The effect of BaCO$_3$ addition on the sintering behavior of lignite coal fly ash

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**Abstract**
The effect of BaCO$_3$ (witherite) addition on the sintering behavior of lignite coal fly ash taken from the Seyitömer power plant of Kütahya/Turkey was examined at temperatures of 1100, 1150 and 1200 °C in air atmosphere. Bloating of the fly ash samples sintered at 1150 °C was prevented, that is, the decomposition temperature of CaSO$_4$ in the fly ash is shifted to a higher temperature, and their physicomechanical properties (porosity, water absorption, bulk density and bending strength) were improved with BaCO$_3$ addition. Positive effects of BaCO$_3$, however, were not seen on the fly ash samples sintered at 1100 °C. All the fly ash samples sintered at 1200 °C were bloated due to the gas evolving and also they melted. During the thermal treatment at 1150 °C a phase transformation from CaSO$_4$ (anhydrite) to BaSO$_4$ (Barite) occurred in the fly ash with BaCO$_3$ addition as seen from the X-ray diffraction (XRD) patterns and the bar shaped fly ash samples with BaCO$_3$ saved their structural integrity up to 1150 °C.

**1. Introduction**
Fly ash is the finely divided mineral residue resulting from the combustion of pulverized coal in thermal power plants. Every year a large quantity of fly ash is produced in the world. For instance, only in Turkey more than 13 million tons of fly ash is produced annually and this amount is expected to reach 50 million tons per year by 2020 [1,2]. But, only a small amount of this waste fly ash in Turkey approximately 1% is reused in construction industry particularly cement industry [3], the rest is disposed into ash dumps or landfill which is an inconvenient solution both from the environmental and economical point of view. Reusing ratio of fly ash generated in all the world is about 10–20% of the total amount [4]. Numerous studies have been performed in order to find out application areas for the waste fly ash. It has been pointed out that fly ash can be used as additive in cement industry [5–7] and building industry for brick making [8–10], for glass [11–15], light weight materials [16,17], ceramic tableware and artwork [18], mullite [19], composite materials [20], and sintered material [21] production.

The fly ashes collected by electrostatic precipitators of power plants are usually finely sized (less than 100 μm) and spherical shaped particles, and consists of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ as major components and alkali and earth alkali metal oxides (i.e. Na$_2$O, K$_2$O, CaO, MgO) [7]. For this reason, sintering seems to be the most suitable way to convert the fly ash to useful fired products. The sintering behavior of powder materials such as fly ash is dependent on its chemical and mineralogical composition, physical properties, i.e. particle size, shape, and thermal treatment conditions [9,21,22]. Actually chemical and mineralogical components and physical properties of fly ashes vary depending on coal type (i.e. anthracite, bituminous coal, lignite and sub-bituminous coals) and combustion conditions of pulverized coal (i.e. dry combustion (1100–1400 °C), high temperature combustion (1500–1700 °C) and fluidized bed combustion (<900 °C) and fly ash collection operations (i.e. cyclone, electrostatic precipitation, bag filters) [7,21,23]. As a result, it is expected that the sintering behavior of each fly ash may be different from each other. Therefore, sintering behavior of each type fly ash needs to be investigated. On the other hand, sintering behavior becomes more important according to new approach of the production of bricks from 100% fly ash [9,10]. This approach is seemed to be a good way for consumpation of the enormous fly ash waste and environmental protection.

