Utilization of Borax Waste as an Additive in Building Brick Production*

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ÖZET: Türkiyede her yıl tincal cevherinden boraks üretim proseslerinde büyük miktarda boraks atığı oluşmaktadır. Bu atıklar öncelikli olarak kil bileşenlerini ikincil olarakta B2O3 ve bir miktarda safsızlık içermektedir. Bu atık materyaller kimyasal bileşimleri nedeniyle inşaat tuğlası üretimine uygun ham maddelerdir. Bu çalışmada inşaat tuğlası üretiminde katkı olarak boraks atığının kullanılabilirliği incelenmiştir.Bu amaçla öncelikle atıktaki B2O3 miktarı liç prosesi ile soda çözeltisi kullanılarak uzaklaştırılmış ve toksik etkisi düşürülmüştür. Liç prosesi sonrasında tuğla kompozisyonuna kuru örnek üzerinden % 10, 20, 30 oranlarında atık katılıp 10 bar basınçla preslenmiş ve 970, 1000 ve 1030°C lerde pişirilmiştir. Pişme sıcaklığının ve katkı yüzdesinin inşaat tuğlasının soğukta basma mukavemeti, porozite, su absorpsiyonu, hacim yoğunluğu ve kızdırma kayıpları üzerindeki etkisi belirlenmiştir. Test sonuçlan atık oranının ve pişme sıcaklığının tuğla kalitesi üzerinde etkili faktörler olduğunu göstermiştir.Tuğlamn soğukta basma mukavemeti, atığın katkı yüzdesi ve pişme sıcaklığının artmasıyla düşmektedir. İyi kaliteli tuğla üretiminde şartlar % 18 nem içerikli % 10 boraks atığının tuğlaya katılması ve 1000 °C de pişirilmesi şeklinde belirlenmiştir.

ABSTRACT: Large quantities of borax waste form during the production of borax from the tincal ore in Turkey every year. It consists primarily of clay compounds, secondarily of B2O3, and some other impurities. Because of its chemical composition, the waste is regarded as a suitable raw material for brick production. In this study, the use of borax waste as an additive in brick production was investigated. For the purpose of leaching treatment by soda solution was applied to recover $B_2 0_3$ and therefore to reduce the toxic effect of the waste. After the leaching process, composition of the bricks was adjusted to contain 10, 20, and 30% by weight-dried waste. These mixtures were molded in 10 bar squeezing pressure and fired at 970, 1000 and 1030°C. At the end of this process, the effects of firing temperatures and the percentage of the added waste on the compressive strength, porosity, water absorption, bulk density and loss of ignition of building bricks were determined. Results of the tests indicated that the waste proportion and firing temperatures were affecting factors the brick quality. It was determined that compressive strength for the bricks decreases with increased waste addition and firing temperatures. The conditions for producing the good quality bricks are found as 10% borax waste with 18% of moisture content, fired at 1000°C.

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1. INTRODUCTION

About 63% of the known world boron reserves are found in the western part of Turkey. Boron reserves include various minerals. Of these minerals, tincal, colemanite, and ulexite have very important commercial value. Products such as boric acid, hydrated borax, anhydrite borax and sodium perborates are produced from these minerals. Boron and its compounds have a wide field of applications in the industry. Particularly, borax has found wide areas of use such as borosilicate glasses, glass wool, ceramics, detergent, cement, and fireproof materials, etc. (Ekmekyapar et. al., 1997).

Borax production from tincal is produced by batch process. In this process, concentrate tincal is fed to a stirred reactor containing water heated to 98°C. After the treatment, undissolved part of the tincal, is discharged. The tincal solution containing colloidal clay in the reactor is passed to thickener (Boncukçuoğlu et.al., 2003). The precipitate in thickener is called as borax waste. Annually, 25.000 tons borax waste from in the concentrated tincal unit and the borax unit during the production in Bandırma Etibank Borax Plant. The borax waste contains boron oxide (B2O3), which is in quite high concentration of 14-18%.

When this waste discharged to soil, boron compound dissolving by rains waters causes to soil pollution as well as economical loss.

Some useful methods have been developed to recovery of boron from the wastes, which formed in boron industries, or usage of these wastes as additive in building sectors.

