CIMETURI PORTLAND DE TIP COMPOZIT MODIFICATE PRIN AGLOMERARe ELECTRICĂ
PORTLAND-COMPOSITE CEMENTS MODIFIED BY ELECTRICAL AGGLOMERATION

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In order to optimize the grain size composition of Portland cement with the addition of silica fume and to activate the hardening process of composite cement the method for surface modification in high-voltage electric field is proposed. The electrical agglomeration setup to produce modified composite cement has been designed. An observation of a cross-section of a cement particle by scanning electron microscopy and an analysis of the element distribution on the surface of modified composite cement particles are shown. According to the test results, cement pastes based on the modified composite cement possess the 28-day compressive strength of up to 89.3 MPa, a 37% increase over the reference.

Keywords: Portland-composite cements, silica fume, spherical cement, agglomeration

1. Introduction

Portland-composite cements based on industrial byproducts (pozzolanic materials) like fly ash, metakaolin, silica fume, granulated blast furnace slag, etc., are the best examples of alternate cementitious materials. This class of cements is better known for their improved long-term strength and durability [1]. However, most pozzolanic materials, especially metakaolin and silica fume, tend to increase the mixing water requirement for concrete. The most common reason is that fine mineral particles raise the water demand due to increasing surface area [2].

On the other hand, fumed silica consists of very fine particles that have a strong tendency to form agglomerates. So, to reduce the water demand of composite Portland cement the particle size distribution should be optimized. This problem can be realized by surface modification of components of composite cements, in particular by dry particle coating process.

Dry particle coating to change the surface properties and/or functionality of powders appears as a very important process for many industries. Typical applications include modification of flowability, wettability (hydrophobic/hydrophilic properties), solubility, dispersibility, flavour, particle properties [3-5]. In such coating processes, powders with relatively large particle sizes (host particles: 1–500 µm) are mechanically coated with the fine particles (guest particles: 0.1–50 µm) in order to create a new functionality or to improve their initial characteristics [4].

Dry impact blending to produce co-called "spherical cement" described in a series of papers by a Japanese group [6–9]. The high fluidity of spherical cement comes from its round shape and particle size distribution. In particular, the particle size is distributed in a narrow range and the volume of fine particles under 3 µm is less than that in ordinary Portland cement.

The packing ratio of spherical cement increases and the fluidity and workability of concrete using spherical cement also increase as compared to those of ordinary Portland cement. Furthermore, the strength and durability of spherical cement concrete are improved because less water is required for mixing. The adiabatic temperature rise of spherical cement is smaller than ordinary Portland cement due to a reduction of the unit weight of cement for the same strength appearance. The authors [6–9] believe that spherical cement is a new type of cement that can be used for several high-quality concrete types including self compacting, high strength and high-durability concretes.

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* Lucrare prezentată la / Paper presented at: Consilox XI
Spherical cement is prepared by a dry impact blending method (microhybridization technology), where a mixture is formed by covering the surface of large cement "host" particles with ultra fine mineral, in particular silica fume "guest" particles.

The adhesion driving forces between particles of spherical cement are due to the van der Waals interaction and electrostatic attraction [8] as well as liquid bridge forces. In turn, the electrostatic interaction between particles is realized by their triboelectric charging. However, it is well known [10] that triboelectric charging is extremely sensitive to environmental conditions. So, if the electrostatic forces between host and guest particles are relatively weak, insufficient adhesion strength takes place. Thus the fine particles are often peeled off from the surface of core grains during the technological processing such as mixing, pneumatic transport or compression forming where relatively strong mechanical forces are applied to the components of concrete mixtures [11].

To overcome this problem and to increase the attraction of particles in "spherical cement" a selective electrostatic charging of single particles can be used [10]. For this reason the method of electrical agglomeration of Portland cement and silica fume particles as well as the laboratory experimental setup has been developed.

