PRODUCTION OF FIRED CERAMIC MATERIALS FROM FLY ASH WITH WITHERITE ADDITIVE

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ABSTRACT

In this study, the effect of witherite ($BaCO_3$) addition on the sintering of lignite coal fly ash taken from the Seyitömer power plant of Kütahya/Turkey was examined at temperatures of 1100, 1150 and 1200 ^0C in air atmosphere. Bloating of the fly ash samples sintered at 1150 ^0C was prevented by shifting the decomposition temperature of $CaSO_4$ in the fly ash to a higher temperature, and their physico-mechanical properties (porosity, water absorption, bulk density and bending strength) were improved with $BaCO_3$ addition owing to the phase transformation from $CaSO_4$ (anhydrite) to $BaSO_4$ (Barite) as supported by XRD analysis. Positive effects of $BaCO_3$, however, were not seen on the fly ash samples sintered at 1100 ^0C. All the fly ash samples sintered at 1200 ^0C were bloated due to the gas evolving during the thermal decomposition metal sulphates, and also they melted.

Key Words: Coal fly ash, Witherite, Sintering, XRD.

1. INTRODUCTİON

Every year a large quantity of fly ash is produced as waste 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] and the rest is disposed into ash dumps or landfill which is an inconvenient solution both from the environmental and economical point of view. Recycle 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 [5-7], construction [1, 8-10] and glass industries [11-15] and for production of light weight materials [16, 17], ceramic tableware and artware [18], mullite [19], composite materials [20], and sintered material [21].

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]. 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, some problems such as swelling and bloating resulting from the thermal decomposition of anhydrite ($CaSO_4$) existing in fly ashes may be occurred during production of the fired ceramic materials such as tile and brick. $BaCO_3$ is used in brick industry to prevent the efflorescence [31, 32] forming undesirable white deposit on fired building materials resulting from water-soluble salts such as $CaSO_4$ and Na_2SO_4, through converting reaction from soluble salt to insoluble salt (i.e. $BaSO_4$). Moreover, the existence of alkaline and alkaline earth metal salts such as $CaSO_4$ in ceramic raw materials might damage fired ceramic product (i.e. brick)'s structure due to its thermal decomposition during firing [8,21,32] and additionally the temperature of decomposition of

$CaSO_4$ is lowered in the presence of SiO_2 [33]. According to the knowledge of the authors, the effect of $BaCO_3$ addition on the sintering behavior of coal fly ash has not been studied. Therefore the main objective of this study is to see how $BaCO_3$ affects the sintering behavior of the Seyitömer fly ash including $CaSO_4$ (anhydrate) at relatively high temperatures of 1100, 1150 and 1200 ^{0}C.

2. MATERIALS AND METHODS

The fly ash used in the experiments was taken from the electrostatic precipitator bag of Seyitömer Power Station in Kütahya-Turkey. Fly ash samples were characterized by using EDXRF (Energy-dispersive x-ray fluorescence) spectrometry (Spectro™ X-LAB 2000), combustion and IR absorption technique (Multilab™ - CS Determinator), laser diffraction method (Malvern™ Mastersizer 2000), N_2 gas adsorption method by BET (Micromeriticies™ Gemini 2360) and helium-picnometer (Micromeriticies™ Autopycnometer 1320). Analysis results showed that the samples has specific gravity 2.08 g/cm^3, carbon content 1.47 wt%, Particle size D90=92 µM, D50 (average particle size)= 64 µM and D10= 16µM, and chemical composition as wt %; SiO_2 53.1, Al_2O_3 19.2, Fe_2O_3 10.4, CaO 4.6, K_2O 1.8, MgO 3.9, Na_2O 0.8, SO_3 3.0 and loi 3.2.

