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The Effects of Addition Two Different Types of Trass to the Clinkering Reaction

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ABSTRACT

In this study, instead of clay the effect of trass - which is used as a component for clinker production in the cement industry and has properties that are significant for agriculture - are researched. The clinkering properties of raw material compositions which are prepared according to the constant Lime Saturation Factor (LSF) degree were considered in relation to sintering at fixed temperature (1450 ºC). Two different clinkers - namely trass 1 which is added to clinker 1 and trass 2 which is added to clinker 2 - were produced from the raw material compositions prepared at a constant LSF. The clinkering reaction was determined by the measurement of the free CaO (FCaO) value. According to the FCaO content and the amount of C3S test results, clinker 1 is preferable to clinker 2. Because of the C3S phases are 70,43 % and 42,72 % respectively.

Key Words: *Clinker, surface properties, Trass.*

1. INTRODUCTION

Cement is the most produced and commonly used binding material in the world with of annual production of 1.6 billion tons [1]. The use of high energy in production causes high levels of emissions due to the nature of the process and the raw materials. The cement industry is responsible for 7 % of total CO_2 emission [2-3]. Thus, the cement industry plays a crucial role in global warming. CO_2 is emitted from the thermal treatment of limestone and from the combustion of fuels in the kiln as well as from power generation.

The clinker of Portland's cement production is conventionally made by sintering a mixture of limestone and clay - or other materials of a similar bulk, composition and with a sufficient reactivity - to a temperature of about 1450 °C. The next step in the production of a blended composite cement process is the finish grinding of clinker and a small amount of gypsum

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(3–4%) together with at least two other components so as to produce a composite blended cement powder to meet the specific surface area and strength requirements.

Use of natural pozzolans - also known as ‘‘trass’’- in cements or concrete systems have an important effect on several of the properties of cement mortar and cement clinker, such as their strength, their setting time, their soundness, the amount of C_3S and their durability, depending on their substitution ratio and its fineness [4-10]. In addition, since these materials enter cement production after the kiln process they also provide important economical and ecological benefits [11-12].

Turkey is rich in natural pozzolans. Almost 155,000 km^2 of the country is covered by Tertiary- and Quaternary-age volcanic rocks, among which tuffs occupy important volumes. Although there have been many geological investigations of these volcanic, their potential as a natural pozzolan is not well-established [13].

In this study, the effect of trass usage in place of clay (which is used as a component for clinker production in the cement industry) and its properties are researched. The surface properties of the raw materials used for clinker production - like limestone, clay and two different trasses - were determined. Trass can be used to produce cement clinker production as an alternative to the cement clinker of raw materials. It is expected that, with the data collected through the application of analytical techniques and the standard characterisation tests performed in this study, the aims of the research on clinkers will be characterised with mineralogical and microstructural analysis (XRD and SEM). The clinkering reaction was determined by the measurement of a free CaO value. Therefore, in terms of the C_3S value in clinkers C1 and C2, two different additions of trass have an effect on clinkering as the result of the sintering of the clinker of raw materials that are prepared at a constant LSF at a fixed temperature.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The raw materials used in this study were: limestone, clay and trass (1 and 2). The chemical compositions of all the materials are given in Table 1. Limestone, trass 1 and trass 2 were supplied by Çimsa Cement Plant (Eskişehir, Turkey) and the clay was provided by the Ceramic Factory (Kütahya, Turkey).

In addition, Merck was preferred for the solutions HCl and NaOH so as to reach the desired pH value during the Zeta potential measurements in the experiments.

Table 1. Physical properties of the raw materials (wt%).

Materials	Particle size distribution (on sieve), %			Blaine, *(m^2/g)*	Specific Gravity, *(g/cm^3)*
	> 45µm	> 90 µm	>200 µm		
Limestone	22.5	5.0		4.01	2.70
Clay	2.1	1.5	-	23.30	2.62
Trass 1	25.5	5.9	-	41.97	2.60
Trass 2	23.2	5.0	-	26.85	2.30

2.2. Method

The experiments performed on the raw materials are physical, chemical, mineralogical and electrokinetic analyses.

The physical properties of the raw materials were defined according to TS EN 196-6 [15]. The specific gravity of the raw material samples was measured with the air comparison Picnometer (Beckman 930 model) and their specific surface area (Blaine) values were measured with the Blaine instrument. As for the over sieve values, the Alpine Air Jet Sieves (A 200 LS) with sieve values of 45, 90 and 200 µm were used to measure the samples. The results obtained are given in Table 1.

