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Kazakh national research technical university named after K. I. Satpayev

ГЕОЛОГИЯ ЖӘНЕ ТЕХНИКАЛЫҚ ҒЫЛЫМДАР СЕРИЯСЫ

♦

СЕРИЯ ГЕОЛОГИИ И ТЕХНИЧЕСКИХ НАУК

♦

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S. K. Kurbaniyazov, [1], A. M. Igibaeva[2], A. A. Koptic[2], Z. C. Tadjibaeva[2], G. Sh. Shalabayeva[1], G. Zh. Aripzhan[1]

[1]A. Yasavi International Kazakh-Turkish University, Turkestan, Kazakhstan,
[2]PI "Regional Social-Innovation University", Kazakhstan.
E-mail: saken_geo@mail.ru igibaeva80@bk.ru tadzhibaeva81@list.ru
gulshat.shalabaeva@ayu.edu.kz gulnur.aripzhan@mail.ru

PROPERTIES AND APPLICATION OF DOLOMITE BINDER

Abstract. The article describes the area of building materials, namely, the preparation of a dolomite binder, dolomitized magnesite which can be used in the manufacture of heavy concrete, wall, heat-insulating, finishing products, cellular concrete, xylolite and other materials for civil and industrial construction. The result of the study showed an increase in the strength and uniformity of the change in the material volume, while reducing the firing temperature and, correspondingly, the energy consumption for obtaining the binder. The possibility of obtaining a qualitative high-strength binder from various dolomite rocks was also considered. The processes occurring in the dolomite during firing were investigated. The effectiveness of using firing intensifiers in the production of dolomitic binder was established.

Key words: dolomite, binders, building materials, concrete, cement, calcium, magnesium.

Introduction. Dolomite is a unique mineral. Even those stones that were mined in one deposit can be completely different in color. A wide range of colors, together with excellent technical parameters, allow the use of dolomite in various areas. Dolomite is a magnesium and calcium carbonate. Its formula is $CaCO_3 \cdot MgCO_3$. The actual composition almost completely corresponds to the theoretical one. It has about 45% of carbon dioxide, 30% of calcium oxide and 20% of magnesium oxide. It can also contain iron impurities, potassium and other metals. It received its name according to D. Dolomie, the surname of the discoverer Frenchman.

There are several types of dolomite, the differences between which are due to their different nature. Minerals can be saddle, large, accreted, transparent, marble, etc. They can have a gray, white or pale yellow color; stones of black color are less common. There is a matte, pearlescent or glass shine on the faces. A feature of dolomite is the existence of colored spots on its surface. They can flow from one tone to another or be separated from each other.

Dolomite is often found in hydrothermal deposits. It can also be formed by replacing calcite under the influence of sea or groundwater.Since dolomite is a sedimentary rock, its strength is determined by the depth of occurrence. The deeper is the mineral layer, the stronger it is. Deposits of dolomite are in Switzerland, Spain, on the North American continent. The largest of them are in Mexico and Lake Ontario. It is also found in the Caucasus, in the Moscow Region, in the Ural Mountains, in Central Asia. In quarries, the dolomite extraction is carried out by drilling and explosion methods or with the use of charges for wells. Its processing includes crushing, firing and, in some cases, grinding. The material is crushed into pieces using hammers or jaw crushers. The dolomite is usually fired in furnaces of a mine type with outboard furnaces. Ball or other mills are usually used for grinding.

When firing at different temperatures, different materials are obtained. Firing of caustic dolomite is performed at a temperature of up to 750 degrees. Dolomite cement is formed at a higher temperature (up to 850 degrees). Dolomitic lime, which is capable of quenching, is produced at a temperature of the order of 950 degrees [1-3]. The purpose of this work is to study the possibility of obtaining a qualitative high-strength dolomitic binder in industrial conditions with an interval of variation in the firing temperature of at least 50°C. To achieve the purpose, the following tasks were set:

- to study the features of dolomites decomposition during thermal processing to obtain a high-strength binder;
- to investigate the possibility of separating the processes of decarbonization of $MgCO_3$ and $CaCO_3$ in the presence of additives-intensifiers;
- to choose the most effective additive - intensifier, get the binder and study its properties.