$BaCO_3$ (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 determined as 8,1 – 8,4 µm (Mastersizer 2000). The milled suspensions were dried in an oven at 105 ^{0}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 10x10x50 mm were uniaxially pressed under the load of 98 MPa and dried at room temperature for two days followed. Dimensions and weight of the samples were determined. The samples were sintered at 1100, 1150 and 1200 ^{0}C in air atmosphere with the heating rate of 240 ^{0}C/h for 1 h in an electrical furnace. Then, water absorption tests were applied on the sintered samples according to Archimedes principle and thus water absorption (wt. %), bulk density (g/cm^3) 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 1mm/min (Instron™ 1150). The phase analysis of both the as-received fly ash and the sintered fly ash without and with $BaCO_3$ additive were performed by XRD (Rigaku™ miniflex) using CuKα radiation.

3. RESULTS AND DISCUSSION

The photographs of the fly ash samples without and with $BaCO_3$ (witherite) additive (5 and 10 wt %) sintered at 1100, 1150 and 1200 ^{0}C are seen in Fig.1. The photographs shows that all samples (without additive and with $BaCO_3$ additive) sintered at 1200 ^{0}C were bloated totally due to the gas evolving and lost their structure entireness. A melting behavior is clearly seen at this temperature for the all samples. 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, melting behavior is promoted due to its fluxing effect increasing with the amount of $BaCO_3$ additive. While the vitrified samples without $BaCO_3$ had heterogeneous large porous, the $BaCO_3$ addition results in small sized and homogenous porous in samples because of 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]. At 1150 ^{0}C and under the working conditions, the samples with $BaCO_3$ additive save their structural integrity, whereas the non-additive sample is bloated.

