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Hydration properties of boron modified active belite cement concrete

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Abstract

In this study, hydration heat and speed of Boron Modified Active Belite (BAB) cement concretes were determined using by semi-adiabatic method. After the development of the theory and analysis of the BAB cement concrete production, the current work includes analyzes of hydration heat in BAB cement concrete. The same experiments were repeated in 6 different cement types including BAB cement, and their hydration properties were determined. For samples hydration heat-time and hydration velocity-time graphs for all types of cement were prepared comparatively. Additionally in order to determine the strength properties of hydration relations, Schmidt hammer, unit weight, compressive strength tests are applied to samples and the test results are interpreted with the help of graphs. As a result, hydration properties of steam cured and non-steam cured boron modified active belite cement concrete were comparatively analyzed and heat of hydration of BAB cementitious mortar samples were found significantly lower than other types of cement. As the cause of this situation is the lack of Alite (C_3S) phase and low C_3A (Belit) content of boron modified active belite cement.

Keywords: *Boron, belite, hydration, curing, cement, concrete.*

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Borlu aktif belit çimentolu betonun hidratasyon özellikleri

Özet
Bu çalışmada, Borlu Aktif Belit (BAB) çimentolu betonların hidratasyon ısıları ve hızları yarı adyabatik yöntem kullanılarak belirlenmiştir. BAB çimentolu beton üretimi teori ve analizinin geliştirilmesinden sonra, BAB çimentolu betonun hidrasyon ısısı analiz edilmiştir. BAB çimentosuyla beraber 6 farklı çimento tipi üzerinde de aynı deneyler tekrarlanmış ve hidratasyon özellikleri belirlenmiştir. Çimento tiplerine ait hidratasyon ısı-zaman, hidratasyon hızı-zaman grafikleri bütün çimento tipleri için karşılaştırmalı olarak hazırlanmıştır. Ayrıca hidratasyon özellikleriyle dayanım ilişkilerini belirleyebilmek amacıyla ısıl işlem görmüş ve görmemiş 3 farklı çimento tipindeki betonlara; basınç dayanımı, Schmidt çekici, birim ağırlık gibi çeşitli deneyler uygulanmış ve deney sonuçları grafikler yardımıyla yorumlanmıştır. Sonuç olarak BAB çimentolu ısıl işlem görmüş ve görmemiş betonların hidratasyon özellikleri karşılaştırmalı olarak analiz edilmiş olup BAB çimentolu harç numunelerinin hidratasyon ısılarının diğer çimento tiplerinden oldukça düşük olduğu tespit edilmiştir. Bu durumun nedeni olarak, borlu aktif belit çimentosundaki Alit (C_3S) fazının olmayışı ve (C_3A) Belit içeriğinin düşük olduğu değerlendirilmiştir.

Anahtar kelimeler: B*or, belit, hidratasyon, kür, cimento, beton.*

1. Introduction

A new type of cement was produced in Turkey, and named as Boron Active Belite (BAB) cement. BAB cement is a byproduct of Boron ore, and it's some trial properties indicated very encouraging technical characteristics. The main purpose of this cement production process was to minimize heat of hydration while cement mixed with water. As a result of hydration process, many times durability-related problems may occur. Especially, the concrete industry tries to control the heat evaluation of cement while mixing, placing and also at the curing period. Thus, anyone in concrete and/or cement industry has to take into consideration not only the cement hydration process, but also the curing process and period. Due to potential of cement based composites wide usage, all over the world, concrete manufacturers are very interested in that type of cement and its effect on the concrete properties [1-11].

Concrete consists of natural sand, gravel and crushed rock or other artificial aggregates, bound together by a hardened paste of cement and water. It has been seen that concrete has been shrinkage as it is in many construction materials with increasing temperature. This has the greatest prospect for massive concrete structures where the initial temperature of the hydration can cause high temperature gradients and cracks in the restraint zones that cause thermal stresses. As a result of the chemical reaction between the cement and the water, hydration of the cement occurs. Hydration is a chemical reaction in which the main compounds in the cement form chemical bonds (C_4AF, C_3A, C_3S and C_2S) with water molecules, resulting in hydrates or hydration products. When the PC reacts with water, the heat becomes clear. This heat is known as the hydration heat as a result of the exothermic chemical reaction between the cement and water. As a result, the heat released increases the temperature of the concrete. Hydration heat has been observed to increase up to temperatures of 55 ° C in mixtures containing high cement. In other words, concrete and cement paste show shrinkage and settlement during the hydration process. Speed of gaining bonding nature and amount of cement paste depend on how much hydration is formed between cement and water [1-8].

