Effective Composite Gypsum Binders On The Basis Of Raw Materials From The Middle East Countries

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ABSTRACT

This paper is devoted to the study of the properties of composite gypsum binders using active mineral additives produced from typical raw materials of the Middle East. It has been found that binders with application of concrete breakage have better strength characteristics in comparison with compositions containing the quartz sand and volcanic tuff.

INTRODUCTION

An important task of construction in Middle East countries is to provide them with materials and products manufactured mainly from local natural and man-made raw materials, keeping in view the traditional unique architecture.

Since ancient times in Palestine, Saudi Arabia and other countries gypsum stone has been used for construction. Due to their important advantages (environmental cleanliness, good heat insulating properties and sound absorption, fire resistance, positive impact on people's health by creating a favorable microclimate in the premises, etc.) gypsum materials are ideally suited for the construction of residential and office buildings. These properties have a positive effect on the maintenance of gypsum concrete walls and buildings as a whole, as well as on the health of people staying in them. In terms of the level of comfort and environmental safety gypsum concrete is on the second place after wood. But gypsum materials are known to be unstable to atmospheric impact. Therefore, nowadays it is required to improve physical and mechanical properties of gypsum-containing building materials produced from local natural materials, as well as to update construction technologies according to the latest scientific advances (Lesovik, V.S., 2012; Lesovik, V.S., 2012; Lessowik, V.S., et al., 2011; Fisher, H.-B., Weimar, 2012; Ronald, A., et al., 2008; Belov, V.V., et al., 2012; Ferronskaja, A.V., 2002).

These countries have all opportunities for the production of rapid-hardening gypsum-containing building materials on the basis of composite gypsum binders. In Jordan (in the north-east) there are several deposits of Quaternary zeolite volcanic tuff, which can be used as active mineral additives in the composite gypsum binder.

In Saudi Arabia there are huge reserves of natural resources: limestone, chalk, and others. There are many deposits of gypsum and anhydrite (Maqna district, etc.). The largest deposit of gypsum is in the Maqna district, along the coast of the Red Sea. It covers the area of about 270 km², the layer of the mineral is 17 m, reserves of 6 million tons of gypsum material containing 83.63% – 90.5% of calcium sulfate dihydrate.

In recent decades, as a result of armed conflicts involving the use of heavy weapons, there is a mass destruction of buildings in the Middle East (Palestine, Iraq, Syria, Egypt, etc.), resulting in formation of large amounts of concrete breakage. Its rational utilization will provide valuable raw materials for construction and reconstruction work, and in many ways it will solve the environmental problems associated with the disposal of large amounts of construction waste.

The use of modern rapid-hardening gypsum-containing building materials for house construction will allow creating a comfortable pre-fabricated accommodation for living, taking into account the local social and climatic conditions of those countries, and also it will give an opportunity for people with low incomes to have their own house.
**Methodology:**

To obtain composite gypsum binders we have conducted a series of tests: the optimal size distribution of the active mineral additives in the composite gypsum binders was determined by a laser granulometry method, the required amount of mineral additives in the binder was selected according to the concentration of calcium oxide contained in special formulations comprising an aqueous suspension of hemihydrate gypsum, portland cement and active mineral additives. The structure of the solidified matrix was determined by the methods of DTA, XRD and electron microscopy.

The composite gypsum binder was prepared by co-grinding of mineral additives (silica sand, volcanic tuff, elimination of crushing concrete breakage), Portland cement CEMI 42.5N and super plasticizer S-3, followed by mixing with gypsum binder of brand G-5B II.

**The main part:**

Most of the composite gypsum binders (CGB), and products based on them are obtained from the mixture (consisting of gypsum binder (GB), Portland cement, active mineral additives and water) being able to set rapidly and harden. The structure of obtained lithoid mass is formed by the hydration of gypsum binder and Portland cement. (Lessowik, V.S., et al., 2011).

