Ultra-disperse modifying zeolite-based additive for gypsum concretes

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Abstract. Under modern construction conditions it is important to find the ways of cost reduction without deteriorating physical and mechanical properties of construction materials and their environmental properties. That is why the construction materials on the basis of the gypsum binder remain competitive and the increase of their operation properties is one of the relevant today tasks. In this paper the authors presented a way of increasing water resistance and strength of gypsum concrete by adding ultra-disperse modifying zeolite-based additive from available raw materials. The authors find out zeolite grindability and its chemical composition. The ultra-disperse modifying zeolite-based additive is a paste dispersed in water and added into a concrete mix as water solution. When 14% of the additive is included in gypsum paste the softening factor grows from 0.31 to 0.84 while the grade strength increases by 30%, the ultimate compression strength of dry samples - by 2.5 times and amounts to 30 MPa. Studying physical and mechanical properties and the micro-structure of gypsum and concrete samples proves the efficiency of using the developed ultra-disperse modifying zeolite-based additive.

1. Introduction
Modern construction is hardly possible without the use of environmentally friendly gypsum materials. The analysis of global references demonstrates that the share of materials based on gypsum binders reaches 20...27% in technically advanced countries of the total volume of products on mineral binders. A high potential of growth is mainly observed in the sector of gypsum sheet materials [1-5]. However, it is also known that high humidity causes the solvability of calcium sulphate CaSO₄·2H₂O characterized by a high permeability of the crystalline structure. The disjoining action of water molecules at the penetration into intercrystalline void spaces weakens the bonds and washes off gypsum. All these factors result in significant reduction of strength and eroding plaster casts because of water action.

By today multiple methods of increasing the water resistance of gypsum binders have been developed by scientists from various countries. The increase in gypsum stone water resistance due to the reduction of gypsum solvability, selecting the method for gypsum substance packing, treatment of the set stone with the substances preventing moisture penetration into the product. The most cost-effective and effective way is incorporating additives for decreasing gypsum solvability into the mix composition as these additives induce the formation of slightly soluble substances.
2. Relevance
In recent years the scientific community of the Republic of Sakha (Yakutia) frequently uses the zeolite-containing mine rock from the deposit Khonguru of the Suntarsky district in their research in various scientific areas. This can be explained not only by the unique absorbing ion-exchanging and other zeolite properties but also by extensive deposits of these raw materials developed and extracted by a simple open and cost-efficient method [6]. The development of zeolite-containing rocks of Yakutia is a priority task as zeolite-bearing districts have estimated reserves of approximately 3.5 billion tons [7].

Zeolite belongs to volcanic tuffs and is quite a wide-spread and well-studied rock [8,9]. At the same time zeolite can be synthesized from the evils and pepl of different materials [10-12], it is applied in the concrete of portland cement and of silicate [13,14].

Hongurin’s zeolite consists of the minerals from the clinoptilolite&heulandite group (70-90%), quartz, feldspars, silica rocks fragments, calcite, volcanic glass and clay matters. Their chemical composition is provided in Table 1.

| Table 1. Chemical composition of Hongurin’s zeolite |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| SiO₂            | Al₂O₃           | Fe₂O₃           | CaO             | MgO             | K₂O+Na₂O        | TiO₂            |
| 65.11           | 12.16           | 1.08            | 2.62            | 1.88            | 3.30            | 0.13            |
| H₂O             |                 |                 |                 |                 |                 | 8.89            |
|                 |                 |                 |                 |                 |                 | 4.26            |

The previously conducted research [6] demonstrated the efficiency of applying Hongurin’s zeolite in concretes based upon portland cement. The relevant task is studying the impact of the developed modifying additive on the gypsum stone structure formation and properties.

3. Experimental studies
The ultra-disperse modifying additive contains Hongurin’s zeolite and quite a wide-spread liquid organic plasticizer - dibutylphthalate. The latter substance is added for reducing energy losses at grinding and providing for longer storage time of fine-dispersed powder without its activity loss.

Many researches [15-18] proved efficiency of mehano&chemical activation of mineral additives. The conducted research on defining the properties of Hongurin’s zeolite breaking demonstrated that, at the activation in the laboratory planetary ball mill RETSCH PM 400, the dimensions of zeolite particles reach 1.3 um on average. Up to 11 % of a total of the particles amount have the dimensions of 3-30 newton-meters, i.e., in the first approximation this additive can be considered as a nano-modifier which is confirmed by the sample research at a laser particle-size analyzer HORIBA [19].

