SUPERSULPHATED CEMENTS WITH TECHNOGENIC RAW MATERIALS

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ABSTRACT

The paper presents the results of the application of technogenic raw materials in the composition of supersulphated cements and the results of study of the cement matrix porosity based on these binders. The porosity defines the structure and strength characteristics of the cement composite. The method of paramagnet-resonance and the method of secant were used for determining the volume of the pores. The quantitative analysis of porous structure of the supersulphated cement matrix in comparison with the Portland cement matrix indicates the prospective use of the complex approach for the study of the matrix structure based on supersulphated cements.

Keywords: Supersulphated Cements; Multicomponent Binders; Lime-Containing Activator; Sulphate-Containing Activator; Technogenic Raw Materials; Porosity, Granulated Blast Furnace Slag.

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1. INTRODUCTION

Recently the application of multi-component binders based on technogenic raw materials to create the efficient building composites has become essential [1-5]. One type of such binders is supersulphated cement. It should be noted that supersulphated cement has greater water-demand, lower exothermy, lower value of frost resistance but higher resistance in some aggressive environments than Portland cement. For instance fly ash-lime-phosphogypsum bricks with optimal quantity of content have shown better performance in strong sulfate environments [6,7]. The authors of paper [8] have shown that supersulfated cements have higher workability compared to Portland cement at the same water-to-binder
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Supersulfated cements based on the low-alumina slag have had lower porosity, higher compressive strength and degree of hydration. Supersulfated cements based on the high-alumina slag have had the high strength and a more complex mechanism of hydration that was strongly influenced by the solubility of anhydrite [9].

However, the detailed study of porous structure and phase composition of supersulphated cement matrix and concrete considering the application of by-products of chemical industry as hardening activators is of great interest [10].

Based on the above the aim of the paper is to assess the influence of lime-containing and sulphate-containing by-products of chemical industry as hardening activators on the strength and cement matrix porosity of composites based on supersulfated cements with high-alumina slag.

2. MATERIALS AND METHODS OF RESEARCH

The ground granulated blast furnace slag (ggbfs) with the module of basicity (Mo) equal to 0.91, lime- and sulphate-containing by-products of the chemical industry were used. The chemical compositions of components are presented in Table 1. The lime-containing by-products with different chemical compositions were marked as LC1, LC2 and LC3. The sulphate-containing by-product was marked as SC.

Table 1. Chemical compositions of materials, % by mass

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Active CaO+MgO</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Active CaO+MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>ggbfs</td>
<td>35.7</td>
<td>40.1</td>
<td>5.5</td>
<td>14.4</td>
<td>0.9</td>
<td>1.2</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>35.7</td>
<td>40.1</td>
<td>5.5</td>
<td>14.4</td>
<td>0.9</td>
<td>1.2</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LC1</td>
<td>5-12</td>
<td>40-50</td>
<td>1.8-2.6</td>
<td>2.8-4.7</td>
<td>1.3</td>
<td>-</td>
<td>1.5</td>
<td>0.2-1.0</td>
<td>-</td>
<td>5-12</td>
<td>3-12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>LC2</td>
<td>2.4-5</td>
<td>58-62</td>
<td>1.0-2.5</td>
<td>2.0</td>
<td>1.3-4.0</td>
<td>2.3</td>
<td>-</td>
<td>0.15-0.25</td>
<td>22-35</td>
<td>-</td>
<td>3-0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
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</tr>
<tr>
<td>LC3</td>
<td>13-15</td>
<td>42-45</td>
<td>2-3</td>
<td>3.6</td>
<td>2.5-4.0</td>
<td>-</td>
<td>0.7</td>
<td>1.0-1.5</td>
<td>6.7</td>
<td>-</td>
<td>0.3-0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SC</td>
<td>3.3</td>
<td>1.3</td>
<td>-</td>
<td>0.2</td>
<td>0.2</td>
<td>-</td>
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</table>

Portland cement (CEM I 32.5) was used. Experimental binder compositions were prepared by the method of separate grinding of slag and by-products activators. Activators had the dispersity approximately equal to slag dispersity that was 6000 sm²/g. The ratio of slag to sulphate-containing by-product was 80:20 percent by mass. The quantity of lime-containing component varied from 0 to 20 percent from the mass of slag. Cubes of 20×20×20 mm size were prepared for strength definition. The cubes were kept in a wet room at 20°C and more than 95% of relative humidity and were tested at the age of 28 days. Statistical methods were used to investigate the cement stone strength.