The discussion of the results. At present, extensive work is being done to study the use of mineral raw materials for the industry building materials and to organize new productions. Natural dolomite $CaCO_3{\cdot}MgCO_3$, whose deposits are very numerous in the CIS and abroad, contains impurities as lime, sand, clays, iron compounds in its composition. The quantitative content of these impurities depends on the quality of the binders being manufactured. In theory, dolomite consists of 30.41% of CaO, 21.87% of MgO and 47.72% of CO_2.

In order to develop a waterproof binder based on the dolomite raw material of Southern Kazakhstan, the processes taking place during the dolomites dissociation of various chemical and mineralogical compositions were investigated. The search for ways to increase the water resistance of the binder on the basis of caustic dolomite was carried out and the properties of binders were investigated. Dolomite decomposition occurs in the temperature range 700-900°C, with two endothermic effects on the thermogram: the first takes place in the range 720-760°C, the second in 895-910°C. Consequently, the process proceeds in two stages. The most likely is the dissociation scheme, in which magnesium oxide and calcium carbonate are formed in the first stage: $CaMg\ (CO3)_2 = CaCO_3 + MgO + CO_2$. In the second stage, decomposition takes place: $CaCO_3 = CaO + CO_2$.

Investigations of the firing processes of small-crystalline dense dolomites in the south of Kazakhstan have shown that in order to obtain a highly active dolomite with a low content of free calcium oxide, its firing temperature should correspond to the endothermic decomposition temperature of $MgCO_3$. For the investigated dolomites this is 720-760°C. The resulting caustic dolomite contains not less than 15% of magnesium oxide and not more than 2.5% of free calcium oxide. The binder properties of caustic dolomite are significantly improved with finer grinding, so the firing products were ground to a residue on sieve No. 008 of 22%. The resulting magnesia binder was covered with a solution of MgSO4 with a density of 1.2 g/cm^3, as well as a brine of Kyzylkol salt lake of the same density containing MgSO4 and MgCl2. The ratio of dry material to mixing is assumed equal to 0.3-0.34, which ensures a normal density of the test. Samples with a size of 2x2x2 cm were prepared, some of which were tested after 28 hours of air hardening, and some were hardened in a drying cabinet at a temperature of 60-90°C for 1-3 hours.

When the caustic dolomite hardens, hydration of magnesium oxide occurs and the formation of oxysulfate or magnesium oxychloride, depending on the chosen mixing. Calcium carbonate increases the density of the hardening mass and, creating crystallization centers, promotes the carbonization of lime, which can be formed in a small amount during the dolomite firing [4, 5]. Dolomite decomposition occurs in the temperature range 700-900°C, with two endothermic effects on the thermogram: the first takes place in the range 720-760°C, the second in 895-910°C. The most likely is the dissociation scheme, in which magnesium oxide and calcium carbonate are formed in the first stage: $CaMg\ (CO_3)_2 = CaCO_3 + MgO + CO_2$. In the second stage, decomposition takes place: $CaCO_3 = CaO + CO_2$: $CaMg\ (CO3)_2 = CaCO_3 + MgO + CO_2$ and $CaCO_3 = CaO + CO_2$ in the second stage.

The production process of caustic dolomite does not differ from the production of caustic magnesite. Depending on the dolomite firing temperature, materials of various composition and purpose can be obtained: caustic dolomite consisting of MgO and $CaCO_3$ at a temperature of 750°C, dolomite cementation of MgO, CaO at 800-850°C, and $CaCO_3$, dolomitic lime, consisting of MgO and CaO, at 900-1000°C, metallurgical dolomite at 1400-1500°C, fired to sintering. For the caustic dolomite production, firing should be conducted so that the product contains as much MgO as possible and the minimum amount of CaO. The density of caustic dolomite should be in the range of 2.78-2.85 g/cm^3. A higher density indicates a high content of free lime.

When solidifying the caustic dolomite, magnesium oxychloride arises. $CaCO_3$ creates crystallization centers, increasing the density of products. $Mg\ (OH)_2$ can interact with highly dispersed SiO_2 already at normal temperature. Most quickly such a reaction is carried out in an autoclave at 174°C and depending on the ratio of MgO: SiO_2 and temperature, kerolite, sepiolite or serpentine are formed in the form of gels, and then converted to fibrous crystals. They not only increase strength, but also act as reinforcing material.

