ГИАБ. Горный информационно-аналитический бюллетень /
MIAB. Mining Informational and Analytical Bulletin, 2024;(10):51-61
ОРИГИНАЛЬНАЯ СТАТЬЯ / ORIGINAL PAPER

УДК 628.511 DOI: 10.25018/0236_1493_2024_10_0_51

ФИЗИКО-ХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ НЕМАЛИТСОДЕРЖАЩЕГО ХРИЗОТИЛ-АСБЕСТА ЖИТИКАРИНСКОГО МЕСТОРОЖДЕНИЯ

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Аннотация: Приведены физико-химические исследования немалитсодержащего хризотил-асбеста (НХА) – попутного минерала от добычи хризотил-асбестовой руды Житикаринского месторождения, который не используется и складируется в специальных отвалах, представляя собой экологически опасный техногенный отход, влияющий на окружающую среду и здоровье населения региона. В ходе исследований пробы немалитсодержащего хризотил-асбеста подвергались химическому и дифрактометрическому анализам с целью определения химическо-элементного и минералогического составов отобранных образцов проб. Исследован состав как природного немалитсодержащего хризотил-асбеста, так и измененного в результате термообработки в интервале температур 450–850 ºС с целью определения возможности его использовании в качестве вторичного сырья для получения соединений магния. По результатам проведенных исследований установлено, что около 60% Mg в составе немалитсодержащего хризотил-асбеста находится в виде минерала – брусита и 40% Mg – в виде компонента, содержащего серпентинин. Проведенные эксперименты и полученные результаты рентгенографических исследований подтверждают, что термообработка способствует качественному улучшению физико-химических и технологических свойств немалитсодержащего хризотил-асбеста при использовании его как вторичного сырья для получения соединений магния.

Ключевые слова: немалитсодержащий хризотил-асбест, брусит, периклаз, серпентинит, форстерит, отход, окружающая среда.

Благодарность: Статья подготовлена при финансовой поддержке грантового финансирования научных и (или) научно-технических проектов и программ на 2023–2025 годы Комитетом науки Министерства науки и высшего образования Республики Казахстан (грант № АП19676952).

Для цитирования: *Ауешов А. П., Ескибаева Ч. З., Арынов К. Е., Колесникова О. Г., Алжанов К. Б.* Физико-химические исследования немалитсодержащего хризотил-асбеста Житикаринского месторождения // Горный информационно-аналитический бюллетень. – 2024. – № 10. – С. 51–61. DOI: 10.25018/0236_1493_2024_10_0_51.

Physico-chemical studies of nemalite-containing chrysotile asbestos from the Zhitikarinsky deposit

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Abstract: This article presents physico-chemical studies of nemalite-containing chrysotile asbestos (NCA), an associated mineral from the extraction of chrysotile asbestos ore from the Zhitikarinsky deposit, which is not used and stored in special dumps, in fact representing a man-made waste that poses an environmental hazard to the environment and the health of the region's population. During the research, samples of nemalite-containing chrysotile asbestos were subjected to chemical and diffractometric analyses in order to determine the chemical-elemental and mineralogical compositions of the selected samples. The composition of both natural nemalite-containing chrysotile asbestos and modified as a result of heat treatment in the temperature range 450–850 ºC has been studied in order to determine the possibility of its use as a secondary raw material for the production of magnesium compounds. According to the results of the conducted studies, it was found that about 60% Mg in the composition of nemalite-containing chrysotile asbestos is in the form of a mineral – brucite and 40% Mg is in the form of a component containing serpentine. The experiments carried out and the results of X-ray studies confirm that heat treatment contributes to the qualitative improvement of the physico-chemical and technological properties of nemalite-containing chrysotile asbestos when using it as a secondary raw material for the production of magnesium compounds..

Key words: nemalite-containing chrysotile asbestos, brucite, periclase, serpentinite, forsterite, waste, environment.

Acknowledgements: The article was prepared with the financial support of grant financing of scientific and (or) scientific and technical projects and programs for 2023–2025 by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No AP19676952).

For citation: Abdrazakh Auyeshov, Chaizada Eskibayeva, Kazhmukhan Arynov, Olga Kolesnikova, Kurmanbek Alzhanov Physico-chemical studies of nemalite-containing chrysotile asbestos from the Zhitikarinsky deposit. *MIAB. Mining Inf. Anal. Bull.* 2024;(10):51-61. DOI: 10.25018/0236_1493_2024_10_0_51.