Collepardi et al. [6], have performed the work related with determining the effect of the main component in the control of cement hydration, it is found that substitution of natural pozzolan reduces hydration rate of C_3A main component. C_3A is about 10.5% of cement under normal conditions. C_3A causes the first set to release high hydration heat, and is more prone to volume changes causing cracking. In addition, with the increase in C_3S content, the permitted limits increase the hydration temperature of the water and the solubility of the cement in the water [1].

In this study, Plowman [7], has detected that natural pozzolan reduces hydration rate of C_3A. Moreover Demirboğa et al [8], revealed that fly ash (FA) and blast furnace slag (BFS), which are used as mineral additives and replaced with cement, improve the mechanical properties of concrete, decrease the hydration heat, and the alkali aggregate reactivity and permeability of concrete. Examination of setting and hardening processes of cement is determined by various methods. Two European standards are present within many different methods that heat of hydration of cement could be determined. The first method is solution method. According to EN 196-8 [9], this European Standard is defined as the method of determining the hydration temperature of cement through solution calorimetry. The heat of hydration is expressed in joules per gram of cement anhydrous and definite time hydrated samples of cement are dissolved in acid mixture and the heat of hydration of cement is determined by the difference between the heats they release. The second is semi-adiabatic method. This method is applied according to EN 196-9, the paste prepared with cement sample, standard sand and water is placed in semi- adiabatic calorimeter and heat of hydration is started to be measured from that moment on. Temperature versus time and correspondingly heat of hydration profile are obtained with the data collected in calorimeter [10].

According to the Yeşilmen and Gündüz [11]., BAB cement offers the advantage of high durability, low heat of hydration, and improved long term strength along with reduced energy and emissions during its production process compared to conventional cement. The production of BAB cement is yet to be continued in industrial scale. Present paper, also compares some of the hydration properties of conventional and BAB cements, including their effect on the compressive strength according to curing types and Schmidt hardness.

2. Materials and methods

Crushed aggregate is used in preparation of concrete mixtures. Aggregate sizes are taken as 0–2, 2–8 and 8-16 mm. Specific gravity of aggregates are 2.71, 2.59 and 2.65 respectively. The quality of the concrete depends on the aggregate used, expressed in terms of aggregate specific gravity (SG) or specific gravity factor (SGF). The SGF, the ratio of the weight of aggregates, including all moisture, as introduced into the mixer to the effective volume displaced by the aggregates [12]. Aggregate is washed before using. Then, water-saturated aggregate in a ventilated oven at 105 ^oC for not less than 24 h and two successive weightings at intervals of 2 hours show an increase of loss not greater than 0.2% of the last previously determined weight of the aggregate size.

Besides, standard sand with a size of 0.8-2.00 mm in (1350±5) g plastic bags, having the characteristics determined in TS EN-196-1 standards [13] is used in formation of reference concrete sample and for Strength Test of cement. Many adiabatic calorimeters use water, air and oil circulation around the sample to maintain the temperature of the sample [14]. For this purpose, thin machine oil is used in this research. Oil is filled into the thermometer pocket by the help of syringe. By the oil placed in the thermometer pocket experiment, thermal touch is fully provided between the sample and the thermometer.
Standard calorimeter, which a section of it is demonstrated in Figure 1, is used in the experiments. In Figure 2, network system where the measurements are recorded is shown. While one of the calorimeters displayed in Figure 2 records heat changes of concrete sample, the second one performed the measurements of the reference concrete sample.

