HMTW processing of quartzite was carried out at temperatures $100 - 240^\circ\text{C}$ in Teflon containers with a volume of 100 ml in a multimode microwave applicator in a 1000 Watt microwave oven MC-6 (VOLT Company) at a frequency of 2.45 GHz (Fig. 13).



Fig.13. Microwave oven MS-6.

Temperature and pressure were automatically controlled by corresponding monitoring devices. In the course of the experiments, pressure in the containers varied from $5 \cdot 10^5$ to $2 \cdot 10^6$ Pa, power from 50 to 100 W, temperature from 100 to 220°C , exposure from 15 to 120 minutes. Concentration of the initial solutions of sodium hydroxide was 1.0-3.0 M, that of potassium hydroxide - 1.0 M, and the ratio of moles of sodium/potassium oxide solution and silica rock (C) varied from 0.1 to 1.0. For comparison, hydrothermal treatment of quartzite was also performed by conventional heating in an electric furnace using stainless steel autoclaves. After treatment, the solution of sodium/potassium silicates was

separated from the residue by filtration. Solutions of sodium silicates $\text{Na}_2\text{O} \cdot \text{SiO}_2$ and potassium silicates $\text{K}_2\text{O} \cdot 3\text{SiO}_2$ were obtained from quartzite.

Stage A2. Study of the impact of hydrothermal-microwave treatment parameters on the process kinetics when obtaining sodium, potassium silicates. Radiative stability of initial materials and end products irradiated by electrons and UV will be determined. Experimental samples of sodium, potassium silicates solutions will be obtained by the hydrothermal-microwave method.

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. Here, an important determinant of the properties and functional activity of a particular type of sodium silicate is Silica Modulus, M , which indicates the ratio of SiO_2 and Na_2O moles. On the basis of the carried out experiments, the following relationships were investigated:

$$M = f(C); M = f(t); g = f(C); g = f(t);$$

where M is the silica modulus (the ratio of SiO_2 and $\text{Na}_2\text{O}/\text{K}_2\text{O}$ moles); C is the ratio of the absolute amount of alkali solution to the absolute quantity of the rock silicon oxide; g is degree SiO_2 extraction from the rock as a result of the alkaline treatment; t is the processing time.

The process kinetics obtaining of silicate solutions from diatomite. Fig. 14-18 show the kinetic curves of diatomite interaction with sodium hydroxide at hydrothermal and hydrothermal-microwave treatment when obtaining sodium metasilicate and trisilicate from diatomite.

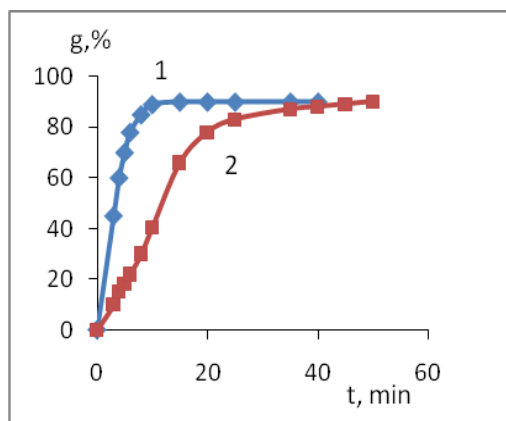


Fig.14. Degree of dissolved SiO_2 from diatomite in obtaining $\text{Na}_2\text{O} \cdot \text{SiO}_2$ (Na-metasilicate) vs. the treatment time for: 1-MW-heating; 2- conventional heating.

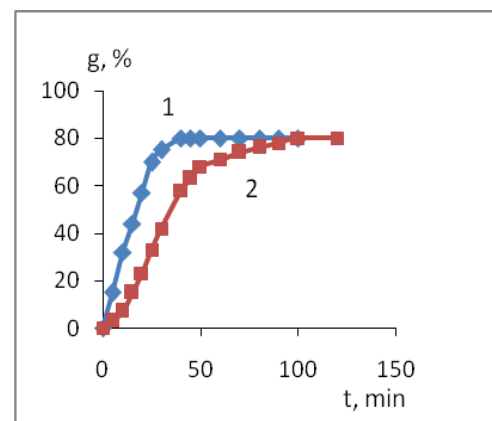


Fig.15. Degree of dissolved SiO_2 from diatomite in obtaining $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ (Na-trisilicate) vs. the treatment time for: 1-MW-heating; 2- conventional heating.

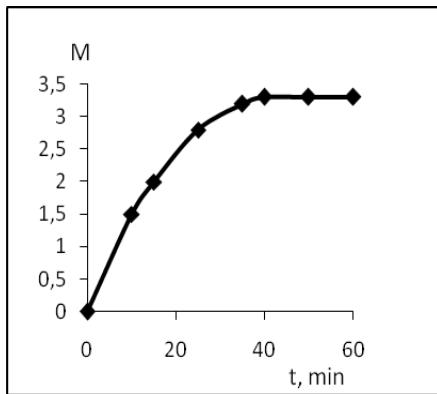


Fig. 16. Silica Modulus, M, (SiO₂/Na₂O) vs. the treatment time (t).

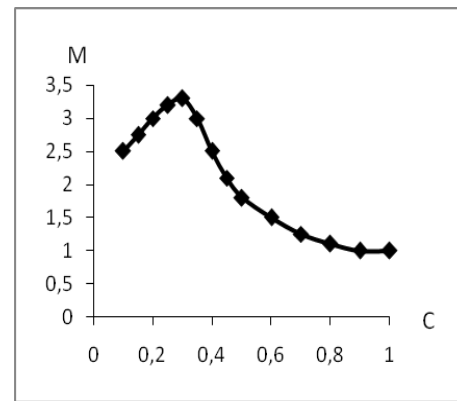


Fig. 17. Silica Modulus, M, (SiO₂/Na₂O) vs. C.

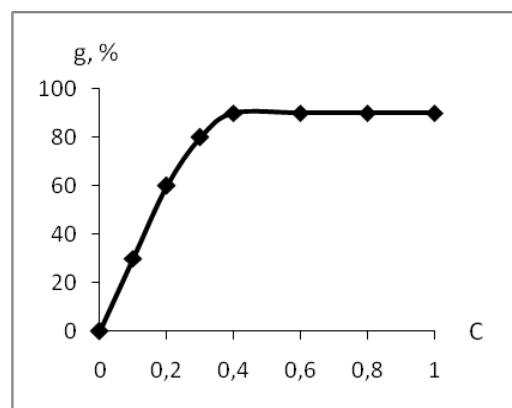


Fig. 18. Dependence of the extraction degree SiO₂ vs C

The processes of producing potassium silicate solutions by HTMW processing of diatomite using potassium hydroxide solution were studied. Fig. 19,20 show kinetic curves of obtaining potassium silicate from diatomite.

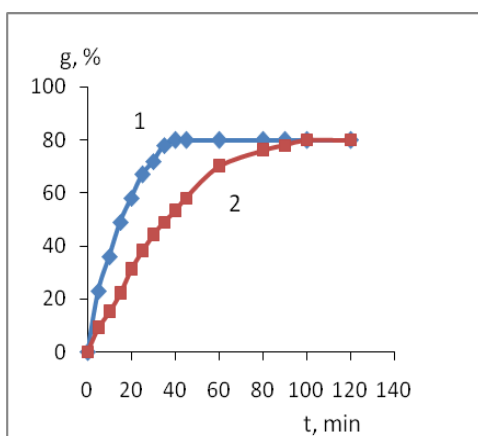


Fig. 19. Degree of dissolved SiO₂ from diatomite in obtaining K₂O· 4SiO₂ (K-tetrasilicate) vs. treatment time for: 1-MW-heating; 2- conventional heating.

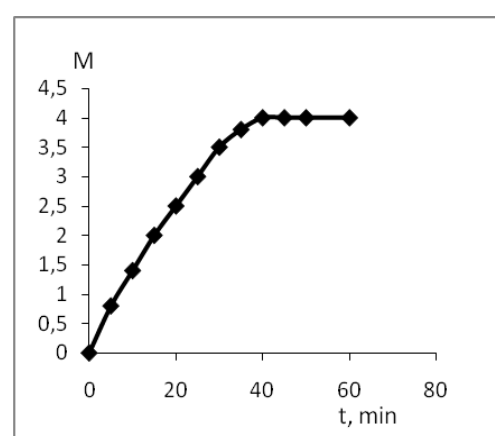


Fig. 20. Silica Modulus, M, (SiO₂/K₂O) vs. treatment time (t).

As it is seen from Fig. 14-20, 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, whereas the reaction yield is practically the same. When preparing solutions of sodium metasilicate, SiO_2 yield is 90%, and when preparing sodium trisilicate and potassium tetrasilicate - 80% of the rock silicon oxide.

Silicate solutions from annealed diatomite become lighter than from the initial the initial unannealed, however the kinetic characteristics during their processing are in principle same.

The kinetics process obtaining of silicate solutions from perlite. Figure 21 shows the dependence of the degree of SiO_2 extraction from perlite on time and the heating method (conventional or MW) under the following conditions: Na_2O concentration 65g/l, temperature 150°C , pressure $5 \cdot 10^5$ Pa. As can be seen, the maximum amount of silica dissolved during the hydrothermal treatment with the formation of sodium trisilicate is about 33% of the rock for both MW and conventional heating method, however in the first case the equilibrium time is achieved within 30 minutes (curve 1, Fig. 21) whereas in the second case within 180 minutes (curve 2, Fig. 21).

Figure 22 shows the degree of SiO_2 extraction vs. the processing time during the formation of sodium metasilicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$) using the microwave and conventional heating methods (the concentration of Na_2O is 150 g/l, $T = 150^\circ\text{C}$, $P = 5 \cdot 10^5$ Pa). Comparing the amounts of sodium metasilicate after reaching a constant concentration, it was found that for both heating methods, the maximum of SiO_2 extraction from the rock was 60%. MW heating reduced the perlite processing time from 100-150 minutes to 25 minutes with obtaining of the sodium silicate solution.

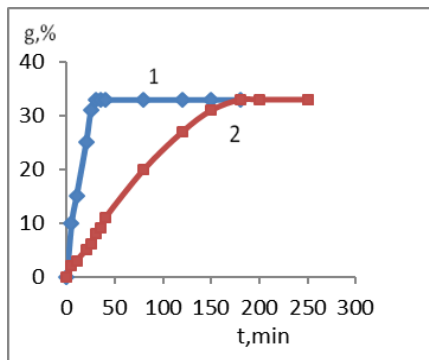


Fig.21. Degree of SiO_2 extraction from perlite when obtaining $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ (Na-trisilicate) vs. the treatment time for 1-MW-heating; 2- conventional heating.

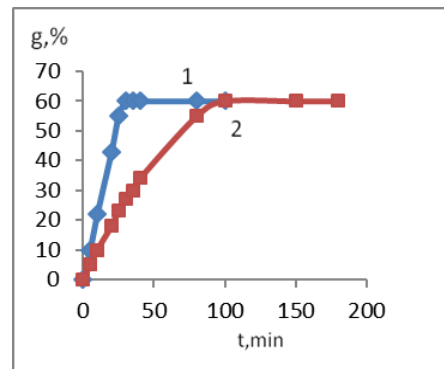


Fig.22. Degree of SiO_2 extraction from perlite when obtaining $\text{Na}_2\text{O} \cdot \text{SiO}_2$ (Na-metasilicate) vs. the treatment time for 1-MW-heating; 2- conventional heating.

Fig.23 presents the amount of dissolved SiO_2 depending on the ratio of Na_2O content in the alkaline solution to the total amount of rock silica (C) in case of MW and conventional heating methods at $T = 150^\circ\text{C}$ and $P = 5 \cdot 10^5$ Pa. The Figure 23 shows (curve 1) that at $C \leq 0.9$ the maximum yield of SiO_2 extraction (60%) is already achieved. Further increase in the initial amount of alkali in the solution does not increase the amount of the dissolved silica.

An important parameter determining the properties and functional activity of the alkali silicate solution is M, the silica modulus or SiO_2 and Na_2O mole ratio. Fig. 24 shows the silicate module values depending on C. Maximum of M equal to 3 ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$) is obtained at C equal to 0.18 - 0.20. The study of SiO_2 yield vs. C has revealed that it increase with increasing C up to a certain value under all selected conditions. Accordingly, the silica modulus reduces (Fig.24). The optimal value of C is 0.18 - 0.20 to obtain high-modulus sodium silicates with maximum yield.

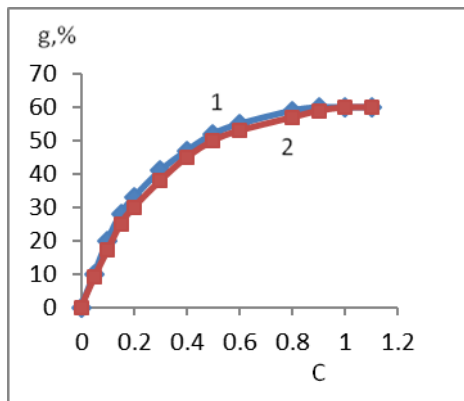


Fig.23. SiO₂ extraction degree vs. C
1-MW-heating; 2- conventional heating.

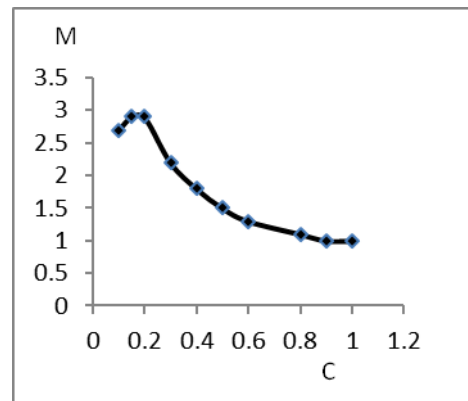


Fig.24. Silica modulus, M vs. C
1-MW-heating; 2- conventional heating.

Fig. 25 shows the dependence of the maximum degree of silica extraction on treatment temperature when preparing sodium trisilicate by MW and conventional heating methods. The initial alkali solutions were identical. The treatment was carried out until a constant SiO₂ concentrations in the solution was reached: for 30 minutes in the case of MW heating and 3 hours in the case of conventional heating. The results of HTMW and HT treatment show that the heating method has no effect on the degree of silica extraction from perlite: the temperature dependence are described by the same curves. The maximum degree of silica recovery (33%, M=3) was obtained when treating perlite at 150°C. This is explained by the transformation of the perlite structure due to changes in its composition in the course of chemical reactions.

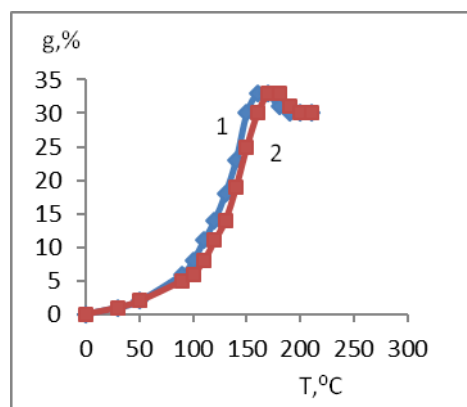


Fig. 25. Temperature dependence of the degree of SiO₂ extraction from perlite
1 - MW heating for 30 min, 2 - conventional heating for 3 hrs.