The seizure timing of the caustic dolomite is stretched. The start of seizure is after 3-10 hours. The end is after 8-20 hours. When tested in a plastic consistency test, caustic magnesite, immobilized with a solution of $MgCl_2$ of density 1.2 g/cm^3, at 1 day age of air hardening, has a tensile strength of at least 1.5 MPa, and 3.5-4.5 MPa after 28 days. The compressive strength of tamped samples from a solution with sand (1:3) after 28 days of air hardening is 40-60 MPa. With high quality of magnesite, the strength can reach 80-100 MPa. In the first period of hardening, hardening rate of strength increase is high. Usually at 1 day age, the strength of concretes and mortars reaches 30-50, and it is 60-90% of the maximum possible at 7 days age. After 28 days, the strength increase is very small or completely absent.

Caustic dolomite is an air binder. In water and in a humid atmosphere, its strength sharply decreases [6-9].

Conclusions. Caustic dolomite should be reduced to the remainder on sieve No. 02 of no more than 5%, and on sieve No. 008 of no more than 25%. Its binder properties are significantly improved with finer grinding. Caustic dolomite is closed with aqueous solutions of chloride and magnesium sulfate salts, usually of the same concentration as caustic magnesite. The seizure and hardening of caustic dolomite and magnesite is mainly due to the hydration of MgO and the formation of magnesium oxychloride or other basic salts.

The true density of caustic dolomite is within the range of 2.78-2.85 g/cm^3. Its increase indicates the appearance of a significant amount of free calcium oxide in the caustic dolomite. The density in the loose-lopped state is 1050-1100 kg/m^3 on the average. The beginning of seizure at room temperature comes in 3-10 hours, and the end after 8-20 hours after mixing.

Caustic dolomite, fired at a temperature below the dissociation temperature of $CaCO_3$, is characterized by a uniform change in volume. Unevenness is observed only in the presence of 2-2.5% of free calcium oxide in it and at the wrong ratio between MgO-$MgCI_2$ and water. In this case, cracks appear and the cement stone collapses. Caustic dolomite is less durable than caustic magnesite. Samples from a tamping solution of 1: 3 composition by weight on this binder after 28 days of air hardening have a compressive strength of 10-30 MPa. Like magnesite, hardened caustic dolomite is destroyed in water due to washing out soluble salts $MgCI_2$, etc from it. Along with caustic magnesite, caustic dolomite is used for the production of xylolite, fibrolite, heat-insulating materials, etc.

Application area. In nature, dolomite occurs no less frequently than calcium. The application area of these minerals is almost identical. Dolomite is used: for the production of refractory materials instead of magnesite; for the production of metallic magnesium; in the production of steel; as a raw material for fluxes in the metallurgical industry; for the production of building materials, such as mineral wool, magnesia cement, sovelit, etc.; as a wall and facing material in the construction of housing and industrial facilities; for building roads; to increase the strength and chemical resistance of glass; for the production of rubber; as a filler in the production of paper; as an abrasive material for polishing metal and glass surfaces; as a raw material for the production of glazes for porcelain; as a means of combating various insects; in landscape design [10-13].

Easiness of processing determines the popularity of this stone among builders. It can be given any shape, a flat or embossed surface. It has good strength; therefore it is used as facing material for walls, windowsills, stairs, for floors in shopping malls and other public buildings.

The dolomite tile has filtering qualities and allows maintaining a favorable microclimate in the room. Rocky tiles are used for finishing socles and facades. Plain tiles usually polish the floor. Polished tiles are well suited for interior decoration. Buchard tiles, which have anti-slip properties, are used for paving paths.

It is used for the design of wells, pools, decoration of fireplaces and stoves, restoration of palace ensembles. With the help of original polishing technologies, designers create products that look like natural marbles. Dolomite flour is an ingredient for obtaining dry construction mixtures. Since the grains of this mineral are cubic in shape, they provide a better level of adhesion than sand. That is why dolomite powder is popular in Russian enterprises. Mixtures with its addition have the highest quality.

In addition, dolomite flour is used to create various sealants, mastics, in the production of paint products, linoleum, etc. Another area of its application is liming, loosening and fertilizing the soil. It reduces the acidity of the soil and enriches it with magnesium and potassium. It can be used both for open ground, and for greenhouses.