Studies on sintering behavior of fly ash without chemical additive reported that the fly ash was bloated at high temperature (1200 °C) in which Seyitömer fly ash sample was used similar to that in this study [8], but the study does not cover the temperatures between 1100 and 1200 °C. Bulk density and bending strength of the fly ash samples sintered between at 900 and 1050 °C was enhanced with decrease of particle size of fly ash [9]. The fly ash based glass-ceramic obtained at 924 °C consists of only the diopside phase and indicated that fly ash can be used to produce glass-ceramic [11]. The sintering process between 1130 and 1190 °C reduced the amount of glass, quartz, gehlenite and anhydrite phases which are present in milled fly ash with average particle size of 5.6 μm, but increased formation of...
anorthite, mullite, hematite and cristobalite, in addition, the best density was obtained at 1170 °C while bloating was occurred at 1190 °C due to the decomposition of alkaline metal salts [21]. Considering the shrinkage curve of the fly ash sintered between 600 and 1200 °C, two densification stages were obtained, the first operates in the 800–1070 °C range and the second one at temperatures higher than 1180 °C, while between the two stages the densification remains constant, densification process observed above 1180 °C is controlled by liquid phase [24]. Even though the tridymite is more stable phase than cristobalite at temperatures ≥900 °C, cristobalite phase was seen in the sintered fly ash at between 1000 and 1200 °C [25]. A detailed study has been performed by Erol et al. [26] on characterization of sintered (at between 1000 and 1200 °C) fly ash, it reduces to about 1170 °C in air at a heating rate of 10 °C/min according to our DTA analysis (data not given here). The fly ash used in the experiments was taken from the electrostatic precipitator bag of Seyitömer Power Station in Kütahya-Turkey, burning the pulverized lignite coal. Its chemical analysis by EDXRF (Energy-dispersive X-ray fluorescence) spectrometry technique (Spectro X-LAB 2000), carbon content using combustion and IR absorption technique (Multilab® – CS Determinator), particle size using laser diffraction method (Malvern® Mastersizer 2000), specific surface area using N₂ gas adsorption method by BET (Micromeritities® Gemini 2360) and specific gravity using helium-pycnometer (Micromeritities® Autopycnometer 1320) were carried out. These analyses are given in Table 1. Besides, in order to check the obtained results related to the negative influence of BaCO₃ on the sintered samples with BaCO₃ at 1100 °C, pore structure analysis (average pore diameter and total pore area) on the two different samples without and with 10 wt% BaCO₃ were performed by mercury porosimeter technique (Micromeritities® Autopore II 9220). Table 1 indicates that the main chemical components of the Seyitömer fly ash are SiO₂ and Al₂O₃, and the other important amounts of oxides are Fe₂O₃, CaO, MgO and SO₃. Loss on ignition (LOI) of the fly ash mainly results from the unburned carbon content. According to ASTM C618, which considers basically the chemical components of fly ash, the Seyitömer fly ash is a class F (SiO₂ + Al₂O₃ + Fe₂O₃ ≥ 70 wt%) fly ash [34]. The both chemical and particle size analysis results are in generally agree with Yilmaz et al. [8], whereas they do not agree with these analysis of Erol et al. [26]. This indicates that the differences between the fly ash samples even in the same type of fly ash may be possible. BaCO₃ in 99% purity was from Lancaster firm (England) and the other properties of the BaCO₃ used are: specific gravity 4.3 g/cm³, solubility 0.02 g/l (H₂O, 20 °C), melting point 811 °C, boiling point 1300 °C and appearance white powder. BaCO₃ (0.5 and 10 wt%) was added into the fly ash and the mixture was wet milled in a ball mill using alumina balls for 3 h. Subsequently, 10 ml of sample was taken from each suspension and their average particle size distributions were between 8.1 and 8.4 µm (Mastersizer 2000). The milled suspensions were dried in an oven at 105 °C for 5 h and then passed from a blender for 10 min to comminute. Water was added into the powdered samples at the ratio of 15 wt% for shaping, and then mixed. The moistened samples were passed from a sieve of 355 µm to obtain granulated particles. The bar shaped samples (or representative bricks) in dimensions of 10 × 10 × 50 mm were uniaxially pressed under the load of 98 MPa and dried at room temperature for two