The solid phase after filtration and washing was investigated using X-ray phase diffraction analysis. The analysis showed that the powder filtered after treatment of perlite by NaOH solution using HTMW or HT method, was characterized by filipsite ($K\cdot Na$)₂O·Al₂O₃·4SiO₂·4.5H₂O crystal structure (JCPDS file # 73-1419) as early as at 100°C (Fig. 26, left column). At 160°C or higher ($P = 6 \cdot 10^5$ Pa), the formation of a new crystalline phase, analcite (Na₂O·Al₂O₃·4SiO₂·5H₂O) took place (JCPDS file # 19-1180), see Fig. 26, right column. This phase transition is the reason for the decrease of the degree of silica extraction from the rock when temperature increases to 160°C and higher (Fig.26).

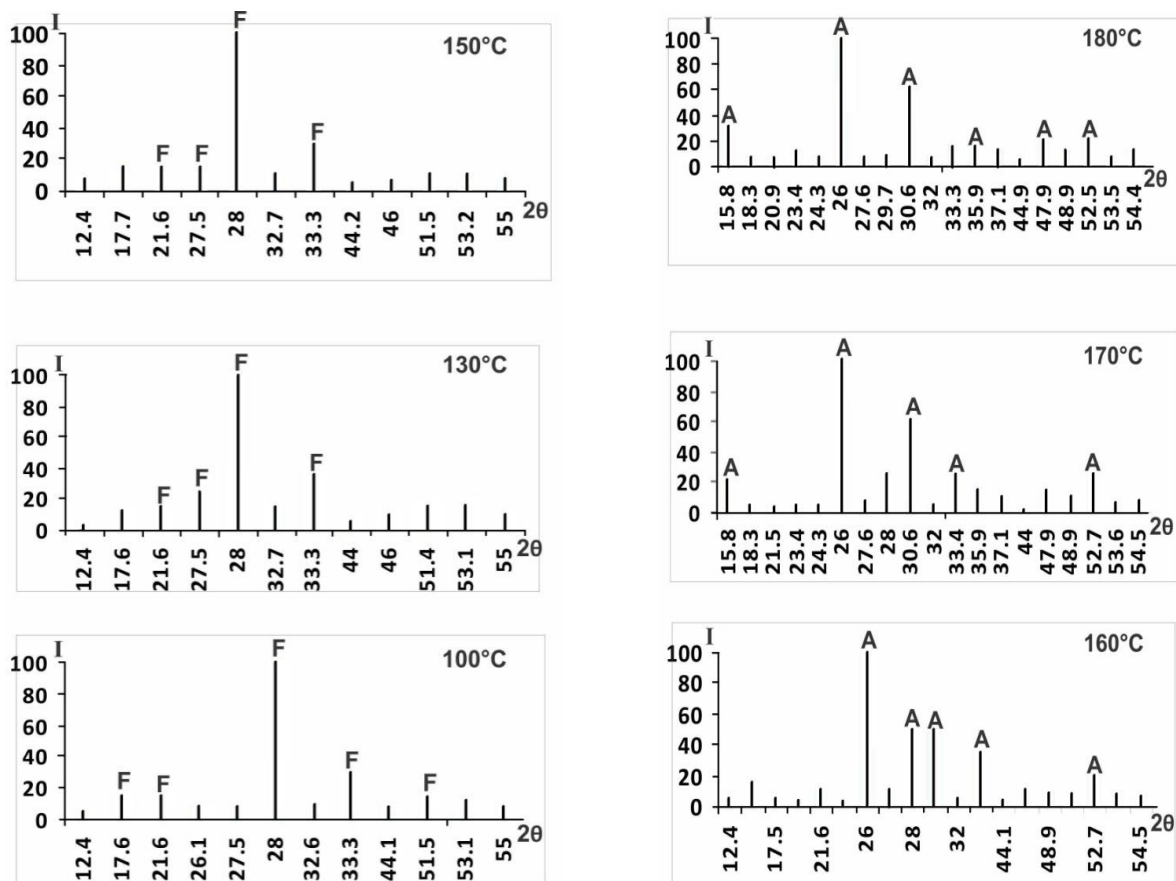


Fig. 26. XRD histograms of the solid phases formed in various temperatures during microwave assisted hydrothermal dissolution of perlite (F- filipsite, A- analcite).

Obtaining of potassium silicate solution: To obtain the potassium silicate solution, perlite was treated with KOH solution. The temperature conditions of the HTMW treatment were chosen within the 100 - 200°C range, the treatment time was about 4 h. K_2O/SiO_2 mole ratio was 0.1-1.0. The experiments were conducted in 4-12 ml autoclaves of capacity, the amount of perlite was 1- 6 g, the ratio of liquid and solid phases was is 1.5 - 7. Fig.27-29 present the kinetic curves of the processes of interaction between potassium hydroxide and perlite. It is obvious from Fig.27 that the equilibrium is fixed in 50 minutes in the case of HTMV processing and 200 minutes in the case of conventional heating with the obtaining of liquid glass with the modulus equal to 3.8. The further increase of treatment time is not expedient. When obtaining potassium metasilicate, the equilibrium is achieved in a shorter time (40 minutes, see Fig. 28) than when obtaining high-modulus liquid glasses. Fig.29 shows the temperature dependence of the degree of SiO_2 extraction from rocks for a 60 min. HTMW processing. Apparently, interaction of KOH with the rock has an "inductive" period with respect to temperature - the reaction proceeds slowly up to 100 °C, then speeds up sharply by 180 °C, and then slows down again. This is due to some changes in perlite structure as a result of interaction with potassium hydroxide. Analysis of the precipitate showed that a part of the potassium ions becomes interconnected in perlite aluminosilicate frame forming alkaline aluminosilicates, the structure of which depends on the temperature of HT processing. Potassium liquid glass and water-insoluble products are obtained as a result of treatment. The amount of precipitate depends on treatment conditions. The maximum yield of silica extraction from rock (60%) and the minimum amount of wastes (40%) are observed when obtaining potassium silicate with modulus 1 ($K_2O \cdot SiO_2$). The reaction yield decreases with increasing silica modulus.

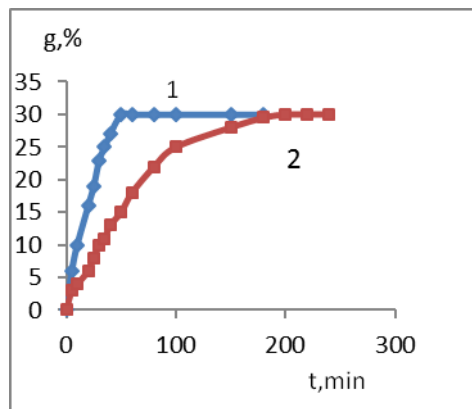


Fig.27. Degree of SiO₂ dissolution from perlite when obtaining K₂O · 4SiO₂ (K-tetrasilicate) vs. the treatment time for: 1- MW heating; 2 - conventional heating.

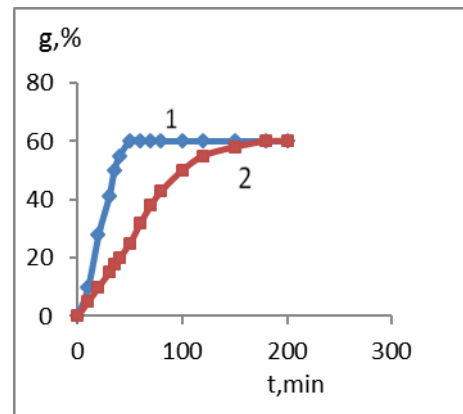


Fig.28. Degree of SiO₂ dissolution from perlite when obtaining Na₂O · SiO₂ (K-metasilicate) vs. the treatment time for: 1- MW heating; 2 - conventional heating

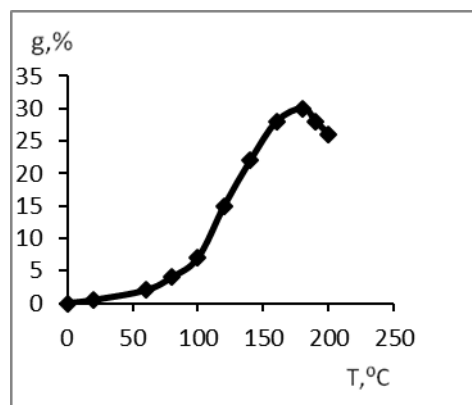


Fig.29 Temperature dependence of the degree of SiO₂ extraction from perlite (η%), t = 60min.

When obtaining the potassium silicate solution with modulus 1- 4, the rate of perlite processing by HTMW method is 4-5 times higher than that by HT method, however the reaction yield is practically the same. When obtaining the potassium tetrasilicate solution, maximum SiO₂ extraction from perlite makes 30%. This is explained by the fact that the content of aluminum and alkali-earth metal oxides in perlites is rather high (14-15%).

Based on the carried out study, optimal conditions of the formation of a high-modulus silicate solution (M = 3,8) were selected; the optimal conditions of HTMW treatment were chosen on the basis of the data on the concentration of potassium hydroxide in terms of K₂O (80-120 g/l K₂O), temperature (180°C), time (50 min), frequency (2.45 GHz), power of the MW oven (500 W).

Hence, when preparing the sodium/potassium silicate solutions with M equal to 1 - 4 under the same processing conditions, the rate of MW perlite processing increased by a factor of 4-5 compared with the conventional heating method, and the reaction yield was practically unchanged. When preparing metasilicate solutions, the SiO₂ yield was 60%, and when preparing of tri- and tetra-silicates – 30 -33% of the rock. It is found that the use of MW radiation energy significantly intensifies the process of HT treatment of silicic rock compared to the conventional heating method. MW heating is especially effective

for the reactions carried out at elevated pressures, since the contactless of energy supply to reactive liquids, high power density and short heating times lead to an accelerated reaction. The use of pressure allows delivering much higher microwave power to the liquids than in the case of atmospheric pressure due to increased dielectric breakdown limit and possibility to avoid electrical discharge without difficulty. On the other hand, microwaves allow delivering high power to liquids under high pressure without contacting electrodes or heating elements that can cause contaminations or temperature gradients. Besides, the proposed method decreases the reaction time to minutes instead of hours. The carried out research has revealed the effectiveness of microwave heating to obtain sodium and potassium silicate solutions from perlite. Thus, for the first time a systematic investigation of the possibility of using microwave energy to produce silicate solutions from perlite was carried out. Kinetic regularities were studied and the conditions for obtaining sodium and potassium silicate solutions using MW heating were revealed. Experimentally, the rate of heating of the reaction mixture and the exposure time for obtaining silicate solutions of certain compositions were determined. The optimum parameters of HTMW processing of perlite 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 conventional. It was revealed that the use of microwave energy can significantly intensify the process of hydrothermal treatment of perlite compared with conventional heating methods.

The kinetics process obtaining of silicate solutions from quartzite. For determine the optimum HTMW treatment conditions of quartzite studied kinetics of the process. Fig. 30-33 presents the kinetic curves interaction of quartzite with solution hydroxides of sodium and potassium for HTMW and HT treatments depending on temperature and processing time. When obtaining sodium metasilicate solutions, SiO_2 yield from quartzite made 90%. HTMW processing by potassium hydroxide solution was slower compared with sodium hydroxide: the reactions yields made 78% when obtaining potassium trisilicate.

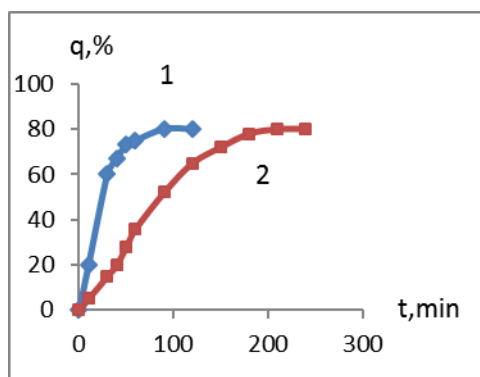


Fig. 30. Degree of SiO_2 dissolution from quartzite when obtaining $\text{K}_2\text{O} \cdot 3\text{SiO}_2$ (K-trisilicate) vs. the treatment time for: 1- MW heating; 2 - conventional heating.

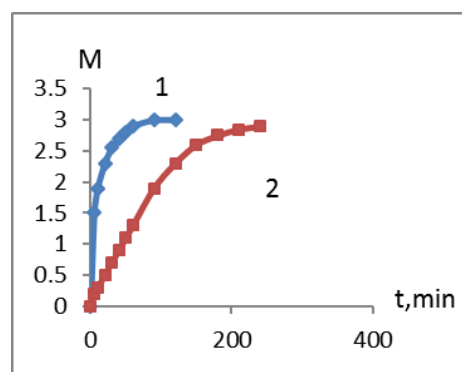


Fig.31. The dependence of silica module (M) when obtaining $\text{K}_2\text{O} \cdot n\text{SiO}_2$ from quartzite vs. the treatment time for: 1- MW heating; 2 - conventional heating

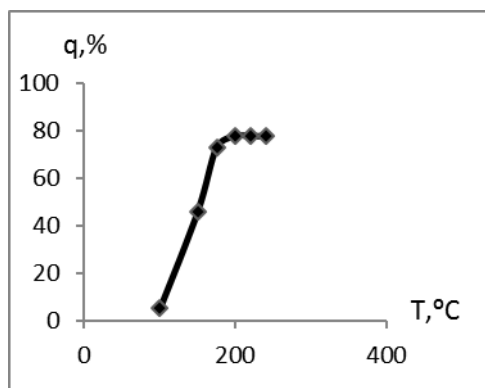


Fig. 32 Temperature dependence on the degree SiO₂ extraction from quartzite (t=1,5 h) when obtaining K₂O·3SiO₂ (MW heating).

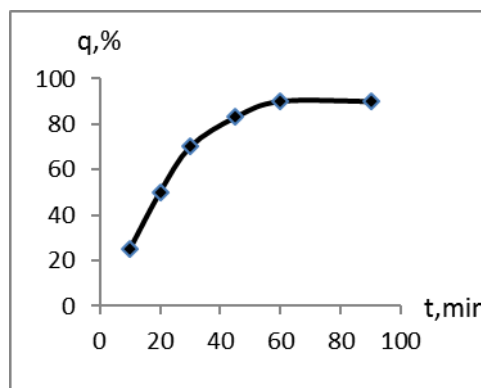


Fig. 33. Degree of SiO₂ dissolution from (Na-metasilicate) vs. the treatment time T=150 °C (MW heating).

