A b s t r a c t

This paper discusses the effects of partial replacement of cement with fluidized bed bottom ash on the properties of mortars. The analyzed ash samples originating from four Polish power plants were separated by grain size selection into fine and coarse-grained fractions. This process leads to a creation of derivative samples of differing physical properties and, partially, phase compositions, as tested in XRD and TG analyses. Despite its high water demand, the obtained fine-grained fraction has the potential for application in cement-based composites as a reactive, pozzolanic additive. An acceptable activity index may be reached when the sulfate content is limited, implying benefits of combining the ash with low gypsum cements. The coarse-grained fraction is significantly less reactive, while a high silica and aluminate content is related to improved mechanical properties of the composite. It can, therefore, potentially be used as a quasi-inert additive or a substitute for sand.

Keywords: fluidized bed, bottom ash, grain size selection, cement mortar

1. INTRODUCTION

The share of coal in electricity production in Poland is extensive, exceeding 81% in 2016 [13]. At the same time, the country is one of the leaders in fluidized bed
combustion (FBC) technology [32]. As a result, the estimated quantity of FBC by-products generated each year in Poland amounts to several million tons [31]. One part of these is a fine-grained material carried along with flue gases and captured on electrostatic precipitators – so-called fly ash. The second part is a mixture of fine- and coarse-grained residues of the fluidized bed, collected from the bottom of the furnace – the so-called bottom ash.

Many years of research and practical experience concerning the use of ashes from conventional coal-fired plants (e.g. with pulverized fuel boilers) enabled extensive, safe, and cost-efficient utilization of these waste materials as additives in cement and concrete. This has been confirmed by numerous papers [2, 14, 16] as well as standards governing their safe use such as EN 450-1 [20]. Ashes originating from FBC have not been similarly researched or widely used. This is due to certain properties deemed as disadvantageous in concrete technology such as high variability of composition, high specific surface area, high water demand, irregular grain shape (leading to low workability), and high sulfate content [8, 36]. On the other hand, FBC ashes exhibit properties crucial for concrete (and other composites) – high pozzolanic activity and hydraulic binding capacity [8, 36].

Practical applications of the material, given the lack of standards and high variability of properties, are usually limited to individual cases. Based on adequate research, FBC fly ash can be used as a raw material in the production of cement [8], as a concrete additive [26, 38], and as a component of cement-free binders [12, 37] or hardening slurries [5]. FBC bottom ash, on the other hand, is used as a component of hydraulic backfill in mining [11], a soil-stabilizing binder in road construction [15], and a material applied in the process of geopolymerization [27]. The possibility of its conditional use in cement production [10, 29] and in concrete mixes [7] has also been discussed.

In response to the observed problematic properties of FBC ashes, a number of modification methods have been developed in order to increase the practical applicability of the material. Modification may serve to alter the chemical composition, e.g., by separation into grain size fractions [7, 10, 26]. Generally speaking, the excessive sulfate content in FBC ash is considered problematic, while the highly desired components are the pozzolanic silica and alumina compounds, as well as the hydraulically reactive calcium oxide [7, 26, 34]. Another group of modification methods is based on the change of certain physical properties without altering the composition. For example, grinding results in the breaking of larger grains of ash, leading to an increased specific surface area and potential release of small reactive particles from larger clusters [9]. This process, also called mechanical activation, leads to an increase in material activity, sometimes at the expense of potentially increased water demand of the resulting mixtures [6, 9].

This research investigates FBC bottom ash and aims at a better understanding of its properties as well as a potential mitigation of difficulties related to its use in
cement-based composites. For this purpose, a simple modification method has been proposed; a division into two fractions of grain sizes with a diameter limit of 0.1 mm. The intention of the authors is to obtain a fine, high specific surface area fraction of 0-0.1 mm, the physical characteristics of which should resemble fly ash in general, enabling the corresponding methods of analysis. At the same time, fine fractions should concentrate most of the reactive components, especially anhydrite and calcium oxide [7, 10]. The resulting coarse-grained fraction (> 0.1 mm) should be a material characterized by a lower reactivity due to a smaller specific surface area and, potentially, different chemical composition. The analysis of both derivative materials can serve as an initial assessment towards a possible utilization of fine fractions as an active additive to composites and coarse fractions as an inert additive or a substitute for aggregate, similarly to, e.g., the studies of Rafieizoonooz et al. [25] on conventional ashes as well as research by Patra and Mukharjee [18] or Sunil et al. [28] on other waste materials. An important aspect of the presented research was the inclusion of ashes of several origins. The aim is to assess whether the chosen modification method leads to similar effects on samples of material stemming from different plants, in the context of the well-known exceptionally high variability of physical and chemical characteristics of FBC ashes.

