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The Effects of Pyrite Ash on the Compressive Strength Properties of Briquettes

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Abstract

The aim of this study is to investigate the utilization of Pyrite Ash (PA) in the production of briquettes as a replacement of clay or soil. To achieve this, first, the characterization of the materials used (clayey soil and pyrite ash) was made using Fourier Transform Infrared Spectroscopy (FTIR/ATR). Particle size distribution and microstructure elemental analyses of these materials were also obtained using a particle size analyzer (Mastersizer) and a Scanning Electron Microscope (SEM). Following the characterization of the materials, the samples of briquettes made with or without addition of PA were prepared and sintered at 950 and 1000ºC in the furnace. The PA replacement ratios with clayey soil were 0, 5, 10, 20% in mass basis (w/w). Compressive strength and bulk densities of briquettes produced were measured and the results were presented. Compressive strength results of the briquette samples indicated that pyrite ash containing briquettes with 35 MPa compressive strength, which was higher than the requirements of Turkish Standard Specification (TS EN 771-1), can be obtained. It is also recorded that for each mixture, compressive strength values obtained at 1000ºC were higher than that of obtained at 950ºC. XRD analyze was performed on sintered briquette sample made with 10% PA which have the highest compressive strength value. The XRD results showed that peaks are Quartz (SiO_2), Hematite (Fe_2O_3), Ortoclase ($KAlSi_3O_8$), Albite ($Na(AlSi_3O_8)$), Anorthite ($CaAl_2Si_2O_8$) and Gehlenite ($2CaO.Al_2O_3.SiO_2$).

Keywords: *pyrite ash, SEM, XRD, compressive strength and briquette*

1. Introduction

In order to contribute the solution or discarding and coping with the environmental pollution that is a great problem in current era, the utilization and management of waste materials in construction industry is a common way.

For this purpose, in this study, PA waste material was considered, and a research was carried out whether PA could be evaluated in manufacturing of construction briquettes. PA is a waste material that is obtained from Sulphuric acid production; details of PA were presented in materials section. Although, there are studies about firing and sintering process with waste materials such as silica fume, fly ash, waste brick, phosphogypsume, slag, recycled glass and borax in producing brick (Baspinar, 2009; Lingling, 2005; Tütünlü and Atalay, 2001; Demir and Orhan, 2003; Abalı *et al*., 2007; Shih, 2004; Vieira, 2006; Loryuenyong, 2009; Kavas, 2006; Uslu, 1996; Uslu and Arol, 2004), the published works on utilization of PA are scant (Pişkin *et al*., 2008; Tuğrul *et al*., 2003; Celik *et al*., 2007). In this work, firing method was chosen since PA contains high ratio of Fe element. These Fe melt at high temperature and make additional bound in the briquettes. In addition to these properties it increases liquid phase.

The aim of this study is to investigate the utilization of pyrite ash as industrial waste in preparation of briquettes and hence to contribute in producing a green construction materials. This is achieved by measuring and examining the compressive strength, bulk density and XRD properties of briquettes made with addition of PA. The chemical and morphological properties, and mineralogy of raw materials used were also investigated. This material can be utilized in not only a variety of fired brick production but also tile, interlocking paving stone, stone roads kerb or channel element production.

2. Materials and Methods

2.1 Raw Materials

The materials used in this work were Soil (S) and Pyrite Ash (PA) supplied from a brick factory and Etibor Sulphuric acid Factory in Turkey, respectively.

2.2 Characterization of Materials

2.2.1 Soil (S)

The following experiments (FTIR/ATR and particle size and DTA-TG) were carried out in order to characterize the soil. Chemical compositions of soil were given in Table 1. SiO_2 component of soil was 58.36%. The Mastersizer-x technique was used for measuring the particle size distribution. Particle size

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Table 1. The Chemical Composition (%w/w) of the Materials Used

Constituents (%)	S	PA
SiO_2	58.36	5.87
Al_2O_3	22.17	2.49
Fe_2O_3	7.09	85.3
CaO	2.61	0.11
MgO	2.46	0.52
K_2O	2.27	0.04
Na_2O	0.71	-
SO_3	0.34	1.15
Loss of ignition	3.35	2.84
Free CaO	0.01	-
Cl^-	-	0.0163