Since quartzite is very strong rock, an important factor of HT treatment is mechanical activation of the process, i.e. crushing quartzite. Quartzite was ground in grinders and then milled in planetary mills. The influence of the degree of quartzite dispersion on the reaction yield was studied. The figure 34 show the dependence of the degree of extraction of silica from quartzite on the degree of crushing for HTMW processing of the rock by sodium and potassium hydroxide solutions. The best results were obtained for the particles sized less than 20 mkm (for 90 min) -80% yield. Large particles (greater than 50 microns dissolve slowly in alkaline solution: for 90 min the yield made 50-60%.

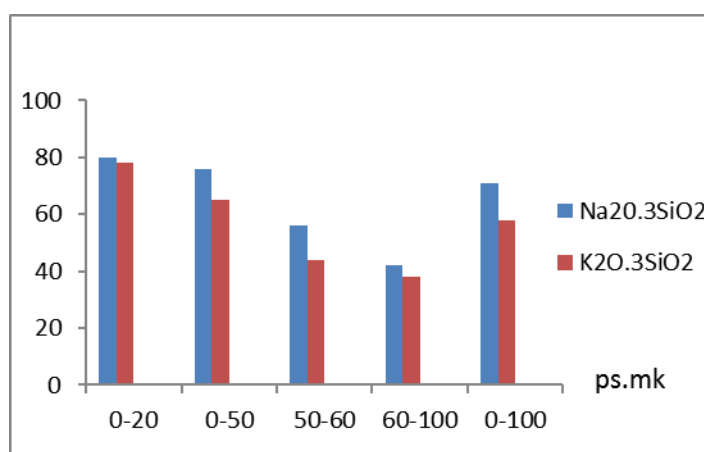


Fig.34. The degree of silica extraction vs. quartzite particle size (microns). T=200°C, t= 90 min.

Study of quartzite reaction with alkaline solutions has shown that at HTMW and HT treatments, the absolute amount of alkali in the solution decreases. This is due to the interaction between the solution sodium/potassium silicate and rock aluminum to form alkali aluminum silicate. According to our chemical analyses, the silicate anion is identical in solution and the residue. When sodium metasilicate forms, the residue has the following composition: $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, and when trisilicate forms, $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ and $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$. Based on this fact, the maximum SiO_2 extraction from quartzite was calculated. According to theoretical calculations, the maximum yield may not exceed 94.0 and 82.0% when obtaining metasilicates and trisilicate, respectively. These data are consistent with the experiment.

The investigations carried out have shown effectiveness of microwave heating in the preparation of silicate solutions from quartzite. Identified the optimal conditions: to obtain sodium metasilicate $T = 150^\circ\text{C}$, the processing time - 60 min, dispersion of quartzite less than 50 microns; for to obtain potassium trisilicate $T = 200^\circ\text{C}$, the time - 90 min, dispersity less than 20 microns. Experimental samples of sodium and potassium silicates ($\text{Na}_2\text{O}\cdot\text{SiO}_2$, $\text{K}_2\text{O}\cdot 3\text{SiO}_2$) were obtained.

As it is seen from experimental dates, the rate of MW processing of obtaining sodium/potassium silicate solutions from diatomite, perlite, quartzite is higher by a factor of 2 – 3 as compared with the conventional method of heating, whereas the reaction yield is practically the same. When preparing solutions of sodium silicate, SiO_2 yield is higher than when preparing potassium silicate. Maximum silica modulus of the potassium silicate reaches 4.0 and that of sodium silicate - 3.3. This is because the potassium ion radius is larger than that of sodium ion: 0.138 nm (K^+) and 102 nm (Na^+), in consequence of which potassium ion binds higher number of siloxane groups (-O-Si-O-), than sodium ion. The rate of the reactions producing silicate solutions also 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 in aqueous solutions is more active than potassium ion. The ionic strengths of solutions of these cations are different because of different ionic radii at the same charges. The completeness of silica transition from the rock to alkaline solution to form silicates depends on the rock cation content (Al, Fe, Ca, Mg, etc.). The degree of silica extraction from the rock into the solution varies depending on the ratio of silica oxide and Al, Fe, Ca, Mg oxides in the initial rock: that form insoluble silicates: the higher this ratio, the greater the amount of SiO_2 goes into solution.

Effect of UV radiation on the radiation-optical properties of potassium and sodium silicates. The effect of UV irradiation on radiation-optical properties of sodium and potassium silicates was investigated for the samples obtained from diatomite, perlite and quartzites. Transmission spectra were measured in the wavelength range from 1 to 2.2 μm (μm) for the samples subjected to UV radiation. Before the irradiation, the potassium and sodium silicates obtained by HTMV treatment of diatomite, perlite, quartzite were dried in drying boxes to form a powdery substance. UV irradiation was carried out using various exposures and cycles: 30 to 150 minutes. After UV radiation the tested samples were compacted mixed with KBr (mass fraction of the tested substance in the formed tablet was about 25%). To eliminate the influence of KBr on the spectrum of the tested sample (KBr often distorts the form of absorption bands), the measurements were carried out in a two-beam mode: pure KBr tablet compacted in the conditions identical to those for the tested samples was placed in the comparison channel. The measurements of transmission/absorption spectra were carried out at regular intervals after UV radiation.

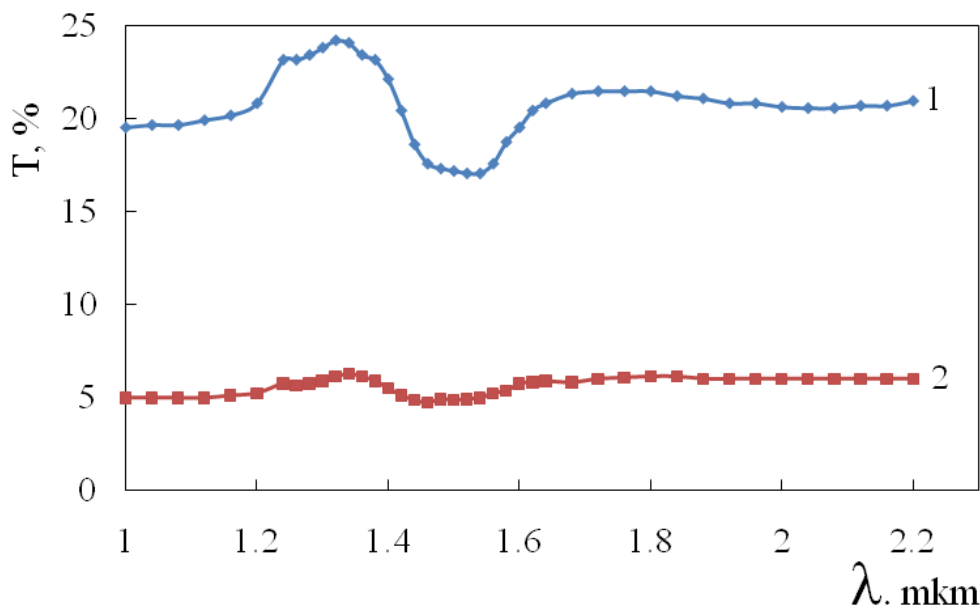


Fig. 35. The optical transmission (absorption) spectra of initial samples obtained by HTMV processing: 1 - sodium metasilicate; 2 - potassium tetrasilicate.

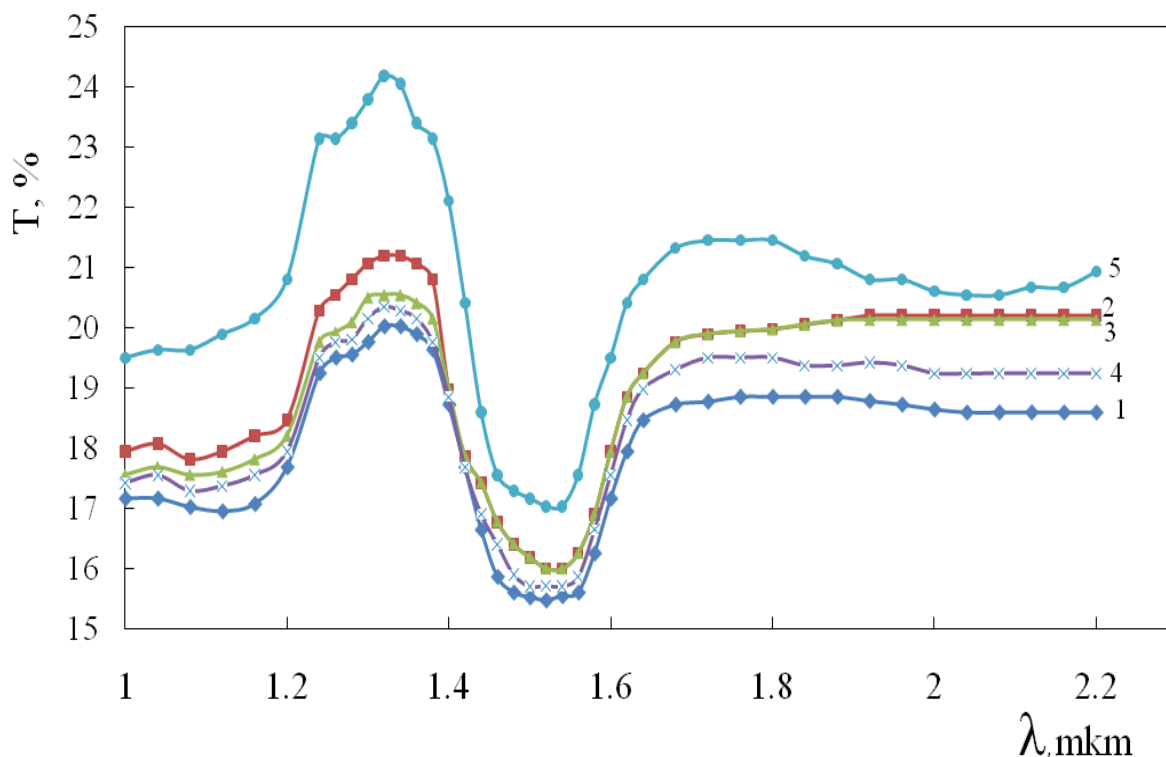
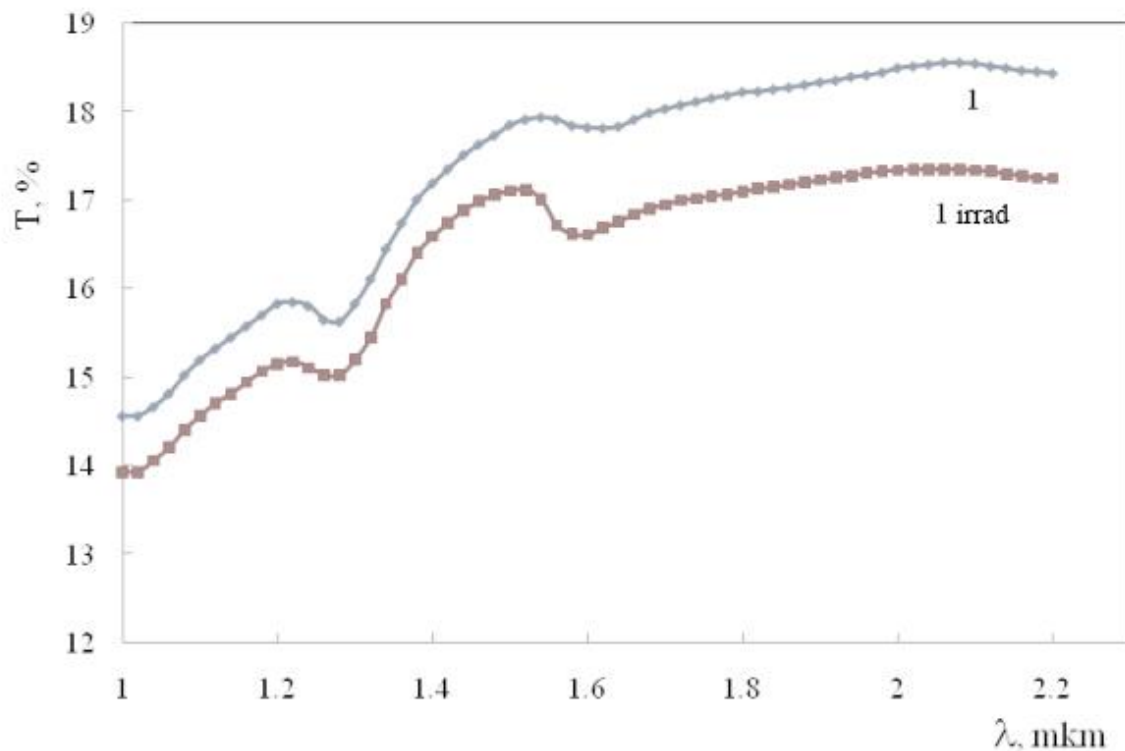


Fig. 36. The optical transmission (absorption) spectra of sodium metasilicate after UV irradiation: 1- Measured after 30 min. irradiation; 2 - Measured after 150 hours following 30 min. irradiation; 3 - Measured after 7 days after following another 60 min. irradiation (total irradiation time made 90 minutes); 4 - Measured after another 60 min. irradiation (total irradiation time made 150 minutes); 5 – initial sample.

Fig. 35 and 36 show the transmission (absorption) spectra of sodium and potassium silicate . It is seen that the behavior of absorption spectra changes depending on the composition of silicate powders. The absorption at 1.3 mkm with a pronounced maximum for the sodium silicate sample and a weak

maximum for the potassium silicate sample are determined by the presence of water valence vibrations $\mu(\text{OH})$ or, probably, by its own structure in non-irradiated samples. The possible presence of water in the structure suggests deformation vibrations (OH) at 1.4 and 1.6 μm . After UV radiation (3KW DksEl-1000-6 xenon lamp) within the wavelength of 240-320 nm, a decrease of intensity peaks in the tested samples was observed. The low intensity peaks at 1.4 - 1.6 μm were related to the presence of deformation vibrations of silicate bonds as a result of UV radiation. The medium intensity peaks at 1.6 - 1.8 μm were also related to the structure of silicates. The high intensity peaks at 1.3 μm corresponded to valence vibrations of crystal lattice $\mu(\text{Si-O-Si})$, whereas the small peak at 1.1 μm was the effect of deformation vibrations of defects (Si-O-Si) as a result of irradiation. It is seen from Fig. 36 and 37 that irradiation reduces the intensity of transmission (absorption) bands, i.e. UV radiation contributes to a redistribution of the intensity peaks responsible for defect formation in the crystal lattice and, thus contributes to an increase of the resistance of materials with respect to radiation sources.

Figure 37 (1, 2) show the transmission (absorption) spectra of the samples of sodium and potassium silicates.