The chemical and mineralogical research of the samples of Hongurin’s zeolite powders conducted at the transmission electron microscope JEM-2100 demonstrate the direct dependence of the particle size on the grinding time. In Figure 1(a) at 500 times magnification the size of the Hongurin’s zeolite particles at coarse grinding varies from 200 to 400 um, the content of silicon oxide SiO₂ is equal to 51.56 % of the total mass of the substance quantity, i.e., 92.8 % of the atomic weight. After 5 minute activation the average size of particles is equal to 80 um. This confirms the softness of Hongurin’s zeolite minerals taking the position 2 at the Mohs' scale.

The chemical analysis shows a high content of silicon oxide SiO₂ - 89.09 %. This element is structure-forming and provides for the stone high strength and water resistance. Its presence in the rock composition allows estimating the possibility of its use as an active mineral additive allowing one to increase operation properties of concretes and providing hydraulic binder propeties due to the formation of waterproof compounds in a formed structure in the course of time. Due to this the stone durability and resistance to external impacts are improved. At this, the organic additive component, plasticizer, also positively influence concrete water resistance.

For determination properties of physic-mechanical of gypsum concrete with the developed additive standard samples – prisms with sizes of edges of 4x4x16 cm of 12 samples on each structure were formed. Indicators of average density, strength at compression in 2 hours of solidification were
defined and at the age of 7 days in an air-dry status and also softening factor. The softening factor was defined as an arithmetic average value from 6 results of the relations of compression strength of the dry samples to the strength of the samples kept in water within 2 hours. Average results of the main properties of gypsum concrete are given in table 2. Water requirement of samples with use of additive decreases in comparison with structure without additive at the expense of the plasticizing component. Therefore density of the samples which are dried up to the constant weight differs on 150 – 200 kg/m³.

| Composition       | Density of samples, kg/m³ | Compression strength of samples, MPa | Softening factor       |
|-------------------|---------------------------|--------------------------------------|------------------------|
|                   |                           | in 2 hours of solidification | dried up up to the constant weight |                      |
| a) 0 % of additive| 1140                      | 4,6                                  | 12,3                   | 0,31                  |
| b) 14 % of additive| 1340                      | 5,9                                  | 28,9                   | 0,84                  |
| c) 22 % of additive| 1290                      | 5,2                                  | 22,7                   | 0,47                  |

The research of the developed additive impact on the gypsum stone structure confirm theoretical assumptions while the micro-photos (Fig. 2) of the gypsum stone structure with and without the additive, obtained at the scanning nano microscope “NtegraPrima” NTMDT, prove the possibility of the efficient application of ultra-disperse modifying zeolite-based additive in gypsum concretes for the premises with a high relative air humidity. This additive also improves the setting time.

The samples of the composition (a) in Fig. 2 have low water resistance due to a high solvability of calcium sulfate dihydrate, high permeability of the crystalline structure and disjoining action of water molecules at penetration into intercrystalline void spaces. Sulfate dihydrate is characterized by rather high volume of interplanar spaces accessible for water weakening the intercrystalline bonds. All these factors result in the significant reduction of strength and eroding plaster casts because of water action, these samples have the arithmetic mean value of the softening factor 0.31, water resistance class - hydrolabile which is the lowest index of all conducted research. One can observe a large amount of micro-pores the average size of which is equal to 80-90 um. The average strength of standard samples after 2 hours of mixing concrete ingredients with water is equal to 4.6 MPa, the one of the oven-dried - 12.3 MPa.

The composition (b) in Fig. 2 at introducing 14 % of the additive is characterized by the formation of the fewer amount of micro-pores comparing with other compositions. The average size of micro-pores is 30-40 um. One can also observe visual changes: calcium dihydrate crystals are almost fully covered by a thin film of a plastifying additive component decreasing the permeability of the crystalline structure and, consequently, improving water resistance. The formed crystalline structure of the composition (b) is similar to the structure of tobermorite-like compounds which can explain the obtained increased stone characteristics. The factor of softening the samples with such composition is equal to 0.84, water resistance class - hydrostable. The average ultimate compressive strength of standard samples in 2 hours reaches 5.9 MPa which improves the strength of gypsum plaster by 30 %. The ultimate compression strength of the oven-dry samples reaches 30 MPa which is 2.5 times higher comparing to additive-free gypsum. Therefore, the additive produces the maximum effect at late setting stages as the processes occurring in the substance, such as absorption, diffusion, changing structural bonds, are quite complicated and require some time.