Introduction

Nemalite is a mineral containing chrysotile, which is a type of asbestos, or sometimes it is called nemalite-containing chrysotile-asbestos. Due to health concerns, most countries have banned the use of asbestos and products containing it [1, 2]. Nevertheless, due to the very valuable technological properties, quite a large number of studies are being conducted in the world aimed at finding the use of chrysotile-containing minerals in various branches of science and technology [3—6], for example, groups of serpentinite minerals from various deposits [7—9], which cannot be said about the granite.

The processing of chrysotile-containing minerals, including graphite, usually includes special processes to neutralize and reduce the danger of asbestos to human health. These processes may include:

- Identification and isolation of the chrysotile-containing mineral from the environment to prevent further spread of asbestos and reduce geoecological risks [10—12];
- Mechanical processing — grinding or crushing of the mineral to reduce the particle size and improve the controllability of the material during processing;
- Heat treatment, to destroy the structure of asbestos or reduce its carcinogenic properties;
- Chemical treatment, in order to neutralize or destroy the structure of chrysotile;
- Control and removal of chrysotile to prevent further spread of asbestos and its effects on the environment and health [13, 14].

It is obvious that projects for processing chrysotile-containing minerals require serious technological improvements and controls to ensure safety and minimize health risks [15, 16]. Apparently, from this point of view, as well as due to the lack of sufficiently scientifically and technologically sound research, most of the deposits of chrysotile-containing raw materials in Kazakhstan do not belong to the industrial categories, especially granite. The calculated reserves of nemalite-containing raw materials for all deposits of the country amount to about 90—120 million tons. Of course, the development of new fields requires a significant allocation. However, non-graphite is often a by-product of the extraction of chrysotile-asbestos ore, for example in the Zhitikarinsky deposits. Nemalite-containing chrysotile has similar properties as other chrysotile-containing minerals and can be used in various industries such as construction and materials production. However, the graphite in the ores is in close fusion with chrysotile fiber — $Mg_6Si_4O_{10}(OH)_8$, as a result of which the reinforcing properties of asbestos in asbestos-cement products are significantly reduced. Purification of chrysotile from non-graphite by selective dissolution of non-graphite is fundamentally possible [17], however, it is not economically justified. Therefore, at this time, during the extraction of chrysotile-asbestos ore, nemalite-containing chrysotile-asbestos is stored in specially designated areas as an environmentally hazardous waste product.

However, nemalite, which mainly consists of $Mg(OH)_2$ brucite, can potentially be a raw material for the production of magnesium compounds. The nemalite-containing chrysotile does not belong to the typical sources of magnesium to date only because of the presence of asbestos. Magnesium is usually extracted from minerals such as dolomite and magnesite. However, if chrysotile is contained in a small amount in the composition of the granite, the remaining minerals may contain magnesium, the amount of which will be acceptable for using it as a source of magnesium, while using thermal and chemical methods of its processing.

So, usually the magnesium content in dolomites ranges from 18 to 22%, in chrysotile-asbestos ores (serpentinite) up to 25%, and in non-graphite (depending on the ratio of brusite and chrysotile components, which in turn depend on the geography of the deposit), it should be assumed theoretically even higher. However, they are certainly justified by the data of physico-chemical studies of hematite chrysotile asbestos of a particular deposit.

The chemical and mineralogical compositions of the nemalite-containing chrysotile-asbestos of the Zhitikarinsky deposit have not been studied from the point of view of its use as a source of magnesium. The timeliness of conducting a study to determine the chemical and mineralogical composition and ratios of brusite and chrysotile components of nemalite (to establish possible areas of its application), associated mineral extraction of chrysotile-asbestos ore is justified by the fact that the results can contribute to the integrated use of mined ores during the operation of deposits [18—20]. To obtain magnesium compounds, which are widely used in various industries.

This paper presents the results of studying the chemical and mineralogical compositions of nemalite-containing chrysotile-asbestos from the Zhitikarinsky deposit (Kazakhstan), which may be useful for identifying applications of nemalite, including as a raw material for the production of magnesium compounds.

