**Influence of the Composition and Dispersion of Mineral Supplements on the Strength of Cement Paste**

Liliia Vladimirovna Il’ina and Nikolai Olegovich Gichko*

Department of Building Materials and Special Technology, Faculty of Engineering and Information Technology, The Novosibirsk State University of Architecture and Civil Engineering (Sibstrin), Novosibirsk, Russia

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**Abstract**

At the initial phase of hardening, it is the limestone component that plays a major role in the hardening process, which acts as the substrate for the crystallization of hydrate tumors due to its chemical affinity with the products of Portland cement hydration. After 7 days, the diopside supplement influences the processes more significantly. Diopside has a high modulus of elasticity compared to the cement paste. As a result, stresses are redistributed within the cement paste and the whole composition is hardened. An increase in the quantity of diopside in the compound supplement to more than 66.7% does not provide a substantial increase in the strength of the cement paste. As the hardness of diopside is higher than the hardness of limestone, much more energy is required to grind it down to a usable component. Therefore, a further increase in the quantity of diopside in the compound supplement is not economically feasible. An evaluation of the optimum quantity of input compound mineral supplements can be made based on the ideas of close packing of spherical particles and the Pauling rules. The optimum content of the supplement is 8-8.5% provided that its dispersion and density are close to the dispersion and density of the binder. An increase in the dispersion of the supplement reduces its optimal quantity. During the addition of mineral supplements, thermo grams show a displacement of the endoeffects' temperatures to the area of higher temperatures. If there are mineral supplements in the cement paste, which may be substrates for the crystallization of tumors, the cement paste’s structure is hardened, which is shown by the integrated thermal analysis.

**Keywords:** Cement Paste, Compound Mineral Supplement, Diopside, Dispersion, Integrated Thermal Analysis, Limestone, Mechanical Strength

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**1. Introduction**

To reduce resource consumption and the cost of building materials that are based on cement, it is expedient to increase its strength properties.

Using dispersed mineral supplements allows largely for the fulfilment of the Portland cement capacity, which determines the improvement of the most important properties of composite cement materials. In many cases, the addition of such supplements allows for a reduction in the consumption of expensive binders\(^5,6,9,10\).

**2. Scientific Hypothesis**

The effective use of dispersed mineral supplements depends on the chemical composition and quantity of the added mineral supplement\(^5,11\).

To improve the efficiency of mineral supplements, it is necessary to control their dispersion\(^3,8\).

The influence of supplements is due to the fact those they:
- Affect the process of hydration hardening in Portland cement.

* Author for correspondence
Prevent the spread of micro-cracks in the cement when under the influence of external stresses.

Cause the redistribution of mechanical stresses between the particles of supplements and the cement paste; at the same time, it is essential for the modulus of elasticity of the supplement material to be higher than that of artificial stone.

Dispersed mineral supplements can serve as substrates, on which the growth of the formed hydrated compounds crystals takes place. It is important for the supplements to be similar enough by composition, type of chemical bonds, and physical and chemical characteristics (specific enthalpy of formation, specific entropy, etc.) to the original binders and products of their hydration.

Thus, it is necessary to examine the degree of increasing the cement stone strength by introducing supplements with various dispersion and mineral composition, and to identify factors that affect on the cement paste hardening process.

The interaction between the fillers and the mineral binders takes place in the area of contact of the particles of those components. Obviously, the optimum concentration of supplement corresponds to the case where the supplement particle is tightly surrounded on all sides by the hydrated binder particles. Lesser quantity of the supplement will reduce their effectiveness. With their increased content, direct contacts between the particles of supplements are possible, which also reduces the effectiveness of their influence.

Assuming that the particles of both cement and supplements have a spherical shape and the same dimensions, and given that the supplement particles are distributed uniformly throughout the entire volume, we find that at the formation of a dense structure, the volume fraction of the supplement is 1/12th of the binder’s volume fraction, or 8.3%. If the density of the supplement is different from the density of the binder, the mass fraction of the supplement (in %) can be determined by the ratio of the densities:

\[ m_s = \frac{8.3 \rho_s}{\rho_b} \]  

(1)

where \( m_s \) is the percentage of the added supplement in the overall weight of the binder,

\( \rho_s \) is the density of the supplement, g/cm³,

\( \rho_b \) is the density of the binder, g/cm³.

