VOL. 13, NO. 10, MAY 2018 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

PRACTICES OF DOLOMITE APPLICATION IN THE PRODUCTION OF CONSTRUCTION MATERIALS

Liliya Nailevna Lomakina, Ivan Nikolaevich Garanykov, Pavel Anatol'evich Fedorov, Ramzi Fajzievich Husnutdinov and Bulat Ramzievich Husnutdinov
Ufa State Petroleum Technological University, Russia, Ufa, Kosmonavtov Street, Russia
E-Mail: liliya.n.lomakina@yandex.ru

ABSTRACT

In this article the authors consider the issues concerning promising areas of dolomite utilization as a component in various applications when forming construction materials. The article presents the structure assessment of the dolomite of Madaevskoe deposit in the Nizhny Novgorod Region (Russian Federation). Besides, the article describes the results of selecting the optimal composition of the putty coat containing the dolomite as fine ground filler. For the purpose of using dolomite as a magnesia binder, the authors have considered phase transformations as a result of dolomite calcination in both pure form and when adding promoters of magnesium component decomposition.

Keywords: dolomite, dolomite calcination, magnesia binder, X-ray phase analysis, structure formation, phase composition, putty coat.

INTRODUCTION

Priority and upcoming trend in creation of new construction materials is the use of natural environmentally sound raw materials. Such materials include dolomite based magnesia binding substances. The application of dolomite when producing construction materials allows solving problems of rational approach to natural resources and reducing the ecological load on the environment.

Total production of dolomite in Russia for all industries is about 5 million tons per year.

The availability of dolomite and its known crystallographic, physical and chemical properties allow obtaining a reliable estimate of the potential application of this material in industrial and civil construction [1].

In [2] the authors investigated the positive effect of dolomite, incorporated as a mineral additive, on the hydration of cement that accelerated the hardening of the main products of hydration. With increasing content of dolomite the volume of the hydration products had also increased. The authors of [3] proposed to incorporate fine dolomite limestone as mineral additive when manufacturing cement mortars that had led to compacting structure and increasing the early strength of the compositions. The research [4] presented studied influence of fine-grained dolomite on important physical and mechanical properties of concrete. The authors tested cement samples with added dolomite powder in quantities of 0, 5, 10, 15 and 20% by cement weight. The results had shown that tested concrete mortars with dolomite provided the increase of compressive strength of concrete, as well as tension breaking strength, and flexural strength.

Studies [5] revealed the possibility of successful replacement of limestone powder by dolomite fine powder when producing self-compacting concrete.

Also, there are known not single cases of using dolomite as magnesia binder, obtained by firing with the addition of intensifiers. Research [6] provides information about the fact that proper firing and proper selection of intensifiers leads to formation of sufficiently high strength of chlorine magnesia stone, comparable to the strength of the binder, obtained from other raw materials, namely magnesite and brucite. It should be noted that issues related to the provision of the necessary resistance of concretes based on magnesia binders under impact of aggressive media, including acidic gases such as carbon dioxide, remain currently insufficiently studied [7, 8].

The authors of [9] considered the effect of different intensifiers, produced by decomposition of magnesium and calcium components of dolomite, on the decrease in $MgCO_3$ decomposition temperature in the dolomite rock.

Of particular interest is the work [10] related to the study of the kinetics of dolomitization reaction in water dispersion composed of dolomite and portlandite with different alkalinity, temperature, and content of silicon dioxide.

The authors of [11] developed a mathematical model to select properties of chlorine magnesia compositions (strength and hydroscopic capacity) depending on the content of the main source material components, such as magnesium oxide, magnesium chloride, and water. This technique allows controlling the final characteristics of the magnesia materials to avoid efflorescence and cracking.

MATERIALS AND METHODS

The dolomite rock from Madaevskoe deposit in the Nizhny Novgorod Region (Russian Federation) was assessed.

