საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 19(193), №4, 2025
BULLETIN OF THE NATIONAL ACADEMY OF SCIENCES OF GEORGIA, vol. 19(193), no. 4, 2025

Physical Chemistry

Influence of Natural Zeolite Minerals on Chemical Processes Occurring in Building-Restoration Lime Mortars

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(Presented by Academy Member V. Tsitsishvili)

Abstract. Lime mortar is the simplest three-component building material used for centuries in almost all countries of the civilized world for construction and restoration work. It is still used for that purpose. Lime mortar is the main binding material, the quality of which largely determines the longevity of a building or a historical monument. The research aims to study the hardening process of lime mortar, the selection of reactive components, and such mineral additives with high activity that can affect its strength. Natural zeolites from the regions of Georgia were chosen as additives for lime mortar, which are characterized by all the properties of pozzolanic additives that facilitate the application process. Their physical and chemical properties, their influence on the hardening process of lime mortar and on its strength were studied. The results of the study showed that the strength of the mortar largely depends on the chemical, phase composition, and structure of its components and additives. The optimal composition of the mortar was determined. Zeolites with different structures have different effects on mortar strength. The best result was shown by zeolite clinoptilolite. *© 2025 Bull. Natl. Acad. Sci. Georg.*

Keywords: lime mortar, natural zeolite, lime, sand, physico-chemical research methods

Introduction

One of the reasons for the deterioration of architectural and cultural monuments is the use of poor-quality building materials, including lime; however, pure lime is practically not used. Lime mortar is used, which is a mixture of lime with sand and water.

The second most important component of lime mortar is sand, which is a mixture of silicates and aluminosilicates (Boynton, 1980; Shuagshuang et al., 2022; Cowland, 2022).

The hardness of silicates depends significantly on the ionic radius of the main cations and the type of chemical bond. Silicates built with cations with small ionic radius have high strengths (Colella et al., 2001).

After adding an appropriate amount of the third mortar component – water – to the lime and sand

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mixture, the mortar hardening process proceeds in several directions. The first is the evaporation of chemically unbound water, the second is the interaction of calcium hydrate with carbon dioxide in the air, in which calcium hydrate gradually loses chemically bound water and calcium carbonate is formed – a solid salt of limestone. Absorption of carbon dioxide occurs rapidly, and since this process occurs mainly on the surface of the mortar, a crust is formed that prevents the reaction from continuing in this direction and complete evaporation of chemically bound water. Therefore, this process takes decades (Colella et al., 2001; Aiello, 1995; Tsintskaladze et al., 2018). In addition to the carbonation process, lime-free particles interact with clay substances, actively decompose them and form gel-like hydrosilicates, which gradually lose moisture and act as binders for various particles. For different aluminosilicates, this reaction proceeds at different rates and depends on the reaction medium. If the medium does not conform to the corresponding norm, the physical property of the mortar may change and it will not harden (Shuagshuang et al., 2022; Cowland, 2022). Therefore, in addition to the quality of lime, the chemical and phase composition of sand is of great importance in the mortar hardening process (Lidin et al., 2019; Orlenko & Shuan, 2016; Tutberidze, 2010).

The goal of the research is to create a high-strength mortar of exceptional quality that will be used in both construction and restoration. To this end, mortar components of various chemical compositions, as well as some mineral additives selected based on their structural features were studied.

Materials and Methods

In order to determine the optimal composition of the building mortar, yellow sand from Sachkhere deposit (Georgia) was selected. Lime was selected taking into account its chemical composition.

The preparation of the desired fraction of the samples was carried out on the devices: Laboratory jaw crusher (RAM 35, Rantek Brand, Turkey); Electromagnetic vibrator-shaker (BIOBASE BK-TS200, Chine). Methods of chemical, X-ray diffractometric, IR spectroscopy and petrographic analysis were used to study the chemical and mineralogical composition and structure of the objects of study.