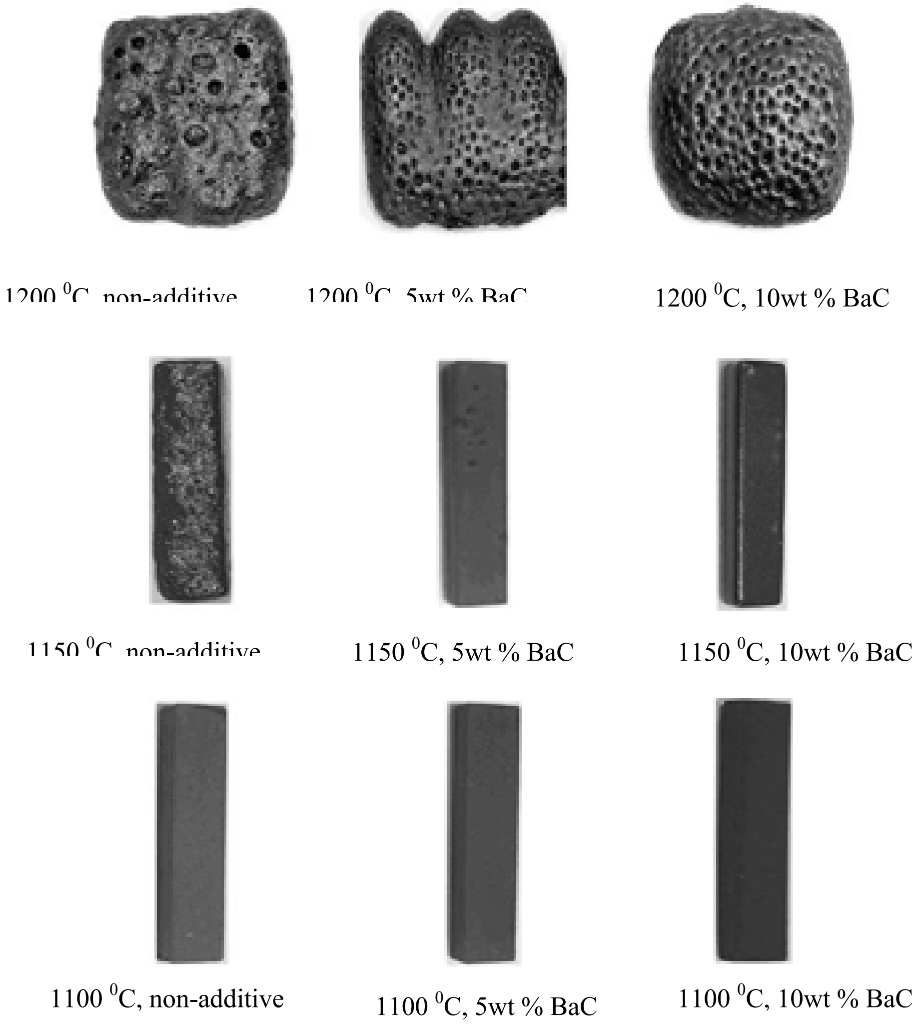


Figure 1. Photographs of the fly ash samples without and with $BaCO_3$ additive (5wt and 10wt %) sintered at 1100, 1150 and 1200 ^{0}C for 1 h.

Moreover, a partly melting or liquid phase formation on the sample surface is observed. Especially, the surface of the sintered sample with 10 wt % $BaCO_3$ additive has a very smooth and a glassy appearance. At 1100 ^{0}C, no significant difference was observed, but only the color gets darker with increasing the amount of additive.

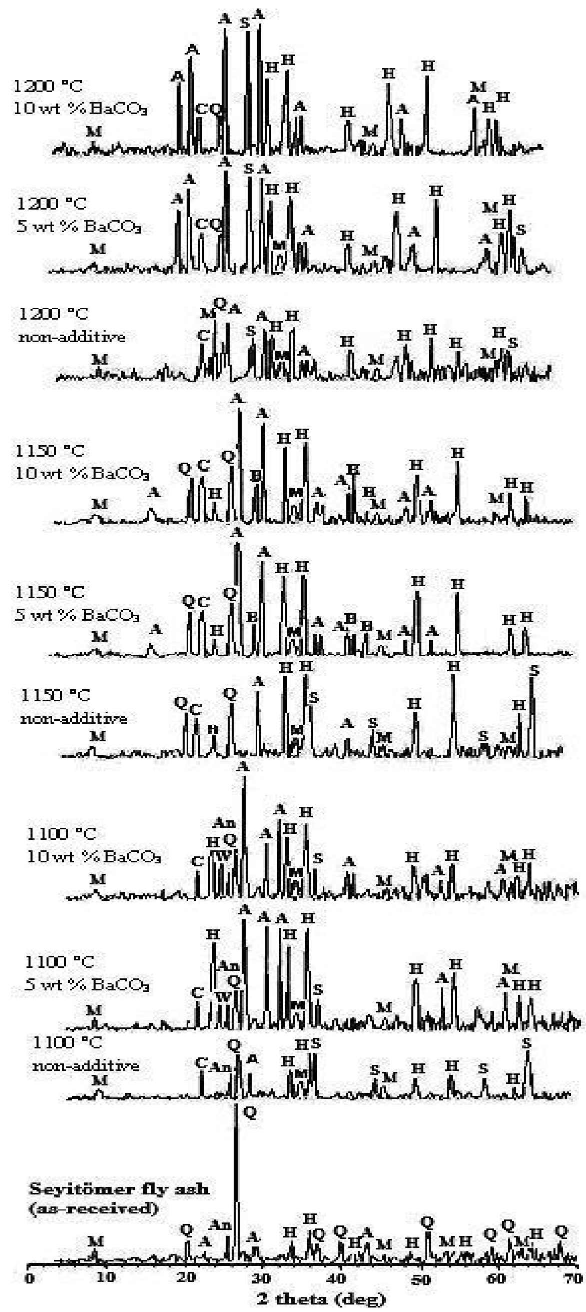
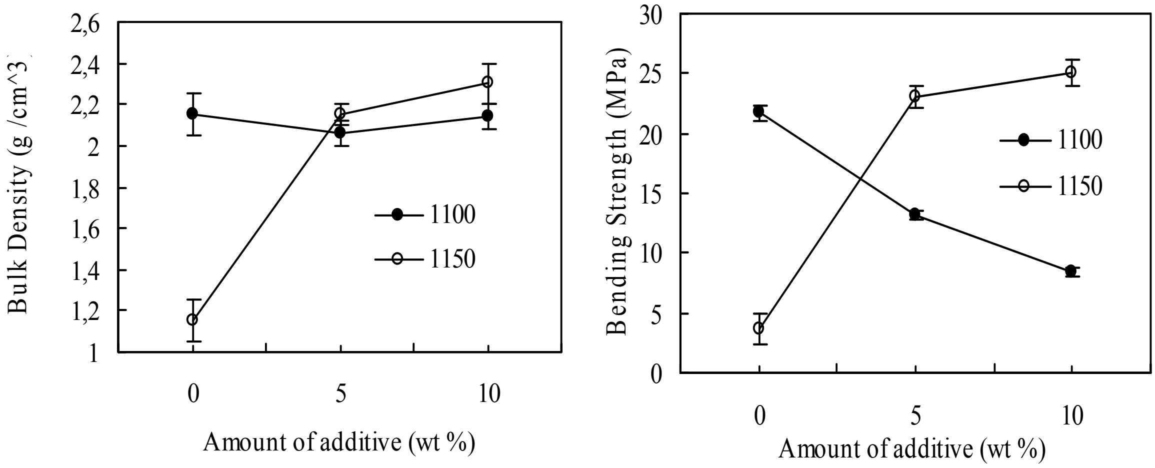