When studying the dolomite phase compositions as well as concrete and magnesia binder produced on its basis, the X-ray phase analysis was used employing the "D2 Phaser" diffractometer (manufactured by "Bruker Corporation", Germany). Radiographs were processed using the "Diffrac. Eva" and "Diffrac. Topas" licensed software versions, as well as the database of "PDF-2 Release 2011 of the Powder Diffraction File". Morphological analysis of the dolomite surface was conducted by scanning electron microscopy technique

using the "JEOL JSM-6610 LV" (Japan) electronic microscope. Dehydration test was carried out using simultaneous thermal analysis, thermogravimetry, and differential scanning calorimetry (TG and DSC) employing "STA 449 F3 Jupiter" apparatus with quadrupole mass spectrometer "QMS 403C" (produced by "Netzsch", Germany).

When selecting putty mixes (for the production in a form of dry mixes) with application of dolomite as a fine filler, cement N produced by Ust-Katav and sand from deposit in Neftekamsk (Russia) were used. The sodium carboxymethyl cellulose was used as water-retaining additive. Water-cement ratio of the studied samples ranged from 0.2 to 0.3 depending on composition to provide the necessary slump of concrete according to GOST 31356-2007 [12].

Selection of mixture compositions was carried out on the basis of operational criteria of dry mixes according to [12, 13, 14], divided into three categories: basic quality indicators of dry mixes (moisture, largest particle size of filler grains, the content of grains with the largest size (sieve residue, corresponding to the grain size of the largest aggregate size), the main quality indicators of ready-to-use mixes (flowability, retainability of the original flowability, water-holding capacity), and the main quality indicators of the mortar stone (water absorption and adhesion bond strength). Obtained compositions met noted requirements [13].

RESULTS AND DISCUSSIONS

The analysis results of the dolomite structure using the X-ray phase analysis method, shown in Figure-1, revealed the availability of the main components of the rocks, namely dolomite ($CaCO_3 \cdot MgCO_3$), cristobalite (SiO_2), and quartz (SiO_2). The presence of silicon oxide impurities had a positive effect on the hardening process of cement mixes.

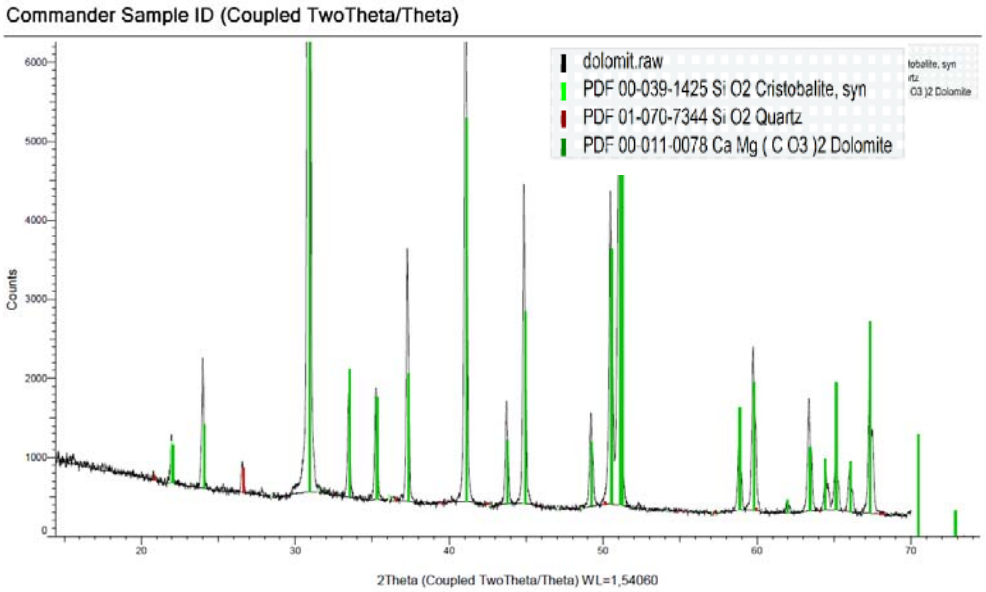

Figure-1. The X-rayogram of a dolomite sample from Madaevskoe deposit (Russian Federation).

Microscopic image of the dolomite surface, presented in Figure-2, showed a porous structure conducive to increased hydroscopic capacity of the material.