Recently, dishes have been produced from dolomite. Dolomite ceramics are inexpensive, have a beautiful appearance and are light in weight, but they are very fragile. Under the influence of high temperature, the outer layer is broken, and microcracks appear in it. Therefore, dolomite dishes are not recommended for hot food. Some scientists argue that dolomite is generally unsuitable for making dishes, since it is sensitive to the action of acids, especially coal. However, this material does not cause harm to health.

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С. К. Құрбаниязов[1], А. М. Игибаева[2], А. А. Коптік[2], З. С. Таджибаева[2], Г. С. Шалабаева[1], Г. Ж. Әріпжан[1]

[1]А. Ясауи атындағы Халықаралық қазақ-түрік университеті, Түркестан, Қазақстан,
[2]ЖМ «Аймақтық әлеуметтік-инновациялық университет», Қазақстан

ДОЛОМИТТІ БАЙЛАНЫСТЫРҒЫШТЫҢ ҚАСИЕТТЕРІ МЕН ҚОЛДАНЫЛУЫ

Аннотация. Мақалада құрылыс материалдарының саласы сипатталған, нақтырақ атап кеткенде, байланыстырғышты доломиттен алу, яғни доломиттелген магнезитті ауыр бетонды жасауда, қабырғалық, жылуизоляциялайтын, әрлеуші құрылымдар, ұяшықты бетондарды алуда, ксилолитті және басқа да материалдарды тұрмыстық және өндірістік құрылыста қолданылуы мүмкін. Зерттеу нәтижелері көрсеткендей, күйдіру кезіндегі температураның төмендеуі және сәйкесінше байланыстырғышты алуда энергошығындарының азаюі беріктіліктің және материалдың көлем біртектілігінің жоғарлағанын көрсетті. Сонымен қатар түрлі доломитті жыныстардан сапалы жоғары берік байланыстырғыштарды алу мүмкіншіліктері қарастырылған. Зерттеу барысында күйдіру кезіндегі жиілегіштерді қолдану, доломитті байланыстырғыштарды өндіруде тиімді екендігі анықталды.

Түйін сөздер: доломит, байланыстырушы заттар, құрылыс материалдары, бетон, цемент, кальций, магний.

**С. К. Курбаниязов[1], А. М. Игибаева[2], А. А. Коптик[2],
З. С. Таджибаева[2], Г. С. Шалабаева[1], Г. Ж. Арипжан[1]**

[1]Международный казахско-турецкий университет им. А. Ясави, Туркестан, Казахстан,
[2]ЧУ «Региональный социально-инновационный университет», Казахстан

СВОЙСТВА И ПРИМЕНЕНИЕ ДОЛОМИТОВОГО ВЯЖУЩЕГО

Аннотация. В статье описывается область строительных материалов, а именно получение вяжущего из доломита, доломитизированного магнезита которое может быть использовано при изготовлении тяжелых бетонов, стеновых, теплоизоляционных, отделочных изделий, ячеистых бетонов, ксилолитовых и других материалов для гражданского и промышленного строительства. Результат исследования показал повышении прочности и равномерности изменения объема материала при одновременном снижении температуры обжига и, соответственно, энергозатрат на получение вяжущего. Также рассмотрена возможность получения качественного высокопрочного вяжущего из различных доломитовых пород. Исследованы процессы, протекающие в доломите при обжиге. Установлено, что в производстве доломитового вяжущего эффективно применение интенсификаторов обжига.

Ключевые слова: доломит, вяжущие вещества, строительные материалы, бетон, цемент, кальций, магний.

Information about the authors:

Kurbaniyazov S. K. – Ph.D., A. Yasavi International Kazakh-Turkish University, Turkestan, Kazakhstan, saken_geo@mail.ru

Igibaeva A. M. – Master, sen. Lecturer, PI "Regional Social-Innovation University", Kazakhstan, igibaeva80@bk.ru

Koptic A.A. – Master, sen.lecturer, PI "Regional Social-Innovation University", Kazakhstan,

Tadjibaeva Z.C. – Sen.lecturer, PI "Regional Social-Innovation University", Kazakhstan, tadzhibaeva81@list.ru

Shalabayeva G. Sh. – c.tech.s., associate prof., A. Yasavi International Kazakh-Turkish University, Turkestan, Kazakhstan, gulshat.shalabaeva@ayu.edu.kz

Aripzhan G. Zh. – teacher, A. Yasavi International Kazakh-Turkish University, Turkestan, Kazakhstan, gulnur.aripzhan@mail.ru

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