It is known (Belov, V.V., et al., 2012) that the filler with a high surface area due to “the asymmetry of the structure of the surface of dispersed particles forms a layer of adsorbed polarized and structured water with increased density and decreased dielectric conductivity (Belov, V.V., et al., 2012). In that layer there will be intensive crystallization of dissolved substances. It is assumed that the polarization of water molecules results in ordering of structure of crystalline hydrate neoplasms with a consequent increase in physical and mechanical properties of the binding matrix.

Based on the modern concepts of gypsum cement-silica systems hardening mechanism, it is necessary to comply with the following conditions to ensure their durability: supporting of binding of most aluminates with gypsum to form ettringite in the initial period of hardening of the system with the increase in the level of hydration of portland cement, for example, by the mechanical and chemical activation; upholding the concentration of calcium hydroxide on the desired level during hardening to provide the conditions for the formation of various hydrate tumors, including low-basic calcium hydroaluminates (Ferronskaja, A.V., 2002).

Great interest as an object of research and utilization of industrial wastes is the use of recycled concrete breakage as a mineral additive in CGB. In the previous studies (Bazhenov, Y.M., et al., 2006) suitability of using concrete breakage for obtaining fillers for cement systems was established.

It should be noted that its binding part consists of calcium hydrosilicates of group C3SH2 according to Bogg’s nomenclature, calcium hydroxide and residues of not hydrated clinker minerals, mainly belite. This material has the appreciable secondary binding properties. Herein, the “younger” concrete, from which concrete breakage was obtained, demonstrated its secondary binding properties.

In this paper, raw materials of the Middle East countries (quartz sand, fine grained screenings of concrete breakage, volcanic tuff) were used as a mineral additive in the composite gypsum binder (CGB).

**Table 1: Chemical composition of used fillers.**

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe (total)</th>
<th>P2O5</th>
<th>CaO</th>
<th>MgO</th>
<th>Na2O + K2O</th>
<th>SO3</th>
<th>TiO2</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartzsand</td>
<td>94.32</td>
<td>2.61</td>
<td>(0.42-0.81)</td>
<td>-</td>
<td>0.46</td>
<td>0.66</td>
<td>0.22+0.65</td>
<td>0.01</td>
<td>0.16</td>
<td>0.65</td>
</tr>
<tr>
<td>Screenings of concrete breakage</td>
<td>90.1</td>
<td>1.3</td>
<td>2.6</td>
<td>1.4</td>
<td>2.0</td>
<td>0.3</td>
<td>1.2</td>
<td>0.4</td>
<td>0.15</td>
<td>0.42</td>
</tr>
<tr>
<td>Colitic tuff</td>
<td>70-75</td>
<td>10-16</td>
<td>Up to 4</td>
<td>-</td>
<td>Up to 1</td>
<td>Up to 3</td>
<td>2-6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

To activate CGB hydration processes mineral additives were ground in the laboratory ball mill followed by mixing with portland cement and gypsum binder, combined with brief milling. The introduction of mineral additives in gypsum cement composition allows influencing the stages of hardening and helping to change the final properties of the material.

For assessment of the properties of mineral additives their activity was determined by absorption of calcium hydroxide in the hardening system up to regulated limits (not higher than 1.1 and 0.85 g/l – converted into calcium oxide), respectively, on the 5th and 7th days. (TU 21-31-62-89 – gypsum-cement-pozzolan binder). CaO concentration in solutions was set: with a fine ground quartz sand with mandatory ratio A/C = 1:1, with a zeolite tuff with mandatory ratio A/C = 0.25:1, which is associated with the formation of disturbed microlayer on the surface of mineral additives while grinding, containing a very limited amount of amorphous SiO2. The increased activity of silica component and its mechanical destruction accelerate hydrolysis of clinker minerals by Ca(OH)2 of Ca(OH)2 with formation of additional portions of CSH(B) at the expense of the nanoscale particles, which act as nucleation of cristallisation of new phases, contribute to a substantial increase in the number of active centers per unit volume material, which allows managing the process of ettringite formation and leads to the synthesis of specific morphology of tumors. This provides a significant increase in the strength
of the composites, improves their water-resistance. Having analysed the results obtained, further studies were conducted on CGB of the following composition, mass %: gypsum binder – 60, Portland cement – 20, siliceous additive – 20. In this paper a comparative study of the influence of the specific surface area and particle size distribution of the CGB components were conducted by the laser granulometry methods, allowing direct measurement of particle sizes (from 0.2 to 600 microns) and their percentage in the analyzed material. It was stated that the optimal surface area of siliceous additive was 500 m²/kg.