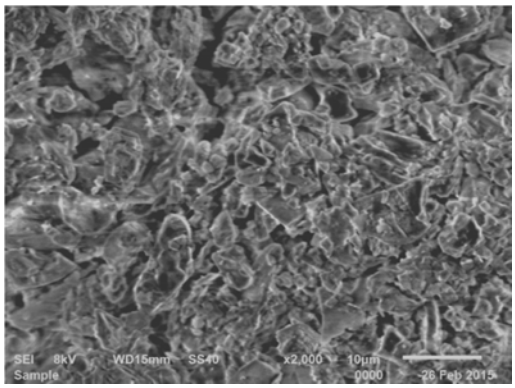

Figure-2. Pattern of the dolomite sample surface at x2000 magnification.

ARPN Journal of Engineering and Applied Sciences

The composition of the dolomite proves that in the normal conditions it is inert with respect to chemical interaction with water. Therefore, in a "primordial form" by grinding to fine fractions, it can be used primarily as inert fine powder filler to replace fine fractions of sand, for example as part of the dry putty coat construction mixes' composition [1]. Additional effects of using fine dolomite powder (dolomotized calcite) as filler of portland cement based compositions are shown in the work [3].

Phase composition was analyzed for all hardened compositions selected in the course of all the conducted tests. The X-rayogram of major phases of the stone mortar compositions containing dolomite is shown in Figure-3.

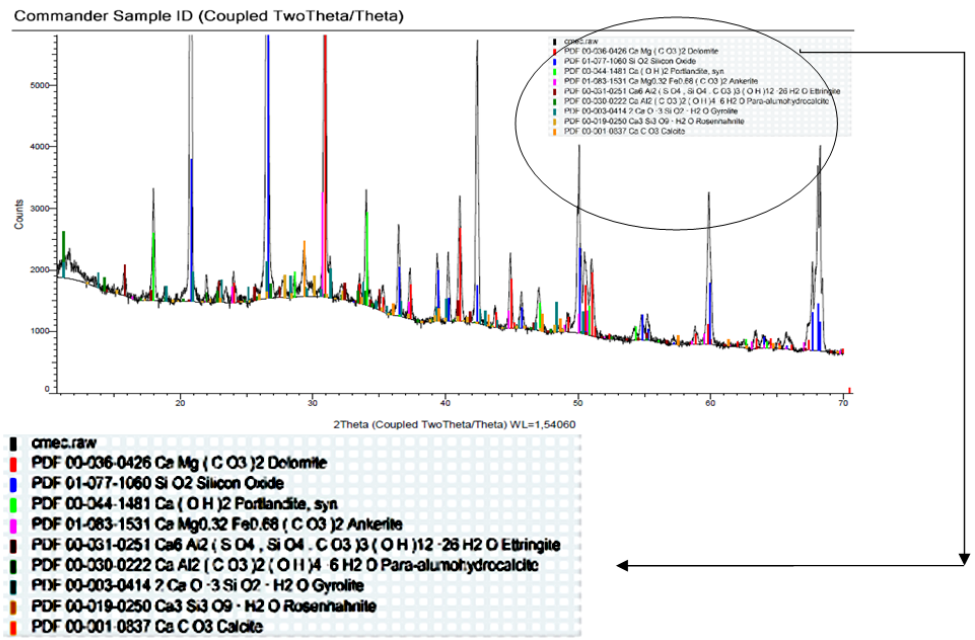

Figure-3. The X-rayogram of the major phases of the stone mortar compositions of dolomite containing putty mixes.

The presence of undecomposed dolomite and portlandite in the compositions indicates the fact that dolomite does not react under normal solidification conditions of portland cement. However, when using it as fine filler it is possible to solve the problems such as the improvement of differential porosity of cement stone through its approaching to fine structure. In addition, the filler particles act as additional crystallization grains to accelerate the cement hydration process, resulting in higher compressive strength [2, 3]. Besides, there is some increase in the plasticity of the mixture and the adhesion of the solidified formulations.