### 2. Experimental procedures

The fly ash used in the experiments was taken from the electrostatic precipitator bag of Seyitömer Power Station in Kütahya-Turkey, burning the pulverized lignite coal. Its chemical analysis by EDXRF (Energy-dispersive X-ray fluorescence) spectrometry technique (Spectro X-LAB 2000), carbon content using combustion and IR absorption technique (Multilab® – CS Determinator), particle size using laser diffraction method (Malvern® Mastersizer 2000), specific surface area using N₂ gas adsorption method by BET (Micromeritities® Gemini 2360) and specific gravity using helium-pycnometer (Micromeritities® Autopycnometer 1320) were carried out. These analyses are given in Table 1. Besides, in order to check the obtained results related to the negative influence of BaCO₃ on the sintered samples with BaCO₃ at 1100 °C, pore structure analysis (average pore diameter and total pore area) on the two different samples without and with 10 wt% BaCO₃ were performed by mercury porosimeter technique (Micromeritities® Autopore II 9220). Table 1 indicates that the main chemical components of the Seyitömer fly ash are SiO₂ and Al₂O₃, and the other important amounts of oxides are Fe₂O₃, CaO, MgO and SO₃. Loss on ignition (LOI) of the fly ash mainly results from the unburned carbon content. According to ASTM C618, which considers basically the chemical components of fly ash, the Seyitömer fly ash is a class F (SiO₂ + Al₂O₃ + Fe₂O₃ ≥ 70 wt%) fly ash [34]. The both chemical and particle size analysis results are in generally agree with Yilmaz et al. [8], whereas they do not agree with these analysis of Erol et al. [26]. This indicates that the differences between the fly ash samples even in the same type of fly ash may be possible. BaCO₃ in 99% purity was from Lancaster firm (England) and the other properties of the BaCO₃ used are: specific gravity 4.3 g/cm³, solubility 0.02 g/l (H₂O, 20 °C), melting point 811 °C, boiling point 1300 °C and appearance white powder. BaCO₃ (0.5 and 10 wt%) was added into the fly ash and the mixture was wet milled in a ball mill using alumina balls for 3 h. Subsequently, 10 ml of sample was taken from each suspension and their average particle size distributions were between 8.1 and 8.4 µm (Mastersizer 2000). The milled suspensions were dried in an oven at 105 °C for 5 h and then passed from a blender for 10 min to comminute. Water was added into the powdered samples at the ratio of 15 wt% for shaping, and then mixed. The moistened samples were passed from a sieve of 355 µm to obtain granulated particles. The bar shaped samples (or representative bricks) in dimensions of 10 × 10 × 50 mm were uniaxially pressed under the load of 98 MPa and dried at room temperature for two

### Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>wt%</th>
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<tr>
<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<tr>
<td>Fe₂O₃</td>
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<td>MgO</td>
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<tr>
<td>Na₂O</td>
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<tr>
<td>SO₃</td>
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<td>LOI</td>
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<tr>
<td>Total</td>
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<tr>
<td>Specific gravity (g/cm³)</td>
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<tr>
<td>Carbon (wt%)</td>
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<tr>
<td>Specific surface area (m²/g)</td>
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</tr>
<tr>
<td>Particle size (µm)</td>
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<tr>
<td>D90</td>
<td>92</td>
</tr>
<tr>
<td>D50 (average particle size)</td>
<td>64</td>
</tr>
<tr>
<td>D10</td>
<td>16</td>
</tr>
</tbody>
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days followed by determining dimensions and weight of the samples. The samples were sintered at 1100, 1150 and 1200 °C in air atmosphere with the heating rate of 240 °C/h for 1 h in an electrical furnace. The cooling rate was 240 °C/h. After firing linear shrinkage (%) of the samples were determined. Then, water absorption tests according to Archimedes principle were applied on the sintered samples and thus water absorption (wt%), bulk density (g/cm³) and apparent porosity (vol%) of the samples were calculated. Three-point bending strength was measured with 35 mm span length at the cross-head speed of 1 mm/min (Instron™ 1150). The each data used in the curves in Fig. 5 is average of the test results taken from the six samples. Physical and mechanical tests were not able to apply on the samples sintered at 1200 °C due to their unsuitable forms as seen from their photographs in Fig. 1. In order to clarify the effect of BaCO₃ addition on the sintering behavior of the fly ash, X-ray diffraction and electron microscopy techniques were used. Phase analysis of both the as-received fly ash and the sintered fly ash without and with BaCO₃ additive were performed by XRD (Rigaku™ miniflex) using Cu Kα radiation (at 2θ scanning speed of 2°/min). The secondary electron images of fracture surfaces of the sintered samples were obtained from a scanning electron microscope (SEM, Leo™-1430 VP) equipped with an energy dispersive (EDS) spectrometry. Before SEM analysis, the fractured surfaces of the samples were coated with gold.