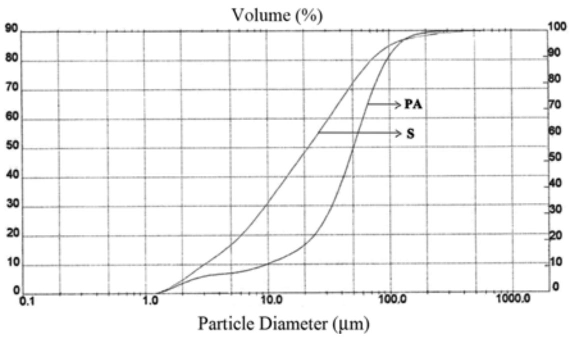

Fig. 1. Particle Size Analysis of Materials Used

analyze of S was presented in Fig. 1. Granulametric data for the size fractions of S showed that the $d_{(90)}$ and $d_{(50)}$ values were 73.41 and 17.44 µm respectively.

Infrared spectroscopy of the powdered S sample was run using Perkin-Elmer Spectrum 1. FTIR/ATR results are shown in Fig. 2. The sample was scanned 25 times in the region of 4000 to 600 cm^{-1}. As a result two characteristic bands centred at around 1000 and 800 cm^{-1} have been identified. These bands are due to (Si-O-Si or Si-O-H) asymmetric stretching vibration (C-O) highly conjugated at 1632 cm^{-1}. The sharp peak at 1427 cm^{-1} indicates the presence of CH group in carbohydrates. In addition to these bands at 3399 cm^{-1} corresponding to non-hydrogen bonded (N-H). The last peak at 3622 cm^{-1} is due to O-H stretching.

After the FTIR/ATR analyze, DTA-TG analyze was carried out on soil sample (Fig. 3). To obtain thermal behaviour of S,

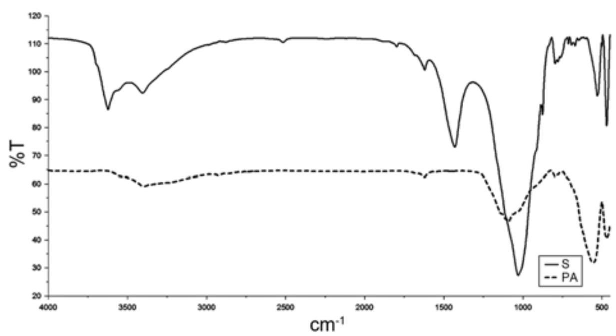

Fig. 2. FTIR/ATR Analyze Results of Materials Used

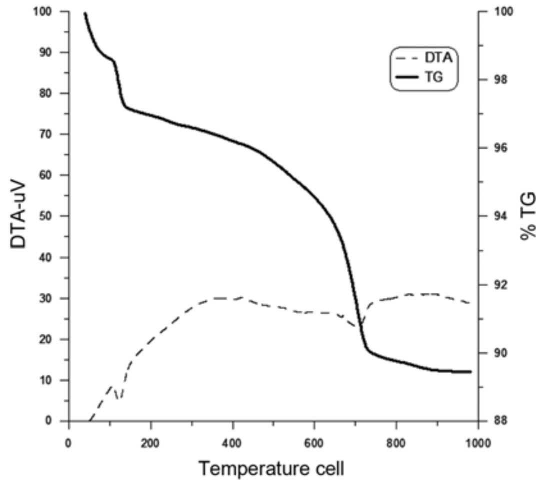

Fig. 3. DTA-TG Analyze Results of S

DTA-TG analyses were carried out between 25-1000ºC in air atmosphere, at a rate of 10 ºC/min. It was found that there was 10.5% weight loss in total.

100-200ºC range shows that the dehydration of the water, 300-500ºC range shows exothermic effects due to the combustion of the organic matter, phase transformation of quartz at 570ºC is detected, endothermic peak at 720ºC corresponds to decomposition of calcite, exothermic peak around 900ºC shows that new minerals occurred (Biçerler, 2008).

SEM photo (X500) of the soil sample to observe microstructure was taken and shown in Fig 4. There is mainly one phase on the matrix; it is related to chemical composition of soil.

2.2.2 Pyrite Ash (PA)

Pyrite ash used in the experiments was supplied by Eti Holding Bandirma Sulfuric Acid Plant in Turkey. It is formed as an industrial waste from pyrite ore is used for sulphuric acid production. Pyrite ore treated with flotation process and pyrite concentrate was obtained. The concentrate contains 41.44 pyrite in % w/w is roasted in fluid bed at 700ºC. Therefore 122.845 tones waste pyrite ash is manufactured annually. The reactions are exothermic and they are occurred in two steps by using oxygen.

