МРНТИ 61.35.33

***B.Ch. Nurimbetov, **Sh.N. Turemuratov,**
***G.B. Chimbergenova, * G.A. Sultanov**

*Karakalpak State University, Nukus, Uzbekistan
**Karakalpak Branch of the Academy of Sciences of the Republic of Uzbekistan, Nukus, Uzbekistan,
(E-mail: nbch2010@mail.ru, tsharibay@mail.ru, chimbergenova2002@gmail.com, gulomjon.sultanov.85@mail.ru).

Effects of finely dispersed filler on the β-C_2S and CaO formation

Abstract. *The article discusses the results of the study of joint heat treatmentmarlarls and ground quartz sand. It was shown that the optimum sand content in the raw mix should be 10 %, with such proportions of heat-treated raw material components, their interactions result in the formation of a relatively large amount of belite.*
Keywords: *marl; heat treatment; ground quartz sand; belite; lime-belite binder.*

DOI: https://doi.org/10.32523/2616-6771-2022-141-4-27-33

Introduction

Researches aimed at the comprehensive and rational use of local raw materials are rrelevant since after the collapse of the USSR, economic relations between the former soviet republics were broken and the national economic need of the republic for industrial products, especially building materials, should be satisfied mostly through local production. Output products based on local raw materials in terms of quality and other parameters should not be inferior to imported products, to ensure full import substitution.

The Republic of Karakalpakstan is rich in natural minerals that serve as raw materials - gypsum, ganch, limestone, including marls, which are represented by Mo‘ynoq, Ustyurt, Porlytau, Aqborili, Khodzhakul deposits, of which the Aqborili and Porlytau fields are the most promising.

At the same time, these marls are practically not studied and are not used in the national economy, although they can be excellent raw materials for the production of binders, widely used for the production of silicate blocks (wall materials), bricks, antifiltration coatings on side channel walls. A premise for such judgments is the presence in the literature of studies carried out with marls from deposits of various other regions in order to obtain binders.

This work is devoted to the development of ways to control the processes of obtaining lime-belite binders with the highest content of belite, based on marls of the Aqborili and Porlytau deposits of Karakalpakstan and to study the phase composition of the obtained products.

Materials and methods

Marls from the Aqborili and Porlytau deposits of Karakalpakstan were used for obtaining a lime-belite binder material, various local minerals were used as fillers to control the properties of the obtained binders.

Chemical (Table 1), X-ray phase, thermogravimetric, petrographic, and IR-spectroscopic analyses of marls were carried out.

Table 1. Chemical composition of marl samples, %

Marl deposit	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	ignition losses	Σ
Aqborili	7,48	2,08	0,79	48,18	1,03	0,23	1,03	0,43	39,65	100,9
Aqborili	7,50	2,07	0,84	47,27	1,17	0,20	0,94	0,49	39,53	100,01
Aqborili	7,55	2,03	0,80	47,75	1,20	0,21	0,92	0,50	39,24	100,18
Porlytau	9,70	3,67	1,01	44,95	0,69	0,10	0,80	0,73	38,45	100,10
Porlytau	9,86	3,54	0,96	45,24	0,71	Сле.	0,95	0,62	37,91	99,79
Porlytau	9,91	3.51	0,89	45,20	0,78	Сле.	0,97	0,58	38,06	99,90

As can be seen from the chemical analysis data, the samples used in the analysis belong to lime marl. Chemical-mineralogical composition of marls is a mixture of calcium and magnesium carbonates, silica compounds, alumina, and iron hydroxide in the composition of montmorillionite, a certain amount of calcium sulfate in the form of gypsum, a small number of soluble salts of sulfuric and hydrochloric acids.

Physico-chemical studies of marls from the Aqborili and Porlytau deposits of the Republic of Karakalpakstan show that they can be excellent raw materials for obtaining binders widely used in the national economy.

For research, washed and processed Volga sand was used as quartz sand. According to chemical analysis, the used quartz sand has the following composition, %: SiO_2 - 99,60; (Fe_2O_3+Al_2O_3)-0,63; CaO-traces; Na_2O - 0,08.