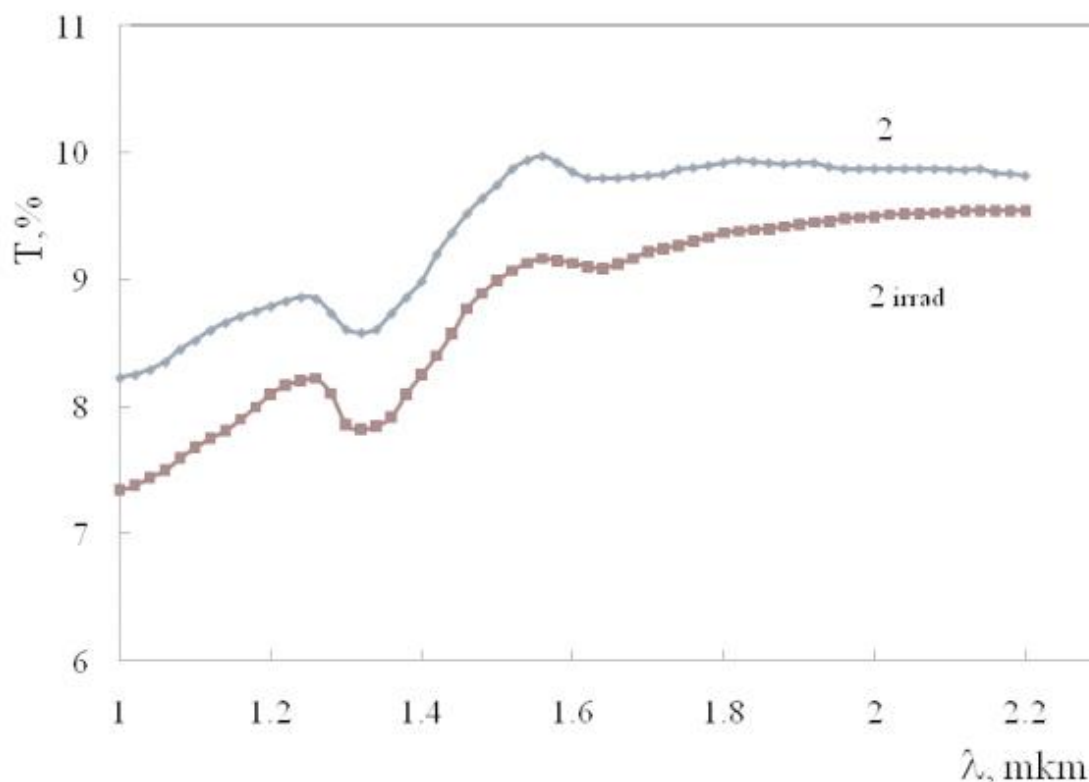


Fig. 37. (1, 2,) Transmission spectra of non-irradiated (1: powdered sodium silicate, 2: powdered potassium silicate) and UV irradiated samples (1_{irrad}, 2_{irrad}. : exposure 3 hr at 100 - 150°C).

As it is seen, the character of the transmission/absorption spectra does not depend on the content of silicate powders. There is a difference in the transmission percentage of spectra and no significant changes of the samples are observed (Fig.37). After UV radiation within the wavelength of 240-320 nm using ~3 kW DKsEI-1000-6 xenon lamp, the investigated samples revealed a general decrease in the intensity maxima. The peaks at 1.2 -1.6 mkm are due to deformation vibrations of silicates. As a result of exposure to UV radiation, there are some violation of the vibrations bonds, and therefore a decrease in the intensity within the entire scope of the investigated transmission spectra. The strong variation of intensity (by a factor of 2) is observed in potassium silicate samples and is presumably due to the structure. Potassium silicate has crystalline structure (Fig.38).

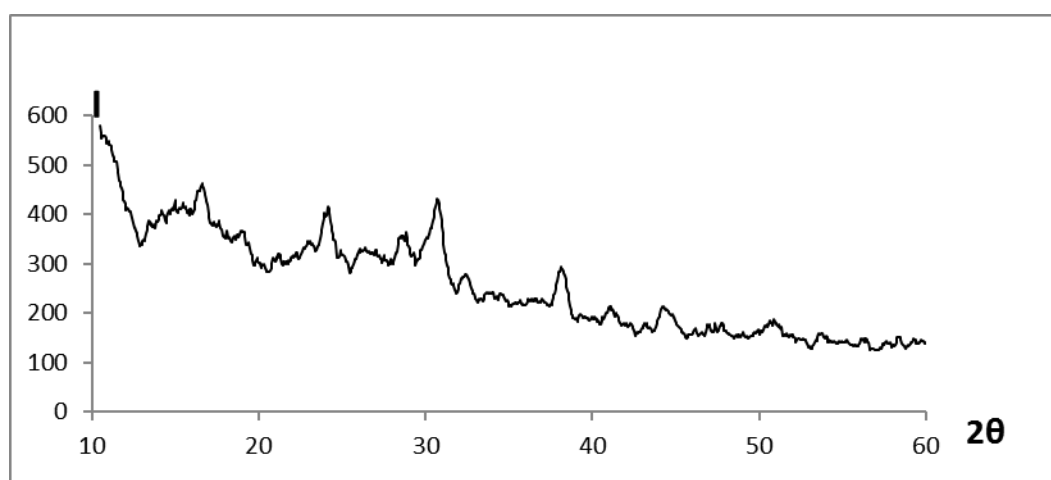


Fig.38. Diffraction patterns of K₂O · 3SiO₂ dried at 200 °C.

Sodium silicate samples have more amorphous phase, and in this case UV irradiation should not affect the redistribution of the intensity of deformation vibrations. The observed decrease in intensity at 1.6-1.8 mkm is associated with own structure of initial silicates. The irradiation was carried out using ELU-5 linear electron accelerator at 90K. The measurements were performed within the wavelength range from 1 mm to 2.2 mm under identical conditions for all the samples. Figures 39 and 40 present some experimental results of the measurements. It is seen from the absorption spectra shows that the initial non-irradiated samples (Fig.39, curve 1, Fig.40, curve 2) exhibit more complex behavior. The absorption spectra clearly reveal intense absorption bands at $\lambda=1.38$ mkm and $\lambda=1.91$ mkm in the case of sodium silicate samples and at $\lambda=1.2, 1.38$ and 1.5 microns in the case of potassium silicate samples. In potassium silicate samples the absorption band at $\lambda=1.38$ microns is weak, however there is a new intense absorption band at $\lambda=1.5$ mkm. Irradiation with fast electrons leads to changes in color or color tone of the samples: white powder becomes gray, which is accompanied by changes in the transmission spectra structure (as Figures 39 and 40 show). The changes in samples color confirm the appearance of new defects as a result of both recharging of own growth defects and violation of local regions in the sample crystal structure. The samples of sodium silicate reveal a new broad absorption band at $\lambda=1.52$ mkm. In the potassium silicate samples completely disappears the intense band at $\lambda=1.5$ microns, but appears a new, no less intense absorption band at $\lambda=1.3$ mkm.

Thus, it follows from the absorption spectra that in all investigated samples electron irradiation results in a strong decrease in transparency within the entire studied spectral region.

The observed absorption band at $\lambda=1.91$ mkm in sodium silicate is interpreted as a combination of valence and molecular vibrations of hydroxyl (OH) groups, the fundamental oscillation frequencies of which are in the far infrared region (~ 3500 cm^{-1} and 1600 cm^{-1}). The nature of the rest of absorption centers, including radiation damages in the crystalline structure (bands at $\lambda=1.52$ microns in irradiated sodium silicate samples and $\lambda=1.3$ mkm in irradiated potassium silicate samples) requires further study using theoretical modeling of physical processes in disordered structures (disorder order type).

The presented figures also show the changes in the transmission of the irradiated samples relative to non-irradiated ones (curve 3). They clearly reveal the irradiation effects.

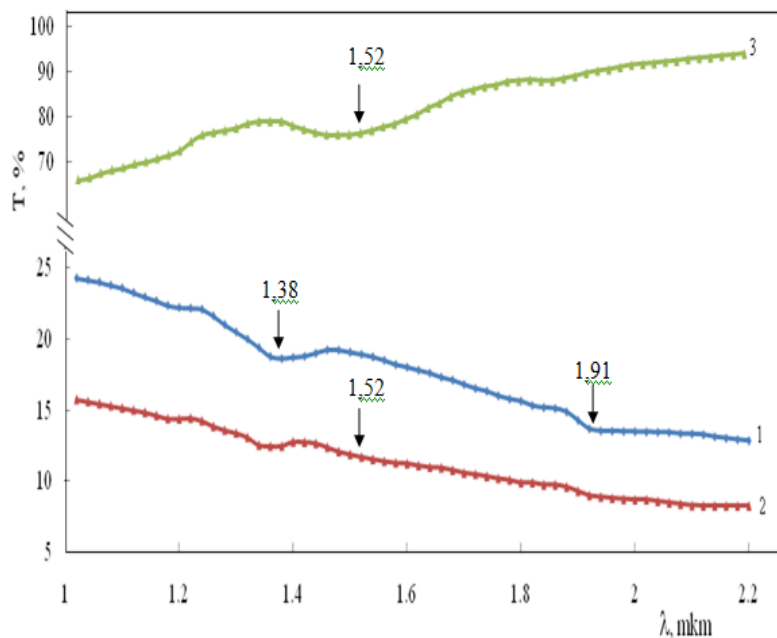


Fig. 39. Optical absorption spectra of sodium silicate in the near infrared spectral region: 1 - non-irradiated; 2 - irradiated with a dose of 10^{16} electrons/ cm^2 ; 3 - induced absorption, the difference in absorption between non-irradiated and irradiated samples.

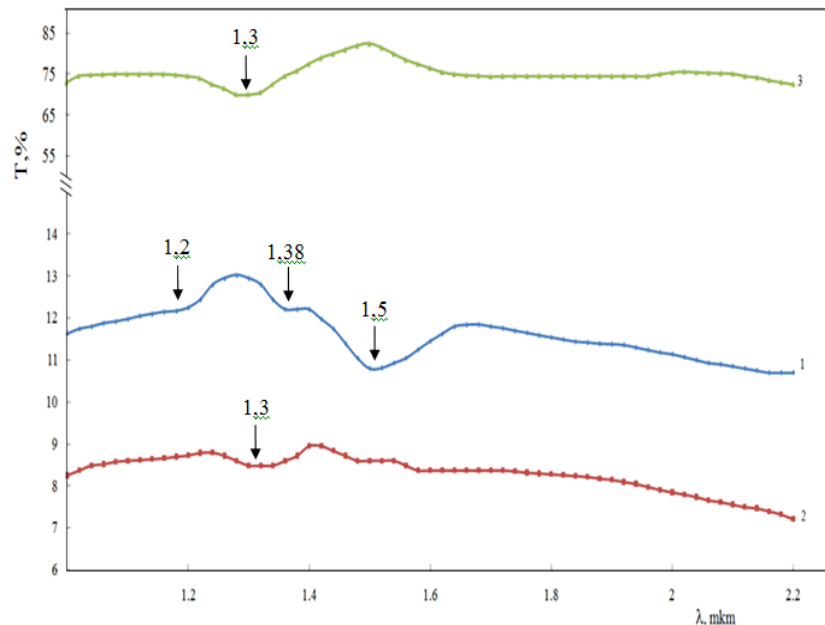


Fig. 40. Optical absorption spectra of potassium silicate in the near infrared spectral region: 1 –non-irradiated; 2 - irradiated with a dose of 10^{16} electrons/cm²; 3 - induced absorption, the difference in absorption between non-irradiated and irradiated samples.

Thus, as a result of UV exposure, redistribution of intensity of crystal lattice vibrations μ (Si-O-Si) takes place due to violations of valence bonds, as well as an increase in deformation vibrations, (Si-O-Si) defects, as a result of exposure. These processes promote an increase of radiation-optical resistance of materials.

Stage A3. Study of electromagnetic treatment jointly with microwave heating for clearing of silicate solutions. Study of the impact of the parameters of hydrothermal-microwave treatment on purification degree of silicate solutions.

At this stage, optimum conditions of electromagnetic and hydrothermal-microwave treatment of solutions will be determined for the purpose of obtaining of high-purity silicate solutions.

The samples of high-purity solutions of sodium, potassium silicates will be obtained, and their testing will be conducted.

Purification of silicate solutions. To obtain high-quality silicate materials (zirconium, zinc, etc. silicates pigments) on the basis of sodium/potassium silicates solutions, purity of solutions is one of the main quality indicators. When obtaining silicate solutions from rocks (perlite, diatomite, quartzite) by hydrothermal-microwave (HTMW) treatment of rocks by NaOH or KOH solutions, the impurities containing in rocks (basically, iron compounds) also pass to the solution. From the literature it is known that alkali metal silicate solutions are among the hard-to-clean systems. . Analysis of patents and scientific publications shows that the known methods for purification of silicate solutions only allow reducing the concentration of coloring impurities by one order of magnitude. For deep cleaning of silicate solutions of iron compounds is necessary to develop more effective methods. We have developed a method for purifying alkali metal silicate solutions by a simple and effective manner: combination of electromagnetic treatment and microwave activation of silicate solutions in the presence of a precipitation agent (CaO) with the subsequent precipitation of impurities in the form of silicates; here the amount of coloring impurities after purification makes 0.001 mg/l or lower. The essence of the method is as follows: liquid glass is passed through a multipolar electromagnetic device and then added to a solution of freshly prepared lime milk (the precipitating agent), and with intensive stirring the reaction mixture is maintained at MW oven for one hour at boiling temperature. Purification of liquid glass was carried out at microwave frequency of 2.45 GHz and power of 200-300 watts.

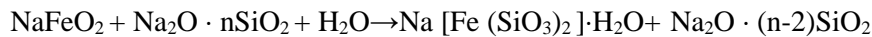
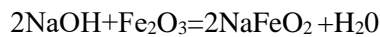
To reveal the mechanism and develop a method of deep cleaning of the obtained silicate solutions from trace iron, the solubility of iron oxide and iron silicates was investigated. To this end, the following model systems were chosen to study the solubility of iron oxide at HTMW processing.

1. NaOH - Fe₂O₃ - SiO₂ - H₂O
2. NaOH - Fe₂O₃·nSiO₂ - H₂O
3. Na₂O·nSiO₂ - Fe₂O₃·nSiO₂ - H₂O

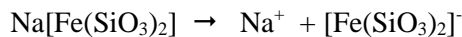
The NaOH and Na₂O·nSiO₂ concentration corresponded to their concentrations at HTMW processing of rocks, and the amount of iron compounds – to their content in the rocks. The investigation of above systems has shown that in the first system

(NaOH - Fe₂O₃ - SiO₂ - H₂O) after HTMW treatment, maximum amount of iron (in terms of Fe₂O₃) in the solution made 0.3 g/l, in the second system (NaOH - Fe₂O₃·nSiO₂ - H₂O) 0.9 g/l, in the third one (Na₂O·nSiO₂ - Fe₂O₃·nSiO₂ - H₂O) 0.5 g/l. The X-ray and IR spectroscopic analyzes showed that iron oxide and iron silicate pass into the solution in the form of complex salts Na[Fe(Si₂O₆)]·H₂O that form polymer chains of sodium ferrous silicate.