2. MATERIALS

Ash samples were obtained from 4 large power plants in Poland in November 2016 (Table 1). From a formal point of view, they constitute industrial waste non-hazardous to human health. The oxide composition of the analyzed ashes is given in Table 2.

Table 1. List of bottom ash batches used in the research, along with the source boilers characteristics

<table>
<thead>
<tr>
<th>Ash code</th>
<th>Circulating-FBC boiler type</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘1’</td>
<td>Compact</td>
<td>hard coal</td>
</tr>
<tr>
<td>‘2’</td>
<td>Compact</td>
<td>hard coal, coal slurry</td>
</tr>
<tr>
<td>‘3’</td>
<td>Steam-cooled cyclone</td>
<td>hard coal, coal slurry</td>
</tr>
<tr>
<td>‘4’</td>
<td>Hot cyclone</td>
<td>hard coal</td>
</tr>
</tbody>
</table>
Table 2. Oxide composition of raw fluidized bed bottom ashes

<table>
<thead>
<tr>
<th>Oxide group</th>
<th>Content in samples [% weight]</th>
<th>‘1’</th>
<th>‘2’</th>
<th>‘3’</th>
<th>‘4’</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td></td>
<td>5.5</td>
<td>9.9</td>
<td>15.8</td>
<td>15.2</td>
<td>11.6</td>
</tr>
<tr>
<td>Chlorides</td>
<td></td>
<td>0.042</td>
<td>0.052</td>
<td>0.036</td>
<td>0.104</td>
<td>0.060</td>
</tr>
<tr>
<td>P₂O₅ [mg/kg]</td>
<td></td>
<td>2.3</td>
<td>0.9</td>
<td>2.0</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>SiO₂ total</td>
<td></td>
<td>48.1</td>
<td>32.3</td>
<td>33.8</td>
<td>24.5</td>
<td>34.7</td>
</tr>
<tr>
<td>SiO₂ reactive</td>
<td></td>
<td>17.4</td>
<td>14.8</td>
<td>10.8</td>
<td>11.6</td>
<td>13.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td>4.5</td>
<td>3.1</td>
<td>3.9</td>
<td>3.1</td>
<td>3.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>16.8</td>
<td>12.8</td>
<td>15.2</td>
<td>10.4</td>
<td>13.8</td>
</tr>
<tr>
<td>CaO total</td>
<td></td>
<td>11.3</td>
<td>31.9</td>
<td>22.2</td>
<td>36.3</td>
<td>25.4</td>
</tr>
<tr>
<td>CaO free</td>
<td></td>
<td>4.9</td>
<td>14.5</td>
<td>6.0</td>
<td>16.4</td>
<td>10.5</td>
</tr>
<tr>
<td>CaO reactive</td>
<td></td>
<td>7.3</td>
<td>24.6</td>
<td>14.5</td>
<td>28.2</td>
<td>18.7</td>
</tr>
<tr>
<td>SiO₂ + Al₂O₃+ Fe₂O₃</td>
<td></td>
<td>69.4</td>
<td>48.2</td>
<td>52.9</td>
<td>38.0</td>
<td>52.1</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>2.0</td>
<td>0.4</td>
<td>1.3</td>
<td>3.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Total alkali</td>
<td></td>
<td>0.82</td>
<td>0.43</td>
<td>0.41</td>
<td>0.44</td>
<td>0.53</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td></td>
<td>0.95</td>
<td>2.19</td>
<td>4.15</td>
<td>0.80</td>
<td>2.03</td>
</tr>
</tbody>
</table>

The average gradation curve for all four ash samples, obtained in the sieve analysis, is shown in Fig. 1. The grain size composition of the material resembles medium sand. The thick dashed line marks the limit of division into fractions (0.1 mm), achieved in the sieve shaker. As a result of the separation, the following derivative ash samples were obtained:

- fine-grained - ‘1F’, ‘2F’, ‘3F’, ‘4F’ with grain sizes smaller than 0.1 mm,
- coarse-grained - ‘1C’, ‘2C’, ‘3C’, ‘4C’ - grain sizes greater than 0.1 mm.

