1. Introduction

Fly ash presence in cement result in modification of the rheological properties of cement pastes, which means the influence on the rheological properties of the fresh concrete mixes and mortars [1-4].

Analysis of studies of many authors concerning the influence of the fly ash on the rheological properties of cement paste shows, that the addition of fly ashes to cement can have the result in improvement or deterioration of rheological properties [5-9]. Different rheological reactions have been observed of cement pastes from cement with additions of fly ash and are the summary of influence of many factors superposition [10-11]. They are mainly such factors as type and quantity of fly ash in cement, particle size, shape and porosity of grains of ash and also contents of unburned coal in ash.

In this study the researches were carried out aiming at the defining the role of factors which have influence on rheological properties of pastes from cement including fly ash.

2. Experimental

2.1. Materials

Low-calcium fly ashes (A, B) from the bituminous coal combustion were used. The chemical composition of the materials used is given in table 1.

The phase composition of fly ashes was characterized by XRD. The following crystalline phases have been detected: quartz, mullite, hematite.

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**Chemical composition of fly ashes A and B**

<table>
<thead>
<tr>
<th>Component</th>
<th>fly ash A</th>
<th>fly ash B</th>
</tr>
</thead>
<tbody>
<tr>
<td>% by wt.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>1.0</td>
<td>3.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>50.4</td>
<td>51.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.6</td>
<td>8.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.8</td>
<td>26.1</td>
</tr>
<tr>
<td>CaO</td>
<td>4.3</td>
<td>3.1</td>
</tr>
<tr>
<td>MgO</td>
<td>2.6</td>
<td>1.9</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.4</td>
<td>3.2</td>
</tr>
<tr>
<td>CaO free</td>
<td>0.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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**Specific surface area of fly ashes (Blaine)**

<table>
<thead>
<tr>
<th>Fly ashes</th>
<th>Specific surface area of fly ashes (Blaine) [m²/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>288</td>
</tr>
<tr>
<td>B</td>
<td>271</td>
</tr>
<tr>
<td>B-1</td>
<td>379</td>
</tr>
<tr>
<td>B-2</td>
<td>425</td>
</tr>
</tbody>
</table>

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Fly ash - cement blends designed for rheological studies were obtained by homogenizing the components. The ashes A and B were applied in the raw state (A, B) and the B fly ash was ground in a laboratory mill to obtain a larger Blain’s specific surface area (B1, B2). The fly ash content in cement was 20, 40,
60 and 80 percent wt. The Blain’s specific area of the fly ash used are given in table 2.

2.2. Methods

The rheological measurements were carried out using the rotative viscosimeter type Rheotest RV - 2.1, with the modified surfaces of both cylinders. All the cement-fly ash samples were prepared and measured following the same procedure and in the same conditions. The tests were performed at a constant temperature 21 °C and at a constant water to solid ratio 0.4. Measurements started 10 minutes after mixing with water. The rheological properties of pastes with fly ashes were determined from the flow curves at growing and reduced rates of shearing in the range from 0 to 146 s⁻¹. The yield value and plastic viscosity were determined from the descending part of flow curve, according to the Bingham’s model.

The particle size analysis of fly ash was made by the laser analyser type LAU -10.32 fractions were determined in range 0.5 - 200 μm. On the base of size analysis of fly ash the following parameters characterised the file of particles of fly ash were determined [12]: average diameter of particle \( \bar{d} \), conventional diameters \( D_{25}, D_{50}, D_{75} \), spherical shape coefficient \( \Psi \) and contents of grains less than 24 μm in % wt.

They were calculated by equations:

\[
\bar{d} = \frac{\int_{\phi_{\text{min}}}^{\phi_{\text{max}}} \phi \cdot q(\phi) \, d\phi}{\int_{\phi_{\text{min}}}^{\phi_{\text{max}}} q(\phi) \, d\phi} \tag{1}
\]

\[
\int_{\phi_{\text{min}}}^{\phi_{\text{max}}} q(\phi) \, d\phi = 1 \tag{2}
\]

\[
\bar{d} = \frac{\int_{\phi_{\text{min}}}^{\phi_{\text{max}}} \phi \cdot q(\phi) \, d\phi}{\int_{\phi_{\text{min}}}^{\phi_{\text{max}}} q(\phi) \, d\phi} \tag{3}
\]

\[
\Psi = 6 \frac{\int_{\phi_{\text{min}}}^{\phi_{\text{max}}} \phi^2 \cdot q(\phi) \, d\phi}{\rho \cdot \phi_{\text{max}} \cdot \int_{\phi_{\text{min}}}^{\phi_{\text{max}}} \phi \cdot q(\phi) \, d\phi} \tag{4}
\]

where: \( \phi_{\text{min}} \) - diameter of finest fraction, 
\( \phi_{\text{max}} \) - diameter of coarsest fraction, 
\( d\phi \) - elementary fraction, 
\( q(\phi) \) - fly ash particles distribution, 
\( \rho \) - density of grains of fly ash, 
\( \phi_{\text{powvl}} \) - specific surface area of fly ash.