In the electrokinetic analyses, the Zeta-meter 3.0 device was used. For the Zeta potential experiments, and at a stage when the consistency was right, pH measurements were performed with of the Inolab pH Meter device.

In order to determine the electrokinetic features of the samples, the particle size of the samples was reduced to -45 µm with a ring mill and to +10 µm with a ball mill. For measuring the Zeta potential, each sample was weighed to 0.5 g and mixed in a magnetic mixer containing 50 mL of distilled water. Their pH values were determined with the HCl and NaOH solutions. While mixing, the heat of the mixture was kept at 25 ± 2^oC and the suspension pH was kept between 7 and 12. The movement rates of 20 particles were calculated at each pH value according to the Smoluchowski equation and transformed into ζ potential values.

In order to determine the mineral structure of the raw materials and produced clinkers, XRD analysis was conducted by using Cu Kα (λ= 1,54056 A^o) radiation on a Rikagu Miniflex brand ZD 13113 series X-ray diffractometer (Figure 1). The microstructure of sintered samples was determined by means of a ZEISS EVO 50 Vp variable pressure Analytic FESEM (Figure 4).

3. EVALUATION OF THE EXPERIMENTAL STUDIES

Physical Analyses: In looking at the results of the physical experiments (Table 1), limestone is milled more difficultly than the other materials and takes different values with regard to the Blaine values and the specific gravity.

Chemical Analyses: The chemical analyses of raw materials were performed according to Table 2. The chemical structure is in accord with the values given in EN 196-2 [16]. In terms of the Lots of Ignition (LOI), trasses 1 and 2 have less LOI than either clay or limestone.

Mineralogical Analyses: The natural pozzolans which are used in the cement industry generally contain pyroclastic rocks. These rocks generally contain carbonate, clay and the zeolite group of minerals as filling/binding materials. Trass samples containing the zeolite group minerals were found in volcanic tuff [14]. The mineralogical structure of the raw materials was determined with XRD (Figure 1).

Table 2. Chemical analysis of the raw materials (%).

% Compounds	*Limestone*	*Clay*	*Trass 1*	*Trass 2*
SiO_2	4.22	35.14	68.32	69.29
Al_2O_3	1.10	9.13	12.86	12.82
Fe_2O_3	0.55	4.84	2.07	2.12
CaO	50.80	25.01	2.33	2.71
MgO	0.85	1.36	1.51	0.73
P_2O_5	0.01	0.11	0.06	0.06
K_2O	0.14	0.89	3.33	2.81
Na_2O	0.22	0.23	1.59	1.62
SO_3	0.03	0.08	0.07	0.08
LOI	41.50	22.24	7.50	7.35
Total	99.42	99.03	99.64	99.59

The pattern of the XRD which can be seen in Figure 1 shows that the major minerals of trass 1 and trass 2 are quartz, zeolite and anorthite. With the exception of limestone, the most common mineral in all materials - quartz - has different proportions. This can also be deduced from the differences between SiO_2, CaO and Al_2O_3 (Table 2). The other minerals are clinoptilolite, dolomite and anorthite, which were formed - basically - by K, Na and Ca's being taken by aluminium silicates as cation.

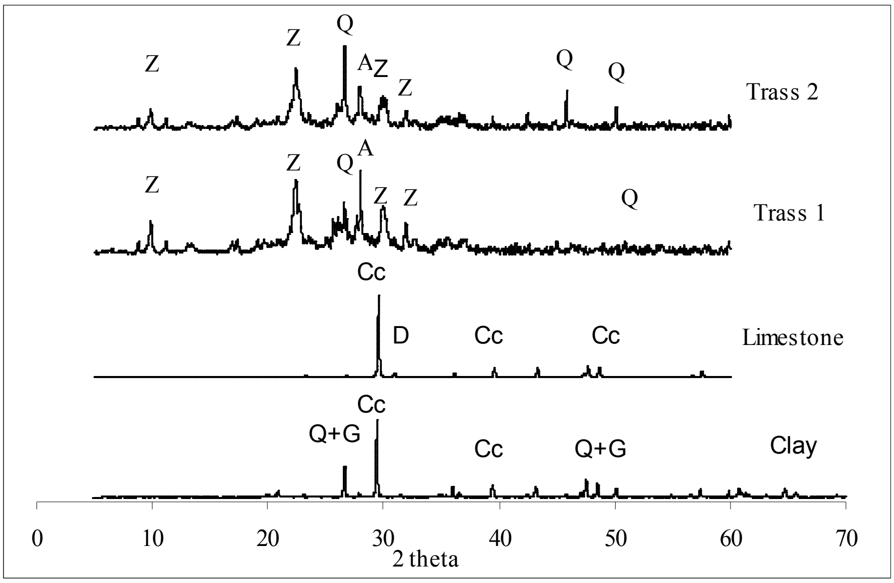


Figure 1. XRD analysis of the raw materials limestone, clay, trass 1 and trass 2.