The micro-photos of the samples of the composition (c) in Fig. 2 demonstrated a center-directed crystal intergrowth of calcium dihydrate. One can assume that such center orientation is connected with a large amount of the incorporated additive – 22 % by mass which is a center of crystal intergrowth. This micro-structure only slightly increases the water resistance of samples. The softening factor 0.47 - medium water resistance. The strength of samples with such composition is also lower comparing with the second composition samples. The size of micro-pores reaches 60 um and they are observed virtually in each center of crystal intergrowth.
Figure 1. General view of particles at 500 times increase and zeolite chemical composition:

- a) coarse grinding
- b) after 5 minute grinding
- c) after 15 minute grinding
- d) after 25 min grinding

| Element                  | Weight, % | Atomic, % |
|--------------------------|-----------|-----------|
| $O_2$ in the composition of $SiO_2$ | 35.99     | 74.45     |
| Sodium feldspar          | 1.54      | 2.22      |
| MgO                      | 0.39      | 0.53      |
| Al$_2$O$_3$              | 2.99      | 3.67      |
| Si in the composition of $SiO_2$ | 15.57     | 18.35     |
| Biotite                  | 0.25      | 0.21      |
| Calcium silicate         | 0.46      | 0.38      |
| Fe                       | 0.31      | 0.19      |

| Element                  | Weight, % | Atomic, % |
|--------------------------|-----------|-----------|
| $CaCO_3$                 | 0.03      | 3.43      |
| $O_2$ in the composition of $SiO_2$ | 0.80     | 65.33     |
| Sodium feldspar          | 0.03      | 1.58      |
| MgO                      | 0.01      | 0.65      |
| Al$_2$O$_3$              | 0.09      | 4.21      |
| Si in the composition of $SiO_2$ | 0.51     | 23.76     |
| Biotite                  | 0.01      | 0.43      |
| Calcium silicate         | 0.02      | 0.61      |

| Element                  | Weight, % | Atomic, % |
|--------------------------|-----------|-----------|
| $O_2$ in the composition of $SiO_2$ | 31.70     | 74.49     |
| Sodium feldspar          | 1.42      | 2.32      |
| MgO                      | 0.35      | 0.53      |
| Al$_2$O$_3$              | 2.72      | 3.78      |
| Si in the composition of $SiO_2$ | 13.46   | 18.01     |
| Biotite                  | 0.28      | 0.26      |
| Calcium silicate         | 0.50      | 0.47      |
| Fe                       | 0.18      | 0.12      |

| Element                  | Weight, % | Atomic, % |
|--------------------------|-----------|-----------|
| $O_2$ in the composition of $SiO_2$ | 32.29     | 74.52     |
| Sodium feldspar          | 1.25      | 2.02      |
| MgO                      | 0.44      | 0.66      |
| Al$_2$O$_3$              | 2.81      | 3.84      |
| Si in the composition of $SiO_2$ | 13.75   | 18.08     |
| Biotite                  | 0.19      | 0.18      |
| Calcium silicate         | 0.51      | 0.47      |
| Fe                       | 0.35      | 0.23      |
Figure 2. Micro-photos of the gypsum stone structure with an ultra-disperse modifying zeolite-based additive at the increase of content by 10,000 times, %: a) 0; b) 14; c) 22.

4. Conclusions
Therefore, the research confirm the alignment theory on water resistance and material strength [20].

The optimal structure characterizing virtually even distribution of discrete particles and continuity of the binder spatial mesh at minimum thicknesses of its film distribution can be observed at the addition consumption up to 15%. When increasing the additive consumption its structure violates the order of particle location and causes the reduction in water resistance and strength.

The analysis of the research on the impact of ultra-disperse modifying zeolite-based additive on gypsum concrete properties makes it reasonable to apply this substance for increasing strength by 2.5 times and improving water resistance to the hydrostable class. The obtained physical&mechanical results of the research of the micro-structure of gypsum stone samples with/without the additive prove the drawn conclusions.

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