The ratio of the masses of part ‘F’ to part ‘C’ is on average 1:10, so the resulting division is strongly asymmetrical.
3. METHODS

3.1. Phase composition

The raw ash samples and the ‘F’ and ‘C’ type derivatives were analyzed by powder X-ray diffraction (XRD). A Bruker D8 Advance instrument was used, with a LYNXEYE detector working in Bragg-Brentano geometry, utilizing Cu-Kα radiation ($\lambda = 0.15418$ nm) with a nickel filter. Measurements were taken within a 2θ angle range of 8-75⁰, with a step size of 0.03⁰ and a sampling time of 960 s/step. Samples ground by mortar and pestle were placed in a layer about 1 mm thick on crystalline silicon plates with orientation <7 1 1>.

Samples of fractionated ashes ‘F’ and ‘C’ were also subjected to thermogravimetric analysis (TG/DTG) via TA Instruments SDT 2960 apparatus at temperatures up to 1000⁰C, with growth rate 10⁰C/min, sample weight 15-25 mg, in air and nitrogen atmospheres. Type ‘C’ samples were ground and homogenized before the test.

Based on the results of XRD and TG tests, the content of anhydrite in the tested samples was estimated as it is a key component important for the practical applications of the ashes.
3.2. **Physical properties**

Basic physical characteristics of fine-grained ‘F’ samples were determined in accordance with the Polish-European standard PN-EN 450-1:2012 [20], which regulates the use of conventional fly-ash as a concrete additive. The tested properties are:

- grain density according to PN-EN 1097-7 [19],
- Blaine's specific surface area according to PN-EN 196-6:2019 [24],
- fineness according to PN-EN 451-2:2017 [23].

3.3 **Properties of cement-based composites with the addition of bottom ash**

The final part of the research considered selected properties of grouts and mortars modified by a partial replacement of cement (25 or 30% of mass, depending on the test) with ashes of types ‘F’ and ‘C’. The compositions and methods of mortar preparation were in accordance with the provisions of the standards mentioned below. CEM I 42.5 R cement was used and the samples were cured in a water bath at a temperature of 21°C. The tested properties included:

- water demand according to PN-EN 450-1 Annex B [20],
- initial setting time according to PN-EN 196-3 [22],
- soundness according to PN-EN 196-3 [22],
- bending and compressive strength according to PN-EN 196-1 [21],
- activity index according to PN-EN 450-1 [20].

Due to the grain size, the ‘C’ samples differ significantly in their properties from the materials for which the above-mentioned test methods were developed, therefore, in their case the results should be treated as roughly indicative.

4. **RESULTS**

4.1. **Phase composition**

The qualitative XRD analysis (Figs. 2-5) indicates the presence of similar crystalline phases in all tested samples. The three main components are quartz (SiO₂), calcium oxide (CaO), and anhydrite (CaSO₄). Secondary components include aluminosilicates - muscovite, microcline, gehlenite, illite, and calcite (CaCO₃). Observable differences in peak sizes of diffractograms of raw, fine-grained ‘F’, and coarse ‘C’ samples suggest some quantitative differences between the analyzed materials and their separated fractions.
Fig. 2. X-ray diffractogram, samples ‘1’, ‘1F’, and ‘1C’

Fig. 3. X-ray diffractogram, samples ‘2’, ‘2F’, and ‘2C’
Fig. 4. X-ray diffractogram, samples ‘3’, ‘3F’, and ‘3C’

Fig. 5. X-ray diffractogram, samples ‘4’, ‘4F’, and ‘4C’

XRD analyses confirm the complexity and diversity of the composition of the analyzed ashes. The main components, observed in each ash sample in varying amounts, can be reactive and influence the properties of cement-based composites.
The unburnt calcium oxide in the FBC ashes, stemming from thermal decomposition of calcite present in sulfur sorbent, reacts quickly on contact with water and forms calcium hydroxide while releasing heat [8, 36]. Anhydrite, resulting from the capture of gaseous sulfur oxides by calcareous sorbent molecules, also reacts with water, forming dihydrate gypsum and ettringite, the crystallization of which leads to binding of the ash grout [8]. Silica, considered to be the most important pozzolanic component of conventional ashes, rarely occurs in FBC ashes as a vitreous phase and therefore exhibits low reactivity [8, 34]. Dehydrated clay minerals (aluminosilicates), often highly porous, usually exhibit significant pozzolanic properties [26]. Non-observable or relatively small peaks characteristic for calcite (only ‘2’ ash) may indicate that the sulfur sorbent is spent to a high degree, likely as a result of a prolonged stay in the furnace. Based on the surface area under the anhydrite-related peaks obtained by XRD analysis, the approximate mass content of this component in the test samples was determined. A series of quartz-anhydrite samples with adjusted proportions, tested using the same apparatus, served as a base for content estimation. The results are given in Table 4.