In these studies, solid and liquid wastes of boron industries were investigated with cement, lime and sand and it was determined their effects on some properties of the concrete and cement (Boncukçuoğlu et. al., 1998, Elbeyli et. al., 2003, Boncukçuoğlu et. al., 2002). At work, the use of the borate wastes in the Masonry cement production was used for solidification of the concentrated borate slurry at nuclear plants. It was found that properties of Masonry cement were better than Portland cement(Tsai, 1989). In some studies on the removal of solid boron wastes, the recovery of boron from boron wastes or the stabilization of boron wastes with cement, lime and sand has" been studied (Erdoğan et. al.,1993, Boncukçuoğlu, et al., 2002, Boncukçuoğlu et. al., 1999). Solid wastes such as borax waste, has become one of the most serious problems of today, and the use of these wastes in the building industry as raw materials offers a potential alternative for environmental protection.

In this study, the effects of firing temperatures and the percentage of the added waste on the compressive strength, porosity, water absorption, bulk density and loss of ignition of building bricks were investigated. The suitable conditions of using dried borax waste in production of bricks under the criteria of Turkish Standards (TSE 705) were determined.

2. MATERIALS AND METHODS

2.1 Materials

Borax waste used in study was provided from Eti Holding Borax Plant in Bandırma. The brick clay sample was obtained from Işıklar Holding m Istanbul, Turkey. Process of production of borax from the tincal is shown in Fig.l. Borax waste was supplied from the outlet of the thickener unit.

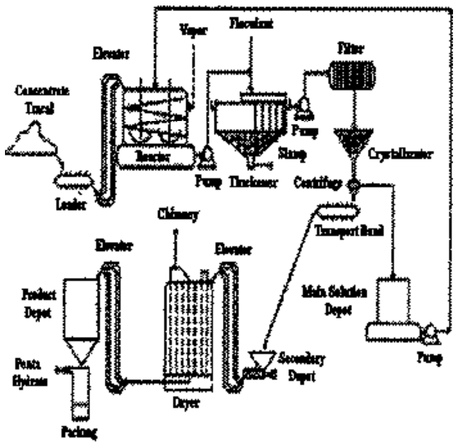

Figure 1. Process of production of borax from the tincal (Boncukçuoğlu et. al., 2003)

The main constituents of the waste and clay samples are given in Table 1. Relatively high B2O3 content of the borax waste can be observed in the table.

Table 1. The chemical composition of cement and borax waste by weight percent (%).

Constituent (%)	Brick Clay	Borax waste (dried)
$Si0_2$	60.22	16.67
AI2O3	15.13	0.94
Fe_20_3	11.83	0.35
MgO	1.04	11.80
CaO	1.15	13.53
Na_20	1.20	6.87
B2O3	-	14.09
Heating lost	9.43	35.75

2.2 Leaching process of the borax waste

The borax waste was dried in oven at 105°C for 2 h, crushed, ground and sieved in a 200um. Leaching process was applied to borax waste before being added to the mixtures for recovery of B_2O_3 from the waste. Experiments were carried out at 98°C with solid/liquid ratio of 1/5 and dissolving for 40 minutes by Na2CÛ3 and NaHCC>3 solutions. The solutions of 2.5, 5 and 10% were prepared for determining the optimum solution yield amounts. The end of the reaction, solid and liquid parts of waste was extracted with vacuum filtration system. B2O3 component and water-soluble materials are passed to filtrate. Thus, boron is recovered by decreasing of its content in waste. The amount of boron remaining in cake and filtrate forms were determined by titration method (Pişkin, 1983). Results of leaching yield obtained by soda solutions are given in Table 2.

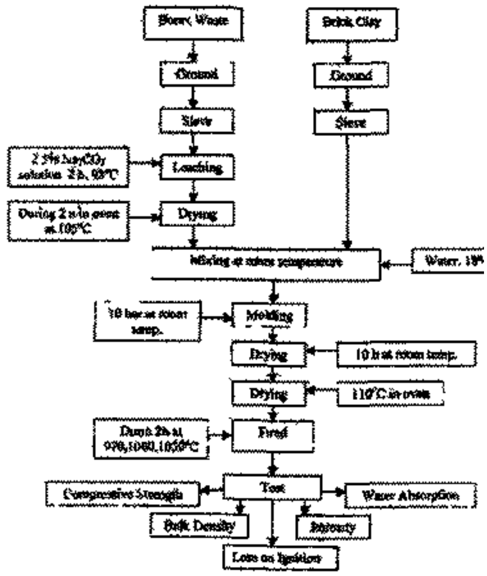

Figure 2. Flow diagram

2.3 Preparation and testing of the brick samples

To produce the brick, borax waste both leached with Na_2CO_3 solution and heated at 105°C for 2 h after leaching with soda solution was added to brick clay in ratio of 10%, 20% and 30% (wt/wt) (Fig.2). In the experiments, brick clay with borax waste and water (18%) was well mixed and the mixtures were molded by using a cylindrical steel mold (23 mmIDx30mm height) at ambient temperature in a universal test apparatus (model Mohr Feddehoft) under 10 bar squeezing pressure.