3. RESULTS AND ANALYSIS OF USE OF TECHNOCENIC RAW MATERIALS IN MULTICOMPONENT BINDERS

Experimental data of the use of the slag binder as well as the activators of hardening such as lime- and sulphate-containing wastes are presented in Figure 1. One can see from Figure 1 that there is the optimal amount of lime-containing component to obtain the higher strength.

The x-ray phase analysis has shown that these compositions have the optimum ratio between Al₂O₃ and CaSO₄, contributing to one-stage formation of the highly-sulfate type of
calcium hydrosulfate-aluminate-ettringite \((3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O})\) that performs the reinforcing role in cement matrix structure without showing the increase of its volume, expansion and destruction [10,11]. The criterion that ensures the optimum rate of dissolution of the \(\text{Al}_2\text{O}_3\) phase is the content of calcium oxide in the amount of 0.6-0.8 g/l in the liquid phase which corresponds to the content of the lime or its substitutes in the amount of 1-1.2 % (based on calculation of \(\text{CaO}_\text{free}\)) in the binder composition.

![Figure 1. Dependence of the binder strength from the quantity of lime-containing component](image)

In these conditions the following relation holds: \(\text{Al}_2\text{O}_3/\text{CaSO}_4 \approx 1/(3...5)\). The relation is favorable for the formation and sustainability of ettringite to its recrystallization in monosulfate [10,11]. Chemical binding of lime with alumina and sulfate with formation of ettringite under these conditions causes the dissolution of new quantities of these oxides and ensures the optimum mode of dissolution and hydration. Along with ettringite (0,973; 0,388; 0,277; 0,256; 0,222 nm) the main hydration products of the binder are: tobermorite-like calcium silicates (0,307; 0,280; 0,183; 0,167 nm), hydrogranats (0,272; 0,280 nm) and calcium hydroaluminates (0,336; 0,280; 0,230; 0,204 nm) due to which there is the increase of strength after complete binding of gypsum.

The structure and strength properties of matrix depend on the products of hydration as well as on the size and number of pores. There are gel pores with size less than 0.1 µm, intermediate pores (0.1 - 1 µm), capillary pores (from 1 to 10 µm) and macropores with size more than 10 µm. Accordingly, the total porosity is defined by the sum of the relative volume of pores: gel pores (PH), intermediate pores (PP), capillary pores (PC) and macropores (PM), i.e.: \(\text{PO}=\text{PH}+\text{PP}+\text{PC}+\text{PM}\). The size, concentration and the form of pores have significant impact on the cement matrix properties.

The electronic images are presented in Figure 2. Analyzing cement matrix structure with the addition of LC1 in the amount of 10% one can see the clear heterogeneity of the structure and existence of various new phases as shown in Figure 2a. Submicro-pores and submicro-cracks are visible on the surface in amount of more than 1%.

Considering the cement matrix structure based on sulfate-slag binder with the addition of LC2 in amount of 10% one can see the closed pores of very rough inner surface and size of less than 50µm as well as particles of new phases and inclusions on the surface of submicropores as shown in Figure 2b. It is possible to see the reaction (hydration) zone of surface of new phases at the boundary of the contact zone. Defects of the contact zone are not observed. One can see the very small capillary pores as well as unlike Figure 2a the more uniform mono-disperse distribution of the new phases.
The matrix structure is less porous than in previous cases with a more uniform distribution of the new phases and the local distribution of the closed spherical pores with using LC3 in amount of 10% as shown in Figure 2c. One can observe the formation of micro-cracks as concentrates of stresses.

Figure 2d shows that the matrix structure is characterized as looser, more multi-porous, defective structure with nonhomogeneous density. In this case the ordinary Portland cement CEM I32.5 was used as alkaline activator of slag.

Thus, one can state that the alkaline activator based on lime-containing by-products of chemical industry is very effective in comparison with the activator based on CEMI32.5 for sulfate-slag binders from the point of view of the pore structure development and strength.

Two methods of data processing to obtain more reliable information about the pore structure of matrix were used. The length of the selected secants was determined. As a rule several dozens of secants were drawn on the samples to get the statistical results. Full length of secants (the sum of the lengths of all secants) was determined for each sample. The same number of cross-sections with pores (approximately 200) was selected for providing the necessary accuracy for all samples.