Thus, it can be assumed that the optimum content of the supplement under the conditions that its dispersibility and density are close to the dispersion and density of the binder is 8-8.5 %. But if the density of the supplement is markedly lower than that of the binder, its optimum quantity will also be correspondingly less.

By considering the particles of the binder and the supplement as spherical, we can estimate the mass fraction of the supplement with various dispersion ratios in the case of the closest possible packing of the particles by the ratio:

\[ n_s = \frac{\pi D_s^3 - 6 \rho_s}{k \pi D_b^3 - 6 \rho_b} = \frac{1}{k} \frac{D_s^3}{D_b^3} \frac{\rho_s}{\rho_b} \]  

(2)

\[ n_s = \frac{\pi D_s^3 - 6 \rho_s}{k \pi D_b^3 - 6 \rho_b} = \frac{1}{k} \frac{D_s^3}{D_b^3} \frac{\rho_s}{\rho_b} \]  

(3)

Here, \( D_s \) is the diameter of the supplement particles, \( D_b \) is the diameter of the binder particles, \( C \) is the coordination number, i.e. the number of the binder particles tightly surrounding a particle of the supplement. It can therefore be roughly determined in accordance with the first Pauling rule.

### 3. Raw Materials

In this article, we studied Portland cement produced by LLC “Iskitimcement” (Novosibirsk Region), grade PTs 400 D-20 with a mineral composition, % of weight: C₅S – 50-55, C₃S – 18-22, C₆Å – 7-11, C₄AF – 12-15 and a specific surface area of 300 m²/kg. The chemical composition of the cement, % of weight: SiO₂ – 20.7; Al₂O₃ – 6.9; Fe₂O₃ – 4.6; CaO – 65.4; MgO – 1.3; SO₃ – 0.4; loss on ignition – 0.5.

As the dispersed mineral supplements, we used diopside and limestone, which are mining wastes. The diopside microfiller selected was crushed host rock that is waste of phlogopite ore processing of the Bugotaksky deposit (Irkutsk Region). The volume average particle size was 27 µm.

The limestone meal was crushed rock - limestone (Iskitim, Novosibirsk Region). The volume average particle size was 12.3 µm. Their chemical compositions are provided in Table 1.

The true density (kg/m³) of these supplements was: diopside-3,300, limestone-2,600.
4. Experimental Part

When evaluating the interphase interaction of the mineral supplement and the cement paste, the dispersion of the supplements plays an important role\(^1\). Their grain-size distribution was determined with a laser analyzer of dispersion of the PRO-7000 type made by Seishin Enterprise Co., LTD, Japan. The indicators of dispersion of the supplements under study are provided in Table 2.

Table 2. Dispersion of mineral supplements according to the results of the particle size analysis

| Indicators                                      | Type of mineral supplement |
|------------------------------------------------|-----------------------------|
| Average particle size, µm                       | diopside  | limestone  |
| Specific surface area, m\(^2\)/kg               | 27.0      | 12.3       |
| Volume fraction of particles with the size less than 4 µm, % | 16.3 | 12.3 |
| Volume fraction of particles with the size less than 16 µm, % | 31.9 | 49.3 |
| Volume fraction of particles with the size less than 32 µm, % | 46.9 | 78.6 |

The supplements were added in the quantity of 1, 3, 5, 7, 9, and 11% of the cement weight. Herewith, we added both diopside and limestone separately, and the compound supplement consisting of limestone and diopside in the proportions 1/2, 1/1, and 2/1. Portland cement was mixed with the above supplements in a ball mill for 1.5 hours.

The samples of the cement paste for determining tensile strength had the dimensions of 20x20x20 mm. Curing was carried out under normal conditions (over the water during the first day, and in the water at 20°C during the next 27 days) for 1, 3, 7, and 28 days, and under conditions of steam treatment. Steam Treatment (ST) was carried out according to the following procedure: increasing the temperature for 3 hours, holding it at 90°C for 6 hours, reducing the temperature for 2 hours.

In order to determine the tensile strength of the samples at compression, we used a press with the full load of 500 kN, providing sample loading in the mode of pure compression. The average rate of rise of the load during the test was \((2.0 \pm 0.5)\) MPa/s. To offset spatial deviation from the non-parallel reference faces of the sample, the press had a movable ball joint and was equipped with a device for centered setting of push plates passing the load to the sample.