Methods and materials

Samples of nemalite-containing chrysotile-asbestos were presented by the Kostanay Minerals JSC plant (Zhitikara, Kostanay region, Kazakhstan), which are a by-product during the extraction of chrysotile-asbestos ore in the Zhitikarinsky locality. The characteristic is not small. The color of stony samples of nemalite-containing chrysotile-asbestos (NCA) can be conditionally characterized as a mixture of formations of gray, white and black solids: externally, stone-like crushed stones, some of them have shine, tree-like chips with a cross section of 0.5—3.0 cm and a length of 2—7 cm, consisting of long filamentous fibers and ordered in one the direction of the layers.

The strength of the threads is much stronger in length than in cross-section (you can break them with your hands). NCA pieces of size (l = 5—10 cm, d = = 2.5 cm, h = 1—2 cm) are susceptible to magnetic influences.

Chemical analyses were carried out on a JSM-6490LV device, JEOL (Japan), complete with INCAEnergy 350 energy dispersion microanalyzer systems.

Diffractograms of samples were taken on a D8Advance (Bruker) diffractometer, Cu—Ka, tube voltage 40 kV, current 40 mA.

The processing of the obtained diffractograms and the calculation of interplane distances were carried out using EVA software. The decoding of samples and the search for phases were carried out using the Search/match program using the PDF-2 Powder Diffractometric Database (JCDD).

Results and discussion

The presented samples of NCA externally differ in color, shape and are hetero-

Table 1

Elemental composition of the average NCA samples
Элементный состав усредненных образцов НХА

Element	**Samples**				
	No. 1	**No. 2**	**No. 3**	**No. 4**	**No. 5**
	weight %				
Mg	30.37	31.66	29.53	30.17	28.97
Si	9.63	6.26	10.03	9.48	5.33
Cl	—	0.22	—	—	—
Ca	—	—	0.55	—	0.23
Mn	0.35	0.39	0.49	—	0.34
Fe	10.70	15.01	7.37	8.56	17.74
Total	100.00	100.00	100.00	100.00	100.00

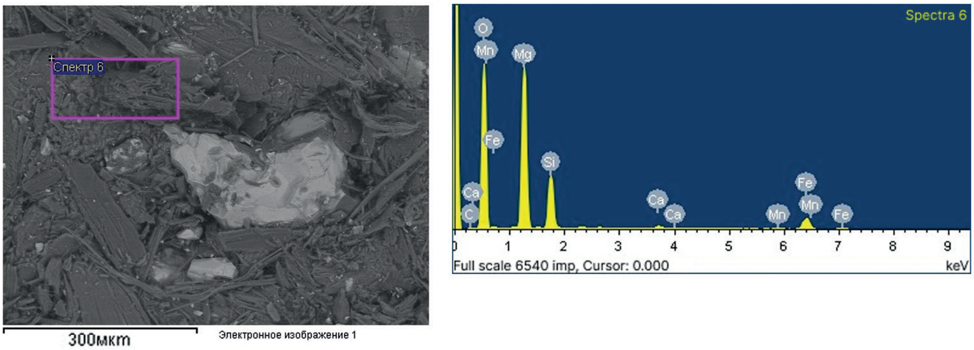

Fig. 1. SEM analysis of the average sample No. 3 (natural nemalite)
Рис. 1. СЭМ-анализ усредненного образца №3 (природного немалита)

geneous. Therefore, 5 average samples of NCAs were prepared for a more detailed study of their natural composition. The results of the elemental composition of these samples are presented in Table 1.

As can be seen from Table 1, in the compositions of the samples, there are no special variations by elements in weight%: Mg (29.5 – 30.5) and Mn (0.34 – 0.49); a higher variation is found for Si (5.5 – 10.0) and Fe (7.4 – 15.6); some samples contain Ca (0.2 – 0.55) and Cl (0.2).

A more complete package of detected elements is contained in sample No. 3, therefore, conditionally, the composition of sample No. 3 was accepted as natural NCA, including all basic elements. SEM analysis and its diffractogram of sample No. 3 are shown in Figures 1 and 2.

X-ray phase analysis of nemalite-containing chrysotile-asbestos ore (NCA) records the interplane distance reflexes (IPD) (d/n) of brucite – $Mg(OH)_2$ d/n = 4.77 – 2.365 – 1.794 Å with clear high peaks, IPD reflexes of serpentinite group minerals (Ch – chrysotile, A – antigorite) denoted by a common the formula is $Mg_6Si_4O_{10}(OH)_8$, d/n = 7.38 – 4.619 – 3.661 – 2.487 Å they are recorded in small peaks (Fig. 2). Iron hydroxide (II, III) does not appear in the derivatogram due to the renntgenoamorphic state of the mineral. The initial ore of NHA consists of brucite, chrysotile (serpentinite) and amorphous magnetite.

