Effect of Dolomite Limestone Powder on The Compressive Strength of Concrete

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Abstract

The purpose of this work is to describe the effect of fine ground dolomite limestone on important physic and mechanical properties of concrete. The present examinations indicate that the use of dolomite limestone as component instead of limestone is a viable solution for producing Portland dolomite limestone cement, especially for quarries with dolomitic inclusions or overburden.

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1. Introduction

One of the major achievements of the cement and concrete industries during the past years is the increasing use of mineral additions. The high cost of energy, diminishing energy sources in the world and the greenhouse effect require that energy consumption be reduced by all industries. The benefits of addition of supplementary materials to Portland cement are well documented [1-6].

Firstly, since the production of Portland cement clinker is an energy-intensive process, a partial substitution of clinker by mineral additions obviously represents considerable energy savings [7].

Secondary, it makes economic sense to reduce the energy used in the production of cement and concrete [2] and at the same time make a safe use of what sometimes can be classified as an industrial waste.

Lastly, the substitution of mineral additions for clinker lowers the CO\textsubscript{2} emission of the cement and concrete industries [8], [9]. Common mineral additions are granulated blast furnace slag, silica fume, fly ash and limestone filler [10].

Limestone powder blended cement is manufactured and used in many countries as limestone is naturally available, cheap and it's a basic raw material in clinker production. Many papers on research of influence of limestone powder on hydration of Portland cement were reported [11]. Research data revealed that limestone powder does not play the role of an inert mineral (inert additive) but also accelerates the hydration rate of Portland cement in an early stage [12].

Finely, powdered limestone helps to reduce water demand and segregability mixtures to increase their water-holding capacity, plasticity, and the homogeneity of mortar, reduce shrinkage and improves the water-and frost-resistance of the solution [13-14].

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In France finely limestone is widely used, which is added to Portland cement in amounts up to 27%. Used limestone consists mainly of calcite with small amounts of quartz or amorphous silica, and occasionally dolomite. Influence of limestone is partly physical and partly chemical. Also limestone accelerates hydration alite and aluminate phases, because of its dispersed material fills the space between the grains of clinker, improving interaction [15].

In Latvia dolomite in powder was studied for making dolomitic cement [16]. Some investigations confirmed that finely ground dolomite can be used as cementitious material to produce cement with dolomite [17–19].

Some authors [20-21] investigate a positive influence of limestone filler on the increase of early strengths of conventional concrete. They present two reasons for explaining this. The first is the effect of limestone on hydration $C_3A$ and $C_3S$ and the second reason is the fact that small limestone particles constitute nucleation sites of hydration products.

2. Materials and research methods

Portland cement PC-500 D-0 produced by OJSC “Gornozavodskcement” per GOST 10178-85 was used as the main binding material. To prepare a mix, gravel sand size up to 2.5mm was used as an aggregate, in the ratio 3:1 with Portland cement. Besides, limestone obtained from screenings of Pudingov Aggregate Preparation Plant located in the Sverdlovsk Region, was added.

Two kinds of dolomite limestone fine powder with mean particle size 4μm and 2.79 μm and specific surface 5500cm$^2$/g (Fig. 1) and 7523 cm$^2$/g, respectively, were examined. To determine specific surface and mass-average particle size of disperse powder to be examined Khodakov tester (PSKh-12) was used. Limestone powder particle size distribution was analyzed by means of Horiba Laser Partical Size Distribution Analyzer LA-950.

Mixtures containing finely dolomite limestone from 0 to 30% by weight of cement were prepared. Water/binder ratio of control specimens was 0, 5.

The mortar mixture is poured into prismatic molds with 40×40×160 mm. Specimens were demolded after 24 ± 2 hours and kept in water until the testing day for 7, 14 and 28 days. Test results for compressive strength obtained from the average of six broken pieces of specimens for each age.

Aggregate mineral composition as per powder X-ray pattern (Fig. 2) is represented by carbonate, dolomite, and silica. Silica is mainly represented by crystal phase which does not predermine its activity. So, this dolomite limestone powder is inert additive – filler in Portland cement.

Fig. 1. Dolomite limestone powder particle size distribution (specific surface 5500cm$^2$/g)

Fig. 2. X-ray pattern dolomite of limestone powder
Dolomite limestone powder thermogram is shown in Fig. 3. Differential thermal analysis was carried out with instrument METTLER STAR SW 9.01.