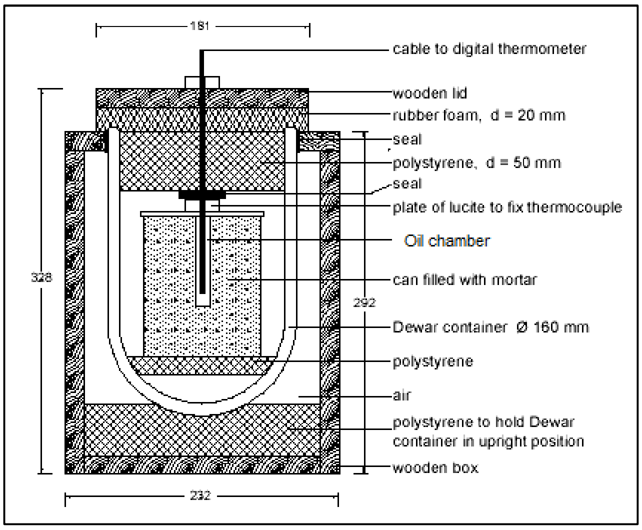

Figure 1. Longitudinal section of the standard calorimetry.

Figure 2. Calorimeters and the networking system.

In this study, hydration temperature of cements is determined by using semi-adiabatic calorimetry methods. As described, TS 196-9 [15] standard, which is also known as the Langavant method, which is a method of measuring the hydration temperature of cements by means of semi-adiabatic calorimetry. The purpose of the test is to measure the continuous cement hydration heat during the first few days. The measured hydration temperature is defined in terms of joules per gram of cement.

Besides, the hydration temperature of the cement is generally determined according to the ASTM C 186 [16] standard test method for the hydration temperature of the hydraulic cement. For both European standards about heat of hydration, one standard have citation to other and it is declared that 41 hour heat of hydration determined by TS EN 196-9 [15] is well correlated with 7 day heat of hydration determined by TS EN 196-8 [9].

When results obtained in 41 hours by semi adiabatic method is compared with results obtained in 7 days by solution method, a very well correlation is seen between these two methods [15]. Accordingly, 41 hour data is taken as the basis in our experiments.

In Figure 3, atmospheric steam cure machine where concrete samples are cured is seen.

Figure 3. Atmospheric steam curing machine (steam chamber).

In this study, five different cement types are used along with BAB cement to compare the heat of hydration of BAB cement with the heat of hydration of other cements. These cements are as the following:
1-CEM II B-M (P-LL) 32.5 R,
2-CEM I 42.5-R,
3-CEM II A-M (P-LL) 42.5 R,
4-CEM II B-M (P-LL) 42.5 N,
5-CEM I 52.5 R (Super White Portland Cement)

Besides, for determining hydration – strength relation, compressive strength, Schmidt hammer strength and unit weight values of concretes made of CEM II B-M (P-LL)32.5 R, CEM I 42.5-R and BAB cement, and which atmospheric steam cure and water cure are applied are examined. Chemical properties of these cements are given in Table 1. The mechanical, physical and chemical properties of the BAB Cement used in this study are summarized in Table 2.

Table 1. Chemical properties of the cement type.

Type of cement	Chemical compound (%)									
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**K_2O**	**Finenes (%)**	**Specific gravity**
CEM II B-M (P-LL) 32,5 R	18.73	4.84	3.12	55.28	2.10	2.48	0.15	0.70	10.34	2.93
CEM II B-M (P-LL) 42,5 N	18.08	4.68	3.05	59.05	2.09	2.69	0.11	0.67	9.41	2.98
CEM II A-M (P-LL) 42.5 R	18.09	4.69	3.07	60.85	2.26	2.66	0.20	0.68	7.76	3.04
CEM I 42.5 R	18.11	4.60	2.96	64.49	2.34	2.95	0.13	0.66	8.03	3.13
CEM I 52.5 R	21.60	4.05	0.26	66.70	1.30	3.30	0.30	0.35		

PCC= Portland Compose Cement
NPC=Normal Portland Cement
LL : Lime
P= Natural Pozzolan
R= Rapid ,N= Normal, L=Low Hardening Cement

Table 2. Properties of BAB cement.