5. Results and Discussion

The change in the strength of the cement paste depending on the quantity of the introduced supplement and the composition of the supplement is shown in Table 3.

An analysis of the results of the experiment showed that in all cases of the supplements addition in the quantity of 1, 3, 5, 7, 9, and 11 % of the Portland cement weight, the compressive strength of the cement paste increases at the hardening time of 1, 3, 7, and 28 days. Herewith, we clearly trace the optimum quantity of the supplement that provides maximum strength. The optimum quantity of the supplement (diopside) with the dispersion close to the cement’s is 7%, which is close to the above theoretical estimation. For the much more dispersed supplement -limestone flour - the optimum quantity is 1% of the cement weight.

The rate of curing does not depend on the quantity of the added supplement and is approximately identical at its content from 1 to 11 %. The strength of the cement paste at 3 days of age, obtained by the addition of limestone, compared to the strength at 28 days of age, was slightly higher than in other mixtures.

When analyzing the effect of mineral supplements on the mechanical strength of the cement paste, we need to consider their elastic properties. If the modulus of elasticity of the mineral supplement is more than that of the cement paste, then more stress will affect the supplement’s material, which is stronger than the cement paste, at external loads. It enhances the strength of the cement paste as a whole\(^4\).

Among the considered silicate materials, diopside has the highest value of hardness (6.5-7 on the Mohs scale), that is the greatest value of the modulus of elasticity. This
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will determine the redistribution of stresses between the components of the cement paste.

Calcite that forms the basis of limestone meal has a rather low value of hardness (3 on the Mohs scale). It is less than that of the cement paste. That is, in this case, we can hardly expect effective micro-reinforcement of the cement paste, and the effect of the supplement is determined by other causes.

The effect of CaCO$_3$ will be manifested to the greatest extent in the contact area of the system. The optimum content of the supplement is determined by its effect on the cement hydration process and formation of the contact area between the particles of the supplement and cement paste. In this case, the optimum content of limestone meal is 1% by weight.

An analysis of the results of the compound supplement effect on the compressive strength of the cement paste showed the following:

At the early stages of hardening, less than 7 days, with the introduction of supplements in the quantity of 1-5%, limestone has a predominant effect, i.e. at the increase in its quantity in the compound supplement, the strength increases. However, with the transition to the late stages of hardening, the role of diopside increases, and its effect on the strength of the cement paste becomes more significant.

### Table 3. Influence of the quantity of the compound mineral supplement on the compressive strength of the cement paste