Table 1. Chemical composition of the dolomite limestone

| Content of Chemical Elements, % | Ignition loss, % |
|---------------------------------|------------------|
| SiO₂                            | 21.7             |
| Al₂O₃                            | 2.40             |
| Fe₂O₃                            | 0.65             |
| TiO₂                             | 0.14             |
| CaO                             | 23.16            |
| MgO                             | 15.6             |
| SO₃                             | 0.09             |
|                                 | 35.7             |

Chemically free water evaporation takes place at 80 °C. DTA may identify dolomite as a contaminant of lime material. Dolomite is characterized by two endothermic effects: at 800 and 950 °C. The first one is due to pre-calcining of MgCO₃ contained in dolomite, and the second one is due to pre-calcining of CaCO₃, contained in dolomite limestone. It is known [22], that dolomite contained in lime material in the form of contaminant, peak temperature is slightly displaced towards greater heats. In Fig. 3 there are two endothermic effects 830 and 880 °C, corresponding to dolomite contaminant of limestone.

Fig. 3. Thermogramm of dolomite limestone powder

3. Results and Analysis

3.1. Mechanical properties

Strength test results of samples in the age of 14 and 28 days are provided in Fig. 4. As we can see, partial cement replacement with dolomite limestone powder results in compression strength increasing. Strength of samples containing 25% of dolomite limestone powder increased by 16.7% and 23.5% at 14 and 28 days age, respectively, in comparison with reference samples.

Fig. 4. Effect of dolomite limestone fine powder (specific surface 5500cm²/g) content on cement concrete compression strength: 14 and 28 days age
Dolomite limestone ultrafine particles act as nucleation site [23], [24], where silicates crystallization rate increasing takes place, that facilitates Portland cement minerals hydration, hydrosilicates CaO – SiO ratio changing.

When limestone content is optimal (25 % of binder weight), strength gain is higher than in the reference sample (0% additives) by 56 %. As per test results it may be concluded, that grinding fineness improving results in concrete ultimate compressive strength increasing (Fig. 5), and, at the same time, density increasing, see Fig. 6.

3.2. Microstructure

In order to investigate filler influence, microstructure was examined with the help of scanning electron microscope (Phenom G2 pure).

Fig. 7. SEM microstructure of concrete: (a) without dolomite limestone, 7 days age at ×6000 magnification; (b) – with dolomite limestone, 7 days age at ×6000 magnification; (c) – with dolomite limestone, 7 days age at ×5000 magnification; (d) – with dolomite limestone, 90 days age at ×7000 magnification
Microstructure analysis results demonstrated that 7 days cement composition (Fig. 7a) without fine limestone powder has porous open-grain structure with macropores predominance. Dolomite addition results in increasing of quantity of centres which initiate more intensive crystallization that, in turn, results in hydration rate increasing. A thin layer of growths appears at the surface of cement particle. These growths consist of calcium hydroxide (plate crystals with perfect cleavage) (Fig. 7b). This results in structure densification and growth at early stages (Fig. 7c). With time this layer increases up to 4 μm at the age of 90 days. As the result, pronounced densification of the concrete structure can be seen (Fig. 7d). In this case interface layer possesses good adhesion resulting in modified concrete strength and density increasing.

Thus, dolomite limestone ultrafine particles act as additional crystallization grains; optimal content of dolomite limestone is 25% of cement weight. At this amount fine concrete has the best compression strength.

3.3. DTA

Differential thermal analysis of the cement composition (Fig. 8) demonstrated that chemically bound water evaporates at 130 °C, sharp weight decrease takes place in the reference sample.

Endothermic effect about 480 °C corresponds to calcium hydroxide dehydration. Dolomitic component is characterized by endothermic effect at 830 °C due to Ca(CO$_3$)$_2$ pre-calcining. Peak value, presented in Fig. 8b, is displaced as compared with Fig. 8a, prompting suggestion that dolomite limestone presents in the cement composition.

3.4. X-ray phase analysis

The X Ray diffractogramme of the cement sample shows the main reflection lines corresponding minerals C$_3$S and C$_2$S, calcium hydroxide Ca(OH)$_2$ and calcite CaCO$_3$, see Fig. 9a.

![Fig. 8. Thermogram of cement composition: a – without additive, b – with dolomite limestone additive (specific surface 5500cm$^2$/g)](image)

![Fig. 9. X-Ray diffraction of cement composition: without additive (a); with dolomite limestone additive (specific surface 5500cm$^2$/g) (b)](image)
XRD analysis of the modified cement sample (Fig. 9b) indicates quartz (composed of dolomitic limestone) which is dominated. Also there are lines corresponding to calcium hydroxide, calcite and dolomite. However, the reflection line corresponding minerals of Portland cement are very weak, which means that hydration of the cement with additives in the form of finely dolomitic limestone is more intensive.

4. Conclusion

Investigations confirmed that finely ground dolomite limestone in fact can be used as cementitious material to produce cement with dolomite limestone.

Incorporation of 5 wt. % and more than 25 wt. % dolomite limestone into cement always reduces compressive strengths after 14 and 28 days. Specimens containing 25% dolomite limestone powder by weight have the maximal compressive strengths.