Q: Quartz (SiO_2),G:Gismondine ($CaAl_2SiO_84H_2O$), A: Anorthite ($CaAl_2Si_2O_8$), Cc: calcite ($CaCO_3$), Z: Clinoptilolite ($KNa_2Ca_2(SiO_29A_{l7})O_{72}24H_2O$), D: Dolomite ($CaCO_3MgCO_3$).

Electrokinetic Analyses: The results of the experiment (Figure 2) showed that while limestone and trass 2 got -ζ degrees depending on the proton (H^+) transfer from water (which is at the same pH values as the surface particles), clay and trass 1 had +ζ values. This was because the SO_3^- ions in the content of limestone covered the surface of the particles, and the limestone particles were negatively charged. Besides, as the pH value turns alkaline, the zeta potential value gets closer to positive values, depending on the dissolution of SO_3. This tendency also shows that the surface charge structure has changed. The change in the charge structure explains why the crystalline structural framework of limestone deteriorates at a high pH value.

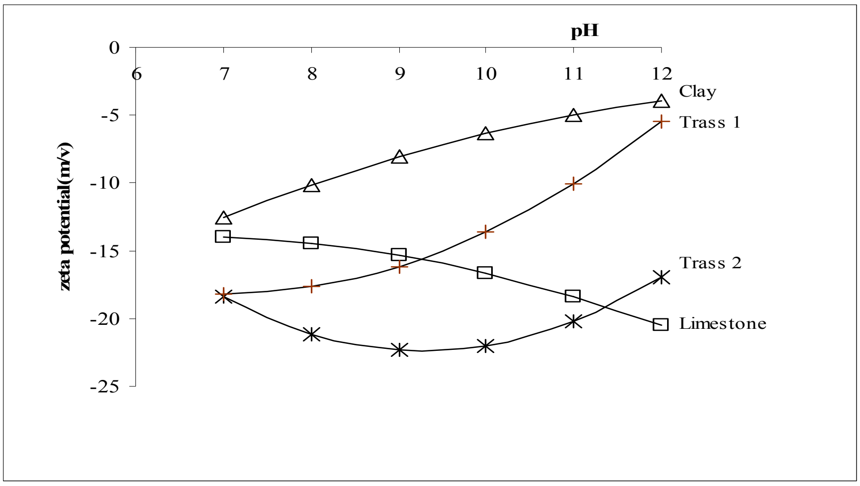


Figure 2. The change of the zeta potential depending on the pH value of limestone, clay and trasses 1 and 2.

For clay and trass 1 - which are crystalline raw materials - because the pH value of the medium turns alkaline their crystalline frameworks deteriorated depending on the increase in hydroxyl (OH^-) ions within the medium, and with the increase in the negative charges on their surfaces their zeta potential values turns negative.

According to the mineralogical analyses, clay is composed of quartz and calcite. Therefore the zeta potential values of clay and limestone have parallel results. Trass 1 consists of anorthite clinoptilolite. The surface charge of these minerals caused an increase in the pH of trass 1 while the ζ potential of raw materials close to each other those materials pushing each other electrically. So those materials have powerfull impulse. Because of this impulsion, the limestone pulls the trass 1 strongly and pushes the clay. Thus, limestone and clay particles coming together of particles with trass 1 is easier.

Preparation of Clinker Samples: Two samples of clinker raw materials (Farine) were synthesised by mixing the Portland cement raw materials with trasses 1 and 2 in appropriate proportions. Both of them were compared with each other according to their clinkering reaction, as either mineralogical or FCaO. So two type of clinker were prepared using two different trasses including clay materials. Farine compositions are shown by Table 3. The scale grain size process was carried out in a two-stage laboratory type ball mill of 5 kg with a raw mix capacity. The materials were crushed to a maximum size of 16 mm by a jaw crusher before feeding into the mill.