Elements	**Amount of %** (< requirement by mass %)
Silicon dioxide (SiO_2)	19.1
Aluminum dioxide (Al_2O_3)	4.68
Ferric oxide (Fe_2O_3)	3.42
Calcium oxide (CaO)	57.1
Magnesium oxide (MgO)	1.32<5
Chloride (Cl-)	% 0.001<0.1
Sulfur trioxide (SO_3)	2.68<3.5
Loss on ignition	3.82<5
Insoluble residue	0.70<5
Equivalent alkanies	0.86
Boric oxide (B_2O_3)	3.00
Clinker	86.1
Gypsum	4.85

For determining heat of hydration –strength relation of the samples, 10x20 cm cylinder concrete samples with properties shown in Table 3 are prepared for steam and water cure. For water cure, they are filled with water, made lime saturated and the temperature of it is provided to be 23±2^{o}C before samples are placed in curing pool. Samples in water cure are removed from the curing pool at the end of the 28th day. Required experiments are performed after waiting for 24 hours at normal room temperature.

Table 3. Specification of hydration heat-compressive strength relationship concretes.

Curing type	Type of cement	Slump (mm)	W/C	Adjusted W/C	Fresh Unit Weight (kg/dm^3)
For Steam Cure	CEM I 42.5 R	15	0.57	0.52	2.393
	CEM II B-M (P-LL) 32.5 R			0.51	2.388
	BAB			0.49	2.360
For Water Cure	CEM I 42,5 R			0.52	2.396
	CEM II B-M (P-LL) 32.5 R			0.57	2.364
	BAB			0.50	2.365

Samples prepared to explore effect of steam cure to strength are exposed to totally 2190-minute steam cure. Weight, length and diameter measuring of samples are made after resting for 24 hours following steam cure. 28-day samples are subjected to axial pressure test following Schmidt hammer test. Results of the obtained strength are given in Table 4.

Table 4. Schmidt hardness and compressive strength values of different types of cement concrete exposed to atmospheric steam curing and water curing.

Type of curing	Type cement	Mean Schmidt hardness	Mean compressive strength (MPa)
Atmospheric steam curing	CEM I 42.5 R	22.13	32.48
	CEM II B-M (P-LL) 32.5 R	20.60	17.42
	BAB	17.83	16.73
Water curing (7 days)	CEM I 42.5 R	21.80	36.90
	CEM II B-M (P-LL) 32.5 R	14.80	27.13
	BAB	15.47	25.63
Water curing (28 days)	CEM I 42.5 R	29.07	49.17
	CEM II B-M (P-LL) 32.5 R	19.97	36.68
	BAB	21.50	35.64

Semi adiabatic method is based on determining the amount of heat propagation according to temperature rise starting with replacing fresh concrete sample to one calorimeter. At the given time point, heat of hydration of cement in the sample is equal to the total amount of heat accumulated in calorimeter all through the experiment process and the heat loss spread in the atmosphere in the medium. Temperature increase of mortar is compared with the temperature of an inert sample at one reference calorimeter. Temperature increase primarily depends on the characteristics of cement and is normally between 10 K and 50 K. The homogenously mixed concrete sample is placed into the adiabatic calorimetry after about 30 minutes of water being added to the cement. Although the semi-adiabatic calorimetry method is a widely used test method, there is no standard test method for semi-adiabatic calorimetry. [14].
According to TS EN 196-8, total heat of hydration of BAB cement should not be over the value of 70 cal/g at the end of the 28th day or when determined by isothermal conduction calorimeter method at the end of the 28th day [9,18-21].

3. Results and discussion

In Table 3, wet unit weight values of concretes cured in atmospheric steam and water, and made of different cements to examine heat of hydration- compressive strength relation are given. Slump values and W/C rates of these concretes are fixed at 15 mm and 0.57 respectively. It is seen that there aren’t significant differences between unit weights.

The following results are obtained in the research on effects of concretes made of CEM I 42.5 R, CEM II B-M (P-LL) 32.5 R, BAB cement to water and steam cure strength: In Table 4 and Figure 4, Schmidt hardness and compressive strength values of concretes with different cements exposed to atmospheric steam cure and water cure are given.

Compressive strengths of concretes cured in water for 28 day is found higher compared to concretes cured with steam. However, strength of concrete samples cured with steam reaches to 47% to 66% of 28-day strength in such a short period of 36.5 hours. This strength rate provided by steam cure cannot be ignored in constructions in which time is very valuable.