2. Experimental details

2.1. Materials

Ordinary Portland cement CEM I 42.5 N (OPC), silica fume (SF) which is a by-product of the ferrosilicons production and Melment F-10 superplasticizer (SP) as dried powder supplied by Degussa Polymers were used in this investigation. The chemical composition and physical properties of materials used are given in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>OPC</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>21.4</td>
<td>91.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.8</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.4</td>
<td>0.65</td>
</tr>
<tr>
<td>CaO</td>
<td>61.5</td>
<td>2.4</td>
</tr>
<tr>
<td>MgO</td>
<td>1.7</td>
<td>0.05</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.5</td>
<td>0.35</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>1.2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

| Bulk density Densitatea în vrac (kg m⁻³) | 1310 | 215 |
| Finesseness Finețea (m² kg⁻¹) | 365 (Blaine) | 18600 (BET) |
2.2. Experimental electrical agglomeration setup

Agglomeration in an alternating electric field (AC-agglomeration) is a process in which large particles are formed via coagulation of smaller particles. The principle of AC-agglomeration is presented in [12]. Firstly particles are charged by a corona discharge as in a conventional electrostatic precipitator. Next they enter into an alternating electric field where they start to oscillate. The electrical mobility and so also the oscillation velocity depend on the particle size, so that the larger the particle size the larger is the velocity and the amplitude. Velocity and amplitude differences of the particles oscillation cause collisions between the fine and the large particles. So, the particles remain attached to each other.

It is necessary to mention the fact that only the charged particles will be moved in an alternating electric field [13]. Better results are expected using bipolar distribution of large and small particles [14].

The schematic outline of electrical agglomeration setup to produce modified composite cement is given in Figure 1.

Particles are charged previously by a corona charger (CC). In this case they are charged bipolarly – Portland cement (OPC) in the positive corona discharge and the silica fume (SF) in the negative one (U=+/- 25 kV, I=30-50 μA). Then the aerosols of charged particles flow into a chamber of alternating electric field – agglomerator (A). The electric strength of electric field was 3-5 kV/cm. Large charged cement particles oscillate with bigger amplitude and velocity than the small charged silica fume particles. The difference in particle velocities and amplitudes causes their collisions and adhesion (agglomeration).

2.3. The host / guest particles mass ratio

The evolution of the percentage by mass of guest particles used in agglomeration experiment is calculated based on the assumption of 100 % surface coverage of the host particles (OPC) with a monolayer of guest particles (SF). It is assumed that all guest particles are of same size, both host and guest particles are spherical, and that the shapes of host and guest particles do not change during the coating process. Based on these assumptions, the mass percentage (W) of guest particles for 100 % coverage is [3, 5]:

\[
W,\% = \left( \frac{Nd_{\text{guest}} \cdot \rho_{\text{guest}}}{D_{\text{host}} \cdot \rho_{\text{host}}} + \frac{Nd_{\text{guest}} \cdot \rho_{\text{guest}}}{D_{\text{host}} \cdot \rho_{\text{host}}} \right) \cdot 100 \quad (1)
\]

where \(N\) is the number of guest particles per host particle, \(D_{\text{host}}\) is the average diameter of host particle, \(d_{\text{guest}}\) is the average diameter of guest particle, \(\rho_{\text{host}}\) is the density of host particle and \(\rho_{\text{guest}}\) is the density of guest particle.

For \(D_{\text{host}} >> d_{\text{guest}}\) (here, \(D_{\text{host}} / d_{\text{guest}} \approx 10\)), the number \(N\) of guest particles per host particle is given by the expression:

\[
N = \frac{4(D_{\text{host}} + d_{\text{guest}})^2}{d_{\text{guest}}^2} \quad (2)
\]

The average dimensions of particles are accepted: ordinary Portland cement (host particles) \(D_{\text{host}} = 20 \mu m\), silica fume (guest particles) \(d_{\text{guest}} = 2 \mu m\). From Eq. (1), the percentage of guest particles needed to coat host particles is 25.5 %.

2.4. Mix proportions and test methods

2.4.1. Mix proportions

The next samples were investigated during SEM, calorimetric and XRD researches: 1 – ordinary Portland cement – 100 %; 2 – composite Portland cement: ordinary Portland cement – 75 % and silica fume – 25 %; 3 – composite Portland cement modified by electrical agglomeration: ordinary Portland cement – 75 % and silica fume – 25 %.

The composition of cement paste to estimate the fluidity and compressive strength was: OPC=210 g; SF=70 g; SP (Melment F-10)=2.8 g.

2.4.2. Test methods

The particle characteristics of ordinary Portland cement and modified composite cement were assessed by scanning electron microscopy (SEM). In this investigation both an observation of a cross-section of cement particle by SEM and an analysis of the element distribution on the surface of modified composite cement particles by energy dispersive spectrometry (EDS) were used.

The fluidity of cement paste was measured in accordance with [15]. The flow pipe was 50 mm in diameter and 100 mm in height. Flow (F) was measured by averaging two crossing diameters of the spread. The relative flow area ratio (G) as the index of fluidity was calculated by the Eq: \(G = F^2 / 50^2 - 1\).