Colloid-chemical, chemical-analytical, as well as physico-chemical methods of phase analysis were used, which make it possible to establish the relation between the phase composition of the initial product, hydration processes features, and the kinetics of formation and strength of hydration hardening structures arising on its basis.

X-ray phase analysis was used to study the structure, composition and properties of raw materials and calcinates. It was used to study the qualitative, mineralogical and phase compositions [1,2]. The studies were carried out on a desktop X-ray diffractometer MINIFLEX-600.

Differential thermal analysis of minerals and binders was carried out on a simultaneous thermal analyzer STA 449 F1. The simultaneous thermal analysis combines the methods of differential scanning calorimetry and thermogravimetry in one measurement. With the help of STA, measurements of heat fluxes and mass measurements are carried out under completely identical conditions.[1,3].

Electron microscopy studies were carried out using a JEOL Ltd. JSM-6490 (Japan) scanning electron microscope. This method was used to study both minerals and the products of their interaction with water.

IR absorption spectra were obtained on a Specord 75 JR spectrophotometer. Samples of minerals were mixed in an agate mortar with potassium bromide (chemically pure) and pressed in a special mold under a specific pressure of 5 t/cm^2 during pumping for 12-15 minutes.

Discussion

As noted earlier [4,5], the optimum temperature for heat treatment of marls is 1000 °C with a holding time of 90 min. In this mode, in the products of heat treatment, the largest amount of β-C_2S belite is formed (30.37 and 28.09%, respectively, for each deposit). But for the formation of a sufficient amount of belite in the calcinates, the amount of SiO_2 in the raw marl is not enough. It was shown in [6] that during the heat treatment of marl, up to 70.45% of belite can be obtained. In order to increase the content of β-C_2S in the heat treatment products and at the same time obtain a high-strength binder, 5.10 and 20% of ground quartz sand (washed Volga sand) were intjected into the composition of the raw material.

The surface of quartz grains is inhomogeneous and consists of two qualitatively different sites with different energy and adsorption properties: silanol sites, in which surface silicon atoms are bonded to hydroxyl groups, and siloxane sites, in which silicon atoms are not bonded to hydroxyl groups. For a real quartz surface, the ratio between these areas can be different depending on its structure.

The properties of the silanol sites depend on the distribution of OH^- groups on the surface. The most chemically active are the sites where the OH^- groups are located most densely. The siloxane sites are less active than the silanol ones.

According to different authors, as a result of mechanical treatment, a destructured layer 50–100 μm thick appears on the surface of quartz, but the surface layer 0.5 μm thick is most strongly amorphized [7,8].

In addition to defects caused by mechanical processing, the quartz surface can also have other various kinds of defects: point, one-dimensional (dislocation), two-dimensional (boundaries between blocks), various inclusions, and others. Point defects are revealed when the crystal is exposed to various types of irradiation and decoration methods. Research [8] showed that in natural quartz there are from one to four varieties of aggregates of point defects that differ in activity and symmetry.

Quartz sand was crushed in a laboratory porcelain ball mill until it completely passed through a sieve № 008. The specific surface area (according to Tovarov) was in the range of 2500-3200 cm^2/g. Quartz sand was added to the marl, the resulting mixture was thoroughly mixed in closed flasks, then in a porcelain mortar until a homogeneous product was obtained. After that, the mixture was subjected to heat treatment in a laboratory silite furnace at 1000 °C with an exposure of 90 minutes. The composition of the products after heat treatment of the mixture is determined by X-ray phase (Figure 1,2,3) and mineralogical (Table 2) analysis.

X-ray diffraction patterns show that with the injection of 5% quartz sand, the intensity of the lines characteristic of belite (0.274 and 0.217 nm) increases (Figure 1) compared to the lines of belite without the addition of sand. The lines characteristic of free calcium oxide (0.239 and 0.169 nm) are reduced. At the same time, there are preserved lines characteristic of calcium aluminates and ferrites.

An increase in the input amount of sand to 10% (Figure 2) does not make any special changes, only the intensity of the belite lines increases.