The main technical reasons include improvement and densification of the structure and possible increase in early strength with no detrimental effects on long term properties of concrete.

References

[1] Piechówka-Mielnik, M., Giergiczny, Z., 2011. “Properties of Portland-composite cement with limestone”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[2] Nocuń-Wcezelik, W., Łoj, G., 2011. “Effect of finely dispersed limestone additives of different origin on cement hydration kinetics and cement hardening”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[3] Irassar, E. F., Bonavetti, V. L, Trezza, M. A., 2011. “Sulfate attack on portland limestone cements manufactured with low CaA portland clinker”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[4] Li, Y., Do, X. L., Huo, D., 2005. Utilization of limestone as mineral admixture in cement and concrete, Journal of Cement Engineering 34(4), pp. 27-29.

[5] Sato, T., Beaudoin, J. J., 2010. Effect of Nano-CaCO₃ on Hydration of Cement Containing Supplementary, Journal of Advances in Cement Research 23(1), pp. 1-29.

[6] Zotkin, A.G., 2007. Effects of mineral additives in concrete, Journal of Concrete Technology 4, pp. 10-12.

[7] Lagerblad, B., 2011. “Mechanism of carbonation”, Proceedings of the 18th International Baustofftagung “Ibausil”, 12-15 September, 2012, Weimar (CD).

[8] Chaid, R., Rendel, F., Jauberthie, R., 2011. “Impact of marble powder combined with limestone CEM II on concrete”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[9] Antoni, M., Rossen, J., Scrivener, K., Castillo, R., Alujas Diaz, A., Martirena, F. 2011. “Investigation of cement substitution by combined addition of calcined clays and limestone”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[10] Skaropoulou, A., Sotiriadis, K., Kakali, G., Tsivilis, S., 2011. “The effect of mineral admixtures on the sulfate resistance of limestone cement concrete”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[11] Tsivilis, S., Batis, G., Chaniotakis, E., Grigoriakis, G., Thedossis, D., 2000. Properties and behavior of limestone cement concrete and mortar, Journal of Cement and Concrete Research 30(10), pp. 1679-1683. http://dx.doi.org/10.1016/S0008-8846(00)0372-0

[12] De Weerdt, K., Justnes, H., Lothenbach, B., Ben Haha, M., 2011. “The effect of limestone powder additions on strength and microstructure of fly ash blended cements”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[13] Allahverdi, A., Salem, S. 2010. Simultaneous influences of microsilica and limestone powder on properties of Portland cement paste, Journal of Ceramics – Silikáty 54(1), pp. 65-71.

[14] Kopanitsa, N. O., Anikanova, L. A., Makarevich, M. S., 2002. Fine additives filled with binders based on cement, Journal of Building Materials 9, pp. 2-4.

[15] Taylor, H. F. W., 1996. Cement Chemistry. Mir, Moscow. p. 560.

[16] Barbane, I., Vitina, I., Lindina, L., 2012. “Synthesis of portland from Latvia’s clay and dolomite”, Proceedings of the 18th International Baustofftagung “Ibausil”, 12-15 September, 2012, Weimar (CD).

[17] Schöne, S., Dienemann, W., Wagner, E., 2011. “Portland dolomite cement as alternative to Portland limestone cement”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[18] Henning, O., Kudjakow, A., Winkler, K-G., 1980. Influence of dolomite on the hydration of Portland cement, Scientific Journal of the University of Architecture and Civil Engineering in Weimar 4.

[19] Rakhimov, R. Z., Shelikhov, N. S., 2006. Rational utilization of carbonate raw materials for the production building materials, Journal of Building Materials 9, pp. 42-44.

[20] Carrasco M.F., Menéndez G, Bonavetti V, Irassar E.F., 2003 Strength development of ternary blended cement with limestone filler and blast furnace slag, Journal of Cement and Concrete Composites 25, pp. 61-67.

[21] Kadri E.H, Aggoun S, De Schutter, G., 2010. Combined effect of chemical nature and fineness of mineral powders on Portland cement hydration, Journal of Materials and Structures 43, pp. 665-673.

[22] Ramachandran, V. S., 1977. The application of differential thermal analysis in cement chemistry. Ratinov, V. B (Ed.). Translated from English. Moscow: Stroiizdat, p. 408.

[23] Bilek, V., 2011. “Slag alkaline concrete with mineral admixtures”, Proceedings of the 13th International Congress on the Chemistry of Cement (13th ICCC), 3-8 July, 2011, Madrid (CD).

[24] Z’hor Guemmadi, Musa Resheidat, Hacéne Houari, Belkacem Toumi, 2008. Optimal criteria of Algerian blended cement using limestone fines, Journal of Civil Engineering and Management 14(4), pp. 269-275. http://dx.doi.org/10.3846/1392-3730.2008.14.26