Thermo-kinetic analysis (heat evolution rate) was carried out on a differential automatic calorimeter at 30°C. Cement pastes are mixed before inserting in the measuring unit. The sample mass is 0.5±0.001 g.

X-ray diffraction patterns of the samples hydrated for 28 days were recorded using monochromatic CuKα radiation and operating at 40 kV and 20 mA (DRON-3 diffractometer).

Compressive strength of cement paste was determined after 28 days of hardening as a mean of 3 specimens for each mix. 50 mm cubes were
3. Results and discussion

3.1. The shape of cement particles

It was observed that ordinary Portland cement grains have an angular shape with particle size distribution in the range of 1-50 µm (Fig. 2 a). After the treatment of Portland cement and silica fume in the electrical agglomeration setup the particle size distribution became narrower in 5-50 µm with a predominance of larger particles. These results were due to the modification from sharp-cornered grains to spherical shape based on the fixing and embedding of fine silica fume particles (Fig. 2 b).

According to the data of energy dispersion spectroscopy the following oxides were found surrounding the surface of modified cement, %: SiO₂ (84.93); SO₃ (11.91); Al₂O₃ (1.85); MgO (0.84); K₂O (0.45) (point 1, Fig. 2 c) – these elements belong predominantly to the chemical composition of silica fume. For comparison, an angular grain on the spheroid surface (point 2, Fig. 2 c) is represented by the next set of oxides, %: CaO (51.44); SiO₂ (37.31); Fe₂O₃ (4.21) SO₃ (2.24); Al₂O₃ (1.43); K₂O (3.07), which is very close to the chemical composition of ordinary Portland cement.

3.2. Fluidity and compressive strength of cement paste

It has been found that composite Portland cement paste (control sample) with water-to-cementitious ratio w/c=0.32 is characterized by the relative flow area ratio G=1.1. In the case of modified composite Portland cement the value of relative flow area ratio G=1.1 is reached when water-to-cementitious ratio is w/c=0.285 (less than 11 %). 28-day compressive strength of composite Portland cement paste (control samples) is 65.2 MPa when modified composite Portland cement has the figure 89.3 MPa (37 % higher).

3.3. Calorimetric researches of thermal emission kinetics and X-ray diffraction analysis of cement pastes

The height of the first peak of the heat evolution rate curve (Fig. 3) of sample 2 is lower than that of OPC (1). In turn, the height of the first peak of sample 3 (modified cement) is lower than that of sample 2 (control cement). Perhaps this is due to the fact that the layer of ultra fine silica fume particles blocks the penetration of water to the surface of cement grains.

Fig. 2 - Scanning electron microphotographs of particles of ordinary Portland cement (a) and modified composite cement (b, c) with EDS Micrografii SEM ale particulelor de ciment portland normal (a) şi ciment de tip compozit modificat (b,c) şi spectrul EDS.
The height of the second peak of the heat evolution rate curve is recorded at 9.5 hours of hydration for Ordinary Portland cement paste (1) and at 13-14 hours for the control sample (2) and 15-16 hours for the modified sample (3). On the other hand, the maximum quantity of heat evolution is observed for the modified composite cement, which indicates increasing degree of hydration. These data are consistent with the X-ray diffraction analysis of 28 days cement paste (Fig. 4).

The intensity of diffraction reflections lines of tricalcium silicate (d=0.386; 0.277; 0.176 nm) of composite Portland cement pastes (samples 2 and 3) is less in comparison with Ordinary Portland cement paste (sample 1). It appears that incorporation of amorphous mineral addition of silica fume to Portland cement stimulates the hydration reactions. In the absence of SF (sample 1) there is a considerable amount of calcium hydroxide which is indicated by an intense peaks of portlandite (d=0.491; 0.311; 0.263; 0.193; 0.170 nm). These peaks are diminished in the presence of SF (samples 2 and 3) due to pozzolanic reaction forming hydrated calcium silicates C–S–H(I) (main d-spacing is 0.304 nm). Surface modification of composite Portland cement in high-voltage electric field stimulates pozzolanic reaction.

4. Conclusion

The method for surface modification of ordinary Portland cement with addition of ultra fine silica fume in high-voltage electric field is proposed. The electrical agglomeration setup to produce modified composite cement has been designed. It was found that Portland-composite cement modified by electrical agglomeration exhibits higher fluidity as well as higher 28-day compressive strength of cement paste in comparison with control samples. The results of this investigation can be considered as the comprehensive set of the basic principles of the sustainable construction [16].

REFERENCES

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