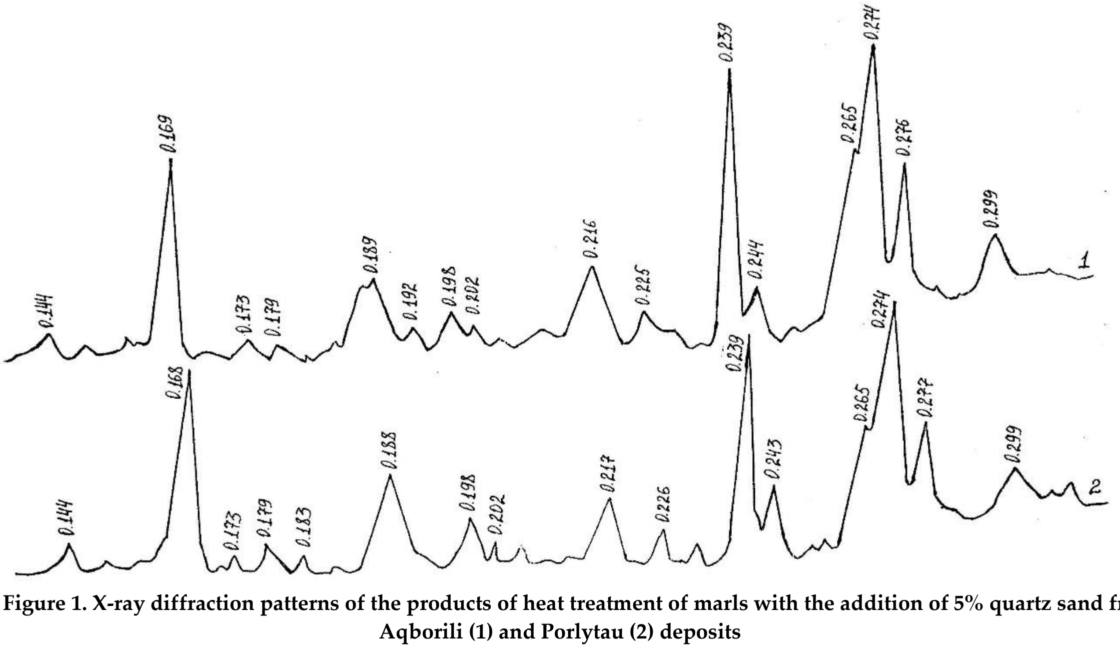

Figure 1. X-ray diffraction patterns of the products of heat treatment of marls with the addition of 5% quartz sand from the Aqborili (1) and Porlytau (2) deposits