Table 3. The raw material mix percentage of the samples.

Raw Materials	*Farine 1*	*Farine 2*
Clay %	82	82
Limestone %	1	1
Trass 1 %	17	-
Trass 2 %	-	17

All the mixtures were homogenised in a laboratory ball mill and their homogenisation was examined by determining the loss of ignition at 1100 °C. After the homogenisation process, the residue at 90 μm of all the mixtures was the same (approximately 7%). The applied clinkering process was common in all off the mixtures.

The cement raw materials were firstly dried at 110 °C for one day. Then, they were placed in an electrical furnace at 1450 °C for 1 h. The samples were rapidly cooled in air. The effect on the combustibility was evaluated on the basis of the content of lime which had not reacted (free lime, FCaO) in the samples sintered at the above temperatures. Free lime was determined according to the standard ethylene glycol method (ASTM C 114-03).

The clinkers that were produced (sintered at 1450 °C) were studied by means of mineralogical analysis so as to ensure the completeness of burning by using a Miniflex X-ray diffractometer with cobalt-filtered CuKα=1.5405 Å. All the patterns were obtained within a scanning range between 5° and 65° in a 2θ scale. The scanning rate that was applied at 2°min-1 for all the samples.

They were milled in a steel mill submicron of 45 micron. Equal quantities of each clinker were milled at equal times in order to make the characterisation. The milling time was selected in order that the specific surface area might remain within the range used in the clinker.

Analysis of the Clinkers by XRF: The two different farine compositions were sintered at 1450 ^{o}C and two different clinkers were obtained from those farine compositions. The farine compositions and clinker samples XRF results are shown by Table 4.

Table 4. The chemical analysis of the farine and clinker samples.

% Composition	*Farine 1*	*Farine 2*	*Clinker 1*	*Clinker 2*
SiO_2	20,52	20,85	27,08	26,41
Al_2O_3	6,30	6,06	0,84	1,09
Fe_2O_3	2,54	2,38	0,65	0,72
CaO	38,01	37,81	69,68	67,78
MgO	1,21	1,11	1,51	2,20
K_2O	1,50	1,33	0,36	0,39
Na_2O	0,24	0,34	0,00	1,31
SO_3	0,07	0,07	0,07	0,07
LOI (Loss of Ignition)	30,02	29,66	0,05	0,16
Total	100,54	99,73	100,19	99,97
LSF	101,1	101,0	90,22	89,54
SiM	1,95	2,07	18,17	14,59
AlM	2,39	2,62	1,29	1,51

Mineralogical Analysis of the Clinkers Produced: Figure 3 shows the XRD analyses of the produced clinkers (sintered at 1450 °C). It should be noted that the main mineralogical phases - C_3S, C_2S, C_3A and C_4AF - are present in all clinkers. In addition, the clinker obtained from trasses 1 and 2 also shows the different peaks of FCaO where the FCaO content for clinker 2 was also higher than that of clinker 1 (Table 5).

Table 5. Calculated using the formula percentage of the clinker mineral phases and the % of the amount of Free CaO (1450 °C and 2 h) that had not reacted.

Component	*Clinker 1*	*Clinker 2*
C_3S	70.43	42.72
C_2S	25.90	53.01
C_3A	2.30	2.40
C_4AF	-	-
% Free CaO	0.30	0.22

