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INVESTIGATION OF SOME VOLCANIC GLASSES OF GEORGIAN DEPOSITS

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The paper presents research materials on some hydrogen-containing volcanic glasses of Transcaucasia of acidic composition, concentrated in areas of late Tertiary-Quaternary volcanism, in particular, the central part of the Akhalkalaki plateau, within the Akhaltsikhe valley (Georgia). Studies of natural materials of perlite, obsidian and pechstein were carried out by geological, physico-chemical: petrography, chemical analysis, X-ray diffractometry, and IR spectroscopic methods. The work shows the genesis, structural features and prospects of using these minerals. It has been found that the chemical composition of the minerals studied is characterized by a different content of aluminum oxide Al_2O_3 . It is shown that silicon oxide SiO_2 , which is a part of volcanic glasses, occurs in an amorphous state. Perlites of the studied deposits differ from each other both visually and in composition. The perlites of the Toloshi deposit are dark gray in color and the Paravani deposits are white. In the perlite spectra of the Tolosh deposit, the vibrational frequencies of both the intratetrahedral and in the intertetrahedral space of Si-O-Si (Al) indicate that silicon is replaced by aluminum to a lesser extent than in the perlite of the Paravani deposit. The prospects of using expanded volcanic glasses are also shown.

Keywords: *perlite, obsidian, volcanic glass, petrography, chemical analysis, X-ray diffractometry, IR-spectroscopy*

INTRODUCTION

Along with perlites, obsidian and pechstein are acidic volcanic glasses. They are formed at the edge of molten magmatic lava as a result of rapid cooling, when in contact with the ground, and differ from each other mainly by the water content in the texture. Perlite contains up to 6 % water and is characterized by concentric shell texture. Obsidian contains less than 1 % water and is characterized by high hardness (≈ 5.6 on the Mohs scale) and a massive texture. The water content in pechstein is 8–10 % [1, 2].

In some cases, perlites associate with obsidian and form species of obsidian-perlite, where obsidian exists as an insert. It is also possible to associate two types of perlite with different water content. In this case, the nucleus of perlite, with a low water content, is characterized by an intracellular shell. In addition, there is a “layered” alternation of volcanic glass with different water content: obsidian-perlite or perlite-perlite.

The chemical composition of perlite is mainly as follows: SiO_2 -70-75 %, Al_2O_3 -12-14 %, Na_2O -3-5 %, K_2O -3-5 %, up to 1 % Fe_2O_3 , CaO and MgO. It also contains water and gases: CO_2 , N_2 , H_2 , SO_3 ,

Ne, Ar. The location of gases and water molecules in volcanic glass is unequal or stream-like [1, 3].

There are two types of water in perlites (structural (up to 2–5 %) and mobile). It may also contain hydroxyls (OH). Structural water is linked to the tetrahedra of aluminosilicium oxygen through hydrogen binding. Its content is 1–3 %. Movable water, that can be 0–7 % in the mineral composition, fills channels and gaps of molecular size. The moving water of the perlites is released during the heating of the mineral from 50 to 250–300 °C and the structural water – after heating above 250–300 °C. Hydroxyl groups act as bridges between the aluminosilicium oxygen tetrahedra [1].

Dependent on the texture, there are massive, layered, breccial and pumice-like perlites. A specific peculiarity of perlites is their capability to swell when heated at high temperatures – i.e. increase the initial volume (5–20 times). Swelling occurs when heated at a temperature of 900–1200 °C, from 1 to 3 min. In the case of obsidian, swelling can occur at the same temperature, but heating takes longer, 3–10 min [2–4].

Swollen perlite is a loose, porous, lightweight, stable material that can be used at temperatures from

-200 to +900 °C. It has thermal- and noise-insulation properties and can absorb liquid in an amount of more than 400 % of its weight; it is biologically stable, does not rot under the influence of microorganisms; it is not a desirable environment for the reproduction of insects and rodents. Perlite is chemically inert – it is neutral to the effects of a weak acidic and basic environment. Perlite is medium friendly and sterile, non-toxic and does not contain heavy metals.

Perlite can be used under both unprocessed and swollen conditions. Mainly, swollen perlites are used. These type of perlites are used as insulating materials in construction, as adsorbents in the oil and gas industry; they are used for the purification of drinking water, as filters – in the food industry, as well as for the purification of water chemically or of nuclide-contaminated one; in medicine they are used for filtering pharmaceutical preparations. Swollen perlites are also widely used in agriculture.