3. Results and discussion

3.1. Photographs

The photographs of the fly ash samples without and with BaCO₃ additive (5 and 10 wt%) sintered at 1100, 1150 and 1200 °C are seen in Fig. 1. The photographs shows that considering their appearance; (i) All samples (without additive and with BaCO₃ additive) sintered at 1200 °C were bloated totally due to the gas evolving and lost their structure entireness. A melting for the all samples is clearly seen at this temperature. That is, three separate bar...
shaped samples exist before firing but they turned a single piece after firing possibly as a result of melting as seen from the Fig. 1. Moreover, with increasing the amount of BaCO$_3$ additive, melting was promoted due to its fluxing effect. While the vitrified samples without BaCO$_3$ had heterogeneous large porous the BaCO$_3$ added samples resulted in samples with a small sized and homogenous porous caused by fluxing effect of BaCO$_3$. On the other hand homogeneity differences on the surfaces of both samples possibly dependent on unique decomposition behavior of CaSO$_4$ and BaSO$_4$ in the samples. Previous study indicated that thermal decomposition kinetics of metal sulphates (e.g. MgSO$_4$ and BaSO$_4$) vary significantly [35]. Fluxing effect of barium in production of ceramic and glass materials is also reported elsewhere [14,28]. (ii) At 1150 °C and under the working conditions, the samples with BaCO$_3$ additive saved their structural integrity, whereas the non-additive sample was bloated wholly because of the presence of CaSO$_4$ in the as-received fly ash as will be explained later. Moreover, a partly melting or liquid phase formation on the sample surface started. Especially, the surface of the sintered sample with 10 wt% BaCO$_3$ additive had a very smooth and a glassy appearance. (iii) At 1100 °C, a significant difference on their structure was not seen, but only their color was getting darker with increasing the amount of additive.

3.2. Phase analysis

X-ray diffraction patterns of the Seyitömer fly ash (as-received) and all the sintered fly ash samples are given in Fig. 2. The Seyitömer fly ash consists of those phases: quartz (SiO$_2$), hematite (Fe$_2$O$_3$), anorthite (CaAl$_2$Si$_2$O$_8$) and anhydrite (CaSO$_4$). This mineralogical composition is very similar to that in the paper [8] using the similar fly ash taken from the same power plant. But, it is not very similar to that in the [26], using the similar fly ash taken from the Seyitömer Power Plant, that is, mullite and enstatite minerals exist in the fly ash sample in that study, while they were not seen in our fly ash sample. After the sintering at 1100 °C, in the non-additive sample cristobalite which is a high temperature phase of quartz and spinel [Mg,AlFe$_2$O$_4$] phases were occurred while the intensity of quartz peak was diminished. Moreover, cristobalite formation from quartz with increasing the temperature is encountered in the all sintered samples. Similar results on cristobalite formation have been obtained for different coal fly ashes [21,25]. With BaCO$_3$ addition, peak intensities coming from anorthite and hematite increased and also witherite (BaCO$_3$) peaks were seen (Fig. 2). When considered the presence of witherite at 1100 °C this might be expressed that this temperature is insufficient to occur barite through ion exchange between Ba$^{2+}$ in witherite and Ca$^{2+}$ in anhydrite.