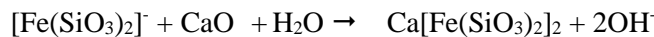
From these data it was revealed that when obtaining silicate solutions from rocks, iron oxides pass into the solution in the form of complex salts - sodium ferrous silicates according to the following reactions:



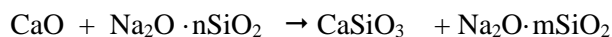
Under the effect of magnetic field on the silicate solutions, de-polymerization of sodium ferrous silicate takes place. The formed sodium ferrous silicate monomer dissociates into ions:



After adding of a precipitation agent - CaO, slightly soluble calcium-ferrous silicate is formed.



These reactions without magnetization proceed very slowly and incompletely. A part of calcium oxide with sodium silicate forms calcium silicate according to the following reaction:



The formed calcium silicate having a high specific surface area with a high adsorption capacity adsorbs on its surface the formed slightly soluble calcium-ferrous silicate, the calcium-ferrous silicate particles become larger, heavier and come out of the solution. Based on the above results, was determined the conditions of electromagnetic - MW purification of the silicate solutions. The concentration of the initial silicate solutions made 0.5 - 0.8 M, the ratio of moles of silicon dioxide and the solution sodium/potassium oxide M made 1.0 - 3.8, and the CaO concentration 0.2-1.0 g/l. The heating time of the reaction mixture from room temperature to the boiling point at microwave treatment was 5-7 min. In parallel (for comparison), purification of silicate solutions at similar ratios of the initial components was carried out magnetic liquid using conventional heating. The purified solution was separated from the residue by centrifugation. The purified silicate solutions after centrifugation was a transparent liquid. Fe₂O₃ identification in solutions was performed by spectrophotometric method using AAS-1 spectrophotometer. The influence of various factors (electromagnetic field strength (H), processing time (t), amount of precipitation agent (CaO), solution feed rate (V) through electromagnetic field, and heating method) on the degree of purification of liquid glass is studied. The dependence of the degree of purification of silicate solutions on the amount of the precipitation agent (calcium oxide) is studied at H

= 1100 kA/m, $v = 4.0$ m/s, $\text{Fe}_2\text{O}_3 = 40$ mg/l. Fig.41 shows the results of our experiments. As the optimum amount of CaO, 0.5 g/l is selected.

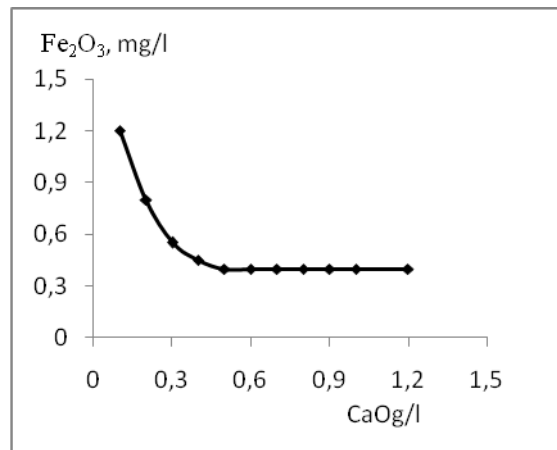


Figure 41. The degree of purification of liquid glass from Fe_2O_3 vs. the amount of precipitating agent (H: 1100kA/m, v : 4.0 m/s, Fe_2O_3 : 40 mg/l).

Fig. 42 shows the dependence of the degree of purification of liquid glass on the speed V of the liquid phase passing through the poles of the electromagnetic device at 0.5 g/l CaO, $H = 1100$ kA/m, $\text{Fe}_2\text{O}_3 = 40$ mg/l.

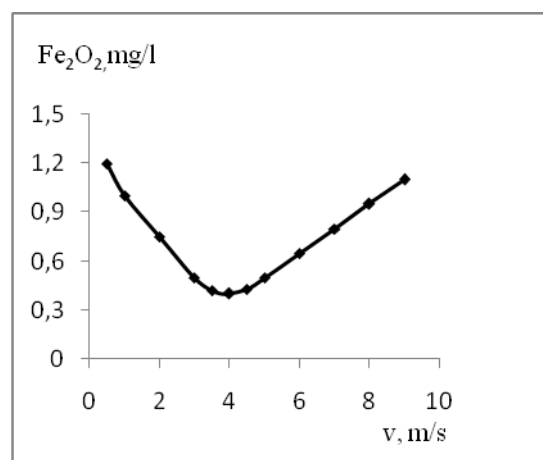


Fig.42. The dependence of the degree of purification of liquid glass from Fe_2O_3 on the feed rate of liquid glass through the electromagnetic field (H: 1100kA/m², CaO: 0.5 g/l, Fe_2O_3 : 40mg/l).

It is seen that the effect of the speed on the degree of purification of the solution from iron oxides is not monotonous: there is an optimal solution feed rate for magnetization. It is 4 m/s at electromagnetic field strength $H = 1100$ kA/m. The reason for this phenomenon is not clear. In all likelihood, at the beginning with increasing flow rate the Lorentz force ($F_l = BqV$) increases, then due to the formation of a turbulent flow at high speeds and cutting the solution stay period in the magnetic field, the cleaning efficiency decreases.

Fig.43 shows the dependence of the degree of purification of liquid glass on electromagnetic field strength (CaO: 0.5 g / l, v : 4.0 m/s, Fe_2O_3 : 40 mg /l). As it is seen from Fig. 43, the effect of electromagnetic field strength on the purification process is complex. The maximum cleaning effect is

observed at $H = 1100$ kA/m. Some publications also describe a similar character of the impact of magnetic field on water system.

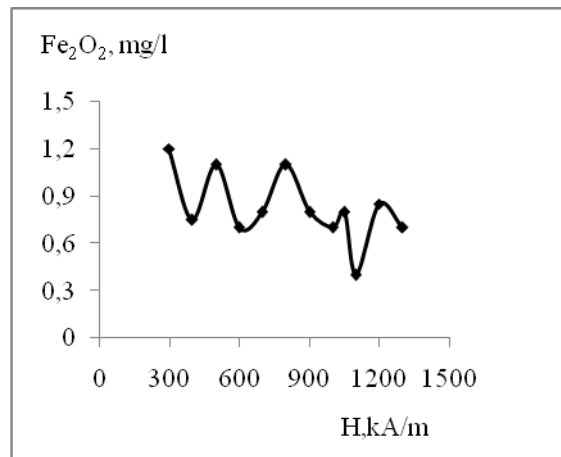


Fig. 43. The degree of liquid glass purification from Fe_2O_3 vs. H (v : 4.0 m/s, CaO : 0.5 g/l, Fe_2O_3 : 40mg/l).

Fig.44 presents the dependence of the degree of liquid glass purification on the heating method at 0.5 g/l of CaO , 40 mg/l of Fe_2O_3 , $H = 1100$ kA/m, $v = 4$ m/s. obviously, the use of microwave energy shortens the cleaning process. The experimental results showed that the microwave activation combined with the magnetic treatment accelerates the formation of calcium iron silicates and their removal from the solutions by a factor of three. Accelerating of the process can be explained by increasing frequency and effectiveness of collisions of reacting molecules due to volume thermal effect in an open microwave system.

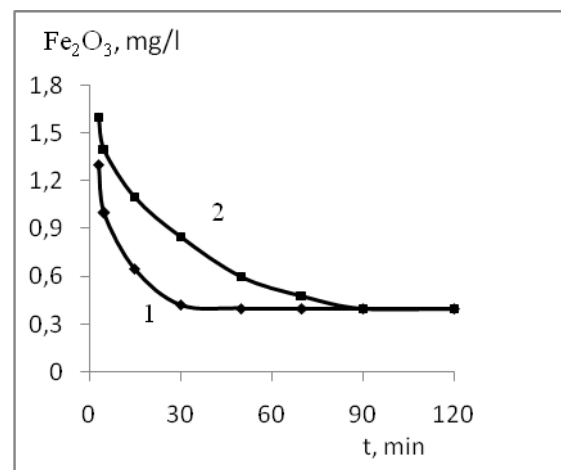


Fig. 44. The dependence of the degree of liquid glass purification on the heating method and time (0.5 g/l of CaO , 40 mg/l of Fe_2O_3 , $H = 1100$ kA/m, $v = 4$ m/s.): 1 - MW-heating; 2 - conventional heating.

The iron oxides content in the purified samples of sodium and potassium silicates is less than 0.0004g/l Fe_2O_3 . It is estimated that when synthesizing zirconium and zinc silicates and a small part of this amount of iron only will pass into the structure of the synthesized zirconium and zinc silicates. A non-monotonic dependence of the degree of purification on the speed of the liquid phase passage through the poles of the electromagnetic unit is determined (Fig. 42) in all likelihood with that at first with increasing flow rate increases the Lorentz force ($F_{\perp} = BqV$), then due to the formation of a turbulent

flow at high speeds and reducing the residence time of the solution in magnetic field, the cleaning efficiency decreases. Also, the effect of electromagnetic field strength on the cleaning process is complex (Fig.43). Several publications describe a similar character of the influence of magnetic field on water systems. Various hypotheses were put forward to explain the mechanism of the impact of magnetic fields on water systems. We believe that the more credible hypothesis consists in the fact that there is a magnetic coagulation of the finest ferromagnetic particles present in the solution. As we pointed out, iron in the silicate solution is in the form of complex salts $\text{Na}[\text{Fe}(\text{SiO}_3)_2]_n\text{H}_2\text{O}$, which form polymer sodium-ferrous silicate chains. The observed (Fig. 43) poly-extreme character of cleaning silicate solutions from iron oxides, depending on electromagnetic field strength, may be due to the fact that under the influence of electromagnetic field de-polymerization of sodium ferrous silicate proceeds intensively at certain values of the electromagnetic field strength. The maximum cleaning effect is observed when the electromagnetic field strength is 1100 kA/m. Periodic changes in the cleaning degree with increasing H can be attributed to Larmor regularity according to which the electron precession in the magnetic field is linearly related to the field strength. As the magnetic field strength changes, resonant phenomena may occasionally occur. With increasing magnetic field, the Larmor frequency that which depends linearly on it, also grows constantly, and the spectrum of molecular frequencies is discrete, so that the equality of three frequencies of neighboring molecules and the Larmor frequency is only possible for certain magnetic field strengths. This fact explains poly-extreme nature of the studied dependencies.

From the obtained results it is obvious that the use of the energy of microwave radiation shortens the cleaning process. Experimental results have shown that the microwave activation in conjunction with magnetic treatment accelerates the formation of calcium iron silicates and their removal from solution by a factor of three (Fig.44). Such acceleration of the process can be explained by increase in the frequency and efficiency of the collisions of the reacting molecules upon a volume thermal effect in an open microwave system. Let us assert again that the use of MW radiation opens manifold possibilities in chemistry, and in particular, shows the efficiency of microwave processing in combination with the magnetic treatment for deep cleaning of silicate solutions from coloring impurities. Studies have shown that in the case of silicate solutions the combination of both methods, electromagnetic processing and microwave activation, greatly improves the performance of each method, used separately: the amount of iron oxides in the solution is reduced by a factor of 100 (0.5 mg/l and lower). Pure samples of sodium and potassium silicate solutions have been obtained.

Task 2

Development of hydrothermal-microwave method for obtaining of high-purity silicate pigments.

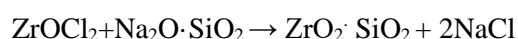
Stage A4. Obtaining of $\text{ZnO}\cdot\text{SiO}_2\cdot m\text{H}_2\text{O}$, $\text{ZrO}_2\cdot\text{SiO}_2\cdot m\text{H}_2\text{O}$ hydrosilicates by hydrothermal-microwave method. Synthesis will be conducted using purified silicate solutions and appropriate soluble salts on the basis of theoretical calculations and elemental analysis data.

The effect of 18 MeV proton radiation on surface properties of silicate materials will be determined depending on the radiation intensity and temperature.

Modelling of physical processes related to the formation of radiation defects in silicate materials with different properties.

Obtaining of Zirconium silicate. Zirconium silicates, due to their specific properties, have been widely used now as absorbing materials, decolorizing agents, catalysts, filling compounds for paints, pigments, in glass and ceramics industry, for thin- layer chromatographic separation of mixtures of substances extracted from biological objects.

Synthesis of Zr silicates by deposition of sodium silicate and soluble zirconium salts from aqueous solutions is easy and economical, however for the past twenty years the growing interest has been shown in chemical reactions using microwave irradiation. We used for the synthesis chemically pure zirconium oxychloride $\text{ZrOCl}_2\cdot 6\text{H}_2\text{O}$ and sodium metasilicate solution $\text{Na}_2\text{O}\cdot\text{SiO}_2$ cleaned of coloring impurities of iron compounds. The amounts of initial reagents were calculated according to the following reaction:



Synthesis of zirconium hydrosilicate was performed in CE1073AR Samsung microwave oven using an open glass flask equipped with a backflow condenser and a stirrer. Synthesis conditions: the microwave frequency of 2.45 GHz, microwave power of 600 watts. The synthesis was carried out by reacting zirconium oxychloride and sodium silicate solutions while maintaining pH at 7.0. Pouring the very first portions of $ZrOCl_2$ to the sodium silicate solution instantaneously caused formation of a white flocculent residue. After keeping at boiling temperature for 10-15 minutes at continued stirring, the residue was filtered using laboratory nutsch filter and washed thoroughly from Cl^- ions by hot water (repulping), and then dried at $120^{\circ}C$. SiO_2 and ZrO_2 identification was carried out by gravimetric method and XRF analysis (Fig.45). Quantitative determination of Fe_2O_3 in silicates was carried out by chemical and spectrophotometric analyses. X-ray analysis of the heat-treated samples of $ZrO_2.SiO_2$ silicate was carried out) as well as differential thermal and thermal gravimetric analysis up to $1500^{\circ}C$.

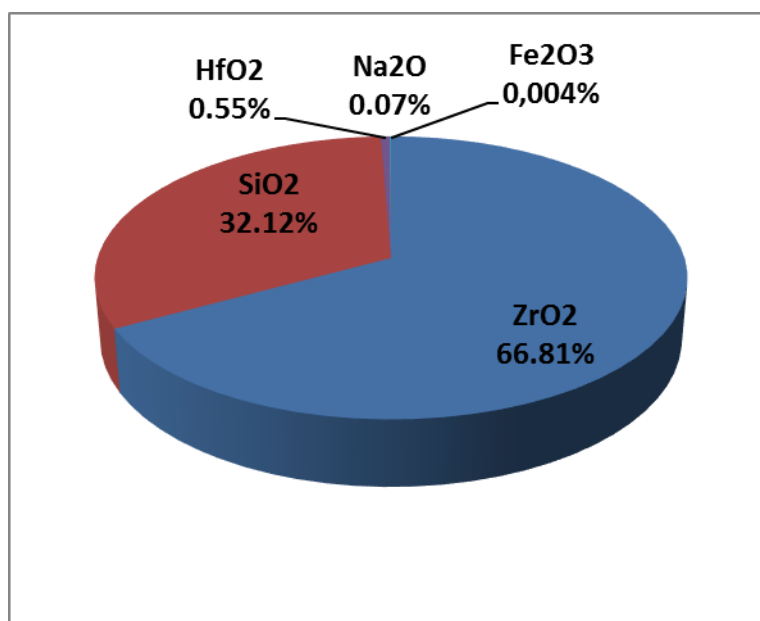


Fig. 45. Chemical composition of Zr silicate, measured by XRF analysis.