EXPERIMENTAL

In Transcaucasia, water-containing volcanic glasses of acid composition are concentrated in areas of late Tertiary-Quaternary volcanism. Large deposits of volcanic glass are known within the western spurs of the Geghama ridge, at the southwestern edge of the Aragats volcanic massif, on the eastern and northeastern spurs of the Zangezur ridge in the western part of the Karabakh upland, in the central part of the

Akhalkalaki plateau and within the Akhaltsikhe valley [5].

The objects of research were perlite and obsidian from two different regions of Georgia: perlite and obsidian of so-called “Korghan” deposits of Ninotsminda region and perlite from the village Toloshi in Aspindza region [6–8].

The chemical composition of these samples was investigated, and petrographic, X-ray diffractometric and IR spectroscopic analyses were also performed. The results of these studies are presented in Table 1 and Figs. 1–6.

X-ray diffractometric analysis was carried out with a device “DRON-4.0”. Infrared spectrographic analysis was performed with an Agilent Cary 630 FTIR Spectrometer.

Petrographic analysis was carried out with an Optika B-383POL microscope.

RESULTS AND DISCUSSIONS

The data of chemical analysis of the samples differ significantly. As expected, SiO₂ in the largest quantities is present in obsidian and Al₂O₃ – in perlite of Paravani deposit (see Table 1). Accordingly, the ratio SiO₂/Al₂O₃ is as follows: Paravani perlite < Toloshi perlite < obsidian. Obsidian also contains large amount of alkaline earth metal oxides. The largest difference in the chemical composition of obsidian and perlite is in the percentages of water and phase. Their total value in the composition of perlites (Paravani, Toloshi) is 17.63 and 15.56 %, respectively, and in the case of obsidian – 3.54 % (Table 1).

Table 1. Chemical composition of the samples studied

Sample	Chemical composition of samples										
	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	CaO	MgO	MnO	TiO ₂	Fe ₂ O ₃	SO ₃	P ₂ O ₅
Perlite (Paravani)	52.19	23.65	2.50	0.38	0.84	0.31	0.10	0.20	1.57	0.50	0.11
Perlite (Toloshi)	60.76	12.21	3.55	2.13	1.65	1.88	0.07	0.19	1.61	0.34	0.05
Obsidian (Paravani)	72.70	12.63	4.95	4.20	0.81	0.02	0.06	0.11	0.92	0.01	0.05

Petrographic analysis of the samples showed that the perlite of the Toloshi location is a rock with a dacite composition and structure, which is built of volcanic glass, where perlite spheroidal cracks, obtained as a result of depletion, are observed. Pure and amphibole-containing crystals

of plagioclase ranging in size from 0.03 to 0.5 mm, are rarely observed in the glass (Fig. 1).

Minerals, probably pyrite, are also rare. Perlite of the Paravani deposit is built with a strong replacement volcanic glass in which perlite spherical cracks are observed. The glass is devoid of any admixtures. The only mineral found is

chlorite, which is a product of volcanic glass replacement. There are also iron-enriched areas

that are likely to be a product of the destruction of some iron-containing mineral (Fig. 2).