The brick samples were obtained cylindrical in shape (Fig.3 and 4). After the molding, the brick samples were left to dry in the atmosphere for 1 day followed by oven drying at 110°C for 10 h. Dried bricks of each composition were fired m a metallurgical furnace at 970,1000 and 1030°C for 2 h. The heating rate of the furnace was 200°C/h. The fired bricks were slowly cooled in the furnace closed overnight and tested for their compressive strength using a test machine of 101 capacity.

The bricks after the determining of compressive strength values were subjected water absorption, porosity, bulk density and loss of ignition tests. Turkish Standard (TSE 705) tests or modified versions of these tests were used in determining the mentioned qualities of the bricks (TSE 705,1979).

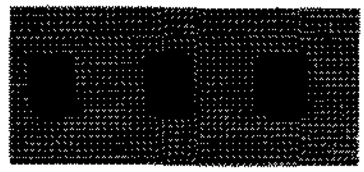

Figure 3. Pictures of the bricks produced with brick clay at 1030°C, 1000°C, 970°C

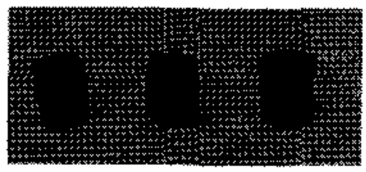

Figure 4. Pictures of the bricks produced with 10 % borax waste at 1030°C, 1000°C, 970°C

3. RESULTS AND DISCUSSION

The study was divided into three stages, consisting of mixing the raw materials, the experiment of brick production using these raw materials, testing the physical properties of the fired bricks. Although commercial red brick manufacturing the firing temperature is usually 900°C. These bricks were fired 970, 1000 and 1030°C due to investigation of the temperature effect.

3.1 Recovery ofB2Ös by leaching treatment

The content of B2O3 in borax waste decreased from 14.09% to 2.80% by using 2.5% Na_2C0_3 solution and boron oxide in waste was recovered at the yield of 80% as sodium borate. The reaction was given below.

$$Na_2B_4O_7\ 10H_2O + Na_2CO_3 \longrightarrow 4NaBO_2 + 10\,H_2O + CO_2 \quad (1)$$

Although the utilization of borax fabric waste in the production of building material is a useful way for the protection of environmental pollution, B_2C>3 content of the waste must be decreased to the least level from the point of brittleness effect of the building materials. For this reason, the brick samples were prepared by treated waste (2.80% B2O3).

Table 2. Leaching yield of borax in waste by different soda solutions

	$NaHC0_3$			Na_2C0_3		
Solutions	2.5%	5%	10%	2.5%	5%	10%
Yield	66%	60%	60%	80%	68%	60%

3.2 Test results of the bricks

The results obtained are given in Fig.5-9. It can be seen from the Fig. 5 firing temperature affected the compressive strength of the bricks. Suitable temperature for the production of bricks observed as 1000°C because of obtaining the highest compressive strength values. All brick samples showed the same compressive strength at 970 and 1030°C firing temperatures. Samples, which produced at 1030°C, showed cracks on the surface due to the various mineral matters arisen from borax waste.

The samples of bricks were obtained by adding borax waste to brick clay at various ratios. The compressive strength, water absorption, porosity, bulk density and loss on ignition values of the brick samples prepared with borax waste were determined. Addition of borax waste amounts in higher ratios has negative effects on compressive strength of bricks (Fig.5). These effects has similar trends all of the firing temperatures. The highest value has found for the one contained 10% borax waste at 1000°C firing temperatures. As seen in Fig.5, it is observed that the bricks obtained by adding borax waste to brick clay had higher compressive strength than that of the brick clay sample. The compressive strength values of these bricks samples were higher than the TS 705 values. The highest values were obtained in the sample containing 10% borax wastes for firing at 1000°C. The compressive strengths with increasing borax waste ratios are 28.00, 27.58, 16.64 (N/mm^2) for control brick sample and 7.80(min)- 23.50(max) (N/mm^2) at TS 705 (Uslu et. al., 2003).