The integral curves of the particle size distribution of CGB with different mineral additives have a similar polyfractional character. The main particle size range which has more than 80% of the material is limited to the fractions of 11–158 microns, CGB with a fine grained concrete breakage waste has four clear peaks – the first one with a maximum amount of particles with size 41.6 microns, the second one – with the maximum content of particles with size 11 microns, the third one – with a maximum amount of particles with size 5.47 microns, and the fourth one – with a maximum amount of particles with size 2.88 microns. The CGB compositions and the study results of their basic properties are presented in Table. 2.

Table 2: Composition and properties of composite gypsum binder.

<table>
<thead>
<tr>
<th>№</th>
<th>Composition of CGB, mass %</th>
<th>Water/Cement ratio</th>
<th>Flow, mm</th>
<th>R_{com}, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>Cement</td>
<td>Tuff</td>
<td>Concrete breakage</td>
<td>Grinded sand</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>20</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>20</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 1: The CGB granulometric composition with mineral additive of concrete breakage waste (1), ceolitic tuff (2), and quartz sand (3).
CGB with fine grained concrete breakage waste have a higher strength index in terms of the compressive strength ($R_{\text{comp}} = 22-29$ MPa).

The phase composition and the structure of gypsum-cement matrix with various mineral additives (binder composition, mass %: gypsum binder – 60%, portland cement – 20%, mineral additive – 20%) in two hours, 14 and 28 days were studied, using the methods of DTA, XFA and electron microscopy.

To study the microstructure a scanning electron microscope Tescan MIRA 3 was used, carrying out X-ray microanalysis at the same time, which can significantly improve the results.

The analysis of the microstructure has shown (Fig. 2-6) that at the early stages of hydration (2 hours) in the compositions with concrete breakage there is a formation of tumors with thickness of 1-2 microns, which, judging by microanalysis and characteristic morphology, can be attributed to CSH-gel (Fig. 2), generally has a variable composition and amorphous nature. In its structure there are also poorly crystallized regions, referred to as CSH (I) and CSH (II).

In the compositions with tuff (Fig. 3) there is a formation of a loose, porous structure with large crystals of gypsum dihydrate, in the compositions of CGB with quartz sand the structure of the material is similar to compositions with tuff. A little later, in 7 days there are fused gypsum crystals, which are in the stage of geometric selection of the growing crystals.

In pores of all the samples the accumulations of needle-shaped crystals were revealed. They grow out of the CSH-gel matrix, penetrate the pores, and increase the number of contacts; calcium hydrosilicates gain the morphology of dendroid formations, creating a sealed shell around the gypsum particles (Fig. 3, 4 b).

Due to hydrosilicates with such morphology gypsum cement stone gains strength.
Fig. 2: The microstructure of hardened CGB with mineral supplement of concrete breakage a) in 2 hrs. b) in 7 days and c) in 28 days.
Fig. 3: The microstructure of hardened CGB with tuff a) in 2 hrs, b) in 7 days and c) in 28 days.
Fig. 4: The microstructure of hardened CGB with milled sand a) in 2 hrs. b) in 7 days and c) in 28 days.

However, in the compositions with concrete breakage, available pores almost completely overgrew with small crystals of calcium hydrosilicate, performing a reinforcing function, as compared with the samples of the other two compositions.

In 28 days the shell of hydrosilicates is thick enough, the particles are combined into a continuous structure with the bond strengthening between the crystals of gypsum. The test results of the strength of solidified samples (Table 2) demonstrate the positive impact of fine crushing of concrete products in the CGB (Klimenko, V.G., A.V. Balakhonov, 2005; Lesovik, V.S., et al., 2012).