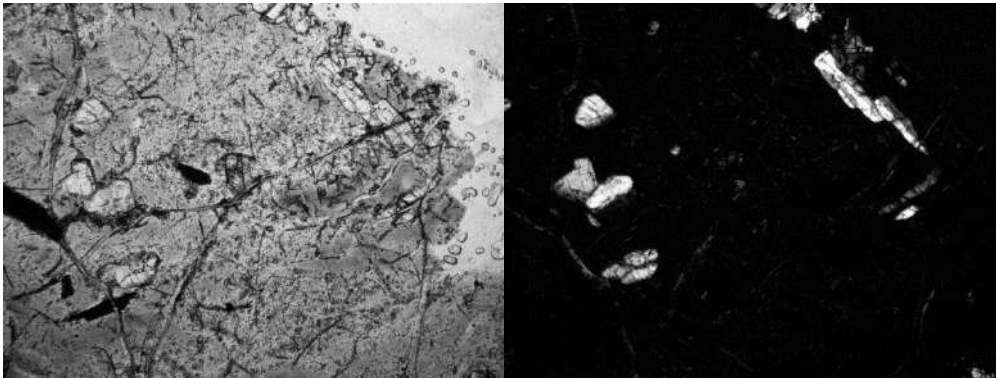


Fig. 1. Perlite of Toloshi location. Magnification – 40×

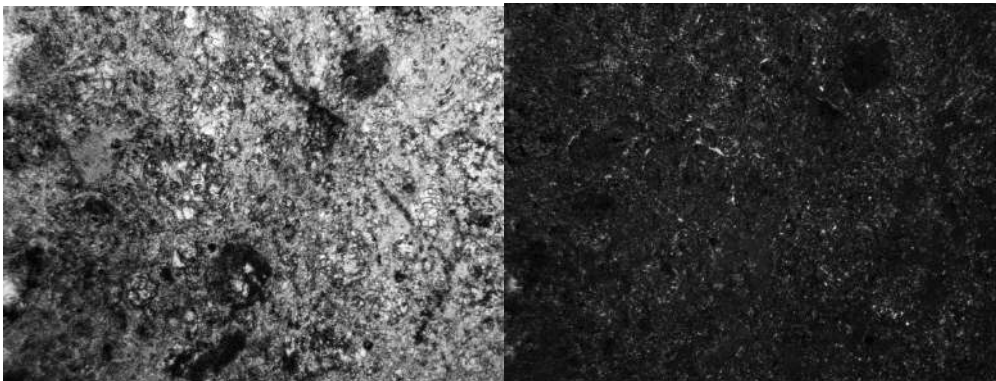


Fig. 2. Perlite at the location of Paravani. Magnification – 40×

The obsidian sample consists entirely of volcanic glass. Rarely, at large magnifications (100× diameter), the smallest grains of plagioclase are observed, as well as cracks, which can be characterized as perlite. Due to the transparency of the sample, it could not be observed.

X-ray diffractometric analysis of the samples showed that they sharply differ from each other. First of all, their structure consists mainly of an amorphous phase. This is especially true for obsidian. Samples vary in degree of dispersion. Except of crystalline silicon oxide, in perlite samples of the Toloshi location, andesite-specific and feldspar-specific peaks are clearly visible and in the perlite sample of the Paravani location, there are peaks of chlorite and feldspar (Fig. 3).

The study of all three samples by IR spectroscopy showed that the spectra of the samples are similar to those of silicates. These are two high-intensity bands of stretching vibrations (ν_1) of Si–O–Si bonds at the frequency of

1073 cm^{-1} – obsidian; 1058 cm^{-1} – perlite (Toloshi); 1041 cm^{-1} – perlite (from Paravani deposit). An increase in the vibration frequencies of the bands is completely consistent with the results of chemical analysis of the samples, since the frequencies of these bands depend on the value of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio [9]. The band of bending vibrations (ν_1) of the same bond is 467, 469 and 471 cm^{-1} , respectively. In addition, the perlite from Paravani deposit, unlike these two samples, has a band of 551, 692 and 912 cm^{-1} . The first two bands can be attributed to Al–O vibrations, and the third at 912 cm^{-1} – to Al–OH vibrations [10–13] (Fig. 4).

It is interesting that in these samples water and hydroxyl groups are represented in different kinds and in all three samples the band of bending vibrations of water is equally fixed (at $\approx 1640 \text{ cm}^{-1}$) [1, 2]. In the stretching vibrations the zone of water obsidian has one band – 3445 cm^{-1} , in the perlite of Toloshi deposit - two bands – 3438 and 3640 cm^{-1} are observed and in

the perlite of Paravani deposit there are three types of hydroxyl groups – at 3440, 3619 and

3696 cm^{-1} . These three species correspond to the data known from literature [1, 7] (Figs. 5, 6).