The next task that was formulated in this work was obtaining effective magnesia binder. To this end, various additives were supplemented during calcination of dolomite. This allowed increasing the temperature interval between starting point of its decomposition to the active MgO prior to the beginning of the decomposition of $CaCO_3$.

Based on the results of thermal analysis of dolomite, the initial temperature of its decomposition to MgO and $CaCO_3$was found to be equal to +724 ºC. However, it was noted that in the inert atmosphere of the apparatus various stages of dolomite decomposition overlapped with each other. In this regard, it was decided to investigate the effect of different additives on reducing the dolomite decomposition temperature by heating in a muffle furnace at certain temperatures and subsequent X-ray phase analysis of the obtained compounds. Conducted studies had shown that the optimal exposure time to obtain a more active binding agent was 180 min interval.

The original starting point when testing all samples was a temperature of +600 °C, which was by more than 100 degrees lower than the temperature of +724 °C, obtained at the firing of the samples in thermal analysis apparatus while studying "pure" dolomite. "Pure" dolomite without temperature additives was used as a control composition.

The results of quantitative X-ray phase analysis after thermal aging of the formulations at a temperature of +650 ºC for 60 minutes are shown in Tables 1-5.

Table-1. Components of the "pure" dolomite decomposition after thermal aging for 60 minutes at different temperatures.

Firing temperature	650 °C	700 °C	750 °C	800 °C
$CaCO_3 \cdot MgCO_3$	88.96	76.05	2.8	-
$MgCO_3$	2.62	8.52	5.27	6.35
$CaCO_3$	1.65	8.71	65.78	58.35
MgO	6.76	6.71	26.15	28.53
CaO	-	-	-	6.78

Table-2. Components of the "dolomite+NaCl" mix decomposition after thermal aging for 60 minutes at different temperatures.

Firing temperature	600 °C	650 °C	700 °C	750 °C
$CaCO_3 \cdot MgCO_3$	33.63	-	-	-
$MgCO_3$	9.92	-	11.88	10.42
$CaCO_3$	39.12	69.32	57.03	58.67
MgO	17.33	25.17	30.06	26.64
$5MgO \cdot 4CO_2 \cdot 5H_2O$	-	-	1.03	-
CaO	-	-	-	4.27

Data in Table-1 show that in the control composition the dolomite decomposes completely at temperatures over 800 °C. However, the presence of a considerable fraction of CaO indicates that the optimum firing temperature of dolomite ranges from 750 to 800 °C.

The results of firing with supplement of temperature additive NaCl are shown in Table-2, which shows that as early as at a temperature of 650 °C there is a complete decomposition of dolomite as well as $MgCO_3$, which is decomposed to MgO and $CaCO_3$. Moreover, CaO still did not begin to form even at 700 °C, while at 750 °C its content did not exceed 5%.

Experimental data with temperature additive of $MgCl_2$ are given in Table-3. They indicate that the additive also "extends" the firing temperature interval between the instant corresponding to formation of MgO and CaO. The optimum temperature is 700 °C.

Table-3. Components of the "dolomite+ $MgCl_2$" mix decomposition after thermal aging for 60 minutes at different temperatures.

Firing temperature	650 °C	700 °C	750 °C
$CaCO_3 \cdot MgCO_3$	-	-	-
$MgCO_3$	14.39	12.75	16.00
$CaCO_3$	55.83	56.34	45.05
MgO	29.78	30.01	32.65
CaO	-	-	6.29

Table-4. Components of the "dolomite + $NaHCO_3$" mix decomposition after heat aging for 60 minutes at different temperatures.

Firing temperature	650 °C	700 °C	750 °C
$CaCO_3 \cdot MgCO_3$	2.1	0.74	-
$MgCO_3$	16.73	5.47	-
$CaCO_3$	56.22	64.08	61.88
MgO	24.96	28.1	29.05
$Na_2CO_3 \cdot 10H_2O$	-	1.6	-
CaO	-	-	4.33
SiO_2	-	-	4.74

When supplementing $NaHCO_3$ additive, temperature of 750 °C is the "boundary" and corresponds to the emergence of CaO in the amount of 4.33%.