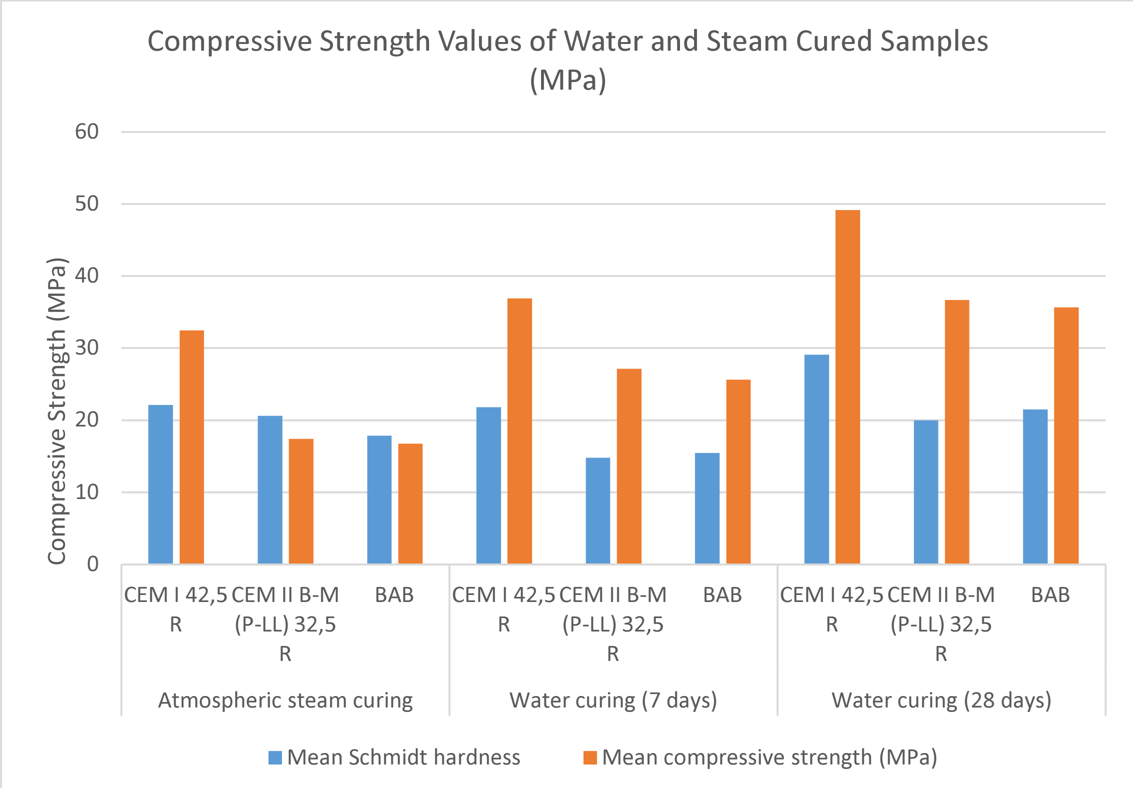

Figure 4. Compressive strength values of water and steam cured samples (mpa).

As is seen in Figure 4, the highest compressive strength is performed in concrete samples poured with CEM I 42.5 R cement. The least difference is seen in samples poured with CEM II 32,5 R cement. Compressive strengths of BAB cement concretes were lower compared to concretes with other type cements, and a linear correlation could not be found.

The structure and fineness of the cement are common methods in which the hydration temperature of any concrete mixture is estimated. Total heat energies released in time in hydration process are compared at the end of the hydration tests of five different cement types along with BAB cement. Besides, rate and development process of hydration are analyzed according to time factor over Heat Amounts expanded in Unit of Time.

In Figure 5, hourly hydration readings taken from calorimeter for six types of cement are given. Hydration readings are taken at every 1 minute by Sirius Program. Graphics are drawn by the help of these data. CEM I 52.5 R cement is known to have an adiabatic temperature increase of about 39.4 ° C.