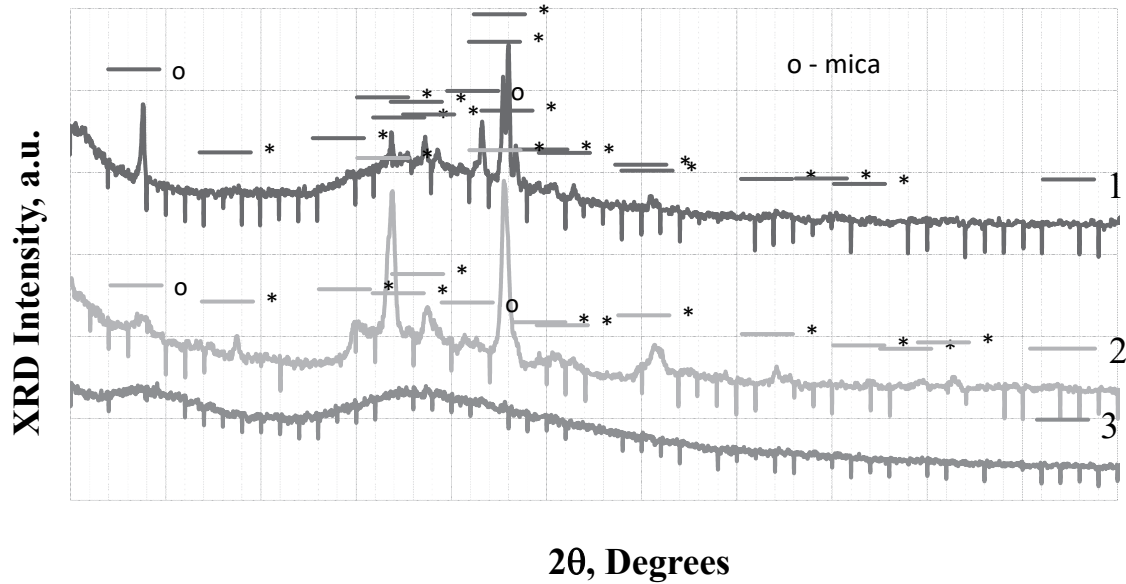


Fig. 3. X-ray diffractograms: 1 – perlite at Toloshi location; 2 – perlite at the location of the Paravani; 3 – obsidian of the location of the Paravani