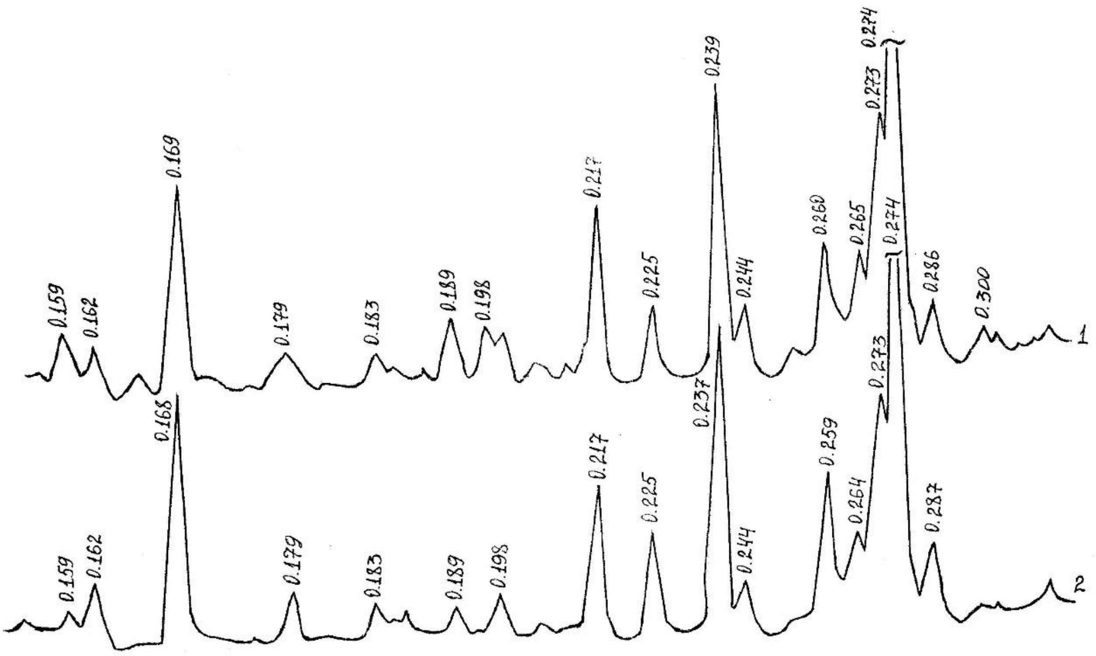

Figure 2. X-ray diffraction patterns of the products of heat treatment of marls with the addition of 10% quartz sand from the Aqborili (1) and Porlytau (2) deposits

With the injection of 20% quartz sand (Figure 3), the intensity of the belite lines slightly increases, as well as the lines characteristic of quartz itself (0.198 nm). At the same time, the intensity of the lines characteristic of free calcium oxide remains unchanged. For complete binding of SiO_2 with calcium oxide, in this case, either exposure or temperature is not enough. This is confirmed by the mineralogical (Table 2) composition of the resulting lime-belite binder.

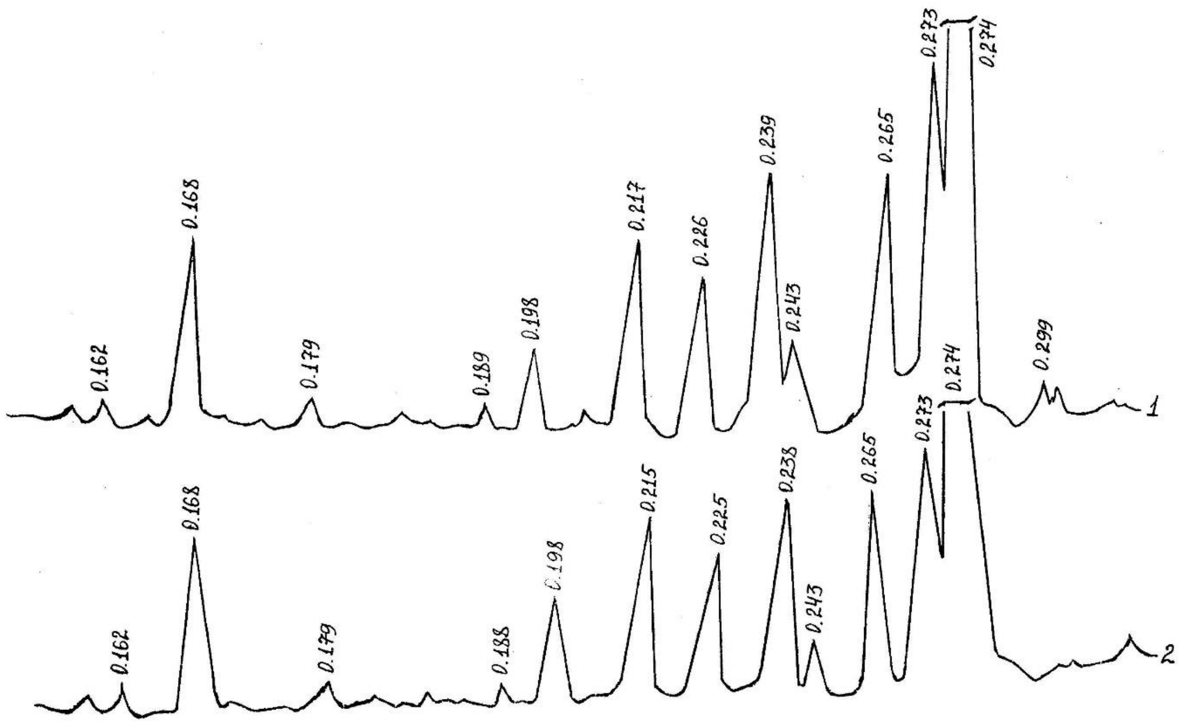

Figure 3. X-ray diffraction patterns of the products of heat treatment of marls with the addition of 20% quartz sand from the Aqborili (1) and Porlytau (2) deposits

Table data shows that the basicity constant K_{bas} decreases with increasing sand content, while the content of aluminates, ferrites and calcium sulfates practically does not change, since there are no clay components in the composition of the sand.