Thus, in consequence of the experiment, the most effective additive is NaCl, the addition of which in the course of firing even at a temperature of 650 °C leads to complete decomposition of dolomite to MgO and $CaCO_3$ without the formation of CaO.

Compositions were prepared at various ratios of calcined dolomite (dolomite calcination with the addition of NaCl with thermal aging during 3 hours at 650 ^{0}C) and grouting fluid $MgCl_2$ (0.44 - 0.53) with the density ranging from 1.26 to 1.28 kg/m^3. The greatest increase in strength was achieved in compositions with a grouting fluid density of 1.27-1.28 kg/m^3 at a binder to grouting fluid ratio of 0.52-0.53.

So, during 3, 7 and 28 days, the highest flexural strength had increased from 7.03 to 9 MPa, while the highest compressive strength of these compounds had increased from 22.58 after 3 days to 34.97 MPa after 28 days. It was revealed that calcined dolomite based compositions had rapid strengthening occurring within the first 3 days, as compared with compositions based on portland cement binder. At that, in 28 days, the strength of the compositions becomes quite similar to that of portland cement compositions. High dispersion of MgO ensures complete hydration of the binder, while the porous structure of the filler $CaCO_3$ contributes to increase in the surface of adhesion with it. At that, $CaCO_3$, in contact points interacts with the hydration products of MgO, thus providing increased strength of stone [5]. Needle-like or fibrous structures of the binder shown in Figure-4 prove in addition to the results of X-ray phase analysis the presence in the formulation of magnesium of 3- and 5-oxyhydrochlorides, which are stone strength indicators.

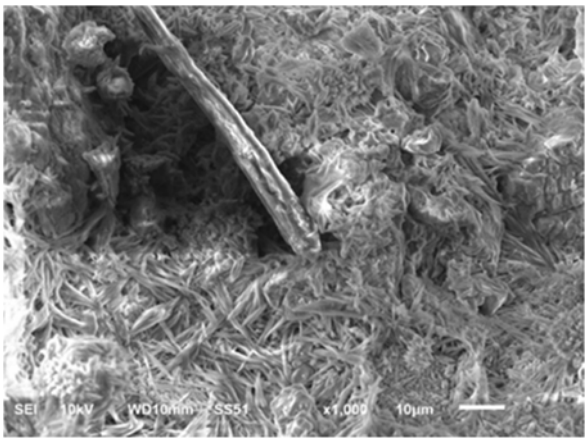

Figure-4. Illustration of the binder sample surface pattern at x1000 magnification.

It is known that adding shavings, sawdust, and other kinds of industrial waste to magnesia binders can result in obtaining solutions with added properties. Several compositions with the addition of various aggregates were prepared adding waste plastic bottles, wood filler, and unburned dolomite powder in different ratios.

The best strength indicators were noted in the compositions containing filler with unburned dolomite powder in the ratio of 1:1 relative to calcined dolomite. So, the compressive strength of such compositions as early as by the 7th day amounted to 32.31 MPa that had shown an increase of strength by 1.3 times comparing to the composition without filler.

Thus, dolomite fine powder has the potential applications not only as filler but also as a formulation that has special binding properties. Compositions based on dolomite binding comparing to those based on standard portland cement, are characterized by a faster strength development, which at the 3rdday of curing reaches about 65% of that corresponding to 28-day strength. This allows applying mortars and concretes based on magnesia binder in the conditions where accelerated curing and strengthening are required.

The development of coupled manufacturing processes of sodium carbonate and cement clinker on the basis of dolomite binders is of special interest due to availability of considerable natural reserves of calcite with different degree of dolomitization in contrast to pure calcite.

CONCLUSIONS

The following conclusions could be drawn in consequence of the conducted research:

- the dolomite structure of the Madaevskoe deposit in the Nizhny Novgorod Region (Russian Federation) had been investigated.
- the optimal composition of putty coat, which was determined based on the use of the investigated dolomite as fine powder filler, had been selected;
- phase transformations of the investigated dolomite had been studied in the course of its firing both in a pure state and with additives of sodium chloride, magnesium chloride, and sodium bicarbonate to accelerate the decomposition of dolomite to magnesium component;
- dolomite based magnesia binder formulations had been selected, and physico-mechanical and physico-chemical investigations of their formulations had been conducted.