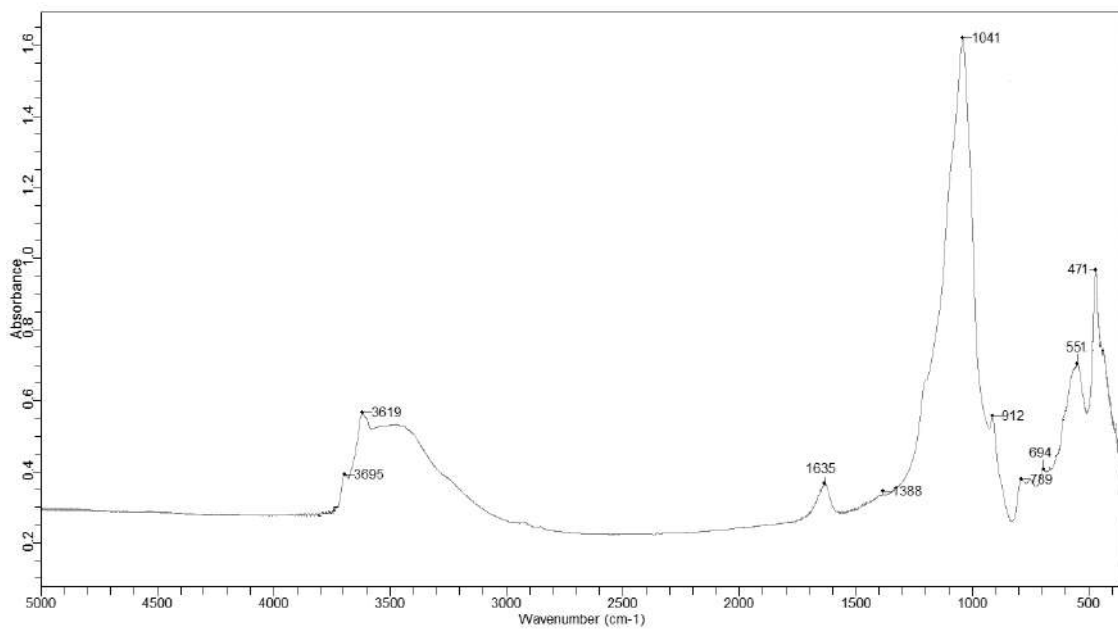


Fig. 4. IR spectra of Perlite from Paravani deposit

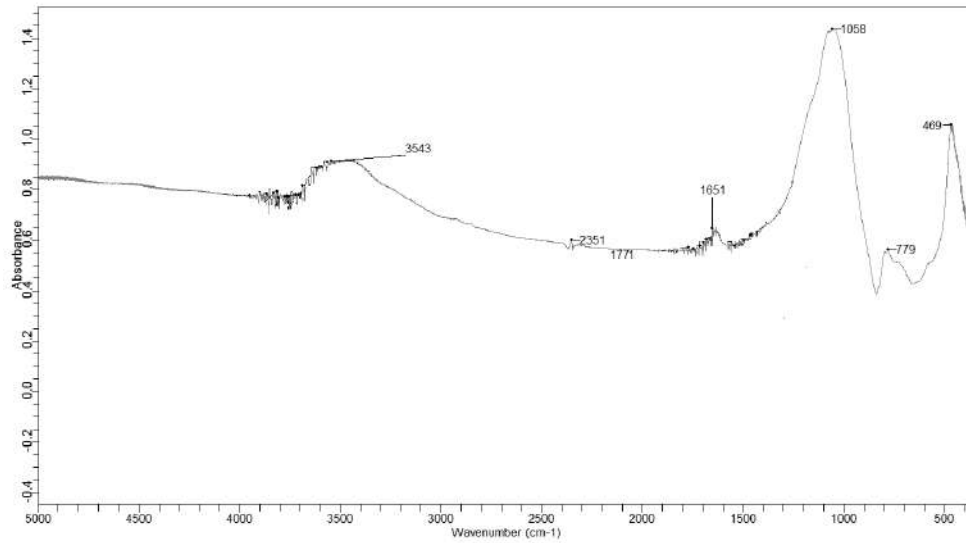


Fig. 5. IR spectra of Perlite from Toloshi deposit

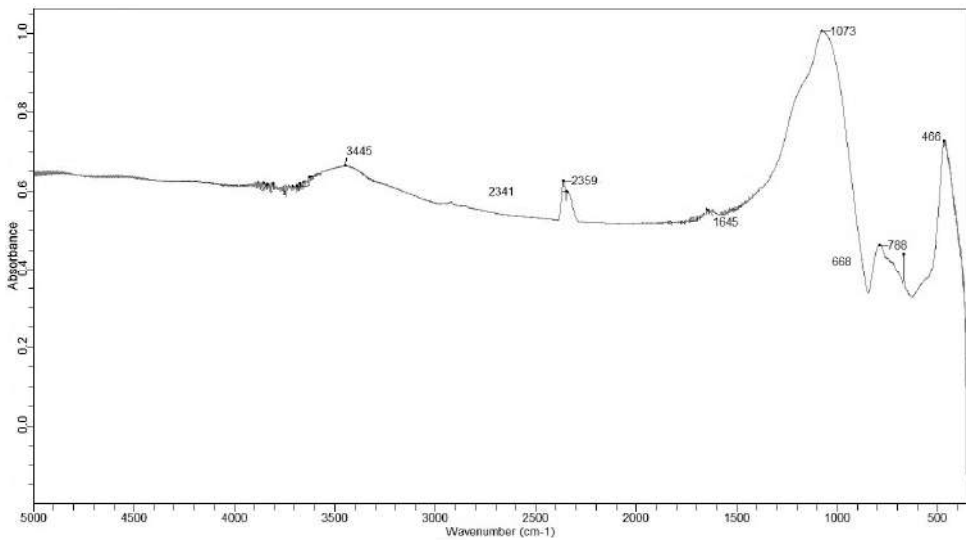


Fig. 6. IR spectra of Obsidian from Toloshi deposit

CONCLUSION

The petrography of obsidian and perlite of Georgia (two different deposits) have been studied. Chemical, X-ray diffractometric and IR-spectroscopic analyses of these samples have been carried out. It has been found that the chemical composition of minerals differs from each other mainly by the content of Al_2O_3 . It has been shown that SiO_2 -containing volcanic glass is mainly in an amorphous state. Perlites differ from each other both visually (perlite of the

Toloshi deposit is dark gray and the other – of the Paravani deposit – is white), as well as in terms of composition. In the perlite spectrum of the Toloshi deposit, in the internal vibration bands, as well as in the vibration bands between the Si–O–Si (Al) tetrahedra, we can see that the replacement of silicon with aluminum is less common than in the perlite of the Paravani deposit. The prospects for the use of volcanic glass are also shown.