Table 2. Mineralogical composition of products of heat treatment of marls with quartz sand

Marl deposit	Addition of sand	K_{bas}	C_3A	C_2F	$CaSO_4$	C_2S
Aqborili	5	5,52	6,60	3,11	0,43	38,05
Aqborili	10	3,24	6,60	3,11	0,43	48,31
Aqborili	20	3,07	6,60	3,11	0,43	64,27
Porlytau	5	2,89	10,06	3,11	5,80	38,29
Porlytau	10	2,37	10,06	3,11	5,80	45,67
Porlytau	20	1,75	10,06	3,11	5,80	61,33

The content of dicalcium silicate increases proportionally with an increase in the amount of additives introduced, respectively, the amount of free calcium oxide decreases (Figure 4).

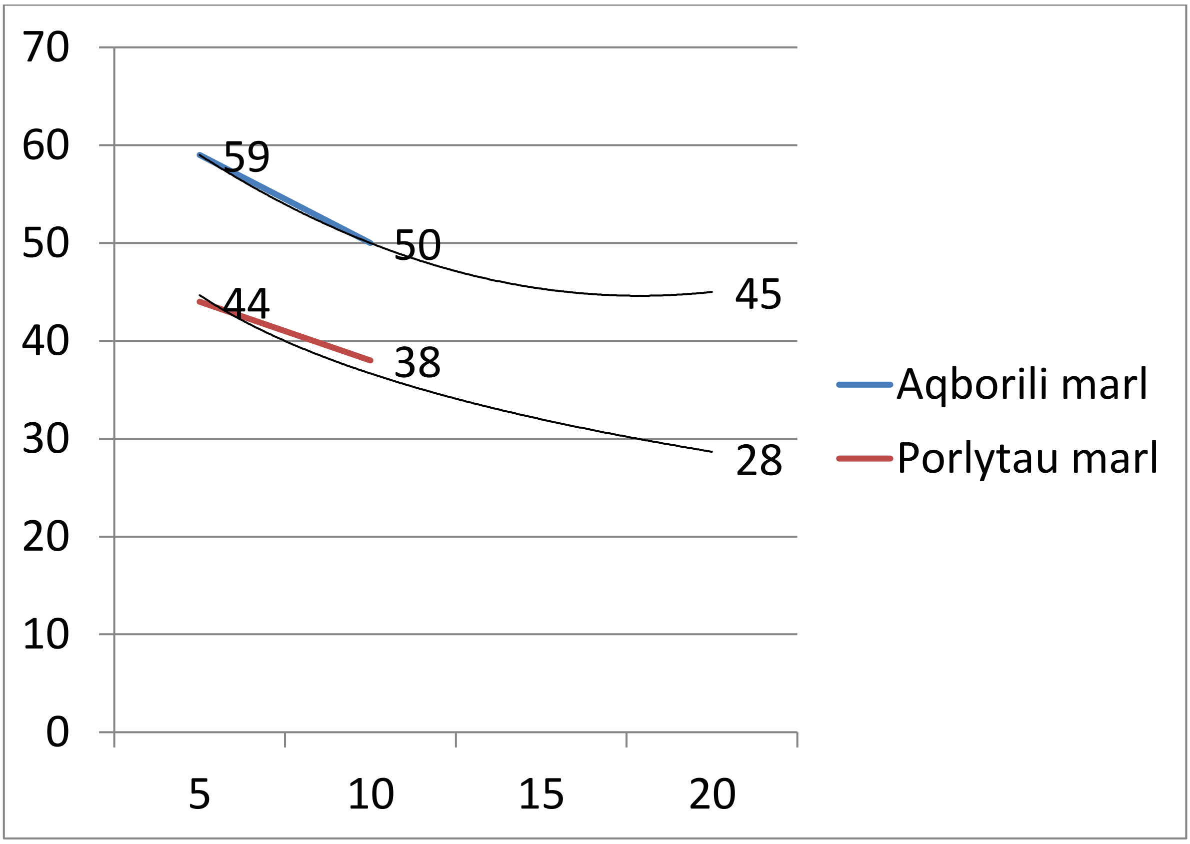

Figure 4. Relation of the content of free calcium oxide on the amount of lime-belite binder additive based on Aqborili (1) and Porlytau (2) marls

This is due to the interaction of quartz with calcium oxide, followed by the formation of bicalcium silicate. Figure 4 confirms the data of X-ray analysis and mineralogical composition.