Fig. 46 shows the results of thermal analysis for $ZrO_2.SiO_2$ samples dried at $120^{\circ}C$. Endothermic effects are accompanied by weight loss: water removal. Here, water loss occurs in 2-3 stages, i.e. apart from the adsorption water which is removed at the first stage, there is chemically bound water.

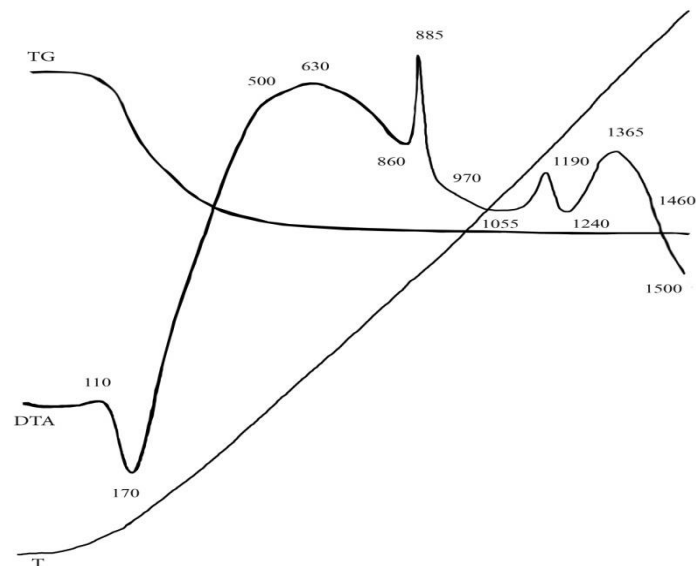
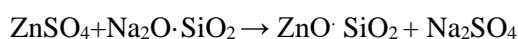


Fig. 46. DTA curves of the $ZrO_2 \cdot SiO_2 \cdot nH_2O$ samples dried at $120^\circ C$

Based on the carried out DTA and X-ray phase studies, it can be stated that in the process of zirconium silicate synthesis a chemical compound $ZrO_2 \cdot SiO_2 \cdot mH_2O$ is formed.

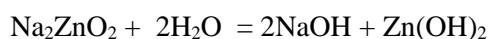
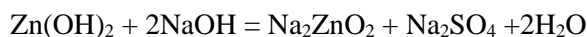
Physico-chemical studies have reveal endothermic effects at $170^\circ C$, and exothermic effects at $885^\circ C$, $1190^\circ C$ and $1365^\circ C$. Endothermic effects are due to removal of the adsorption and chemically bound waters. Exothermic effect at $885^\circ C$ corresponds to the transition of amorphous zirconium metasilicate to crystalline tetragonal ZrO_2 and amorphous SiO_2 , and at higher temperature it converted in crystalline phase $ZrSiO_4$. It is revealed that the silicate modulus of the synthesized silicate correspond strictly to the silica modulus of the initial sodium silicate solution of $(Na_2O \cdot SiO_2)$. It is shown that the microwave heating results in acceleration of the synthesis. It is found that during the heat treatment of the synthesized zirconium silicate, phase transformations of the amorphous structure of the zirconium silicate take place to form zircon. Hence, microwave synthesis gives better results compared with the known methods due to the formation of crystalline centers in the whole volume of the reaction mixture during the silicate synthesis and leads to a reduction in overall process time by a factor of 2-3.

Obtaining of Zinc silicate. Zinc silicate is a promising optical luminescent material due to its high quantum yield upon excitation, stability of its processing characteristics, and resistance to chemical and thermal impacts. Coatings of zinc silicate do not spread flame, withstand high temperatures, are conductive, radiation-resistant materials, and may be used to protect the equipment of cosmic stations, nuclear power and thermoelectric plants, as well as in electrostatic safety systems, etc. Development and application of the directed synthesis should allow controlling the formation of the desired products. Synthesis of zinc silicates from aqueous solutions of sodium silicate and soluble zinc salts is simple and economical process, however chemical reactions which occur at heating by microwave irradiation are more efficient. The HTMW method for obtaining zinc silicates has been developed. To synthesize them, chemically pure zinc sulfate $ZnSO_4$ and sodium metasilicate $Na_2O \cdot SiO_2$ cleaned from coloring iron impurities were used. Synthesis of zinc hydro-silicate was performed in CE1073AR Samsung microwave oven using an open glass flask equipped with a backflow condenser and a stirrer. Synthesis conditions: the microwave frequency of 2.45 GHz, microwave power of 600 watts. Concentrations of the initial aqueous solutions of $ZnSO_4$ and $Na_2O \cdot SiO_2$ were 0.5 mol/l. The synthesis was carried out by interaction between zinc sulfate and sodium silicate while maintaining the medium pH at 7.0. The amounts of the initial reagents were calculated according to the following reaction:

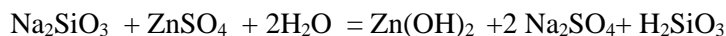


The calculated amounts of the initial solutions were added into the reactor at continuous agitation. Pouring the very first portions of sodium silicate to ZnSO₄ solution instantaneously caused the formation of a white precipitate. After keeping at boiling temperature for 30-60 minutes at continued stirring, the solution was filtered. The precipitate was washed with distilled water (70-80°C) to remove SO₄²⁻ and Na⁺ ions.

As zinc is an amphoteric metal, when synthesizing zinc silicates from solutions an important factor is the method for the solution stirring: if zinc sulfate solution is added to silicate solution, in an alkaline medium (pH of the sodium silicate solution is above 12 (pH < 12) zinc cations Zn²⁺ transfer anionic form ZnO₂²⁻ forming sodium zincate Na₂ZnO₂, which is hydrolyzed to form insoluble zinc hydroxide.

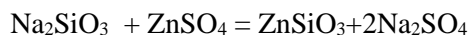


As a result, the reaction proceeds on the following scheme:



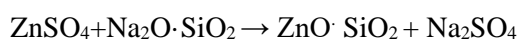
Precipitation entails mutual coagulation of zinc hydroxide and silica. Here, a partial dissolution of the residue occurs, i.e. zinc hydroxide manifesting its amphoteric properties, partially dissolves in alkaline solution. Also, hydrate forms of zinc silicate are present.

If silicate solution is added to zinc sulfate (pH < 7), the zinc cations in acidic medium react with Na₂SiO₃ forming the zinc silicate precipitate



In this case the reaction yield is higher because the solubility of zinc silicate in water is much lower than that of zinc hydroxide.

Synthesis was carried out by reacting of zinc sulfate and sodium silicate solutions while maintaining the medium pH at 7.0. The amounts of the initial reagents were calculated according to the following reaction.



SiO₂ and ZnO identification was carried out by gravimetric method. Quantitative determination of Fe₂O₃ in silicates was carried out by chemical and spectrophotometric analyses. Spectrophotometric analysis was performed using AAS-1 spectrophotometer.

X-ray analysis of the heat-treated samples of ZnO·SiO₂ silicate was carried out), whereas differential thermal and thermal gravimetric analysis up to 1000°C were performed using MOM Derivatograph (Hungary).

Drying of hydrosilicates. The kinetics of microwave drying of zirconium and zinc hydrosilicates was studied. To reveal the optimum regime of drying, it is necessary to determine the drying speed. Our experiments on studying the process of drying the zirconium and zinc hydrosilicates were conducted in the microwave and convection heating modes (the furnaces power was 900 Watt in both cases).

Fig. 47 shows kinetic curves of drying (humidity change u) with time. Drying was carried out until a constant weight of the samples was reached. Fig. 48 shows the drying rate in microwave and convection heating modes. Comparison of the results of microwave and convection drying indicates that the microwave drying is ten times faster than the convective one: at the microwave drying 10% residual moisture is achieved in 8-10 minutes, and at the convective drying during this time for the moisture makes 72-73%. At the convective drying the heat is supplied to the evaporation front at the account of thermal conductivity of the material dry layer, whereas the microwave drying ensures

heating of the entire volume of the material and evaporation occurs in the entire volume. Changes in the material moisture content only take place due to evaporation, and movement of the liquid phase is absent. At the convective drying, there are no phase transformations inside the wet material, and moisture is removed by movement of the liquid phase in the material.

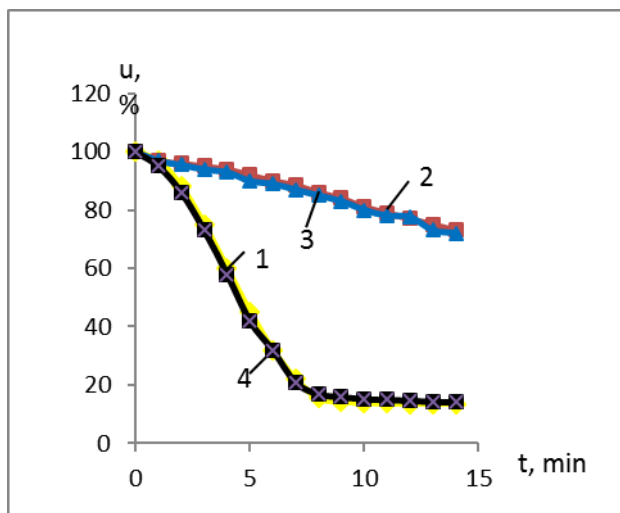
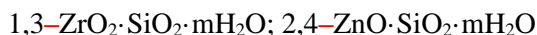


Fig. 47. Curves of MW (1,4) and convective (2,3) drying of hydrosilicates:



The advantage of microwave drying lies in volumetric and high heating rate: after 8-10 *minutes* constant humidity (10%) is reached. In the case of convective drying constant humidity (10%) is reached after 2 hr exposure. Thus, the efficiency of the microwave drying of installed zirconium and zinc hydrosilicate is obvious. Fig. 48 shows the results of thermal analysis $\text{ZnO} \cdot \text{SiO}_2$ samples dried at 120°C . The thermogram of zinc hydrosilicate $\text{ZnO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ reveals three low-temperature and three high-temperature endothermic effects. The low temperature effects at 125°C , 260°C and 380°C correspond to the gradual removal of adsorption, crystalline and loosely bound water. Total weight loss is 14.3% and the low-temperature water loss makes 58.3% of the total loss. X-ray phase analysis of the initial sample indicates the formation of zinc hydrosilicate, testifying to the partial structuralization of zinc hydrosilicate formed due to interaction between sodium silicate and zinc sulfate. In the hydrosilicate $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$ structure, water presents in two structurally nonequivalent positions. On DTA and TG (weight loss) curves the temperature maxima associated with the removal of structural and crystallization water occur at 125°C , 260°C and 380°C . In our opinion, further mass loss with the temperature increases are related to the release of OH groups ($> 500^\circ\text{C}$). In the $\text{ZnO}-\text{SiO}_2$ system at atmospheric pressure only one compound is formed, villemite ($2\text{ZnO} \cdot \text{SiO}_2$) which melts congruently at 1512°C . As can be seen from the DTA curve, the pronounced exothermic effect associated with the formation of zinc silicate, is manifested at 760°C . The narrow temperature interval of the formation of the crystalline compounds indicates the closeness of structural motifs of amorphous (initial) and crystalline ($2\text{ZnO} \cdot \text{SiO}_2$) compound. The formation of eutectics at 1430°C is presumably due to the presence of a sodium containing silicate in the system (taking into account relatively low residual content of Na_2O (less than 0.5%) in the initial zinc hydrosilicate). Consequently, the inconsiderable shift of the system liquidus temperature ($2\text{ZnO} \cdot \text{SiO}_2$ melting) towards low temperatures (1490°C) is associated with the presence of both the impurities and OH groups playing a part of flux ages. The X-ray analysis of the crystallized melt indicates the full identity of reflexes with villemite (Fig.49).

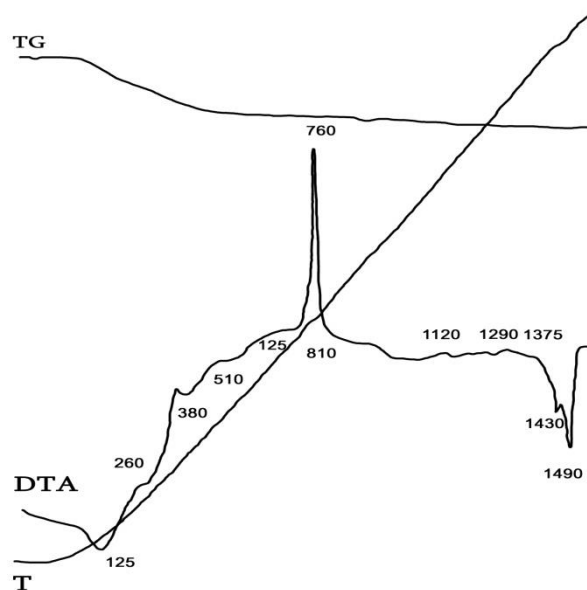


Fig. 48. DTA curves of $\text{ZnO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ samples.