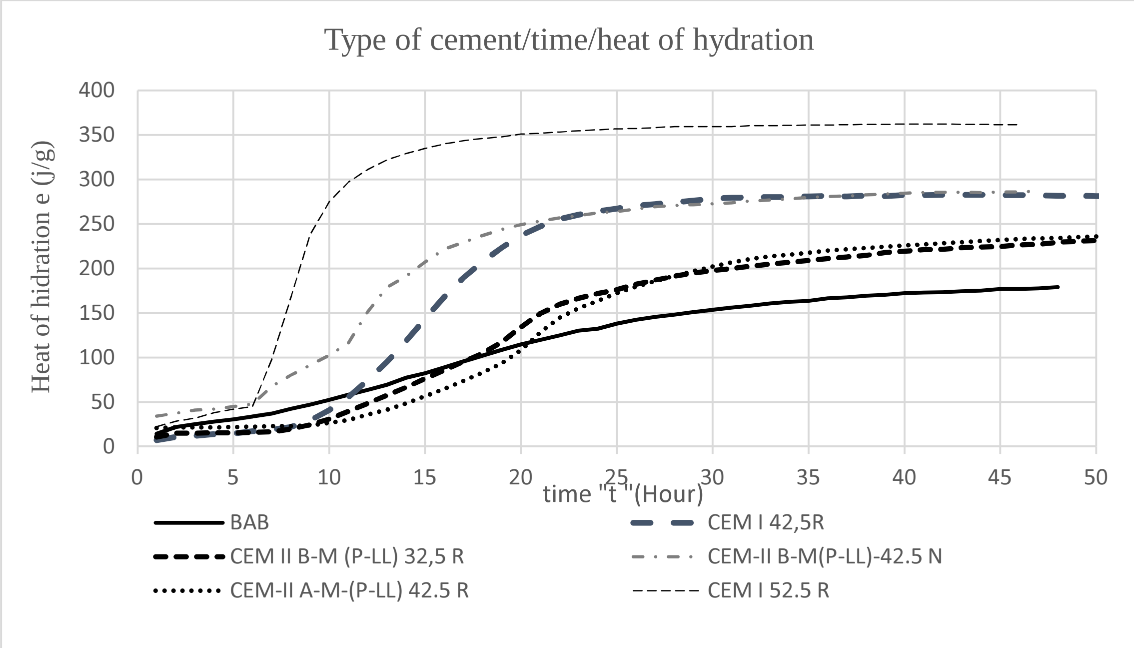

Figure 5. Effects of cement type on semi adiabatic temperature.

The semi-adiabatic curve of a material tested is usually lower than the curve obtained from an adiabatic test. This heat loss is measured in the calculation of the heat flow under adiabatic conditions, and the calculation takes place. Semi-adiabatic calorimetry test methods are generally suitable for mortar, concrete and paste samples [17].
It is determined that heat of hydration of BAB cement is much lower than other cements. (Figure 5) Findings obtained show that BAB cement is an ideal material in buildings which low hydration temperature cements as specifically mass concrete are required to be used.

4. Conclusions

As a result of the experiments conducted, it is seen that there is a parallelism between 36.5 hour atmospheric cure values and hydration values and in cement types with high heat of hydration, compressive strength values are also found high. Although it is thought that this situation is depending on the fineness, oxide composition in chemical composition of cement, it should also be considered that it might change depending on many other variables.

BAB cement's feature of having very low heat of hydration shall create advantages in controlling more easily the cracks which may occur by temperatures, producing high fluidity concrete with high strength and controlling temperature increase.
A significant decline is seen in total temperature and speed of hydration due to failure in formation of alite (C_3S) phase which has a great importance in hydration due to the existence of B_2O_3 in BAB cement and having a low rate of C_3A phase, and this situation brings great advantages in total hydration temperature and processes as mentioned above.

Low heat of hydration helps the occurrence of chemical reactions in warm weathers as well as having contribution in formation of setting, hardening and strength gaining stages in normal periods. On the other hand, in concreting works made with low hydration temperature BAB cement in cold weathers, it may be necessary to use setting accelerator and water reducer chemical additives along with it.

It is an advantage in BAB cement that as it requires less water for hydration than Portland cement, it is easier to adjust the low water/cement ratio. Moreover, thanks to low hydration temperature, shrinkage cracks are minimized and therefore, increase of permeability by shrinkage cracks is prevented.

References

[1] Duggal, S.K., **Building materials**, Thirth edition, New age international limited, publishers, New Delhi, (2008).