Chemical analysis was carried out on a Spectroscout XEP-04 (Germany); X-ray diffractometry analysis was carried out on a Dron-4 device (Russia). The X-ray diffractometer connected to a personal computer via the USB port multimeter AX-18B and the corresponding PC software-PC-Link, which allows the processing of experimental data in Excel format; Infrared spectrometric analysis was carried out on an Agilent Cary 630 FTIR Spectrometer in the range of 350-5000cm^{-1} (USA). Samples were prepared in KBr tablets. Petrographic analysis was carried out on the device Optica B383 polarizing microscope.

To carry out physical and mechanical tests of lime mortar, construction samples were made. Water was added in portions. Then the samples were formed by vibration as cubes of 2 x 2 x 2 cm. Forms containing samples were stored at a room temperature (20 ± 2)°C and 65% humidity.

Physical and mechanical compression tests of the samples were carried out 28 days after moulding. The tests were carried out on a 5-tonne laboratory hydraulic press.

All over the world, zeolites have been used in construction since prehistoric times as a facing material and are still used today. At present, in many countries, natural zeolites are used as additives to cement. Of particular interest is their use in pozzolanic cements (Baerlocher et al., 2007; Tsitsishvili et al., 2005). Zeolites have attracted the attention of their unique mineralogical, chemical and macroscopic properties. For the purpose of structural modification of lime mortar, we used zeolite-clinoptilolite from the Khekordzula (Mtskheta Municipality) location, zeolite-mordenite from the Bolnisi-Ratevani location and zeolite-laumontite from the Tbilisi (Botanical Garden) location.

Results and discussion

The phase composition of clinoptilolite in the samples is as follows: Khekordzula deposit: clinoptilolite – 90%, plagioclase fragments – 5%, chlorite – 3%, ore minerals – 1%, etc. Mordenite is as follows: 70% – mordenite, 12% – plagioclase, 8% – quartz, 5% – chlorite, 3% – ore minerals, 1% – effusive rock fragments, etc. Laumontite is as follows: 80% – laumontite, 10% – amphibole, 5% – clay-shale fragments, 2% – carbonate, 2% – ore minerals, etc.

To test zeolite-added mortar, 7 types of building mortar samples were prepared, consisting of ground quicklime and sand from Sachkhere deposit, to which zeolite was added in the amounts of 30g and 60g respectively. The samples were formed into cubes and after 28 days their physical and mechanical compression tests were carried out. The results are presented in Table 1. The test showed that after 28 days the strength of the lime mortar increased from 20% to 77% with the addition of clinoptilolite, decreased by 15% with the addition of mordenite, and increased by 44% with the addition of laumontite.

The chemical composition of mortars with the addition of clinoptilolite, mordenite, and laumontite is shown in Table 2, which shows that the content of silicium and aluminium cations in the mortar changed dramatically.

In lime solutions with different zeolite additives, the chemical reactions of SiO_2 with CO_2 and CaO proceed differently. This is also indicated by the results of X-ray structural analysis. The high SiO_2 content in the samples with the addition of mordenite indicates that silicon salts are less reactive than in the case of clinoptilolite. In lime solutions containing laumontite, silicon salts are characterized by low reactivity. All this is possible due to the fact that the structure of clinoptilolite is conditionally three-dimensional, it is layered, like feldspars, which play an active role in the process

Table 1. Test results of lime mortar containing zeolites

Mortar composition						Amount of water added, %	Strength after 28 days, MPa
				Zeolite location	%		
Scorched at 1000°C with a 2-hour delay	150g	Yellow sand	150g	Without zeolite additive	–	33.3	2.0
				Clinoptilolite	10	36.7	2.8
					30	46.8	3.1
				Mordenite	10	60.0	1.7
					30	68.7	1.3
				Laumontite	10	43.3	2.88
					30	68.0	1.60