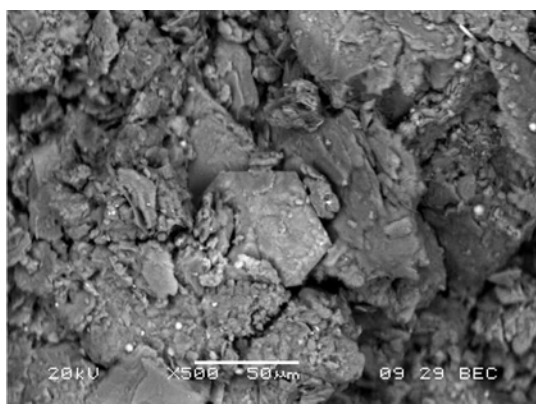

Fig. 4. SEM Micrograph of S

$$4FeS_2 \rightarrow 4FeS + 2S_2 \quad (1)$$
$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2 \quad (2)$$

It can be seen in the second reaction, after the roasting of pyrite, Fe_2O_3 occurs. This waste has very fine particles and, named pyrite ash. SO_2 gases reveals at the end of the reactions and it uses for H_2SO_4 production (EAR, 2009). Forming of pyrite ash and H_2SO_4 production are presented in Fig. 5.

Chemical properties of PA were given in Table 1. Particle size analyze of PA was presented in Fig. 1. Granulametric data for the size fractions of S showed that the $d_{(90)}$ and $d_{(50)}$ values were 99.17 and 46.06 µm respectively. Comparison of particle size between soil and pyrite ash showed that PA has coarser particle size than S (see Fig. 1).

FTIR analyze of PA was shown in Fig. 2. In a study, three spectral domains of interest are exploited : iron environment (oxides, hydroxides and oxyhydroxides) at 400-900 cm^{-1} whereas information concerning sulfur species is at 1000-1200 cm^{-1} (except for the pyrite S-S vibration located at 415 cm^{-1}), sulphite ions (SO_3^{2-}) at 632cm^{-1}. OH stretching is defined at 2500-4000 cm^{-1} (Decostes *et al*., 2002).

In order to obtain thermal behaviour of soil DTA-TG analysis was applied to PA. Thermal behaviour of PA is illustrated by DTA-TG curves in Fig. 6. They were carried out between 25-1000ºC in air atmosphere and at a rate of 10 ºC/min. It was found that there was 5.7% weight loss in total. In a study about pyrite cinders characterization was decelerated that several areas of mass change can be differentiated in their turn: up to 300-400ºC separation of moisture and sulphates degradation; 400-500ºC small increase in mass, corresponding to the oxidation of Fe_3O_4 to Fe_2O_3; 500-700ºC significant mass losses, resulting probably from decomposition of iron sulfides and SO_2 release; 700-1100ºC mass stabilization (Shoumkova and Stoyanova, 2010).

XRD analyze of pyrite ash was shown in Fig. 7. Mean peaks are Hematite (Fe_2O_3) and Magnetite (Fe3O_4).

In order to observe microstructure of the PA samples, SEM micrograph (×500) analyze was applied to the PA sample and the result was presented in Fig. 8. It can be said that there are mainly

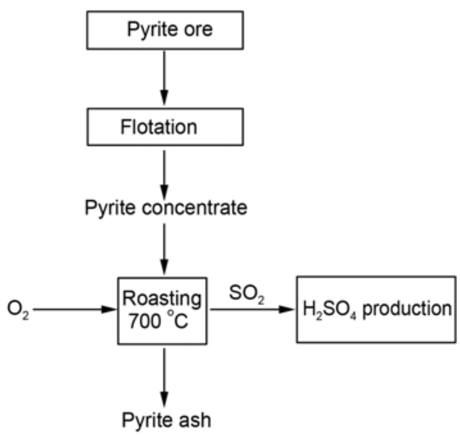

Fig. 5. Formation of Pyrite Ash and H_2SO_4 Production (Canbazoğlu visited time: 06.06.2011)