Even though the anhydrite phase is present in both the as-received and the non-additive samples sintered at 1100 °C, after their heat treatment at 1150 °C it was disappeared as seen in Fig. 2. This is due to the decomposition of anhydrite which leads to bloating of the non-additive sample. The bloating and also swelling of the sample sintered at 1150 °C results from the evolved gases such as SO$_2$, SO$_3$ and O$_2$ during the thermal decomposition reaction of anhydrite. According to the literature [33] this reaction with two steps may be given as

$$\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$$
$$\text{SO}_3 \rightarrow \text{SO}_2 + 1/2\text{O}_2$$

A similar result on sintering of the Seyitömer fly ash fired at 1200 °C has been obtained by Yilmaz et al. [8] using original fly ash, while [21] reported such as bloating on the Yugoslav fly ash fired 1150 °C due to the decomposition of metal sulfates. But, Yilmaz et al. [8] studied at 900, 1000, and 1200 °C, therefore, they were not able to see possible decomposition leading to swelling and bloating occurring at the temperature between 1100 and 1200 °C. On the other hand, as Fe$_2$O$_3$ content of fly ash used by Ilic et al. [21] was relatively lower as compared to current study, therefore, the decomposition temperature of CaSO$_4$ in the fly ash in [21] might be relatively higher than that of CaSO$_4$ in the fly ash in this study. Because Merwe et al. [36] determined that Fe$_2$O$_3$ has a reducer effect on the decomposition temperature of anhydrite (CaSO$_4$) as in the case of alone. However, another study on Seyitömer fly ash fired at 1175 °C does not mention thermal decomposition leading to swelling and bloating. In contrast it states that high density and low porosity sintered products were obtained [26]. It is likely that the absence of anhydrite in the fly ash samples, contrary to the samples of current study, protected the negative effect of decomposition reactions. Essentially, as mentioned before pure anhydrite remains stable up to 1240 °C in an atmosphere of air, but in the presence of 25 wt% SiO$_2$ the temperature of thermal decomposition of anhydrite CaSO$_4$ is lowered to about 1120 °C [33]. However, BaCO$_3$ addition caused a phase transformation from anhydrite (CaSO$_4$) to barite (BaSO$_4$) due to the exchange between Calcium and Barium in the sample during the sintering. Accordingly, BaSO$_4$ peaks are seen in Fig. 2. In order to clearly see the reaction between BaCO$_3$ and CaSO$_4$, a mixture consisting of BaCO$_3$ and CaSO$_4$ 2H$_2$O powders was prepared using 0.01 mol of each powder and sintered at 1150 °C at the same conditions given in the experiment section for fly ash samples, and subsequently its XRD analysis was conducted (Fig. 3). Almost all peaks in Fig. 3 belong to BaCO$_3$ may be considered as a case for barite formation during the firing of the fly ash even though it does not represent the same conditions in the fly ash sample. As a result, it is assumed that BaSO$_4$ shows a better stability against to thermal decomposition at 1150 °C than CaSO$_4$ under the working conditions. Therefore, the bar shaped samples with BaCO$_3$ additive saved their structural integrity at 1150 °C (see Fig. 1) implying that bloating and swelling was inhibited by means of BaCO$_3$ addition. In other words, the decomposition temperature of CaSO$_4$ was shifted to a higher temperature above 1150 °C.

After the sintering at 1200 °C, the BaSO$_4$ peaks are also disappeared because of the decomposition of BaSO$_4$, whereas the peaks are seen at 1150 °C (Fig. 2). Indeed, it is reported that according to the XRD patterns the thermal stability of nearly pure BaSO$_4$ is above 1200 °C [37], which is sintered under the argon atmosphere, but in the presence of fly ash which includes fluxing metal oxides, i.e. Na$_2$, K$_2$O as well as complex mineralogical structure the thermal stability of barite might be decreased, e.g. anhydrite at 1150 °C. Consequently, both of the metal sulfates in the fly ash were decomposed at 1200 °C which leads to totally bloating of the sintered samples (see Fig. 1). On the other hand, relatively higher peak intensities were obtained from anorthite and spinel phases in the sintered samples.