Conclusion

The study results of joint heat treatment of marls and ground quartz sand suggest that the optimum sand content in the raw mix should be 10 %. With such proportions of heat-treated raw material components, their interactions result in the formation of a relatively large amount of belite which will provide the high strength properties of products based on this binder.

References

1. Горшков В. С. Методы Физико-Химического Анализа Вяжущих Веществ: Учеб. Пособие. / В. С. Горшков, В. В. Тимашёв, В. Г. Савельев. – Москва : Высшая школа, 1981. – 335 с.
2. Рамачандран В. С. Применение дифференциального термического анализа в химии цементов / В. С. Рамачандран, М. Стройиздат. – Москва : Стройиздат, 1977. – 408 с.
3. Бутт Ю. М. Практикум По Химической Технологии Вяжущих Материалов / Ю. М. Бутт, В. В. Тимашев. – Москва : Высшая школа, 1973. – 504 с.
4. Синтез и исследования известково-белитового вяжущего на основе мергеля Акбурлинского месторождения / Б. Ч. Нурымбетов, Ш. Н. Туремуратов, Д. К. Адылов, А. Агзамходжаев // Наука и образование Южного Казахстана. – 2000. – С. 223-225.
5. Исследование кинетики гидратационного структурообразования и свойств известково-белитовых вяжущих на основе мергелей. / Б. Ч. Нурымбетов, Ш. Н. Туремуратов, А. Д. Жуков, М. О. Асаматдинов // Вестник Московского Государственного Строительного Университета. – 2016. – Т. 4. – С. 52-56.
6. Маков С. П. Влияния фазового состава продуктов обжига мергелей на свойства автоклавных материалов / С. П. Маков, Х. С. Воробьев // Строительные материалы. – 1958. – Т. 8. – С. 34-36.
7. Айлер Р. К. Коллоидная химия кремнезема и силикатов / Р. К. Айлер. – 1959.
8. Энтель В. Физическая химия силикатов / В. Энтель. – Москва : Стройиздат, 1962. – 312 с.

*** Б.Ч. Нурымбетов, ** Ш.Н. Туремуратов, * Г.Б. Чимбергенова, * Г.А. Султанов**
**Каракалпакский государственный университет, Нукус, Узбекистан*
***Каракалпакское отделение Академии наук Республики Узбекистан, Нукус, Узбекистан*

Влияние тонкодисперсного наполнителя на процессы образования β-C_2S и CaO

Аннотация. В статье рассматриваются результаты исследований совместной термообработки мергелей с молотым кварцевым песком. Показано, что оптимальное содержание песка в сырьевой смеси должно быть 10%: при таких соотношениях компонентов термообрабатываемого сырья происходят взаимодействия с образованием относительно наибольшего количества белита.

Ключевые слова: мергель, термообработка, молотый кварцевый песок, белит, известково-белитовый вяжущий.

*** Б.Ч. Нурымбетов, ** Ш.Н. Туремуратов, * Г.Б. Чимбергенова, * Г.А. Султанов**
** Қарақалпақ мемлекеттік университеті, Нукус, Өзбекстан*
*** Өзбекстан Республикасы Ғылымдар Академиясының Қарақалпақ бөлімшесі, Нүкіс, Өзбекстан*

Жұқа толтырғыштың β-C_2S және CaO түзілу процестеріне әсері

Аннотация.Мақалада мергельдерді ұнтақталған кварц құмымен бірлесіп термоөңдеуді зерттеу нәтижелері қарастырылады. Шикізат қоспасындағы құмның оңтайлы мөлшері 10% болуы керек

екендігі көрсетілген, жылу өңделген шикізат компоненттерінің осындай қатынасы кезінде белиттің ең көп мөлшеріне қатысты өзара әрекеттесу жүреді.