Figure 2. XRD patterns of the Seyitömer fly ash (as-received) and the fly ash samples without and with $BaCO_3$ additive sintered at 1100 and 1150 and 1200 ^{0}C for 1 h. [Q:Quartz, H:Hematite, A:Anorthite, An:Anhydrite, C:Cristobalite, S:Spinel, W:Witherite, B:Barite]

X-ray diffraction patterns of the Seyitömer fly ash (as-received) and all the sintered fly ash samples were given in Fig. 2. The Seyitömer fly ash consists of from quartz (SiO_2), hematite (Fe_2O_3), anorthite ($CaAl_2Si_2O_8$) and anhydrite ($CaSO_4$) phases. This mineralogical composition is very similar to that in the literature [8] using the similar fly ash taken from the same power plant. After the sintering at 1100 ^{0}C, cristobalite phase occurs in the non-additive sample which is a high temperature phase of quartz and spinel [Mg,(Al,Fe)$_2$O$_4$] phases 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 which caused from anorthite and hematite phases increases and also witherite ($BaCO_3$) peaks are observed (Fig. 2). If we considered the presence of witherite peak at 1100 ^{0}C; this might be expressed by insufficient temperature which prevents to formation of 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 ^{0}C, it is disappeared after heat treatment at 1150 ^{0}C. 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 ^{0}C results from the evolved gases such as SO_2, SO_3 and O_2 during the thermal decomposition reaction of anhydrite. This reaction takes place in two steps [33]: "$CaSO_4 \rightarrow CaO + SO_3$" and "$SO_3 \rightarrow SO_2 + ½ O_2$". A similar result on sintering of the Seyitömer fly ash fired at 1200 °C has been obtained by Yılmaz et al (1997) [8] using original fly ash. A bloating behavior on the Yugoslavia fly ash fired 1190 °C due to the decomposition of metal sulfates had reported at [21] . Essentially, as mentioned before pure anhydrite remains stable up to 1240 ^{0}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 ^{0}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 Fig.2. As a result, it is assumed that $BaSO_4$ shows a better stability against to thermal decomposition at 1150 ^{0}C than $CaSO_4$ under the working conditions. Therefore, the bar shaped samples with $BaCO_3$ additive saved their structural integrity at 1150 ^{0}C (see Fig. 1) and this implies that bloating and swelling is inhibited by means of $BaCO_3$ addition. In other words, the decomposition temperature of $CaSO_4$ shifts to a higher temperature above 1150 °C. After the sintering at 1200 ^{0}C, the $BaSO_4$ peaks are also disappeared because of the decomposition of $BaSO_4$, whereas the peaks are seen at 1150 ^{0}C (Fig.2). Indeed, it is reported that the thermal stability of nearly pure $BaSO_4$ is above 1200 ^{0}C under the argon atmosphere according to the XRD patterns [37], but in the presence of fly ash (includes fluxing metal oxides i.e., Na_2O, K_2O as well as complex mineralogical structure) the thermal stability of barite might be lower, e.g. anhydrite at 1150 ^{0}C. Consequently, both of the metal sulfates in the fly ash decompose at 1200 ^{0}C which leads to totally bloating of the sintered samples (see Fig.1). On the other hand, relatively higher peak intensities are obtained from anorthite and spinel phases in the sintered samples.