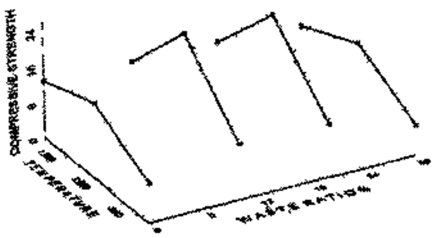

Figure 5. Compressive strength values (N/mm^2) of the bricks

The porosity of the brick samples with 10%, 20%, 30% are 30.60, 30.80, 33.10, respectively while being 31.30 for brick clay sample (Fig.6). It has been seen that porosity of the brick increases with increasing borax waste ratio due to the decomposition of carbonate minerals (CaCOs and $MgC0_3$) in waste. The water absorption of brick samples increase with increasing borax waste ratio due to the some mineral matters in waste.

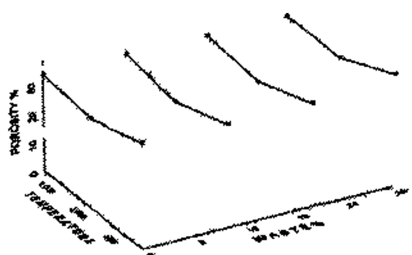

Figure 6. Porosity values (%) of the bricks

Water absorption is an important factor affecting the durability of brick. Fig.7 shows the results of the water absorption values for different proportions of waste in the mixture fired at three temperatures. As it can be seen from Fig.7, water absorption for the bricks increases with increasing waste addition due to increasing the porosity. Porosity takes place from the volatile matter resulting from the gasification reactions of carbonate and sulfate minerals. It was determined that water absorption by increasing 10%, 20%, 30% ratios of borax waste was 15.96, 16.40, 17.81% respectively, while being 13.95 % for brick clay. At the same time, by increasing the firing temperature, the borax waste values are decreased depending on the porosity values of bricks.

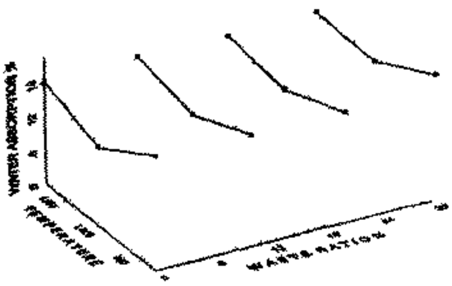

Figure 7. Water absorption values (%) of the bricks

The compressive strength value is increased by raising the firing temperature from 970 to 1000°C as causing to decrease in the porosity values. They are effected in opposite way, so that an increase in porosity and a decrease in compressive strength are shown at 1030°C firing temperature (Fig.5). With the increasing in the firing temperature from 970 to 1000 °C, a liquid phase may be occurred. This occurred phase because of melting of borax in waste at 1000°C is filled the pores in clay and later a fragile and glassy phase is occurred at 1030 °C firing temperature. For this reason, an increase in water absorption plus porosity and a decrease in compressive strength were observed.

The loss of ignition values of brick samples increases with increasing borax waste and firing temperatures (Fig.8). Sulfates and carbonates arisen from the waste decomposed with rising temperature. It was determined that water absorption by increasing 10%, 20%, 30% ratios of borax waste was 7.15, 8.96, 10.50 % respectively, while being 5.30 % for brick clay at 1000°C.

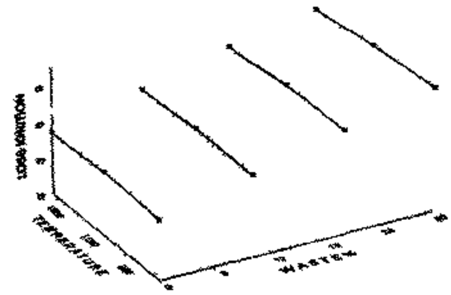

Figure 8. Loss of ignition (%) of the bricks

Bulk density of the brick is changed in the opposite way as compared to the porosity (Fig.9). As it can be seen from the **lïg.** 9 that bulk density by increasing 10%, 20%, 30% ratios of borax waste was 1.854, 1.834, 1.783 (kg/m^3) respectively, while being 1.852 (kg/m^3) for brickclay at 1000°C.