The phase analysis was supplemented by TG/DTG tests, which again indicated the presence of qualitatively similar components in all analyzed samples (Table 3). The measurements under an air atmosphere show weight loss in two distinct ranges - in the temperature range of 450-620°C, which corresponds to the combustion of carbon residues, and in the range of 650-730°C, corresponding to the decay of carbonates. Under a nitrogen atmosphere, a barely visible decrease in weight occurred at a temperature of about 400°C, corresponding to the decomposition of Ca(OH)$_2$ (less than 0.5% of total weight) as well as a significant loss in the range 750-1000°C, associated with CaSO$_4$ reduction [33]. There were significant discrepancies in the total weight loss under air from less than 1% (‘1C’ sample) to more than 5% (‘2F’ sample), and under nitrogen from 3% (‘4C’ sample) to 18% (‘3F’ sample), which suggest a high diversity of sample composition. The high variability was observed mainly in the context of approximate anhydrite content in the samples, which is shown in Table 4. Estimates of anhydrite content obtained independently by XRD and TG/DTG methods are similar and were used in further quantitative analysis.
Table 3. Weight loss of ‘F’ and ‘C’ type samples in TG analysis under air atmosphere in given temperature ranges with corresponding decomposing chemical compounds

<table>
<thead>
<tr>
<th>Temperature range - corresponding chemical compounds</th>
<th>Approximate weight loss of sample in a given temperature range [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under air atmosphere</td>
<td>1F</td>
</tr>
<tr>
<td>450 - 620°C – unburnt carbon</td>
<td>3.5</td>
</tr>
<tr>
<td>650 - 730°C – carbonates</td>
<td>0.5</td>
</tr>
<tr>
<td>0 - 1000°C – total loss</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 4. Anhydrite content in XRD and TG analyses

<table>
<thead>
<tr>
<th>Tested property</th>
<th>Sample type by symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1F</td>
</tr>
<tr>
<td>Anhydrite content [weight %] in XRD</td>
<td>7.3</td>
</tr>
<tr>
<td>Anhydrite content [weight %] in TG</td>
<td>8.0</td>
</tr>
<tr>
<td>* gross error, excluded from analysis</td>
<td></td>
</tr>
</tbody>
</table>

4.2. Physical properties

The basic physical characteristics of the fine-grained ‘F’ samples are presented in Table 5. For reference, exemplary values typical for conventional and FBC fly ash are also presented, according to other papers [1, 3, 4, 26].

Table 5. Test results of the physical properties of fine-grained ‘F’ samples. Common values reported for conventional and FBC fly ash included for comparison

<table>
<thead>
<tr>
<th>Tested property</th>
<th>Sample type by symbol</th>
<th>Conventional fly ash</th>
<th>FBC fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1F</td>
<td>2F</td>
<td>3F</td>
</tr>
<tr>
<td>Fineness [%]</td>
<td>53.7</td>
<td>47.4</td>
<td>57.2</td>
</tr>
<tr>
<td>Particle density [kg/m³]</td>
<td>2910</td>
<td>2880</td>
<td>3120</td>
</tr>
<tr>
<td>Specific surface area [cm²/g]</td>
<td>3030</td>
<td>4380</td>
<td>3450</td>
</tr>
</tbody>
</table>

The results of tests conducted on the ‘F’ samples suggest that their basic physical characteristics resemble those of conventional or FBC class C fly ash (lime ash). However, they are characterized by a higher particle density, which may be
attributable to the fact that the grains of lower density were mostly lifted from the fluidized bed by the flue gases. Thus, further testing by methods derived from standard PN-EN 450-1 [20] seems justified in the case of fine-grained ‘F’ samples. Still, it should be noted that the material under analysis has numerous features different than conventional fly ash and that, due to its composition, 'lime-sulfate ash' would be a more appropriate name.