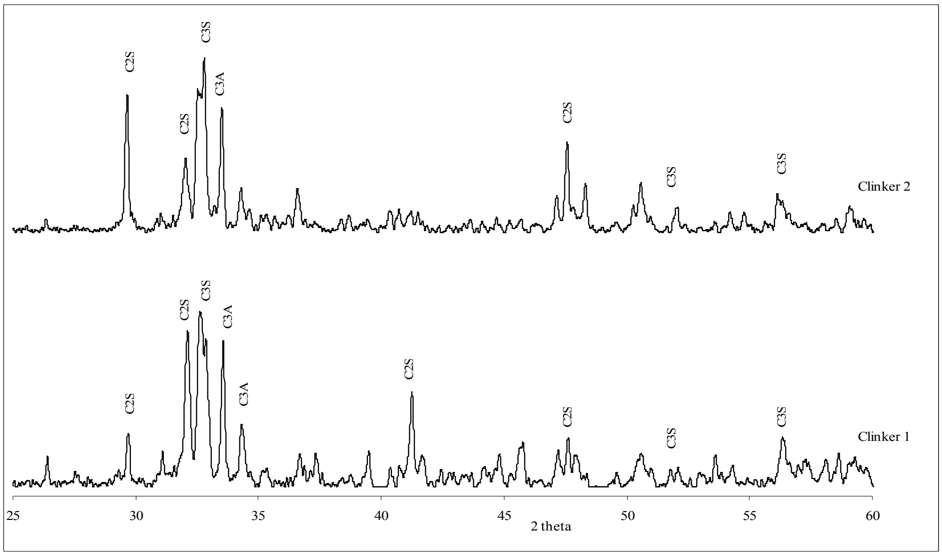


Figure 3. The XRD analysis of clinker 1 and clinker 2.

C_3S-Trikalsiyum silikat 3CaO.SiO_2**, C_2S-**Dikalsiyum silikat 2CaO.SiO_2, **C_3A-**Trikalsiyum alüminat (3CaO.Al_2O_3), **C_4AF-**Tetracalcium alumina ferrit (4CaO. Al_2O_3.Fe_2O_3).

Based on the chemical compositions of the Portland cement raw meal - clinker 1 and clinker 2 (Table 5) - and given the aim to produce clinkers with a constant LSF at the same order and with reference to the raw materials, the required mix proportions were determined. Table 3 presents the syntheses of the cement raw materials used in this paper.

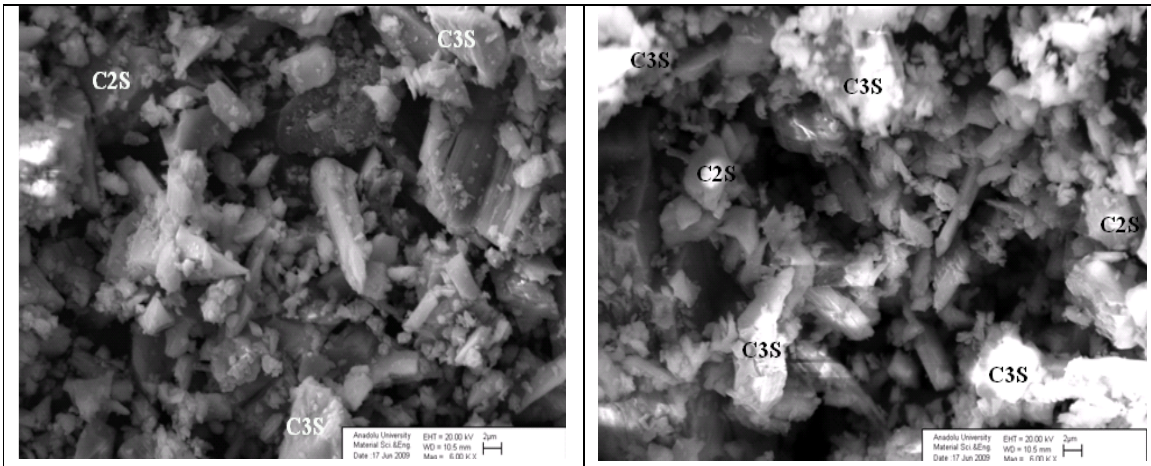
The reactivity of the cement raw materials was evaluated on the basis of the free lime (FCaO) contents after sintering at 1450 °C, which are shown by Table 4.

When the mineralogical structures of the clinkers were calculated according to the Bogue formula, clinker 2 had more C_3S phase than clinker 1. Because of the electrokinetic properties in trass 1, clinker 1 showed itself as more affected than clinker 2 (Figure 2). Figure 4 shows the micro-structure of sintered 1450 °C clinkers. Table 6 gives us these clinkers' average elemental analysis obtained by EDX.

Table 6. EDX analysis of the SEM images.

%Weight	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*CaO*	*MgO*
Clinker 1	27.48	0.87	-	70.04	1.60
Clinker 2	27.48	0.94	-	67.38	2.04

The results of the microstructures for clinker 1 and clinker 2 showed that the XRD results and the results of the calculated Bogue formulas supported each other. The microstructure of the clinkers has wide and square, with round-shaped alite crystals. The addition of Trass for the clinker 1 and clinker 2, the formation of long rod-shaped unbarbered C3S was seen (Figure 4). According to the results of the EDX analysis of clinker 1 and clinker 2, the clinker surface is largely composed of CaO and SiO_2 oxides (Table 6).



Clinker 1	Clinker 2

Figure 4. Clinker 1 and clinker 2 microstructure images.