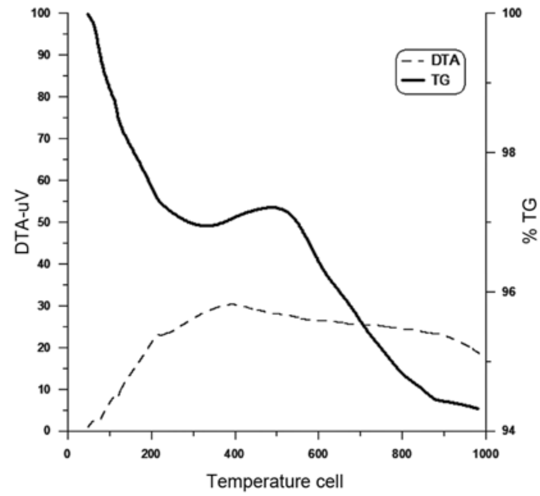

Fig. 6. DTA-TG Analyze Results of PA

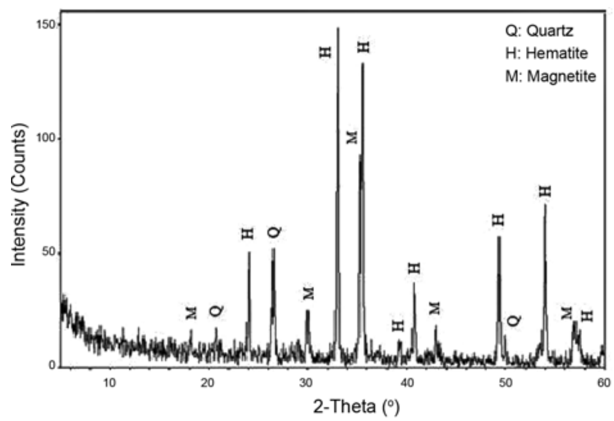

Fig. 7. XRD Analyze Result of PA

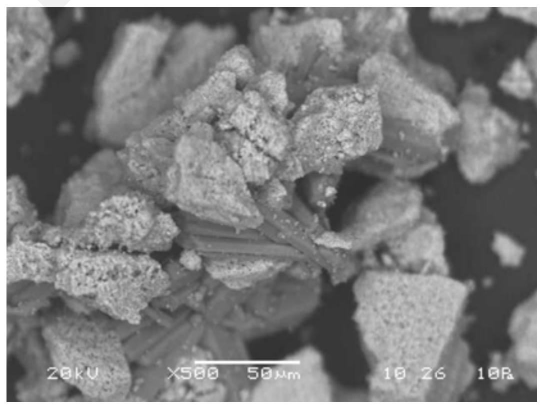

Fig. 8. SEM Micrograph of PA

two phases. Porous matrix defines Hematite (Fe_2O_3) and Magnetite (Fe_3O_4), bar shapes present FeS and FeS_2.

2.3 Preparation and Testing of Briquettes

Control mixture made with only soil and water were prepared. Control mixture was modified by replacing 5, 10 and 20% of PA as a replacement of soil in mass basis. In the preparation of mixtures, soil and PA were used. They were dried at 105ºC for 1 hour in a laboratory drying oven. There was no chemical additive, other than water, used in the mixtures.

Dry powder materials used in briquette production were treated with 6% water to obtain proper workability and casting with enough plasticity. They were blended using an Manual Mortar Mixer (ELE Automatic) to prepare the mixtures at 20ºC during 15 minutes and paddle speed of the mixer was 285 (rpm) ± 10. At the end of the mixing procedure, cylindrical briquette samples were made using stainless steel mould. The samples with 3.5 cm diameter and 3.5 cm height were produced at 19.6 MPa pressure. The samples de-molded and were pre-dried in the drying oven at 105ºC for 1 hour. Then, they were sintered at 950 and 1000ºC in a laboratory sintering furnace. After the furnace had reached the required temperature, the briquettes were removed from the oven. After cooling down the samples, bulk density and compressive strength measurement were carried out complying with relevant standard (TS EN 771-1).

3. Results and Discussion

3.1 Bulk Density of Briquettes

The dimensions of cylindrical specimens were measured using a caliper accurate to 0.1 mm and, the volume of each sample was calculated using cylinder volume formula. Measuring weight of each briquette sample enabled the calculation of bulk densities presented in Table 2. Bulk density measurements were carried out before and after sintering process. An obvious decrease was observed in bulk density of samples before and after sintering process due to the evaporation of mixing water. However, the decrease in bulk density at 1000ºC sintering temperature was higher than that of samples sintered at 950ºC.