4.3. Properties of cement-based composites with the addition of bottom ash

The selected properties of cement-based composites with the addition of the tested ashes are presented in Table 6. The value of water demand higher than 100% means that the partial replacement of cement with ash makes it necessary to add increased amounts of water to achieve the desired consistency. The value described as soundness is a measure of undesirable swelling of the grout samples with the addition of ash as a result of the binding reaction under boiling water conditions. Herein, a higher value means higher swelling. The so-called initial setting time indicates how the addition of ash affects the rate of setting of the grout – a higher value indicates a delay in the process.

Table 6. Test results of cement-based slurries/mortars with addition of ‘F’ and ‘C’ type ash. CEM – pure cement control sample

<table>
<thead>
<tr>
<th></th>
<th>1F</th>
<th>1C*</th>
<th>2F</th>
<th>2C*</th>
<th>3F</th>
<th>3C*</th>
<th>4F</th>
<th>4C*</th>
<th>CEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water demand [%]</td>
<td>111.1</td>
<td>103.6</td>
<td>111.1</td>
<td>103.1</td>
<td>110.7</td>
<td>103.6</td>
<td>105.8</td>
<td>103.6</td>
<td>100</td>
</tr>
<tr>
<td>Soundness [mm]</td>
<td>2.4</td>
<td>4.7</td>
<td>1.5</td>
<td>1.7</td>
<td>1.3</td>
<td>4.8</td>
<td>1.7</td>
<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Initial setting time [min]</td>
<td>238</td>
<td>220</td>
<td>245</td>
<td>205</td>
<td>223</td>
<td>195</td>
<td>247</td>
<td>190</td>
<td>217</td>
</tr>
</tbody>
</table>

* results obtained on type ‘C’ ash samples might only serve as a rough comparison

All tested ash samples are characterized by a high water demand typical for FBC ashes, resulting from the irregular particle shape and relatively high specific surface area. Values of the order of 110% may be problematic and necessitate the use of plasticizing admixtures or have a negative impact on the mechanical properties of hardened composites.

Grouts with the addition of ashes are not at risk of excessive volumetric expansion as defined by PN-EN 196-3 [22], the maximum permissible value is 10 mm. The test method is designed to determine the presence of burnt calcium oxide, which may be responsible for problematic swelling of conventional ashes. In the case of FBC ashes, it would be more appropriate to test the long-term swelling, affiliated,
for example, with the crystallization of ettringite that is associated with the presence of excessive amounts of sulfates.

The addition of ash in place of cement delays the setting of the grout slightly, but in a way that is acceptable according to PN-EN 450-1 [20] – the values do not exceed twice the time measured for the cement control sample. According to the literature, the influence of FBC ashes on the cement composite setting is ambiguous – the presence of active calcium oxide has an accelerating effect, while anhydrite may delay the cement setting [34].

Strength values of mortars with a replacement of 25% of cement mass with respective ash samples are presented in Table 7 and Figs. 6 and 7. Mortar prisms were cured in a water bath and the tests were carried out 28 and 91 days after mixing. The value of the so-called activity index was determined as the ratio of the compressive strength of mortar with an addition of ash, to the strength of pure cement mortar.

Table 7. Tensile strength and activity index results of cement-based mortars with the addition of ‘F’ and ‘C’ type ash. CEM – pure cement control sample

<table>
<thead>
<tr>
<th>Tested property</th>
<th>Cement-based mortars with the addition of ash sample types by symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1F</td>
</tr>
<tr>
<td>Tensile strength after 28 days of curing [MPa]</td>
<td>6.5</td>
</tr>
<tr>
<td>Activity index after 28 days of curing [%]</td>
<td>66.8</td>
</tr>
<tr>
<td>Activity index after 91 days of curing [%]</td>
<td>79.7</td>
</tr>
</tbody>
</table>

Fig. 6 Development of compressive strength of mortars with the addition of ‘F’ type ashes. CEM – pure cement control sample