| Conditions and duration of hardening | Strength of the cement paste, MPa | Quantity of the compound supplement, % of the weight of Portland cement |
|-------------------------------------|-----------------------------------|-------------------------------------------------------------------------|
|                                      | ST                                 | 0 | 1 | 3 | 5 | 7 | 9 | 11 |
| limestone (100%)                     | ST                                 | 56.2 | 64.7 | 64.0 | 62.2 | 53.1 | 52.6 | 51.3 |
| Normal conditions, 1 day             | 10.6 | 13.3 | 13.1 | 12.8 | 10.2 | 11.0 | 11.5 |
| Normal conditions, 3 days            | 18.1 | 27.2 | 26.9 | 25.3 | 24.5 | 22.2 | 21.4 |
| Normal conditions, 7 days            | 33.6 | 42.3 | 41.7 | 40.9 | 35.8 | 36.4 | 34.4 |
| Normal conditions, 28 days           | 62.7 | 74.8 | 73.4 | 70.9 | 68.5 | 64.9 | 60.2 |
| limestone – 2 parts (66.6 % of weight), diopside – 1 part (33.3 % of weight) | ST                                 | 56.2 | 64.8 | 64.8 | 63.0 | 52.7 | 52.6 | 52.0 |
| Normal conditions, 1 day             | 10.6 | 13.0 | 13.4 | 13.1 | 11.7 | 11.2 | 11.3 |
| Normal conditions, 3 days            | 18.1 | 23.7 | 27.3 | 24.4 | 23.8 | 22.0 | 21.0 |
| Normal conditions, 7 days            | 33.6 | 40.6 | 42.2 | 40.5 | 38.2 | 37.2 | 35.2 |
| Normal conditions, 28 days           | 62.7 | 70.8 | 74.3 | 70.8 | 68.5 | 65.8 | 63.4 |
| limestone – 1 part (50 % of weight), diopside – 1 part (50 % of weight) | ST                                 | 56.2 | 62.0 | 65.3 | 65.5 | 65.5 | 60.4 | 58.3 |
| Normal conditions, 1 day             | 10.6 | 12.3 | 14.1 | 12.8 | 12.8 | 12.6 | 11.0 |
| Normal conditions, 3 days            | 18.1 | 22.0 | 24.1 | 23.5 | 23.5 | 23.0 | 18.6 |
| Normal conditions, 7 days            | 33.6 | 39.9 | 43.6 | 43.0 | 42.6 | 42.3 | 36.0 |
| Normal conditions, 28 days           | 62.7 | 70.6 | 77.1 | 75.0 | 75.0 | 75.2 | 63.4 |
| limestone – 1 part (33.3 % of weight), diopside – 2 parts (66.6 % of weight) | ST                                 | 56.2 | 62.5 | 65.1 | 67.4 | 75.3 | 71.2 | 67.0 |
| Normal conditions, 1 day             | 10.6 | 13.0 | 13.0 | 13.7 | 15.0 | 14.0 | 11.8 |
| Normal conditions, 3 days            | 18.1 | 21.1 | 22.1 | 23.8 | 26.8 | 25.3 | 20.3 |
| Normal conditions, 7 days            | 33.6 | 37.4 | 40.9 | 44.3 | 50.3 | 44.1 | 38.5 |
| Normal conditions, 28 days           | 62.7 | 70.8 | 74.7 | 79.0 | 83.8 | 80.2 | 72.8 |
| diopside (100 %)                     | ST                                 | 56.2 | 64.0 | 67.7 | 70.8 | 77.1 | 71.8 | 67.5 |
| Normal conditions, 1 day             | 10.6 | 13.0 | 13.3 | 13.8 | 16.3 | 14.9 | 12.2 |
| Normal conditions, 3 days            | 18.1 | 21.2 | 22.5 | 24.2 | 27.6 | 26.0 | 21.8 |
| Normal conditions, 7 days            | 33.6 | 38.0 | 41.7 | 44.0 | 51.2 | 46.4 | 39.3 |
| Normal conditions, 28 days           | 62.7 | 71.4 | 75.0 | 80.1 | 86.8 | 81.7 | 74.6 |
of the cement paste increases, as well. When over 5% of the supplement is added, there is an increase in the strength of the cement paste with the increasing quantity of diopside in the compound supplement (Figure 1 a, b). Thus, at low, i.e. insufficient, quantity of the supplement from the viewpoint of the closest packing of particles, diopside has no effect. When the optimum quantity of the compound supplement is achieved (7%), increasing the quantity of diopside supplement increases the strength of the cement paste.

• The cement paste has been hardening for seven days in normal conditions. When adding the supplement in a small quantity (1-5 %), it is hard to identify a clear effect of diopside, because its quantity is insufficient to provide the closest packing of particles. The greatest increase in strength can be achieved if we add 7% of the compound mineral supplement (Figure 2 a, b). Herewith, diopside already begins to influence if the compound supplement contains 50% of it, i.e. the content of diopside is 3.5% of Portland cement.

• The cement paste having hardened for twenty-eight days in normal conditions. At low concentrations of the supplement (1-5 %), it is difficult to identify a clear influence of diopside, as well as at the age of 3-7 days. When the quantity of the supplement is large, i.e. sufficient to provide for the closest packing of particles,
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The optimal quantity of the supplement that provides for the maximum increase of cement paste's strength is 7% (Figure 3 a, b). Herewith, diopside already begins to influence if its content in the compound supplement is more than 33.3%.

**Figure 3.** The effect of the quantity of the supplement on the compressive strength of the cement paste having hardened for 28 days under normal conditions, at the addition of the compound supplement in the quantity: 1-1 % of weight; 2-3 % of weight; 3-5 % of weight; 4-7 % of weight; 5-9 % of weight; 6-11 % of weight.

**Figure 4.** The curves of the integrated thermal analysis of the cement paste with no supplements added.

**Figure 5.** The curves of the integrated thermal analysis of the cement paste with the addition of limestone (1% of weight).

**Figure 6.** The curves of the integrated thermal analysis of the cement paste with the compound mineral supplement (3 % of weight) consisting of diopside - 1 part (33.3 % of weight) and limestone - 2 parts 66.6 % of weight.