[2] Jackson, N., Dhir, K.R., **Civil engineering materials**. P. Mc. Millan, (235) 534, Newyork, USA, (1996).

[3] Kurt, M, Kotan, T., Gül, M.S., Gül, R., Aydin, A.C., The effect of blast furnace slag to self-compactability of pumice aggregate lightweight concrete, **SADHANA Academy Proceedings in Engineering Sciences**, 41(2), 253-264, (2016).

[4] Portland Cement Association, Portland cement, Concrete, and Heat of Hydration, **Concrete Technology Today**, 18(2), (1997).

[5] Burg, R.G., Ost, B.W., **Engineering properties of commercially available high strength concrete**, RD104, PCA, Skokie, Illinois, (1994).

[6] Collepardi, M., Baldini, G., Pauri, M., Corradi, M., The effect of pozzolanas on the C3S hydration, **Cement and Concrete Research**, 8(6), 741-751, (1978).

[7] Plowman C., The influence of pulverised fuel ash o the hydration reactions of calcium aluminates", proceedings of symposium on the effects of fly ash incorporation in cement and concrete, Boston, **Materials Research Society**, 10, (1981).

[8] Demirboga, R., Türkmen, İ. ve Karakoç, M.B., Relationship between ultrasonic velocity and compressive strength for high-volume mineral-admixtured concrete. **Cement and Concrete Research**, 34, 2329–2336, (2004)

[9] TS EN 196-8, Methods of testing cement - Part 8: Heat of hydration - solution method, **Turkish Standard**,(2011)

[10] Cement and concrete world, TS EN 196-9, Determination of hydration heat with half-adiabatic method, **Türkiye Çimento Mühtahsisler Birliği (Cement and Concrete World)**, 17(94), (2012)

[11] Yeşilmen, S., Gürbüz, A., Evaluation of boron ore in cement production, **Materials and Manufacturing Processes**, 27(11), 1245-1250, (2012)

[12] Demirboğa, R., Kan, A., Design of specific gravity factor of artificial lightweight aggregate, **Indian Journal of Engineering & Materials Sciences**, 20, 139-144, (2013)

[13] TS EN 196-1, Methods of testing cement - Part 1: Determination of strength. **Turkish Standard**, (2009)

[14] Poole, J.L., Riding, K.A., Folliard, K.J., Juenger, and Schindler, A.K. **ACI**, SP-241 Concrete Heat Development: Monitoring, Prediction & Management, Preface 5, Hydration Study of Cementitious Materials using Semi-Adiabatic Calorimetry, Editors: Kejin Wang & Anton K. Schindler, (2007)

[15] TS EN 196-9, Methods of testing cement - Part 9: Heat of hydration - Semi-adiabatic method, **Turkish Standard**, (2011)

[16] ASTM C 186, Heat of hydration of hydraulic cement. **Annual Book of ASTM Standards**, Vol 04.01., ASTM International, West Conshohoken, PA, (2006)

[17] Wang, K., Ge, Z. Grove, J . Ruiz, J. M., Rasmussen, R., Ferragut, T., Developing a simple and rapid test for monitoring the heat evolution of concrete mixtures for both laboratory and field applications, **National Concrete Pavement Technology Center**, Phase II Report, (2007)

[18] TS EN 13353, **Turkısh Standard**, Boron modified active belite cement – Definitions, composition, specifications and conformity criteria. TSE Ankara, (2008)

[19] Kurt M, Gül, M.S., Gül, R., Aydin, A.C., Kotan, T., The effect of pumice powder on the self-compactability of pumice aggregate lightweight concrete, , **Construction and Building Materials**, 103, 36–46, (2016)

[20] Aydin, A.C., Oz, A., Polat, R., Mindivan, H., Effects of the different atmospheric steam curing processes on the properties of self-compacting-concrete containing microsilica, **SADHANA Academy Proceedings in Engineering Sciences**, 40(4), 1361–1371, (2015)

[21] Kurt, M, Aydin, A.C., Gül, M.S., Gül, R., Kotan, T., The effect of fly ash to self-compactibility of pumice aggregate lightweight concrete, **SADHANA Academy Proceedings in Engineering Sciences**, 40(4), 1343–1359, (2015)