Conventional diameters \( D \) of particles were defined basis on the function of cumulative fly ash grains distribution. They characterise the conventional diameters of fly ash grains equal to the value of cumulative curve distribution 0.25; 0.50; 0.75 and are defined D25, D50, D75 respectively [12].

3. Results of analyses

In table 3 the values of yield value (\( \tau_y \)) and plastic viscosity (\( \eta_{pl} \)) of analysed pastes are presented. Figures 6 - 10 show the particial size distribution in percent wt. of particular fractions of fly ash in range 0 - 200 μm and cumulative curve fly ash A and B raw and grinded B-1 and B-2. Table 4 presents calculated parameters characterising particles of the fly ashes.

<table>
<thead>
<tr>
<th>No</th>
<th>Composition of cement-fly ash mixtures</th>
<th>A</th>
<th>B</th>
<th>B-1</th>
<th>B-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100 % C</td>
<td>69.1</td>
<td>0.83</td>
<td>69.1</td>
<td>0.83</td>
</tr>
<tr>
<td>1</td>
<td>80 % C + 20 % FA</td>
<td>30.0</td>
<td>0.45</td>
<td>57.6</td>
<td>0.89</td>
</tr>
<tr>
<td>2</td>
<td>60 % C + 40 % FA</td>
<td>25.1</td>
<td>0.43</td>
<td>32.4</td>
<td>0.92</td>
</tr>
<tr>
<td>3</td>
<td>40 % C + 60 % FA</td>
<td>16.3</td>
<td>0.39</td>
<td>23.6</td>
<td>0.82</td>
</tr>
<tr>
<td>4</td>
<td>20 % C + 80 % FA</td>
<td>13.1</td>
<td>0.39</td>
<td>15.6</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Fig. 1 Partical size distribution and cumulative curve of fly ash A

Analysis of the results shows, that content of fly ash from bituminous coal in cement causes the decreasing of the yield value and plastic viscosity of pastes. Moreover, it was stated that the cement pastes including low-calcium fly ash A an B with the similar chemical contents and specific surface display significant differences of rheological properties (tab. 3). In aim to explain those differences the size analysis was made of fly ash by the laser diffraction method.
On the base of the calculated parameters of size analysis it can be stated, that the average size of fly ash particles A is 77.2 μm, 25 percent of grains in fly ash has he diameter less than 7.7 μm, 50 percent of grains has the diameter less than 18.2 μm and 75 percent has the diameter less than 66.1 μm. The average size of particles B is 109 μm, 25 percent of grains in fly ash B have the diameter less than 12.8 μm, 50 percent of them - less than 49.4 μm and 75 percent has the diameter less than 88.1 μm. Participation of grains less 24 μm is 34.3 percent in case of B ash, while in A ash it is 53.1 percent. The conclusion is, that the fly ash A are cha-
characteristic for the greater participation of fine fraction comparing with B fly ash. Figures 5 - 6 present quantity and influence of fine fractions participation in fly ash and content of fly ash in cement on plastic viscosity and yield value of cement paste.

The spherical shape coefficient calculation relating to the grains of fly ash A and B (tab. 4) moreover showed, that the shape of fly ash grains A is closer to the spherical shape comparing with B grains. That was confirmed by the microscope analysis SEM.

The above explains, why the pastes containing fly ash with the similar chemical composition and specific surface show differences in rheological properties of cement pastes.

Figure 7 presents the influence of spherical shape coefficient $\Psi$ of fly ash grains and their quantities in cement on yield value of paste. Grinding of ashes results in the growth of participation of fine fractions and increase of spherical shape coefficient of fly ash grains (tab. 4), this explains the improvement of rheological properties of pastes with these ashes (tab. 3).

4. Conclusions

- Content of fly ash from bituminous coal in cement has the result in decrease of yield value and plastic viscosity of pastes - the more significant, the greater is contents of fly ashes in cement.
- Rheological properties of pastes including fly ash from bituminous coal depend mainly on the participation of fine fractions in ashes and on shape of particles of fly ashes. The level of fluidity of cement-ash pastes is more visible at the greater number of fine fractions $< 24 \, \mu m$ in ashes and the more spherical shape of fly ash particles.

5. Literatúra - References