3.3. SEM investigations

The SEM micrographs taken from the fracture surface of the samples sintered at 1100 and 1150 °C are given in Fig. 5a and b, respectively. In general, the samples were poorly sintered at 1100 °C comparing with the samples sintered at 1150 °C. This may be attributed to the heterogeneous packing of the fly ash powders. Likewise, Ilic et al. [21] reported poor sintering behavior of a fly ash without additive at 1130 °C. At 1100 °C, larger pores are seen in the samples containing BaCO$_3$ when compared with non-additive samples, however, pore amount and size distribution of both the samples with 5 and 10 wt% BaCO$_3$ were close to each other. According to physico-mechanical test results BaCO$_3$ addition has an adversely effect on the fired fly ash at 1100 °C. Since as known alkaline (i.e. Na, K, Li) and alkaline earth (i.e. Ca, Mg, Ba) ele-
ments provide liquid phase in powder material during firing [25,32]. Normally, it is expected that BaCO$_3$ as a fluxing agent leads to a better sintering of the fly ash. In order to explain this contrari-ness Hg-porosimeter measurements were conducted. Indeed the obtained results from Hg-porosimeter measurements performed on the two type samples fired at 1100°C without and 10 wt% BaCO$_3$ additive fly ash supports this expectation, namely, the total pore areas are 4.34 and 3.29 m$^2$/g and the average pore diameters are ~0.05 and ~0.12 μm for non-additive and 10 wt% BaCO$_3$ additive fly ash, respectively. With BaCO$_3$ additive the total pore area decreases while the average pore diameter increases. This indicates that the small diameter of pores concentrated in large diameter.

Fig. 2. XRD patterns of the Seyitömer fly ash (as-received) and the fly ash samples without and with BaCO$_3$ additive sintered at 1100 (a) and 1150 and 1200 °C (b) for 1 h. [Q: Quartz, H: Hematite, A: Anorthite, An: Anhydrite, C: Cristobalite, S: Spinel, W: Witherite, B: Barite.]
pores during sintering to eliminate solid–vapor interfaces with higher energy and to occur solid–solid interfaces with lower energy [22,32]. Even though this case, physico-mechanical properties (Fig. 5) of BaCO$_3$ additive fly ash samples were lower than that of non-additive. This contrariness could not be explained at present but it might be an investigation topic for a next study.

The structure of the non-additive samples sintered at 1150 °C was totally bloated and expanded owing to gas evolving during thermal decomposition of anhydrite as mentioned above. A similar bloating on a fly ash fired at 1190 °C is reported in the literature [21]. This difference possibly results from the chemical composition differences of the used fly ashes as explained before. The large pores (or voids) of about 500 μm in diameter were occurred. The pores on the surface of non-additive sample are seen very clearly even by naked eye in Fig. 1. As known from the literature [22] some compounds become oxidized (or decomposed), generating gases as SO$_3$, CO$_2$, CO that are insoluble in the solid and the pressure of the gases can be sufficiently high to produce void in the solid. On the other hand, the sintering capability of the samples increased with BaCO$_3$ addition and consequently the amount of (open or apparent) pore of the sample reduced as supported by Fig. 5b. This may results from the occurring of liquid phase and also promoting it with further increasing of BaCO$_3$ having fluxing property. The best sintering capability of the sample was obtained by 10 wt% BaCO$_3$ addition as seen from Fig. 4b, and this positive effect of BaCO$_3$ on the sintering behavior was also supported by the physico-mechanical tests given in Fig. 5. In addition, in the SEM micrograph of 10 wt% BaCO$_3$ additive sintered at 1150 °C fly ash only some spherical isolated (closed) pores which indicates enhancement of the microstructural property (reduced porosity or water absorption, and increased bulk density and bending strength) with this ratio of the additive.