Түйін сөздер. Мергель; термоөңдеу; ұнтақталған кварц құмы; белит; әк-белит байланыстырғыш.

References

1.Gorshkov V.S., Timashev V.V., Savel'ev V.G. Metody fiziko-himicheskogo analiza vyazhushchih veshchestv [Methods of Physical and Chemical Analysis of Binders: Proc. Benefit]. (Moscow, Vysshaya shkola, 1981).

2.Ramachadran B.C. Primenenie differencial'nogo termicheskogo analiza v himii cementov [Application of differential thermal analysis in cement chemistry] (Moscow, Strojizdat, 1977)

3.Butt Yu.M., Timashev V.V. Praktikum po himicheskoj tekhnologii vyazhushchih materialov (Moscow, Vysshaya shkola, 1973)

4.Nurimbetov B.Ch., Turemuratov Sh.N., Adylov Dzh.K., Agzamhodzhaev A. Sintez i issledovaniya izvestkovo-belitovogo vyazhushchego na osnove mergelya Akburlinskogo mestorozhdeniya [Synthesis and research of lime-belite binder based on the marl of the Akburlinskoe deposit], Nauka i obrazovanie YUzhnogo Kazahstana [Science and Education of Southern Kazakhstan], Shymkent, 223-225(2000)

5. Nurimbetov B.Ch., Turemuratov Sh.N., ZHukov A.D., Asamatdinov M.O. Issledovanie kinetiki gidratacionnogo strukturoobrazovaniya i svojstv izvestkovo-belitovyh vyazhushchih na osnove mergelej [Study of the kinetics of hydration structure formation and properties of lime-belite binders based on marls]. Vestnik Moskovskogo Gosudarstvennogo Stroitel'nogo Universiteta [Bulletin of the Moscow State Construction University], Rossiya, 4, 52-56(2016).

6.Makov S.P., Vorob'ev H.S. Vliyaniya fazovogo sostava produktov obzhiga mergelej na svojstva avtoklavnyh materialov [Influence of the phase composition of marl firing products on the properties of autoclave materials], «Stroitel'nye materialy», 8, 34-36(1958)

7.Entel' V. Fizicheskaya himiya silikatov [Colloidal chemistry of silica and silicates], (Moscow, Strojizdat, 1962)

8.Ajler R.K. Kolloidnaya himiya kremnezema i silikatov[Physical chemistry of silicates] (1959)

Сведения об авторах:

Нурымбетов Б.Ч. - доцент кафедры физической и коллоидной химии, Каракалпакский государственный университет имени Бердака, ул. Ч.Абдирова 1, Нукус, Узбекистан.

Туремуратов Ш.Н. - главный ученый секретарь, профессор, Каракалпакский отделения Академии наук Республики Узбекистан, Нукус, Узбекистан,

Чимбергенова Г. Б. – студентка Каракалпакского государственного университета имени Бердака, ул. Ч.Абдирова 1, Нукус, Узбекистан.

Султанов Г.А. – ассистент кафедры химической технологии, Каракалпакский государственный университет имени Бердака, ул. Ч.Абдирова 1, Нукус, Узбекистан.

Нұрымбетов Б.Ч. – физика-коллоидты химия кафедрасының доценті, Бердақ атындағы Қарақалпақ мемлекеттік университеті, Ч.Абдирова көш., 1, Нүкіс, Өзбекстан.

Төреморатов Ш.Н. - Өзбекстан Республикасы ҒА Қарақалпақстан филиалының бас ғылыми хатшысы, профессор, Өзбекстан, Нүкіс, Өзбекстан.

Чимбергенова Г.Б. - Бердақ атындағы Қарақалпақ мемлекеттік университетінің студенті, Ч.Абдиров көш., 1, Нүкіс, Өзбекстан.

Сұлтанов Ғ.А. - химия-технология кафедрасының ассистенті, Бердақ атындағы Қарақалпақ мемлекеттік университеті, Ч.Абдиров көш., 1, Нүкіс, Өзбекстан.