In order to check the results obtained from the XRD analysis, some physico-mechanical tests were applied on the sintered samples. But it was not possible to apply these tests to the samples sintered at 1200 ^{0}C due to their unsuitable forms as mentioned before (see Fig.1). $BaCO_3$ addition significantly enhances the bulk density at 1150 ^{0}C whereas it causes to a little decrease in the bulk density at 1100 ^{0}C (Fig.3a). This behavior is in agreement with the results of apparent porosity and water absorption data. As well known, bulk density is one of the most important properties of pressed powder since it directly influences bending strength, porosity, and water absorption [9, 22]. The highest (~2,3 g/cm^3) and the lowest (~1,2 g/cm^3) density in the experiments were obtained at the sintering temperature of 1150 ^{0}C with the samples of 10 wt % $BaCO_3$ additive and the non-additive samples due to minimum and maximum apparent porosity, respectively. The variation of mechanical strength as bending strength of the sintered samples versus the amount of $BaCO_3$ additive is given in Fig.3b. The addition promotes the strength at 1150 ^{0}C while it leads to decrease in the strength at 1100 ^{0}C similar to the bulk density. The highest strength (~25 MPa) was obtained with the sample of 10 wt% $BaCO_3$ additive sintered at 1150 ^{0}C accompanying an increase in the bulk density. The physico-mechanical properties of the Seyitömer fly ash with 5 and 10 wt% $BaCO_3$ additive sintered at 1150 ^{0}C are in acceptable level to produce a fired building materials such as tile according to Turkish Standards adapted to European Norms (TSEN 14411) [39].



a **b**

Figure 3. The variation of bulk density g/cm^3 (a), bending strength (MPa) (b) of the samples sintered at 1100 and 1150 ^{0}C versus $BaCO_3$ addition wt%.

4. CONCLUSION

The Seyitömer fly ash (without additive) bloats completely when sintered at 1150 ^{0}C due to the thermal decomposition of anhydrite. $BaCO_3$ additions at levels of 5 and 10 wt% into the fly ash inhibits the bloating and the swelling as a result of phase transformation from anhydrite ($CaSO_4$) to barite ($BaSO_4$) during sintering and this behavior is supported by XRD analysis and photographs. $BaCO_3$ addition had a significant positive effect on the sintering of the fly ash at 1150 ^{0}C, whereas it indicates a negative effect on the sintering at 1100 ^{0}C. The all fly ashes without and with $BaCO_3$ addition sintered at 1200 ^{0}C are totally bloated due to decomposition of metal sulfates ($CaSO_4$ and $BaSO_4$), and melted at this temperature. Both bloating and swelling problems of the fired ceramic products made from the 100 % fly ashes including anhydrite, fired at about 1150 ^{0}C, may be solved by $BaCO_3$ addition. Moreover, the reasonable physico-mechanical properties have been obtained from the sample containing 10 wt% $BaCO_3$ and sintered at 1150 ^{0}C suggesting the Seyitömer fly ash with the aid of $BaCO_3$ could be utilized as a possible raw material to produce fired ceramic materials.

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