3.4. Physico-mechanical tests

In order to check the obtained results from the SEM and XRD analysis, some physico-mechanical tests were applied on the sintered samples. But those tests were not able apply on the samples sintered at 1200 °C due to their unsuitable forms as mentioned before (see Fig. 1). The variation of water absorption (wt%) (Fig. 5a), apparent (or open) porosity (%) (Fig. 5b), bulk density (g/cm$^3$) (Fig. 5c) bending strength (MPa) (Fig. 5d) and linear shrinkage (%) (Fig. 5e) of the samples sintered at 1100 and 1150 °C versus BaCO$_3$ addition (wt%) are given in Fig. 5. At 1100 °C, water absorption increases slightly with BaCO$_3$ addition but the further addition did not importantly affect the sintering behavior of the fly ash. At 1150 °C, water absorption suddenly decreases to 2% ratio at 5 wt% BaCO$_3$, and to zero at 10 wt% BaCO$_3$ addition (Fig. 5a).

Fig. 5 shows that the apparent porosity (vol%) of the sample sintered at 1100 °C increased gradually while that of the samples sintered at 1150 °C reduced sharply with BaCO$_3$ addition. As explained before the sharp decrease at 1150 °C may results from the inhibiting of the bloating and the swelling due to the BaSO$_4$ formation, while the reason the small increase in the open porosity at 1100 °C is unclear. The further addition resulted no significant change on the porosity of the sample sintered at 1100 °C while that brings the porosity to zero after sintering at 1150 °C. The amount of water absorption is a natural result of the amount of apparent porosity [32,38]. So, the porosity curves have exactly the same trends with the water absorption curves which indicates that when the apparent porosity increases (or decreases) the water absorption also increases (or decreases). The maximum porosity (as ~20%) was obtained from the non-additive fly ash sample sintered at 1150 °C due to the wholly decomposition of anhydrite present in the sample and the minimum porosity (as ~0%) was obtained by the sample with 10 wt% BaCO$_3$ additive sintered at 1150 °C because of the good sintering process as well as the phase transformation from anhydrite to barite. The porosity results for 1150 °C in Fig. 5b are in accordance with the photographs (Fig. 1), the SEM micrographs (Fig. 4b) and the XRD patterns (Fig. 2).

BaCO$_3$ addition significantly enhanced the bulk density at 1150 °C whereas it causes to a little decrease in the bulk density at 1100 °C (Fig. 5) agreeing with the results of apparent porosity and water absorption. As well known, bulk density is one of the most important properties of pressed powder since it directly influences bending strength, porosity, linear shrinkage and water
The highest (\(\sim 2.3 \text{ g/cm}^3\)) and the lowest (\(\sim 1.2 \text{ g/cm}^3\)) density in the experiments were obtained at the sintering temperature of 1150 °C with the samples of 10 wt% BaCO\(_3\) additive and the non-additive samples due to minimum and maximum apparent porosity, respectively. This highest density (\(\sim 2.3 \text{ g/cm}^3\)) of BaCO\(_3\) additive fly ash, value obtained in this study is very close to the density (2.43 g/cm\(^3\)) obtained by Erol et al. [26] on the similar fly ash without additive sintered at 1175 °C for 2 h. It is interesting to obtain very close densities for the two studies although there are differences between the properties of used fly ashes. However, it should be noted that in the study of [26] any decomposition process has not been encountered under the working conditions. On the other hand, Yılmaz et al. [8] obtained \(\sim 1.7 \text{ g/cm}^3\) of bulk density at 1100 °C for 1 h using the Seyitömer fly ash very similar to our fly ash samples, and this result is lower from the result \(\sim 2.1 \text{ g/cm}^3\) obtained in this study. This may be attributed to the differences, during the sample preparation, i.e. the moistened ratio of granulated powders which can lead to difference compacting causing different final density [9]. In contrast to our result, Ilıc et al. [21] studied at 1130, 1150, 1170 and 1190 °C on the sintering
behavior of Yugoslavia fly ash without additive showed that the best result for density (2.5 g/cm³) has been obtained at 1150°C by the fly ash milled for 8 h. This indicates that, as expected, particle size and particle size distribution of fly ashes as well as their chemical compositions has a significant effect on the physical and mechanical properties of fired fly ashes.