Table 2. Data of chemical analysis of samples

Constituent elements in the form of oxides	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	SO_3
Sand + lime (without additives)	12.96	1.34	41.75	0.36	0.50	0.13	0.74	0.03	1.40
Sand + lime + 30 g zeolite clinoptilolite (10%)	13.05	1.58	39.19	0.32	0.51	0.13	0.74	0.05	1.32
Sand + lime + 60 g zeolite clinoptilolite (30%)	14.65	1.78	36.28	0.42	0.53	0.13	0.79	0.03	1.33
Sand + lime + 30 g zeolite mordenite (10%)	61.07	8.55	1.76	0.49	2.62	0.13	1.97	0.30	0.21
Sand + lime + 60 g zeolite mordenite (30%)	60.35	8.74	2.11	0.51	2.51	0.13	1.96	0.25	0.30
Sand + lime + 30 g zeolite laumontite (10%)	57.50	9.70	3.20	0.60	2.40	0.10	2.50	0.30	0.20
Sand + lime + 60 g zeolite laumontite (30%)	56.80	9.60	4.00	0.70	2.00	0.50	2.60	0.20	0.10

of lime hardening. Accordingly, clinoptilolite is more reactive than other zeolites. X-ray diffractograms of all solutions with zeolite additions show a quartz (SiO_2) peak at 3.34 Å and a calcite peak at 3.36 Å. Their intensity decreases with time. In 28 days, concrete strength increases compared to 7 days, which indicates the reactivity of the substances contained in the mortar. It should be noted that delaying the cubes for 90 days showed that their strength more than doubled compared to delaying them for 28 days. This again proves that the mortar hardening process is continuous and prolonged.

Petrographic studies of the clinoptilolite-containing mortars showed that their phase composition changes insignificantly. The mortar mainly consists of finely dispersed clay and carbonate masses, as well as fragments of quartz, plagioclase, microcline and basalt. Petrographic analysis of the mordenite- and laumontite-containing lime solution showed that here, as in the clinoptilolite-containing lime, the main indicator is the clayey zeolite mass, in which fragments of different sizes and origins (minerals and rocks) are observed. Namely, small fragments of granite, quartz, plagioclase and spherical formations of carbonate material (presumably, remains of fauna).

IR spectroscopy study of samples obtained with clinoptilolite addition showed that for the mortar without zeolite addition the intensity of Si-O-Si (Al) bond vibrations in the IR spectrum, both in the valence and deformation regions, are much lower than in the spectrum of the mortar with zeolite addition. This is observed for clinoptilolite from all three deposits. The bands of intertetrahedral deformation vibration at 594 and 695 cm^{-1} characteristic of zeolite-clinoptilolite are also present in the mortar composition (Tsitsishvili et al., 2007). In the IR spectrum of the mortar with a zeolite clinoptilolite additive, it is especially interesting to reduce the intensity of the valence vibration bands of hydroxyl groups (by 3495, 3513, 3644 cm^{-1}). Apparently, after a certain time, water present in the zeolite structure participates to some extent in the chemical processes occurring in the mortar composition. This is also evidenced by the decrease in the intensities of the Si–O–Si(Al) intertetrahedral vibration bands (at 633, 595, 1190 cm^{-1}). For the same reason, the intensity of the valence vibrations band of OH-ions (≈3444 cm^{-1}) was reduced. The study of IR spectra of the mortar with the addition of mordenite showed that the intensities of the bands of intertetrahedral vibrations, both deformation (at 524-537, 694-645 cm^{-1}) and valence (at 1162-1168 cm^{-1}), characteristic of zeolite, are high, which allows us to conclude that aluminosilicates of such structure are less involved in the chemical reaction of the zeolite hardening process. This is evidenced by the high intensity of the valence vibration band of the OH- ions at 3645 cm^{-1}. In the IR spectra of laumontite-containing mortars, as in mortars containing mordenite, the intensity of bands of intertetrahedral vibrations both deformation (at 510, 694 cm^{-1}) and valence (at 1160 cm^{-1}), characteristic of the aluminosilicate structure is high. So the process of calcium silicate formation is relatively slow. However, in this case, the compressive strength increases slightly.