Decrease in bulk density of Mix No 1 briquette sintered at 950ºC is 10.39% whereas it is 12.11% for 1000ºC temperature sintering. When PA ratio increases in the mixture, there is a regular decrease in bulk density which was observed for both sintering temperature.

3.2 Compressive Strength Values of Briquettes

After sintering process of the briquette mixtures, compressive strength tests were performed on the samples complying with the relevant Turkish Standard (TS EN 771-1). The results were presented in Table 3. Compressive strengths of the samples containing PA mixture were varied between 11 and 17.5 MPa for 950ºC sintering temperature, while control mixture had 20.9 MPa compressive strength. Similarly, compressive strengths of PA containing samples were varied between 21 and 35 MPa for 1000ºC sintering temperature, while control mixture had 38.3 MPa compressive strength.

Table 2. Effect of Sintering on the Bulk Densities of the Briquettes

Mix no	Bulk densities (g/cm^3)		Decrease (950ºC) %	Bulk densities (g/cm^3)		Decrease (1000ºC) %
	Before sintering	After sintering		Before sintering	After sintering	
1	2.242	2.009	10.39	2.287	2.010	12.11
2	2.242	2.002	10.71	2.324	2.007	13.64
3	2.211	1.983	10.31	2.191	1.906	13.01
4	2.173	1.971	9.30	2.176	1.901	12.64

Table 3. Mixture Ratio and Compressive Strength Results of the Briquettes Produced by the Mixtures

Mixture No	Mixture Ratios w/w %	Compressive strength (MPa)	
		950ºC	1000ºC
1	100% S	20.9	38.3
2	95% S + 5% PA	16.5	29.0
3	90% S + 10% PA	17.5	34.9
4	80% S + 20% PA	11.0	21.3

Strength of the samples decreased by PA addition at 950ºC and fluctuate at 1000ºC. This was because the samples sintered at 1000ºC and had much more glassy phase than that of the bricks sintered at 950ºC. The diminution of the amount of iron oxide phases above 950ºC would explain that recrystallization of the silicate matrix has begun, as iron is quite soluble in the crystalline products such as anorthite and spinel .This products causes to improve compressive strength (Chevalier, 1976).

Compressive strength obtained from all PA containing sample was within acceptable limits (9.8-23.54 MPa) of the relevant standard (TS EN 771-1), however, PA replacement with soil reduced compressive strength of sample for constant sintering temperature. The highest compressive strength value for PA containing mixture was obtained from mixture 3 made with 10% PA replacement for both sintering process. Therefore, 10% replacement of PA with soil can be concluded as an optimum ratio for producing briquettes.

3.3 XRD Results

So as to obtain mineralogical analysis of the briquette produced using PA at 10%, XRD analysis were performed with Rigaku model D/Max-2200 X Ray Powder Diffractometer. XRD results are presented in Fig. 9. The experimental results of XRD analyze of sample indicate that main mineral is Quartz (SiO_2), the others are: Hematite (Fe_2O_3), Ortoclase ($KAlSi_3O_8$), Albite ($Na(AlSi_3O_8)$), Anorthite ($CaAl_2Si_2O_8$) and Gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$).

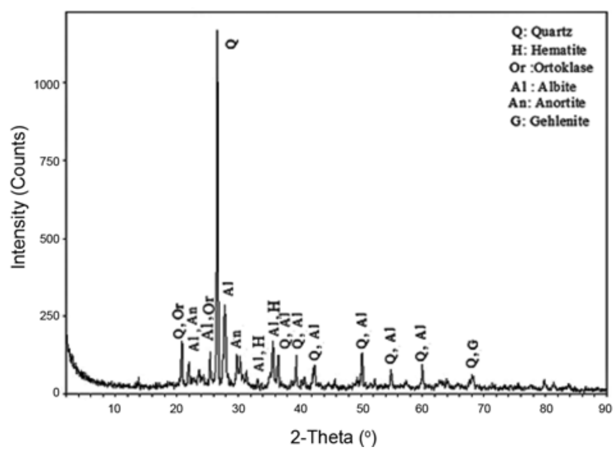

Fig. 9. XRD Analyze of Briquette with PA %10

4. Conclusions

The following conclusions can be drawn from the experimental results. Briquette which contain 10% PA and sintered at 1000ºC, developed 35 MPa compressive strength which complies with the requirements of relevant standard. Therefore, based on compressive strength results, it was concluded that utilization and management of waste PA in the production of briquettes as a construction materials seemed to be possible.

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