**Figure 7.** The curves of the integrated thermal analysis of the cement paste with the compound mineral supplement (7 % of weight) consisting of diopside - 2 parts (66.6 % of weight) and limestone - 1 part (33.3 % of weight).
Table 4. The results of the integrated thermal analysis of the cement paste containing mineral supplements

| The quantity of the mineral supplement, % of weight. | The composition of the mineral supplement, % of weight. | 1st endoeffect | 2nd endoeffect | 3rd endoeffect | Total weight loss, % |
|---------------------------------------------------|----------------------------------------------------------|----------------|----------------|----------------|---------------------|
| limestone | diopside | Temp, °C | Weight loss | Temp, °C | Weight loss | Temp, °C | Weight loss |
| 0        | 0        | 102.54 | 7.080 | 471.43 | 3.483 | 732.74 | 1.850 | 18.74 |
| 1        | 0        | 103.82 | 6.363 | 473.88 | 3.347 | 734.66 | 3.027 | 18.60 |
| 3        | 1        | 103.32 | 6.240 | 474.57 | 3.860 | 741.79 | 3.217 | 18.37 |
| 3        | 1.5      | 106.15 | 5.920 | 475.46 | 3.183 | 743.07 | 3.297 | 18.58 |
| 7        | 2.3      | 105.15 | 6.267 | 481.46 | 3.010 | 756.06 | 2.873 | 18.44 |
| 7        | 0        | 107.35 | 5.337 | 477.12 | 3.217 | 745.49 | 1.910 | 18.02 |

Figure 8. The curves of the integrated thermal analysis of the cement paste with the compound mineral supplement (3 % of weight) consisting of diopside - 1 part (50 % of weight) and limestone - 1 part (50 % of weight).

Figure 9. The curves of the integrated thermal analysis of the cement paste with the addition of diopside (7 % of weight).

6. Conclusion

Increasing the strength of the cement paste containing the mineral supplements may be determined by the hardening of the cement paste's structure, which is confirmed by the results of the differential thermal analysis (Table 4, Figures 4-9).

Differentially thermal and thermogravimetric studies were performed using the derivatograph DTG60H made by Shimadzu, Japan, at a sample heating rate of 10°C/minute.

Endoeffects apparently correspond to the following processes: at the temperature of 102-107°C - to decomposition of hydrate neoplasms; at the temperature of 470-482 °C - to decomposition of portlandite Ca(OH)₂ occurred during cement hydration; at the temperature of about 730-760°C and above - to the decomposition of calcium carbonate CaCO₃, both primary (composed of limestone meal) and secondary (appearing possibly by the reaction of CaO released from Ca(OH)₂ with CO₂ during measurements).

These results show that the strongest hardening of the structure takes place when diopside is added. Deeper hydration of cement takes place when limestone meal is added. It is accompanied by the maximum weight loss in the first endoeffect arising from the decomposition of hydrate tumors.

In the second endoeffect, their temperature and weight loss are close to each other. The largest third endoeffect was obtained with the addition of the compound supplement (7% of weight) consisting of 2 parts of diopside and 1 part of limestone. The total weight loss at the addition of mineral supplements decreases.

Thus, at the introduction of mineral supplements, thermograms record the endoeffects’ temperatures displacement to the area of higher temperatures. If there are mineral supplements in the cement paste that may be substrates for the crystallization of tumors, the cement paste's structure is hardened, which is shown by the complex thermal analysis.

Thus, at the initial phase of hardening, limestone plays a major role in the hardening process, acting as the...
substrate for crystallization of hydrate tumors due to its chemical affinity with the products of Portland cement hydration. After 7 days, on the contrary, the diopside supplement influences more significantly. Diopside hardness on the Mohs scale is equal to 7, and the hardness of the cement paste is equal to 5. That is, diopside has a higher modulus of elasticity as compared to the cement paste. As a result, stresses are redistributed in the cement paste and the whole system is hardened. An increase in the quantity of diopside in the compound supplement to more than 66.7% does not provide a substantial increase in the strength of the cement paste. As the hardness of diopside is higher than the hardness of limestone, much more energy is required for its grinding. Therefore, a further increase in the quantity of diopside in the compound supplement is not economically feasible.

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