The variation of mechanical strength as bending strength of the sintered samples versus the amount of BaCO₃ additive is given in Fig. 5d. The addition promotes the strength at 1150°C while it leads to decrease in the strength at 1100°C similar to the bulk density. The highest strength (25 MPa) was obtained with the sample of 10 wt% BaCO₃ additive sintered at 1150°C accompanying a decrease in the porosity and increase in the bulk density. These results at 1150°C were supported by SEM micrographs. According to the linear shrinkage curves of the fired samples, it decreases with BaCO₃ addition at 1100°C, while it increase sharply with the additive at 1150°C. Shrinkage occurring similarly to the porosity decrease and to the density increase [32] could be supported by Fig. 5b. The porosity of the sample fired at 1100°C increases with BaCO₃ addition while linear shrinkage decreases. However, due to the swelling and bloating on the fired samples at 1150°C as a result of decomposition of CaSO₄ during firing, the linear shrinkage is at the minimum value. The samples reach to almost their original size before heat treatment. It is assumed that a part of BaCO₃ added simultaneously react with CaSO₄ to form BaSO₄ while the other part contribute to liquid phase which enhances sintering process. Benavidez et al. [24] also reported that the densification of the fly ash without additive sintered above 1180°C is controlled by the presence of liquid phase. Accordingly, the BaCO₃ addition either inhibits the bloating or causes to densification accompanying with increase in shrinkage as clearly seen from Fig. 5c and e. Maximum shrinkage occurs at 10 wt% BaCO₃ addition level in

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**Fig. 5.** The variation of water absorption (wt%) (a), apparent porosity (%) (b), bulk density (g/cm³) (c), bending strength (MPa) (d) and linear shrinkage (e) of the samples sintered at 1100 and 1150°C versus BaCO₃ addition (wt%).
which the apparent porosity is nearly zero. The physico-mechanical properties of the Seyitömer fly ash without additive when sintered at 1150 °C due to the thermal decomposition of anhydrite. BaCO₃ additions at levels of 5 and 10 wt% into the fly ash, inhibited the bloating and the swelling as a result of phase transformation from anhydrite (CaSO₄) to barite (BaSO₄) during sintering as supported by XRD analysis and photographs.

BaCO₃ addition had a significant positive effect on the sintering of the fly ash at 1150 °C, whereas it indicated a negative effect on the sintering at 1100 °C.

The all fly ashes without and with BaCO₃ addition sintered at 1200 °C are totally bloated due to decomposition of metal sulfates (CaSO₄ and BaSO₄), and melted at this temperature. The further increase in BaCO₃ level leads to a more melting because of its fluxing effect.

Both bloating and swelling problems of the fired ceramic products made from the 100% fly ashes including anhydrite, fired at about 1150 °C, may be solved by BaCO₃ addition. Moreover, the reasonable physico-mechanical properties have been obtained from the sample containing 10 wt% BaCO₃ and sintered at 1150 °C suggesting the Seyitömer fly ash with the aid of BaCO₃ could be utilized as a possible raw material to produce fired ceramic materials.

4. Conclusions

The results of this study can be summarized as the following:

- The Seyitömer fly ash without additive was bloated completely when sintered at 1150 °C due to the thermal decomposition of anhydrite. BaCO₃ additions at levels of 5 and 10 wt% into the fly ash, inhibited the bloating and the swelling as a result of phase transformation from anhydrite (CaSO₄) to barite (BaSO₄) during sintering as supported by XRD analysis and photographs.

References