ACKNOWLEDGEMENTS

The authors express their gratitude to Narkas B. Khababutdinova, the postgraduate student of the Ufa State Petroleum Technical University (Russia), for her assistance in conducting physical and chemical measurements.

REFERENCES

[1] Lomakina L.N., Gurenkov I.N., Khababutdinova N.B. and Nikitin I.S. 2016. Issledovanievozmozhnostipolucheniyasuhojstroitel'no jsmesidlyashpaklevochnyhrabot s primeneniemdolomita [Investigation of the possibility of obtaining a dry construction mix for puttying works with the use of dolomite] [Text]. Proceedings of the IIIrd International research-to-practice conference Issues of contemporary technical sciences: A fresh look and new solutions. Building and Architecture, Russia, Yekaterinburg, pp. 73-76.

[2] Szybilskia M. and Nocuń-Wczelikb W. 2015. The effect of dolomite additive on cement hydration. Procedia Engineering. 108, pp. 193-198.

[3] Mikhailova O., Yakovlev G., Maeva I. and Senkov S. 2013. Effect of dolomite limestone powder on the compressive strength of concrete, Procedia Engineering. 57, pp. 775-780.

[4] Kumar R.L., Kiran J. and Rangarajan P. 2017. Properties of concrete incorporating dolomite powder. IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE). 14(2): 78-80.

[5] Barbhuiya S. 2011. Effects of fly ash and dolomite powder on the properties of self-compacting concrete. Construction and Building Materials. 25(8): 3301-3305.

[6] Nosov A.V., Chernykh T.N. and Kramar L.Y. 2014. Effektivnost' razlichnyhdobavok-intensifikatorovpriobzhigedolomitov [The effectiveness of various intensifying additives in the

firing of dolomites] [Text]. Construction Materials. pp. 71-71.

[7] Mittermayr F., Klammer D., Köhler S., Leis A., Höllen D. and Dietzel M. 2011. Dissolution of dolomite in alkaline cementitious media. Proceedings of the 13th International congress on the chemistry of cement, Madrid, Spain.

[8] Fedorov P.A., Anvarov A.R., Lutsyk E.V., Latypov V.M. and Latypova, T.V. 2016. Kinetics of fine concrete carbonation in humid operational environment. International Journal of Applied Engineering Research. 11(11): 7439-7445.

[9] Chernykh T.N., Nosov A.V. and Kramar L.Y. 2015. Dolomite magnesium oxychloride cement properties control method during its production. Source of the Document IOP Conference Series: Materials Science and Engineering. 71(1): 012045.

[10] Galí S., Ayora C., Alfonso P., Tauler E. and Labrador, M. 2001. Kinetics of dolomite-portlandite reaction: Application to portland cement concrete. Cement and Concrete Research. 31(6): 933-939.

[11] Chernyh T.N., Kramar L.Y., Trofimov B.Y. and Orlov A.A. Mathematical models for the appointment of the chlorine magnesia composition. Source of the Document Bulletin, South Ural State University, Series: Mathematical Modelling, Programming and Comp.

[12] GOST 31356-2007 Smesisuhiestroitel'nyenacementnomvyazhushchem [GOST 31356-2007. Dry construction mixes based on cement binder] [Text]. Test methods, 2009-01-01, Moscow, Standartinform, 2008, p. 14.

[13] GOST 31357-2007 Smesisuhiestroitel'nyenacementnomvyazhushchem [GOST 31357-2007. Dry construction mixes based on cement binder] [Text]. General technical conditions, 2009-01-01, Moscow, Standartinform, 2008, 12 p.

[14] GOST 5802-86. Rastvorystroitel'nye [GOST 5802-86. Construction mortars] [Text]. Test methods, Introd. 1986-01-07 with ammend. (IUS, 1989, 4), in replacement of GOST 5802-78, Moscow, Standartinform, 2010, p. 16.