This conclusions are confirmed by the microanalysis results. Spectra 1, 7, 13 represent the composition at a particular point of the microprobe analysis whereas spectra 2,9,14 indicate the average composition of chemical elements in the samples (Table 3).

**Table 3:** Compositions of products of hydration in the microprobe analysis points.

<table>
<thead>
<tr>
<th>Elemental composition</th>
<th>Element content, mass % at points of microprobe analysis</th>
<th>With wastes of ground concrete</th>
<th>With tuff</th>
<th>With quartz sand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>22.85</td>
<td>60.70</td>
<td>41.06</td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td>3.31</td>
<td>3.65</td>
<td>21.80</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td>48.55</td>
<td>20.06</td>
<td>14.12</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>-</td>
<td>1.25</td>
<td>4.60</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td>-</td>
<td>0.33</td>
<td>1.70</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>24.16</td>
<td>12.49</td>
<td>1.69</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td>-</td>
<td>0.48</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>1.13</td>
<td>-</td>
<td>4.88</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>-</td>
<td>1.04</td>
<td>10.15</td>
</tr>
</tbody>
</table>
Fig. 5: The hydration products of hardened CGB with mineral additive of concrete breakage (1), tuff (2), quartz sand (3) in the points of microprobe analysis.

The highest strength characteristics are shown by the composites with mineral additives of fine-grained concrete breakage wastes. In the composites with concrete breakage there is a formation of extensive ordered structures having a dense package of tumors with fine-crystalline structure (≤0.01 mcm) of priori calcium-hydrosilicates, hydroaluminates and calcium sulfate dihydrate as a result of hardening of portland-cement and hemihydrate gypsum.
Fig. 6: The multilayered snapshots of the hardened CGB hydration products: 1 – with waste of grained concrete; 2 – with tuff; 3 – with quartz sand.

We can see the formation of hydrafed calcium carboaluminate that contains ions of CO$_3$ of type CaAl$_2$(CO$_3$)$_2$·(OH)$_3$·6H$_2$O in its formula, and also the increase in the contact surface among the crystalline hydrate tumors leads to the increase in the material strength characteristics.

The hydrated CGB thermograms (Fig. 7-9) show an intense multi-stage endothermic effect with a maximum at the temperature of 120 °C due to the removal of free and physically bound by hydrated phases water.

At the ascending stage of this endothermic effect there is a noticeable flex at about 170 °C, caused by dehydration of galled calcium hydroxides. A small exothermic effect at 340 °C is caused by crystallization of anorphous products of dehydration of the mentioned galled phases.

The endothermic effect with a maximum at the temperature of 500 °C is associated with portlandite dehydroxylation. The weak endothermic effect at 770 °C is mainly due to the decarbonization of poorly crystallized metastable forms of calcium carbonate CaCO$_3$, which were formed by the partial carbonization of calcium hydroxide.

The XRD data fully confirm the DTA results. The main cementing substance of the studied samples is calcium sulfate dihydrate (d = 7.62; 4.28; 3.81 ... Å). In the X-ray patterns of CGB with a mineral additive of concrete breakage, besides the peaks of remains of nonhydrated clinker minerals (d = 3.02; 2.86; 2.7 and 2.6 Å), the attention is drawn by the equal dramatic peak with interplanar spacing 4.91 Å, belonging to portlandite. Diffraction lines (d = 3.5; 1.852 Å) indicate a low content of anhydrite CaSO$_4$; there are traces of ettringite (d = 4.73 Å) in the X-ray pattern.

Findings:

Thus, the results of the undertaken study have shown that the fine-grained mineral additives of concrete
breakage, volcanic tuff and quartz sand are the effective components for the production of composite gypsum binders.

Conclusions:
The possibility of controlling the morphology of tumors in the forming gypsum cement matrix with application of mineral additives of various origins was stated. The greatest strength characteristics are shown by composites with the mineral additive of concrete breakage fine-grained wastes.

REFERENCES