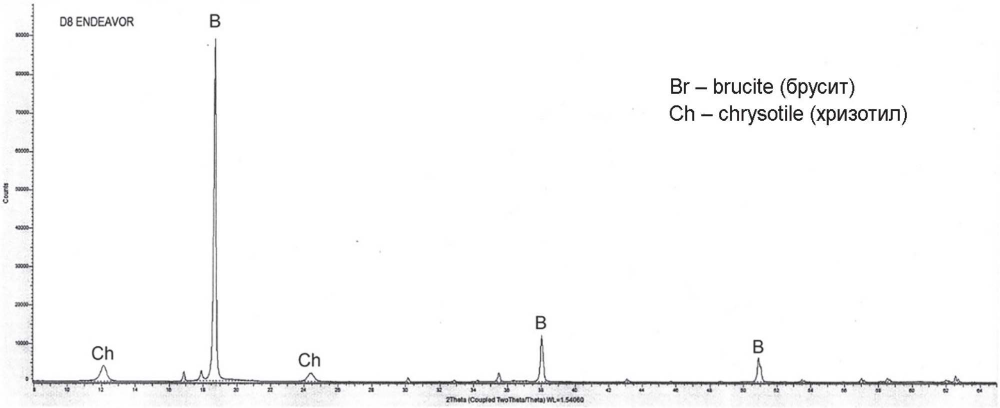

Fig. 2. Diffractogram of the average HC (sample No. 3)
Рис. 2. Дифрактограмма усредненного НХА (образец № 3)

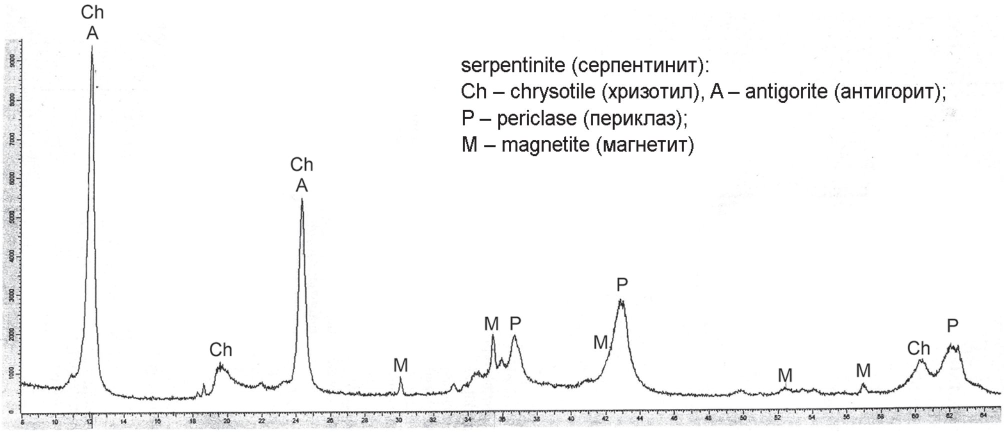

Fig. 3. Diffractogram of NCA heat-treated at 450 °C (1 hour)
Рис. 3. Дифрактограмма НХА термообработанного при 450 °С (1 ч)

In the diffractogram of heat-treated HC at 450 °C (1 hour), brucite IPD reflexes at d/n = 4.77 – 2.365 – 1.794 – 1.55 Å they do not appear (Fig. 3).

Instead of these, IPD periclase reflexes appear – MgO, d/n = 2.432 – 2.108 – 1.485 Å the product of its thermal decomposition. At 450 °C, in addition to periclase, reflexes appear in the HC diffractogram, the IPD of magnetite is d/n = 2.99 – 2.54 – 2.098 – 1.71 – 1.67 Å. Weak reflexes of IPD serpentinitis (Ch, A) at d/n = 7.38 – 4.619 – 3.661 – 2.487 – 2.141 – 1.53 Å they become intense. Heat-treated HC at 450 °C consists of chrysotile (serpentinite), periclase and magnetite.