Дослідження деяких вулканічних стекел грузинських родовищ

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В роботі представлені матеріали досліджень деяких водневоміських вулканічних стекел Закавказзя кислого складу, що концентруються в районах пізньотретинного-четвертинного вулканізму, зокрема, у центральній частині Ахалкалакського плато, в межах Ахалціхської долини (Грузія). Дослідження природних матеріалів перліту, обсидіану і пехитейну були проведені геологічними, фізико-хімічними методами: петрографія, хімічний аналіз, рентгенодифрактометричним, ІЧ-спектроскопічним. У роботі показаний генезис, структурні особливості і перспективи використання перерахованих мінералів. Встановлено, що хімічний склад досліджених мінералів різниться вмістом оксиду алюмінію Al_2O_3 . Показано, що оксид кремнію SiO_2 , що входить до складу вулканічних стекел, знаходиться в аморфному стані. Перліти досліджених родовищ відрізняються один від одного як візуально, так і складом. Перліти родовища Толоші мають темно-сірий колір, а родовища Паравані - білий. В спектрах перліту Толошського родовища частоти коливань як в тетраедрах, так і в міжтетраедричному просторі Si-O-Si (Al) вказують, що заміщення кремнію алюмінієм відбувається в меншій мірі, ніж в перліті Параванського родовища. Також подано перспективи застосування спучених вулканічних стекел.

Ключові слова: перліт, обсидіан, вулканічне скло, петрографія, хімічний аналіз, рентгенівська дифрактометрія, ІЧ-спектроскопія

Исследование некоторых вулканических стекел грузинских месторождений

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В работе представлены материалы исследований некоторых водородсодержащих вулканических стекел Закавказья кислого состава, концентрирующихся в районах поздне-третичного-четвертичного вулканизма, в частности, центральной части Ахалкалакского плато, в пределах Ахалцихской долины (Грузия). Исследования природных материалов перлита, обсидиана и пехитейна были проведены геологическими, физико-химическими методами: петрография, химический анализ, рентгенодифрактометрическим, ИК-спектроскопическим. В работе показан генезис, структурные особенности и перспективы использования перечисленных минералов. Установлено, что химический состав исследованных минералов отличается различным содержанием оксида алюминия Al_2O_3 . Показано, что оксид кремния SiO_2 , входящий в состав вулканических стекел, находится в аморфном состоянии. Перлиты исследованных месторождений отличаются друг от друга как визуально, так и составом. Перлиты месторождения Толоши имеют темносерый цвет, а месторождения Паравани - белый. В спектрах перлита Толошского месторождения частоты колебаний как внутри тетраэдров, так и в межтетраэдрическом пространстве Si-O-Si(Al) указывают, что замещение кремния алюминием происходит в меньшей степени, чем в спектрах перлита Параванского месторождения. Также показаны перспективы применения вспученных вулканических стекел.

Ключевые слова: перлит, обсидиан, вулканическое стекло, петрография, химический анализ, рентгеновская дифрактометрия, ИК-спектроскопия

REFERENCES

1. Kovalsky F.L., Rasadkin V.V., Sergeev K.A. *Mineral raw materials. Perlite*. (Moscow: Geoinformark, 1998).
2. www.petroperl.ru/perlit-vspuchenny
3. www.petroperl.ru/o_perlit
4. www.geolib.net/petrography/obsidian.html
5. Nasedkin V.V. *Water-containing volcanic glasses of acid composition, their genesis and changes*. (Moscow: AN SSSR, 1963).
6. Zaridze G. *Petrology of magmatic and metamorphic rocks*. (Georgia: Ganatleba, 1972).
7. Makaradze L., Khachaturian K., Brokishvili M. The facilities obtained on basis of local raw materials for cleaning oil-contaminated objects using sorbents. In: *Petrochemical conference dedicated to the 100 Anniversary of Academician Leonid Melikadze*. (November 1–2, 2012, Tbilisi, Georgia) P. 141.
8. Khachaturian K., Makaradze L., Brokishvili M. Chromatographic analysis for oil light fractions using perlitic and diatomitic solid lining. In: *Petrochemical conference dedicated to the 100 Anniversary of Academician Leonid Melikadze*. (November 1–2, 2012, Tbilisi, Georgia). P. 147.
9. Tsitsishvili G.V., Tsintskaladze G.P., Tsitsishvili V.G., Tsintskaladze Z.P. Dependence of IR-bands on ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ in zeolites. *Georgia Chemical Journal*. 2005. **5**(2): 140.
10. Plusnina I.I. *IR-spectra of minerals*. (Moscow State University, 1977). [in Russian].
11. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry*. Sixth Edition. (Wiley, 2009).
12. Plusnina I.I. *IR-spectra of minerals*. (Moscow State University, 1967). [in Russian].
13. Vlasova A.T., Florinskaya V.A. *IR-spectra of zeolite silicates*. (Moscow: Khimia, 1970).

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