4. CONCLUSIONS AND RECOMMENDATIONS

- Clay, limestone, trass 1 and trass 2 raw materials have different chemical components. CaO, SiO_2 and Al_2O_3 compounds are the main components of these raw materials.
- Clay, limestone and trass 1's materials' physical properties are affected by their chemical properties and structural shapes. Clay is easier to grind and has a finer grain size than trass 1 and limestone, and therefore clay has OH^{-1} in the structure. The specific surface areas of the raw materials are influenced by the structure of the zeolitic minerals for trass 1. Because clay has layered structure.
- The mineralogical composition, chemical composition and crystalline structure of the raw materials are developed. The mineralogical structure has a linear relationship with grindability. Quartz, calcite and zeolite reduce grindability.
- Electrokinetic analysis indicate a linear relationship between the chemical, physical and mineralogical structures. While the SiO_2 and Al_2O_3 bonds, which exist in the natural structure of clay and trass, increase the negativity of ζ potential values, the zeolitic and CO_3^{-2} groups decrease ζ potential values.
- There is a potential to use the trass component instead of the clay material in clinker production. However, more intensive study on this subject is needed.
- The amount of C_3S in clinker 2 reduces FCaO because of the the amount of trass.
- For clinker production using trass as an alternative to clay is important for world cement sector. Because it is economic benefits for the agricultural sector.

REFERENCES

[1] Worrell, E., Martin, N., Price, L., "Potentials for energy efficiency improvement in the US cement industry", ***Energy 2000***, 25: 1189(2000).

[2] Mehta, P.K., "Greening of the concrete industry for sustainable development", ***Concrete International 2002***, 24-23(2002).

[3] Aída, Z., Pedro, B., "Low temperature preparation of belitic cement clinker", ***Journal of the European Ceramic Society***, 29: 1879–1885(2009).

[4] Uzal, B., Turanlı, L., "Studies on blended cement containing a high volume of natural pozzolans", ***Cement and Concrete Research***, 33:1777–81(2003).

[5] Rodriguez-Camacho, R.E., Uribe-Afif, R., "Importance of using natural pozzolans on concrete durability", ***Cement and Concrete Research***, 32: 1851–1858 (2002).

[6] Colak, A., "The long-term durability performance of gypsum – Portland cement – natural pozzolan blends", ***Cement and Concrete Research***, 32: 109–115(2002).

[7] Vu, D., Stroeven, P., Bui, V., "Strength and durability aspects of calsined caolin-blended Portland cement mortar and concrete", ***Cement and Concrete Composition***, 23: 471–478 (2001).

[8] Cavdar, A., Yetgin, S., "Tane inceliğinin traslı çimento özelliklerine etkisi", In: Ergin A, Özdemir G, editors, ***Türkiye Inşaat Mühendisliği XVII. Teknik Kongresi***, Istanbul, 451–454(2004).

[9] Yetgin, S., Cavdar, A., "Tras Oranı Değisiminin Traslı Çimentonun Bazı Özelliklerine Etkisi", In: Özturan Tet al., editors, ***Advances in Civil Engineering 2004 6th International Conference***., Istanbul, 1084–1092(2004).

[10] Canpolat, F., Yılmaz, K., Köse, M., Sumer, M., Yurdusev, M., "Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production", ***Cement and Concrete***, 2324-2325(2003).

[11] Shannag, M., "High strength concrete containing natural pozzolan and silica fume", ***Cement and Concrete Composition***, 22: 399–406(2000).

[12] Turanlı, L., Uzal, B, Bektas, F., "Effect of large amounts of natural pozzolan addition on properties of blended cements", ***Cement and Concrete Research***, 35(6):1106–1111(2005).

[13] Türkmenoğlu, A.G., Tanku, A., "Use of tuffs from central Turkey as admixture in pozzolanic cements assessment of their petrographical properties", ***Cement and Concrete***, 629–637(2002).

[14] Cavdar, A., Yetgin, S., "Availability of tuffs from northeast of Turkey as natural pozzolan on cement", ***Construction and Building Materials***, 21:2066–2071(2007).

[15]TS EN 196-6, "Methods of testing cement-Part 6: Determination of fineness", Turkish standard according to European Norms, Ankara (2002).

[16] TS EN 196-2, "Methods of testing cement-Part 2: Chemical Analysis of Cement", Turkish standard according to European Norms, Ankara (2002).