It was found that the form of pores was close to spherical as one can see in Figure 2. The obtained values of quantitative distribution of pores by alternative method such as paramagnet-resonance (PMR) gave a good match that confirms the validity of assumptions about the sphericity of the pores in the stone based on sulfate-slag binder.

Two methods were used for experimental data processing. The first method (method of secant) is standard and it makes possible to determine the volume of the pores rather accurately. The value of the volume fraction is equal to:

\[
\frac{\Delta V}{V} = \frac{\sum I_i}{\sum L_i}
\]

where \(\frac{\Delta V}{V}\) – volume of the pores,
\(\sum I_i\) – full length of segments of secant per pores,
\[ \sum L_i \] – the sum of the lengths of all secants.

The second method was used to get the real value of concentrations of pores of different sizes, i.e. their size distribution. This problem is one of the most difficult in stereology due to a number of circumstances. The first two circumstances are related to the fact that the cut is not the pore diameter but some length of secant. In addition, the concentration of pores on the cut depends not only on their real volume concentration, but also on their size. The consideration of these circumstances is very difficult even for spherical pores. To build the true distribution of pore size we used the combination of strict stereological approach with some purely mathematical calculation of the most probable size of the pores by using the secant.

Thus, the value of the volume concentration \((1/\text{sm}^3)\) of pores was determined in the paper. The breakdown by ranges went through 30-50 µm. This is quite a big step of the breakdown. It is explained by the fact that the concentration of small macropores (10-30 µm) and their volume fraction are very small. The size of the volume fraction of pores was determined for each fraction as:

\[
\frac{\Delta V_i}{V} = N_i * V_i
\]

where \(N_i\) – the pore concentration in the appropriate range of sizes,
\(V_i\) – average pore volume in this range.

Full value of the volume fraction is equal:

\[
\frac{\Delta V}{V} = \sum \frac{N_i}{V_i}
\]

Therefore, the summation is performed overall size of fractions.

A criterion of correctness of such approach is the equality of values of volume fractions of porosity (total) defined in two ways: the secant method and the method of summation of fractional volumes. There is good coincidence of these values for all samples that proves the validity of the basic assumptions and, consequently, the correctness of the obtained curves of concentration \(N\) distribution and fractional volume fractions \(\frac{\Delta V_i}{V}\) in size.

3. QUANTITATIVE ANALYSIS OF THE POROUS STRUCTURE OF MATRIX BASED ON SULFATE-SLAG BINDER

An important factor in determining the concrete properties is the ratio between the pores of the above mentioned four ranges. One can give the following distribution of pores by size based on the results of experimental studies as shown in Figure 3.

Strength characteristics of the cement matrix based on sulfate-slag binder are equivalent to similar characteristics of the cement matrix based on CEM I32.5. The overall rate of porosity of the cement matrix based on CEM I32.5 is higher than in cement matrix based on sulfate-slag binder. However, all the samples based on sulfate-slag binder have larger amount of capillary pores. It is known that the increase of amount of C-S-H in cement stone improves the frost resistance of concrete. Capillary pores, on the contrary, are the main defects of dense structure of the concrete, since they favour the migration of water that can freeze in them.
Figure 3 The pores distribution in cement matrixes based on sulfate-slag binders (compositions 1-4) and on CEM I32.5 (composition 5)

The matrix based on sulfate-slag binder had frost resistance of 45-55 cycles because of the high content of capillary pores comparing the control specimens based on CEM I32.5 that had the frost resistance of 115 cycles.

4. CONCLUSION

Presented data allow formulating the following conclusions. Strength characteristics of the cement matrix based on sulfate-slag binder are not inferior to the cement stone based on CEM I32.5. This can be explained by the fact that in the matrix based on sulfate-slag binder with optimum combination of lime and gypsum there is single-stage formation of ettringite crystals as reinforcing elastic fibers in plastic matrix with high modulus of elasticity ($E=75\cdot10^3$ MPa), compared to C-S-H ($E=5-6\cdot10^3$ MPa). The matrix based on sulfate-slag binder had frost resistance of 45-55 cycles because of the high content of capillary pores comparing the control specimens based on CEM I32.5 that had the frost resistance of 115 cycles. The results of the studies demonstrate the prospective use of the complex approach to the investigation of the structure and properties of concrete based on sulfate-slag binders.

REFERENCES