Fig. 7 Development of compressive strength of mortars with the addition of ‘C’ type ashes. CEM – pure cement control sample
The addition of all tested ash types reduced the strength of cement-based mortars after 28 and 91 days of curing. Indeed, very significant discrepancies in activity were observed, taking into account the replacement of only 25% of the cement mass - after 91 days, ‘4C’ type ash reduces strength by 65%, while ‘1F’ type ash does so by only 20%. There are also significant differences between ash fractions of one origin - the activity index after 91 days of ‘4F’ type ash is over 70%, while that of ‘4C’ type ash is 35%. Despite such a drastic individual difference, the effect of separation on activity is quite different depending on the material’s origin. Three out of four analyzed ‘F’ samples are characterized by similar activity rates, ranging from about 60-70% after 28 days, to 70-80% after 91 days. These values are not far from the values required by the standard for ash additives in concrete PN-EN 450-1 [20], i.e. activity rate not less than 75% after 28 days and 85% after 91 days of curing. They also exhibit a visible delayed strength increase, which is illustrated by the graph in Fig. 6.

5. DISCUSSION

5.1. Factors affecting the activity of FBC bottom ash

The discrepancies in the results of tests carried out on bottom ash samples of different origins confirm the notion of inherently high complexity and diversity of their composition and properties. Therefore, it seems important to determine the reasons for the observed differences, especially in the context of the critically low activity of some samples. A correlation analysis has been performed to identify the material characteristics that seem to have a decisive influence on the development of strength of cement composites modified with the addition of bottom ash. The so-called ‘p-value’ was used to assess the significance of linear correlation. This can be defined as the probability of randomly obtaining an observed or better association of the features, assuming the lack of actual association between those features. The lower the p-value, the stronger the linear correlation. The apparent dependencies were assessed in the context of the mechanisms of binding of ash grouts that are described in the literature. Correlations are illustrated in Figs. 8-11, along with the p-values. The contents of compounds used for graphs in Figs. 10 and 11 come from Table 2. They were applied, in an approximate manner, to the ‘C’ fraction of ash as it represents, on average, 90% of their original mass. Moreover, the distribution of components during separation is not drastic (see Table 4).
The anhydrite content of the samples of type ‘F’ and ‘C’ is negatively associated with the ash activity index after 28 days, and also after 91 days in the case of ‘F’ type samples. The possibility of obtaining the correlation randomly is limited because the estimates determined independently by XRD and TG analyses are similar. This association can be explained by the fact that although gypsum (also anhydrite) is a reactive component used in cements as a setting time regulator (about 2-5% by weight), its excess may adversely affect the course of hydration, significantly reducing the strength and durability of the cement composite [30]. Based on the trend shown in Fig. 8, it can be estimated that achieving an activity index after 28 days that is close to 75% or after 91 days that approaches 85% for a type ‘F’ ash sample would require anhydrite content below 2% or 3% by weight, respectively. Similar requirements are placed on conventional ash when used as a
concrete additive, as in PN-EN 450-1 [20]. However, FBC ash is inherently richer in sulfur compounds, mainly anhydrite, which may make such an approach impractical. Limiting the excess calcium sulfates in composites is potentially possible, e.g., by utilizing cement with purposely reduced gypsum content, even pure clinkers. In such a mixture, the setting time regulation function would be fulfilled by the sulfate present in the FBC ash – but such an application requires additional detailed research.

Coarse-grained ‘C’ type samples are characterized by a weaker anhydrite content-activity index relationship after 28 days of curing, and generally lower repeatability of results, which may be due to their lower uniformity and different grain size scale. In general, it can be concluded that with the same anhydrite mass content, they achieve an activity index 10-20 p.p. lower than fine ‘F’ samples after 28 days of curing. This difference probably results from diverse physical characteristics, including mainly grain size and the specific surface area of ashes of different fractions, on the development of strength. Thus, an indirect positive effect of activation of the material is observed, imitating in a way the grinding effect. The strength of mortars modified with ‘C’ ash after 28 days is strongly positively influenced by the total SiO$_2$ content (Fig. 10) (or the sum of SiO$_2$+Al$_2$O$_3$, p=0.019). In the case of reactive silica, the correlation is significantly weaker, p = 0.146. One possible reason could be that a high content of an inert, mechanically strong component (de facto aggregate) is beneficial for coarse-grained samples – as it replaces the potential reactive phases that influence the course of hydration.