EAR treatment at 650 °C (1 hour) leads to quantitative changes in phases (Fig. 4) recorded in a sample heat-treated at 450 °C (Fig. 3).

The reflexes of chrysotile IPD (serpentinite) are very weakly manifested in the diffractogram, more precisely, only the most intense IPD reflexes (dozens) are recorded – d/n = 7.30 – 3.63 – 2.48 Å with small peaks, the IPD reflexes of forsterite, as a product of its thermal transformation, are prescribed from the new peaks, with an

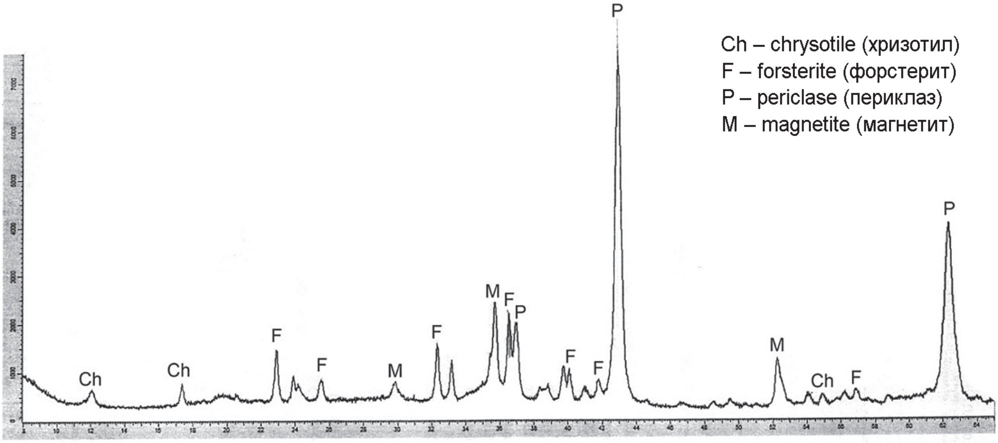

Fig. 4. Diffractogram of NCA heat-treated at 650 °C (1 hour)
Рис. 4. Дифрактограмма НХА термообработанного при 650 °С (1 ч)

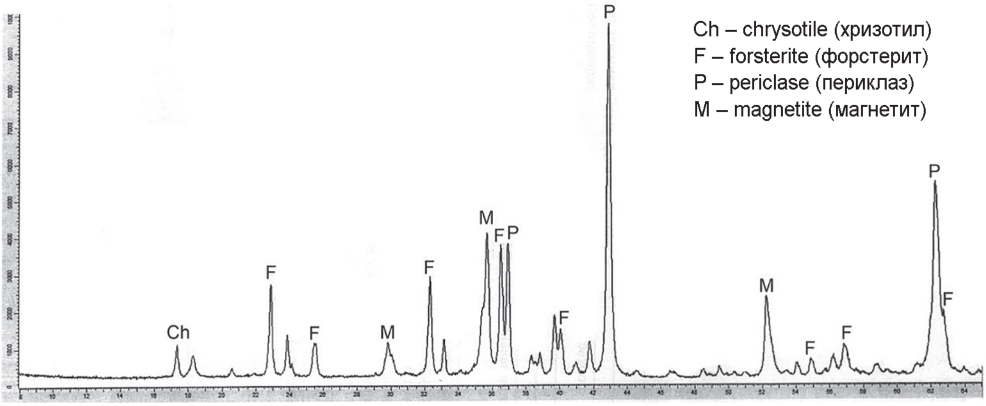

Fig. 5. Diffractogram of NCA heat-treated at 850 °C (1 hour)
Рис. 5. Дифрактограмма НХА термообработанного при 850 ºС (1 ч)

average intensity with IPD reflexes d/n = = 3.87 – 3.47 – 2.75 – 2.49 – 2.25 Å. The main phase of heat-treated NCA at 650 °C becomes periclase, with IPD reflexes d/n = = 2.43 – 2.108 – 1.48 Å however, forsterite and magnetite are present in noticeable amounts. The IPD reflexes of chrysotile (serpentinite) are significantly weakened, which indicates the destruction (at 650 °C) of the serpentinite structure with the formation of forsterite (Fig. 4).