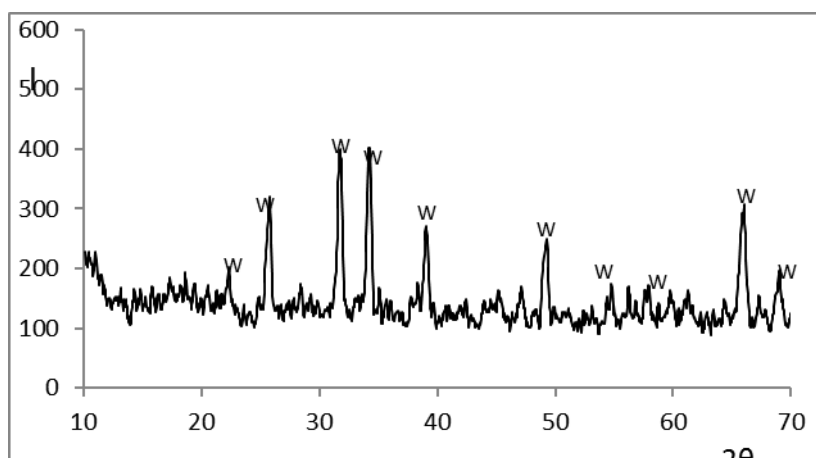
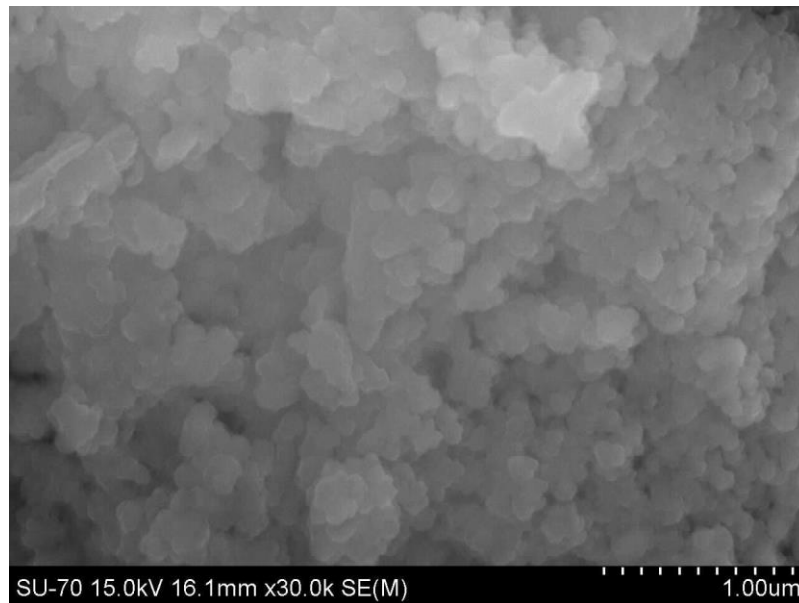


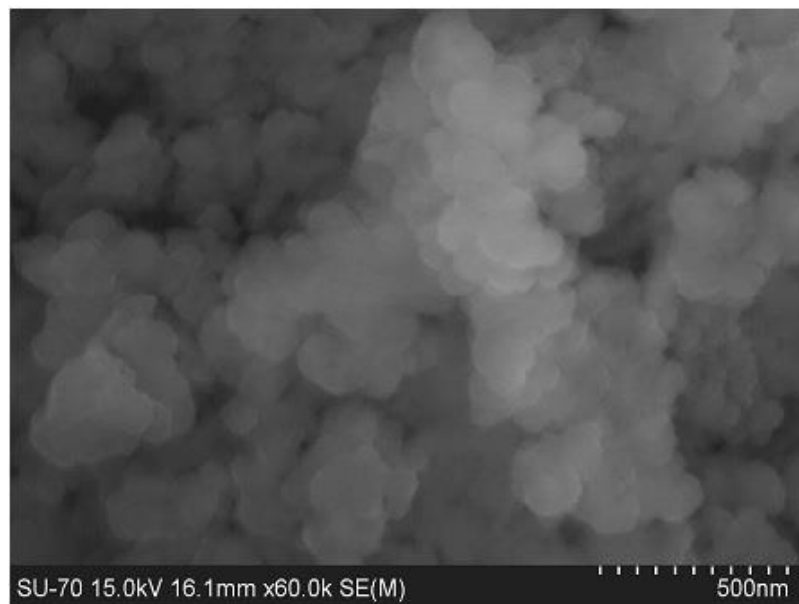
Fig. 49. XRD patterns of samples heated at 1000°C , W-willemite.

Taking into account the described DTA transformations, it is possible to judge in totality the stages of zinc silicate microstructure conversion at heat treatment. The basis of willemite crystalline structure is a framework of SiO_4 and ZnO_4 tetrahedra representing hexagonal hollow tubes surrounded by six populated systems. Fig. 51 shows microstructure of synthesized willemite obtained by HTMW method and heat-treated during 2 hours at 1000°C . The microstructure is loose, with almost uniform distribution of spherical areas sized 100-150 nm. Also, the formation of areas with more compact structure is observed testifying to the formation of liquid phase. The formation of liquid phase with its further crystallization contributes to the increase in the size of crystalline areas to 600-800 nm (Figure 50.1).

Fig. 50.2 of higher resolution (up to 500 nm) allows observing the formation of fibrous structures. However, in general there are uniformly dispersed spherical areas sized 100-200 nm.



1.



2.

Fig.50. Electron micrographs of $2\text{ZnO}\cdot\text{SiO}_2$, firing temperature-1200°C

Thus, it is determined that heat treatment of the synthesized zinc silicate results in phase transformations of the amorphous structure of zinc silicate with the formation of willemite.

Impact of radiation on the surface characteristics of silicate materials. Due to the different conditions of exposure and differences in secondary emission properties of thermo-regulating coatings, there are non-uniform accumulation of excess electric charges on the surface of space vehicles and generation of a large potential difference (up to tens of kilovolts) between separate elements. Therefore, an effective way to prevent radiation-induced breakdowns is the choice of materials for external surfaces of space vehicles that should have, on the one hand, high resistive and dielectric properties, dielectric strength, and on the other hand a reduced tendency to accumulation of

charges and the capability for their rapid relaxation. Here, their physical properties must be maintained at an acceptable level for a long period of radiation and thermal impacts of the space environment. Solving this problem also requires carrying out corresponding accelerated simulation tests. The characteristics of optical absorption spectra of sodium and potassium silicate (both initial and irradiated with 5 MeV electrons at a dose of 10^{16} electrons/cm²) in the near infrared region of the spectrum were studied. The irradiation was carried out using ELU-5 linear electron accelerator at 90K. The measurements were performed within the wavelength range from 1 mm to 2.2 mm under identical conditions for all the samples. Our measurements of the samples irradiated at low temperatures (-100°C) have shown that the intensity of frequency oscillations of silicate bonds decreased due to reduced amplitude as a result of freezing; here the total structure of the spectra did not change, as the pictures for the irradiated and non-irradiated samples show. At high temperatures (150°C) the pattern change, because during UV irradiation a "radiation heat-treatment" takes place, which contributes to increased stability of certain structural disturbances and leads to the relative increase in radiation-stimulated processes contributing to increased material resistance to radiation. Thus, as a result of UV exposure, redistribution of intensity of crystal lattice vibrations μ (Si-O-Si) takes place due to violations of valence bonds, as well as an increase in deformation vibrations, (Si-O-Si) defects, as a result of exposure. These processes promote an increase of radiation-optical resistance of materials.

Stage A5. Study of ZnO·SiO₂·mH₂O, ZrO₂·SiO₂·mH₂O, hydrosilicates doped with rare earth elements directly during the synthesis.

Luminescent properties of rare earth elements doped silicate TRC materials in UV-VUV spectral region at different temperatures.

Determination of the optimum amount of doping elements, providing necessary structure and radiation characteristics of the synthesized pigments.

In recent years, great interest in zircon pigments has been expressed due to their valuable physical and chemical properties. They are characterized by exceptional resistance to high temperatures and aggressive environments. Among the various methods for obtaining zircon pigments it should be accentuate the following ones: baking of salts or hydroxides of the corresponding metals at different temperatures, joint fusion of salts in crystalline form followed by baking of the mixture, sol-gel methods, joint baking of oxides with addition of certain mineralizers. One of the major problems of modern inorganic chemistry and materials science is the development of new methods for the synthesis of substances.

To obtain various pigments zircon group in the synthesis of zircon, various chromophores are introduced to the zircon lattice. In the case of the solid-phase synthesis of pigments, high temperatures and prolonged time up to several hours are required to introduce dopant atoms to the zircon lattice.

In order to reduce the synthesis temperature to obtain a homogeneous structure and uniform introduction of the dopant element in the zircon lattice, the sol-gel synthesis method is used. As initial materials, pure expensive materials (Si and Zr alkoxides, acetates, nitrates in water and water-ethanol mixtures) are used; the synthesis time is prolonged, therefore sol-gel method is not applicable when obtaining of large amounts of pigments is required (on the industrial scale). The gas-phase methods of silicate synthesis are environmentally inappropriate as silicon halogenides are toxic and explosive; besides, harmful gaseous by-products and intermediate product are formed in the synthesis process. More promising are liquid phase synthesis methods in aqueous solutions (hydrothermal method), for example, methods for the synthesis from liquid glass and zirconium oxychloride.

One of the major problems of modern inorganic chemistry and materials science is the development of new methods for the synthesis of substances. Doping of zirconium silicate was performed during the synthesis of zirconium silicate by simultaneous interaction of 0.5 M solutions of zirconyl chloride, and sodium silicate and the solutions of dopant compounds when maintaining pH within the range of 7 - 7.2. To synthesize cerium-doped zirconium silicate, ZrOCl₂·8H₂O, purified Na₂O·SiO₂ solution, Ce(NO₃)₃·6H₂O were used.

The amounts of the initial solutions ZrOCl₂·8H₂O, Na₂O·SiO₂ and Ce(NO₃)₃·6H₂O were taken so as to ensure the following compositions of the final product: (0,95-0,98) of ZrO₂·(0,05-0,02) Ce₂O₃·SiO₂.

To obtain a homogeneous mass, the reaction mixture was kept for 25-30 minutes in a MW oven at a temperature of 100-200°C, and then the residue was filtered off using a Buchner funnel. The residue was thoroughly washed from Cl^- , NO_3^- and Na^+ ions by hot water (repulping) and dried in a microwave oven. To obtain the crystalline cerium-zirconium pigment, the mixture was fired in LHT 08/17 electric furnace LHT (Nabertherm Company).

According to the results of physico-chemical analysis, the synthesized fusion mixture has the following composition: $(0.95-0.98) \text{ZrO}_2 \cdot (0.05-0.02) \text{Ce}_2\text{O}_3 \cdot$

Fig. 51 and 52 present the results of thermographic and X-ray analysis of Ce-ZrSiO_4 pigment samples. The Ce-ZrSiO_4 thermogram reveals a deep endothermic effect at 170°C (within the range of 105 ÷ 435°C) corresponding to the removal of crystallization water. The absorbed water is removed at relatively low temperatures. Analysis of the sample weight loss curve indicates that up to approximately 435°C the loss is 83.8% of the total losses. A pronounced exothermic effect within the temperature range of 1050°C - 1220°C with the maximum at 1170°C is due to the formation of non-aqueous crystalline phase of zircon. The phase of the $\text{ZrO}_2\text{-SiO}_2$ non-aqueous system has only one binary compound - zircon, which composition corresponds to ZrSiO_4 formula.

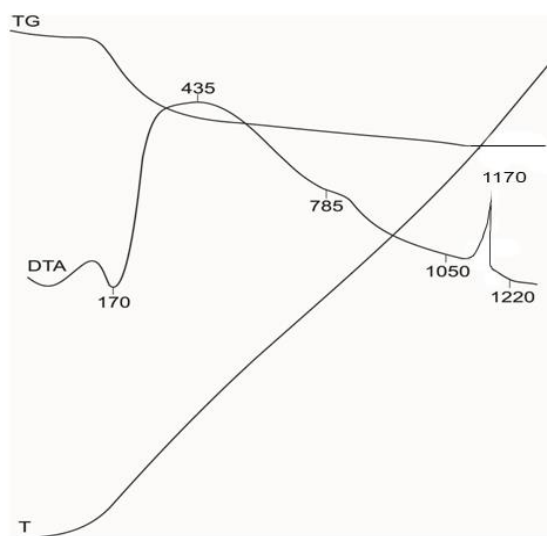


Fig. 51. DTA curves of the $\text{Ce-ZrO}_2 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ samples.

Electron micrographs of Ce-ZrSiO_4 samples were taken. It is seen from the pictures (see Fig. 53) that these crystals are characterized by a developed crystalline structure. The particle sizes are 2 - 5 microns.

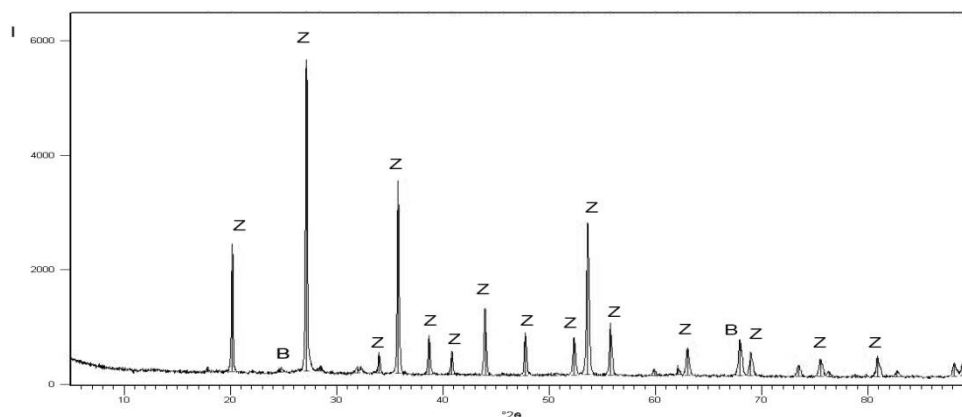


Fig.52. Diffraction patterns of $\text{Ce-ZrO}_2 \cdot \text{SiO}_2$. Firing temperature: 1200°C. Z-zircon, B-baddeleyite

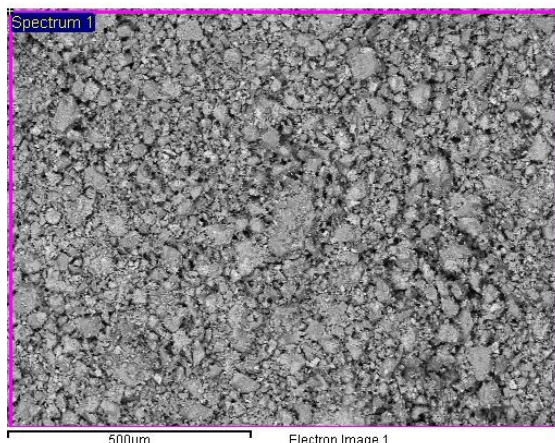


Fig.53. Electron microscope images of Ce -ZrSiO₄. Firing temperature: 1200°C

Thus, the obtained pigment has crystal structure of zircon with homogeneous distribution of all components. On the basis of gravimetric, X-ray and thermographic studies it is revealed that synthesis of the mixture of Ce-ZrSiO₄ pigments from the water -soluble salts of the initial components in microwave oven facilitates faster (at lower temperatures) and uniform implementation of cerium ions in the zircon crystal lattice during heat treatment of the synthesized mixture. The microwave method provides obtaining of a fine and homogeneous zircon pigment powder at lower temperatures and shorter firing times.

We studied the effect of irradiation on the zircon properties. Irradiation was carried out using linear electron accelerator ELU-5 at 90 K and 10^{-5} - 10^{-6} Pa. The optical absorption spectra of the synthesized zirconium silicate (both initial and irradiated with 5 MeV electrons at a dose of 10^{16} electrons/cm²) in the near infrared region of the spectrum were studied. The measurements were performed within the wavelength range from 1 mm to 2.2 mm under identical conditions for all the samples. Fig.54 shows the results of experimental measurements of the absorption spectra. Curve 1 relates to the irradiated sample, curve 2 to non-irradiated one. As it is seen from the absorption spectra, of 1.32 mkm and 1.54 mkm bands responsible for color centers, decrease. This means that the intensity change is due to creation of radiation damages in the structure of the sample after irradiation.