The complete lack of anhydrite-activity association after 91 days of curing for ‘C’ samples suggests the potential existence of other dependencies that determine individually or jointly the delayed activity of the material. This is usually caused by compounds having pozzolanic properties that, in the case of FBC ashes, are typically dehydrated clay minerals in a porous form [17]. This may explain the positive linear relationship between Al$_2$O$_3$ content and activity after 91 days for the ‘C’ fraction. Although the correlation is not strong enough at the significance level of 0.05, worth noting is a seemingly much weaker association of activity after 91 days with the content of anhydrite (p=0.483), silica (p=0.224), and calcium oxide (p=0.188). The lack of data concerning the oxide composition of fine ‘F’ samples makes it impossible to verify this relationship.

The physical characteristics analyzed in the ‘F’ type samples, i.e. fineness, grain density, and specific surface area, are not linearly correlated with the activity of these ashes after 28 days of curing – p-values are 0.529, 0.328, and 0.771, respectively. This fact does not exclude the possibility of such an association but indicates the decisive influence of the chemical composition.
5.2. The viability of bottom ash modification by grain size separation

The samples obtained by grain size selection have inherently different physical characteristics (grain size, specific surface area, etc.), the influence of which on ash activity in cement mortars seems to be confirmed (Fig. 8). In general, separation of the phase composition between the different fractions of ash would take place if the particular compounds present in the material existed in the form of grains of different sizes. The data summarized in Table 4 indicates that a partial separation of anhydrite is achieved by fractionation of the ash on a 0.1 mm sieve, but the effect is not consistent with regard to ashes of different origin – and is negligible in the case of sample ‘2’. These differences are probably due to differing characteristics of individual fluidized bed furnaces, inter alia, combustion conditions, types of sorbent and fuel used, temperature, pressure, and burning time of bed materials. This means that in order to obtain repeatable and desired effects of grain separation of a given ash, it may be necessary to deliberately control combustion process parameters and the physical and chemical properties of the sorbent and fuel. The existence of such relationships is indicated by the strong positive correlation of the mass content of the 0-0.1 mm fraction in the raw bottom ash with the anhydrite content (XRD) in respective ‘F’ type samples (p = 0.023). A possible explanation is that the materials constituting the fluidized bed that burn for relatively long periods of time experience greater fragmentation as a result of chaotic particle movement. At the same time, the limestone sorbent is then used to a greater extent and is transformed into anhydrite in the form of finer grains.

There is another potential benefit of the removal of the finest particles from the ash, regardless of the separation of the phase composition or a lack thereof. Bottom ash is a source of environmental pollution, e.g., the concentrations of sulfates in water leaching through this material may be several times greater than acceptable according to standards [10]. Depriving them of the particles most easily carried away by water and wind may help reduce the migration of pollutants to the environment when the ashes are used, e.g., for earthworks or land reclamation.

6. CONCLUSIONS

The use of FBC bottom ash as an additive to cement composites requires mitigation of some of its adverse properties, mainly high water demand and low activity. The presented studies indicate the possibility of reducing the problem of the latter by selective use of fine ash fraction, in this case of grains smaller than 0.1 mm. Such material is similar to fly ash in terms of physical characteristics, and 3 out of 4 tested samples are characterized by an activity index slightly below
the standard requirements, as well as a visible, delayed increase in strength over 28-91 days of curing.

The presented analysis suggests the possibility of further limiting the problem by regulating the composition of ash or the whole composite made with its addition. The high content of anhydrite in the mass of bottom ash negatively influences the strength of cement-based mortars; however, the selection based on the 0.1 mm grain size limit does not show consistent effects in the form of segregation of this basic component. It seems possible to use FBC ashes in combination with cement of purposely reduced gypsum content.

The coarse fraction of ash, with grains larger than 0.1 mm, is significantly less active due to, among other reasons, low specific surface area. It can, therefore, be used as an almost inert additive, e.g., by replacing part of the fine aggregate. This requires further research, although, on the basis of the presented test results, favorable mechanical properties of mortars with the addition of these ashes can be linked to the high content of silicon compounds (mainly quartz) and aluminum compounds (dehydrated clay minerals, amorphous aluminosilicates).

Grain size separation of FBC bottom ashes might lead to a separation of their components and, as a result, regulate some properties, including activity. However, the effect obtained on the 0.1 mm sieve is not consistent and probably depends, among other issues, on combustion conditions, type of furnace, sorbent, and fuel used.

The effective use of FBC bottom ashes in cement-based composites requires expansion of the research, perhaps according to a new and original methodology appropriate for the unique characteristics of the material.

REFERENCES


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