In the diffractogram of the irradiated HC at 850 °C (1 hour), clear peaks show the IPD reflections of periclase the reflexes of IPD periclase – MgO – d/n = 2,431 – 2.108 – 1.485 Å, forsterite Mg_2SiO_4 – d/n = 3.875 – 3.47 – 2.753 – 2.497 – 2.441 – 2.25 – 2.15 – 1.63 – 1.61 Å and $FeFe_2O_3$ – magnetite d/n = 2.99 – 2.541 – 2.098 – 1.710 – 1.612 Å. The dominant phase in NCA at 850 °C is periclase (Fig. 5), and only fragments of IPD (one peak out of three) remain from serpentinite reflexes, which shows the practical completion of the destruction of the structure of the crystal lattice – $Mg_3Si_2O_5(OH)_4$ (serpentinite) at this firing temperature. The appearance of clear reflexes of $FeFe_2O_3$ magnetite at d/n = 2.99 – 2.541 – 2.099 – 1.710 – 1.612 Å this indicates that in natural NCA iron is mainly in the amorphous form of iron (II) hydroxide, magnesium in the form of brucite $Mg(OH)_2$, which is converted into MgO periclase.

Table 2

Chemical and mineralogical compositions of NCA
Химический и минералогический составы НХА

No.	Chemical composition, by weight, %				Mineralogical composition, by weight, %		
	O	Mg	Si	Fe	Serpentinite $Mg_6Si_4O_{10}(OH)_8$	Iron hydroxide $Fe(OH)_2$	Brucite $Mg(OH)_2$
1	48.95	30.4	9.63	10.7	9.6	17.2	35.5
2	46.46	31.6	6.26	15.0	30.8	24.1	45.0
3	49.93	29.5	10.03	7.4	49.4	11.8	39.0
4	49.85	30.0	9.48	8.6	46.7	13.8	40.0
5	45.0	29.0	5.33	17.7	26.3	28.5	45.0
avg. %	48.5	30.2	8.15	12.3	40.0	19.0	41.0

Thermal decomposition (at 650–850 °C) minerals of the serpentinite group, most likely proceeds by reaction:

$$Mg_6Si_4O_{10}(OH)_8\ 2Mg_2SiO_4 + \\ + 2MgO + 2SiO_2 + 4H_2O \quad (1)$$

Reaction (1) indicates that the serpentinite component of heat-treated NCA may also be a source of magnesium oxide.

Calculations of the component composition of natural NCAs based on elemental analysis (Table 1), based on the average value of the elements in the composition of NCA, showed that NCA contain approximately: brucite $Mg(OH)_2$ — 41.0%, serpentinite $Mg_6Si_4O_{10}(OH)_8$ — 40.0% and iron hydroxide $Fe(OH)_2$ (in amorphous state) — 19.0% (Table 2).

At the same time, 60% of Mg of its total content in NCA is in the composition of brucite and 40% in the composition of serpentinite. Heat treatment of NCA at 650—850 °C can increase the amount of MgO in the composition by about another 5—10% by reaction (1), which increases its solubility during its acid processing, as well as the potential for its use as a raw material for the production of magnesium compounds.

Conclusions

Thus, based on the conducted physicochemical studies, the following conclusions can be drawn:

- the nemalite-containing chrysotile asbestos (NCA) of the Zhitikarinsky deposit (Kazakhstan) consists mainly of minerals of the serpentinite group designated by the general formula $Mg_6Si_4O_{10}(OH)_8$ and brucite, as well as X–ray amorphous magnetite;
- nemalite-containing chrysotile asbestos contains more magnesium than dolomite, which is a traditional raw material for the production of magnesium compounds;
- it was found that natural and heat-treated nemalite-containing chrysotile asbestos (NCA) of the Zhitikarinsky deposit at 450—850 °C show that they are in a better position than dolomites and serpentinites in terms of magnesium content in the component compositions of nemalite-containing chrysotile asbestos (in brucite and serpentinite);
- 60% Mg of its total content in NCA is found in the composition of the mineral brucite and 40% in the composition of the mineral serpentinite;
- heat treatment of nemalite-containing chrysotile asbestos in the temperature range 650—850 °C increases the amount of MgO in the composition by about another 5—10%, and also qualitatively improves their internal and technological properties, which are important when obtaining magnesium compounds using acidic processing methods.

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Получена редакцией 20.05.2024; получена после рецензии 11.07.2024; принята к печати 10.09.2024.
Received by the editors 20.05.2024; received after the review 11.07.2024; accepted for printing 10.09.2024.