Conclusion

Zeolites play a major role in zeolite-containing tuff rocks. They are the main binders in this material. It is an adsorbent that controls humidity and temperature in the building. In addition, it is not enough to consider zeolite tuff only as a building material, it is necessary to study its mineralogical, chemical and macroscopic properties, because its use in construction is the result of synergy of the components that make up zeolite tuff and depends on its general properties. By introducing a zeolite additive in the mortar, the quantity and quality of hydrosilicates involved in the mortar hardening process increase due to the water adsorbed in the pores of the zeolite. This facilitates the prolonging of the hardening process of the mortar and increases its strength.

Introduction of a certain amount of zeolite additive into building mortar had a significant effect on its strength.

- Adding zeolite-clinoptilolite (10%) increased the strength of the mortar – by 77%;
- The addition of zeolite-laumontite (10%) increased the strength of the mortar by 44%;
- In the case of zeolite-mordenite the results were different. The addition of zeolite-mordenite (10%) reduced the strength of the mortar by 15%;

This is due to the phase composition of this zeolite. The zeolite phase here is smaller compared to others, which did not lead to the desired result. Thus, the strength of the zeolite-containing lime solution is greatly influenced by the structure of the zeolite, its chemical and phase composition. The more reactive minerals and cations in the zeolite, the stronger the lime solution.

Acknowledgements

The research was supported by Shota Rustaveli National Science Foundation of Georgia within Grant FR-22-10840.

ფიზიკური ქიმია

სამშენებლო-სარესტავრაციო კირის დუღაბში მიმდინარე ქიმიურ პროცესებზე ბუნებრივი ცეოლითური მინერალების გავლენა

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** ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, საქართველო*

(წარმოდგენილია აკადემიის წევრის ვ. ციციშვილი მიერ)

კირის დუღაბი უმარტივესი სამკომპონენტიანი სამშენებლო მასალაა, რომელსაც საუკუნეების განმავლობაში სამშენებლო სარესტავრაციო საქმეში იყენებდა და იყენებს ცივილიზებული მსოფლიოს თითქმის ყველა ქვეყანა. ეს არის შემკვრელი მასალა, რომლის ხარისხზე დიდადაა დამოკიდებული შენობის ან ისტორიული ძეგლის არსებობის ხანგრძლივობა. კვლევის მიზანია დუღაბის გამაგრების პროცესის კვლევა, აგრეთვე დუღაბის გამაგრების პროცესში რეაქციის უნარიანობის მქონე კომპონენტებისა და ისეთი მინერალური დანამატების შერჩევა, რომელთაც მაღალი აქტივობა ექნებოდა და გავლენას მოახდენდა მის სიმტკიცეზე. დუღაბის დანამატებად შერჩეულია ადგილობრივი ბუნებრივი ცეოლითური ტუფები, რომლებსაც

ახასიათებს პუცოლანური დანამატების ყველა ის თვისება, რომელიც გამოყენების პროცესს უწყობს ხელს. შესწავლილია მათი ფიზიკურ-ქიმიური თვისებები, აგრეთვე მათი გავლენა კირის დუღაბის გამყარების პროცესსა და სიმტკიცეზე. კვლევის შედეგებმა გვიჩვენა, რომ დუღაბის სიმტკიცე დიდადაა დამოკიდებული მისი კომპონენტების და დანამატების ქიმიურ, ფაზურ შემადგენლობასა და სტრუქტურაზე. დადგინდა დუღაბის ოპტიმალური შემადგენლობა. სხვადასხვა სტრუქტურის მქონე ცეოლითები დუღაბის სიმტკიცეზე განსხვავებულად მოქმედებენ.

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Received July, 2025