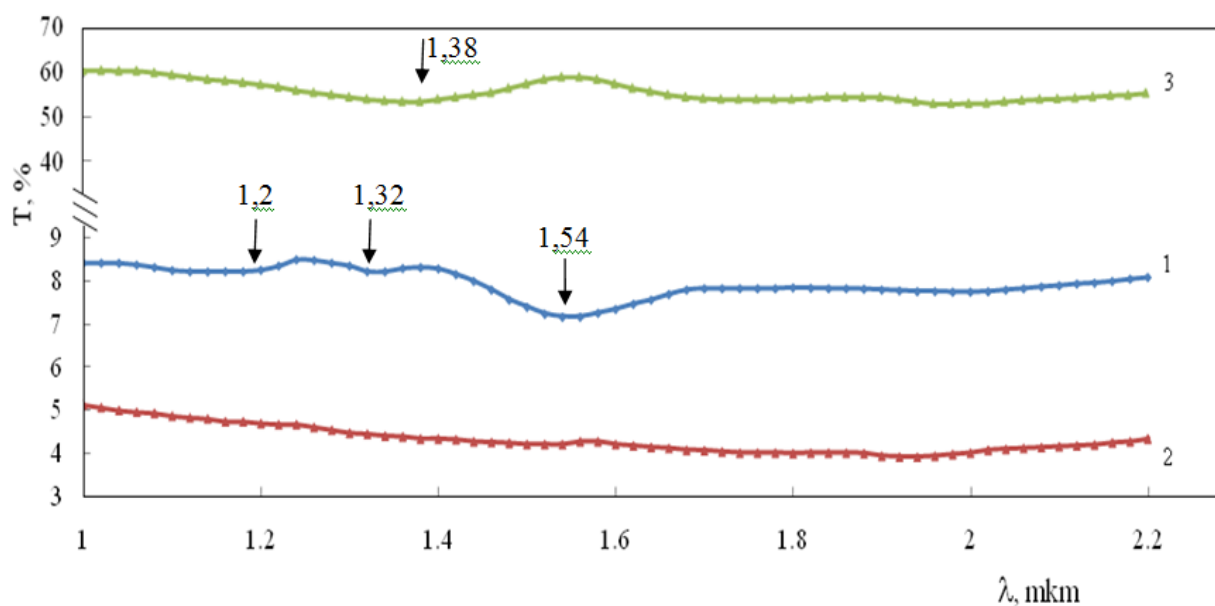


Fig.54. Optical absorption spectra of ZrSiO₄ heat-treated at 1200°C during 2 hr.

Thus, the observed changes in the absorption spectra of the investigated samples after heat treatment and electron irradiation confirm the fact of changing the zircon charge state and formation of structural radiation defects in the form of point defects with different charge states. UV radiation contributes to a redistribution of the intensity of those bands responsible for the defect formation in the crystal lattice, and, thus, promotes increase in the radiation resistance of the materials.

Task 3. Development of thermoregulating coatings.

Stage A7. Elaboration of composites for thermoregulating coatings. Selection of binders from the series of sodium and potassium silicates for the purpose of increasing radiation stability and reduction of out-gassing under the impact of the space.

Thermoregulating coatings of “solar reflectors” type for space vehicles have certain thermal and radiation characteristics: solar radiation absorption capacity (A_s) no more than 0.12, emissivity (ϵ) more than 0.92. Radiation resistance is estimated from A_s change (ΔA_s) under the action of a certain dose of UV radiation from the sun measured in equivalent solar days (e.s.d.), and should be minimal. Rather simple in terms of technology and resistant to UV radiation compared with different types of coatings (varnish-and-paint, plasma, etc.) are silicate coating consisting of binders and pigments. At this stage, the task is to develop a composition for the thermoregulating coating with low absorbance of solar radiation and high radiation resistance, while maintaining the needed emissivity. Investigation of characteristics of both initial and electron irradiated samples of sodium and potassium silicates has revealed that the radiation resistance of potassium silicate was higher than that of sodium silicate (Fig. 7, 8). UV radiation contributes to a redistribution of the intensity of those bands responsible for the defect formation in the crystal lattice, and, thus, promotes increase in the radiation resistance of the materials. Taking in account these data, we have selected potassium silicate with silica modulus 3-3.8 as a binder. A composition is developed for the thermoregulating coatings of “solar reflectors” type, which includes aqueous solution of potassium silicate with silica modulus 3 - 3.8 and density 1.16 – 1.18 g/cm³ and zirconium silicate ($ZrSiO_4$). When preparing the composition, the required amounts of $ZrSiO_4$ and potassium silicate solution are agitated in a planetary agate mill with agate balls for 45-60 minutes to obtain a homogeneous mass. Some laboratory samples of thermoregulating coatings of various compositions have been obtained. Currently, some characteristics of the samples are studied.

Stage A 8. Obtaining of thermoregulating coatings on the basis of the synthesized silicate pigments and their testing by absorption spectroscopy, diffusion reflection, luminescence spectroscopy in UV range, vacuum UV and X-ray irradiation methods.

The developed HTMW method of obtaining thermoregulating coatings comprises the following basic steps:

- Preparation of sodium and potassium silicate solutions.
- Cleaning of sodium and potassium silicate solutions from coloring impurities.
- Synthesis of silicates.
- Drying and heat treatment of silicates.
- Preparation of compositions for thermoregulating coatings.
- Obtaining of thermoregulating coatings.

Preparation of silicate solutions and removal of coloring impurities. Silicate solutions of sodium and potassium have been obtained from perlite, diatomite and quartzite by HTMW processing of rocks using alkaline solutions (processing time 15-60 minutes at 100-200°C). After the processing, the resulting pulp is filtered and washed by hot water for complete extraction of sodium and potassium silicates. The filtrate is fed to a cleaning line and the precipitate (alkaline alumina silicates) to a further processing line. The cleaning line consists of an electromagnetic unit, through which the filtrate (sodium/potassium silicate solution) is pumped at a certain rate. The magnetic solution after

addition of a precipitation agent (milk of lime at the rate of 0.3-0.5 g/l) is fed to the MW furnace reactor, where it is heated to the boiling temperature. After 30 min keeping at this temperature, the silicate solutions are filtered to remove coloring impurities from the solution. Then, the cleaned solutions are fed to a receiver. The cleaned solution of sodium metasilicate from the receiver is fed to the MW furnace reactor, where it is heated to 100°C and where simultaneously a solution of zirconium oxy chloride is added after 30 min. holding at 100°C. The obtained pulp is filtered and washed. The resulting zirconium silicate is dried and heat-treated. The thermoregulating coating composition is prepared on the basis of the heat-treated zirconium silicate and potassium silicate. Research aimed at the selection of optimum compositions for the thermoregulating coatings should be continued.

- compliance with tasks and milestones as described in the work plan

The fulfilled works are in compliance with the tasks and milestones described in the Work plan.

- achievements of the past year

Mineralogical, petrographic, chemical and XRF analyzes of the Armenian siliceous rocks (perlite, diatomite and quartzite) were carried out.

According to chemical analyzes, these rocks have rather stable compositions within a certain deposit. Chemical composition of perlites (in wt.%): SiO₂ - 71.36-74.43; Al₂O₃ - 13.1-15.43; Fe₂O₃ - 0.82-1.47; TiO₂ - 0.07-0.26; CaO - 0.8-1.42; MgO - 0.19-0.39; Na₂O - 2.52-3.87; K₂O - 3.46-4.57. Moisture content: 0.14-0.54. Loss on ignition: 3.13-5.62.

Quartzites generally contain 89.9 - 98.0 wt.% of SiO₂, the rest are Al, Fe, Ca, Mg, Na, K oxides. Chemical composition of diatomites (in wt.%): SiO₂ - 73.43-89.82; Al₂O₃ - 1.93-10.78; Fe₂O₃ - 0.75-4.27; TiO₂ - 0.10-0.36; CaO - 0.95-3.92; MgO - 0.65-1.05; Na₂O+K₂O - 0.17-0.73. Loss on ignition + moisture: 4.82-8.61. Petrographic analysis has showed that perlites are gray, whitish, brown or grey-brown glassy volcanic rocks. The crystal phase content in these rocks is no more than 5%. Quartzites are massive, in some cases laminate, fine- and medium-graded rocks consisting of quartz grains cemented by silica. They are hard materials having a high fire resistance. Diatomites are light, fine-pored rocks with earthy fracture. They consist of a variety of shells and debris of diatomite algae.

A possibility of obtaining of sodium/potassium silicate solutions from these rocks by HTMW processing. The processing of these rocks was carried out in a NaOH/KOH solution at a temperature of 100-240°C. Sodium/potassium silicate solutions with a silica modulus 1.0-3.8 were obtained. Some preliminary treatment conditions were determined for each type of the rocks, and SiO₂ extraction ratio from the rock were identified. Physical and chemical analyzes of intermediate and final products were carried out. Phase transformations in the rocks during the HTMW processing were studied. The content and status of coloring impurities (Fe₂O₃) in the resulting silicate solutions were determined. Several experiments on cleaning the silicate solutions from the coloring impurities were carried out using various physical and chemical methods. The obtained research results have shown a possibility of deep cleaning of silicate solutions of from coloring impurities. On the basis of the obtained sodium silicates, zinc and zirconium silicates of various compositions were synthesized. Their basic physical and chemical characteristics, the conditions for their synthesis were studied. The synthesized silicates are homogeneous, fine, amorphous materials; their surface area and pore volume can be regulated within a wide range by the synthesis conditions. At present, an optimum method of doping the silicates with rare-earth metals is developed. Some characteristics of optical absorption spectra of sodium, potassium and zirconium silicates were studied in the near infrared region - both initial samples and those irradiated with 5 MeV electrons at a dose of 10¹⁶ el/cm². The measurements were performed under identical conditions for all samples within the wavelength range from 1 mkm to 2.2 mkm. UV radiation contributes to a redistribution of the intensity of lines responsible for the defect formation in the crystal

lattice, and thus promotes an increase in the radiation resistance of materials. Several compositions for the "solar reflectors" type thermoregulating coatings have been developed. Some laboratory samples of such thermoregulating coatings of different composition have been obtained. At present, some characteristics of the samples are investigated. A HTMW method of obtaining thermoregulating coatings is developed.

4. Current technical status

- on schedule, behind, ahead
- refining next year schedule if necessary
- recommendation for changes of the work plan, if necessary

5. Cooperation with foreign collaborators

- Contacts with foreign partners during the first year were continued. Quarterly reports were sent to the partner - Air Force Office of Scientific Research (AFOSR).
- signature of protocols (with short description)
- research carried out jointly
- trips to/from foreign collaborators

From May 18 to May 22, 2015 the Project Manager Volodya V. Baghramyan and Scientific Leader Anahit A. Sargsyan visited Arlington, VA (Aerospace Materials for Extreme Environments Program Review). During the business trip they met the foreign partners of Project, PhD Ali Sayir, Program Officer and discussed several aspects related to the Project implementation.

- workshops, topical meetings organized by the project team

Some results of the study was presented at the IV International Conference "Chemistry and Chemical Technology" ([Www.sci.am/download_file_news.php?nid=349&f=1](http://www.sci.am/download_file_news.php?nid=349&f=1)), September 14-18, 2015, Yerevan.

Also, a report on the fulfilled work was presented at the International Workshop on ionizing and non-ionizing radiation influence on structure and biophysical properties of living cells. Tsaghkadzor, Armenia, September 25-27, 2015.

- joint attendance to international conferences

6. Problems encountered and suggestions to remedy

No problems encountered when executing works within the Project program.

7. Perspectives of future developments of the research/technology developed

Based on the results of investigation obtained for last year, it can be asserted that it is expedient to use siliceous rocks: perlite, diatomite and quartzite as raw materials for obtaining solutions of sodium/potassium silicates. The organization of industrial production of solutions of sodium/potassium

silicates on the basis of siliceous rocks will expand a raw-material base for obtaining various silicates and pigments. The zinc, zircon silicates obtained with MW method on the basis of rocks has certain advantages in comparison with the traditional method and can compete with them on the physicochemical and technical characteristics, especially in the field of production of TRC.

- Attachment 1: Illustrations attached to the main text (if)
Attachment 2: Other Information, supplements to the main text
Attachment 3: Abstracts of papers and reports published during the year of reference

1. Bagramyan V. V., Sargsyan A. A.// Liquid glass purification by microwave method with electromagnetic treatment , *Khimicheskaya Tekhnologiya*, 2015, No. 7, pp. 392–398. (in russian)

Abstract:The purification process of liquid glass from coloring impurities has been studied by preliminary electromagnetic treatment with after-heat-treatment in the presence of a precipitant with application of microwave energy (MW) for heating the reaction medium. It has been found out that iron in the liquid glass is in the form of complex salts of sodium ferrous silicate, $\text{NaFe}(\text{SiO}_3)_2 \cdot n\text{H}_2\text{O}$, and during purification the poorly soluble calcium ferrous silicates $\text{CaFe}_2(\text{SiO}_3)_4 \cdot n\text{H}_2\text{O}$ are formed. The influence of various factors on a purification degree of liquid glass, strength of the electromagnetic field, an amount of the precipitant agent, a flow rate through the electromagnetic field, a treatment time was studied. It is determined that use of microwave energy can significantly intensify the process of liquid glass purification and the amount of iron oxide decreases by 2 orders.

2. V. V. Bagramyan, A. A. Sargsyan, C. Ponzoni, R. Rosa, and C. Leonelli.// Microwave Assisted Preparation of Sodium Silicate Solutions from Perlite, *Theoretical Foundations of Chemical Engineering*, 2015, Vol. 49, No. 5, pp. 731–735.

Abstract:Systematic studies on the preparation of sodium_silicate solutions of different compositions via the hydrothermal_microwave treatment of perlite with an NaOH solution were performed. The effect of various factors on the degree of SiO₂ recovery and the reaction rate was studied. The application of microwave energy was established to intensify the process of hydrothermal treatment compared to conventional heating.

3. Baghrmalyan V.V.// Preparation the potassium liquid glass from diatomite by microwave method, *The materials of IV International Conference on the Chemistry and Chemical Technology*, Yerevan, 2015, p, 58-61.(in russian)

4. V.V.Baghrmalyan, A.A.Sargsyan, V.V. Harutyunyan.// Synthesis Natrium, Potassium Silicates for Thermoregulating Coatings Space Vehicles by Microwave Method. Presentations in International Workshop on Ionizing and non-ionizing radiation influence on structure and biophysical properties of living cells radiation influence on structure and biophysical properties of living cells Tsaghkadzor, Abstracts, Armenia , September 25-27, 2015,p 86.

5. V.V.Baghrmalyan, A.A.Sargsyan, V.V. Harutyunyan.// Synthesis Natrium, Potassium Silicates for Thermoregulating Coatings Space Vehicles by Microwave Method. Article sent to *Armenian Journal of Physics*. It will published in No. 1,2016.

Abstract: 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 SiO₂ 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.