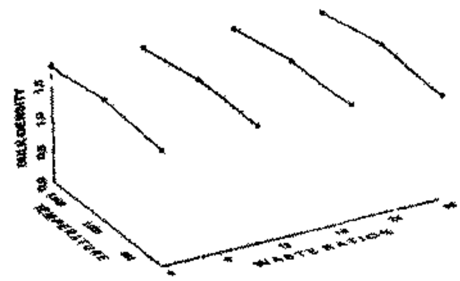

Figure 9. Bulk density values (kg/m^3) of the bricks

4. CONCLUSIONS

It is well known that borax is a good fluxing agent. It combines with silica and alkalis to form a glassy structure and lower the melting temperature, leading to a stronger body upon solidification. The fluxing characteristics of borates have been extensively used in ceramic and glass making (Uslu, 2003). This waste of boron mines is suitable for the production of bricks because of having clay minerals and boron compounds.

The possibility of using borax waste as a brick additive has been investigated. The following conclusions can be drawn from the experimental results:

- If all water-soluble impurities, especially boron oxide (B2O3), are removed from borax waste by a simple leaching process. Recovery of B2O3 is an important process in the prevention of water and soil pollution; recycling of raw materials in borax production and the utilization of waste.
- The compressive strength of the brick decreased with increasing borax waste ratio. The brick samples containing 10% of borax waste had higher compressive strength than brick clay. It has been reported that an increased B2O3 amount in building materials causes a decreasing in strength values (Boncukoglu et.al., 2002).
- As a result, it is suggested that borax waste can be used as an additive to cement 10% by weight after the limitation of boron content by leaching. The conditions for producing good quality bricks is 10% borax waste with
- 18% of moisture content prepared in the molded mixtures and fired at 1000°C.

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An Investigation on the Effect of Potassium Sulphate Salt on the Mechanical Properties of Colemanite Concentrator Waste Blended Portland Cement

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ABSTRACT: The aim of this study is to decrease cost of cement production and environmental pollution with the use of boron waste in cement containing colemanite waste was investigated. Physical and mechanical properties of cement containing different amounts of K_2S0_4 were investigated by XRF method through a number of test such as setting time, volume expantion, compressive strength and grinding time. It was found that the experimental values are in accordence with Turkish Standarts, so the additives used in this study can be utilized as an additive material in cement production.

1. INTRODUCTION

Turkey has the 70% of the reserves of boron which is one of the most strategic ore in the world. Boron minerals are the minerals which contain boron oxide at the different ratios. Tincal, colemanite and ulexide are the most important minerals in Turkey. Tincal reserves are at Eskişehir-Kırka, clemanite reserves are at Kütahya-Emet (Espey and Hisarcık), Balıkersir-Bigadiç, Bursa-Kemalpaşa and ulexide reserves are at Balıkersir-Bigadiç. While the enrichment of these ores and production from these ores, lots of wastes form in the plants.These wastes contain boron oxide in quite high concentration, so this is an environmental pollution. Hence there is a necessity of making use of this waste in large amount in other sectors to avoid environmental problemsin our country the studies about the utilization of these wastes are getting more important day by day. Erdoğan et al pointed out that the wastes containing B2O3 can be used in the production of Portland cement as a cement additive material. In this study, the effects of K2SO4 on the mechanical includes 3 wt% of colemanite waste is investigated (Erdoğan et al).

2. MATERIALS AND METHOD

2.1 Sample

In this work, clinker was supplied from Denizli Cement Plant, gypsum from Denizli-Honaz, colemanite waste from Etibank Boron Plant (Kütahya-Emet), Potasium sulphate salt from Merck Company.

2.2 Experiments Done To Cements Mixtures

Colemanite waste was added to portland cement clinker in 3 wt % proportion. After supplementing of gypsum to this mixture at the 4 wt % ratio, it was taken to a laboratory ball-mill for grinding. After grinding process, cement with additives was ready. At the same time a reference mixture was prepared out of PC and designated as R (PC).

The physical tests of the cement mixes such as particle size analysis, grinding time, specific surface and specific gravity analysis were done according to TS 24 (Table 4). Water requirement, setting times and volume expansion of the cement mixes were determined from the cement paste in accordance to TS 24 (Table 5).

In the continuning study K2SO4 salts were added to cement contaning 3 wt% colemanite waste, in 0,25, 0,50, 0,75, 1 wt% proportion. The kinds and the codes of produced cements are given in Table 1 and also the kinds and the codes of cement mortars from these additive cements are exhibited in Table 2. The relation between the compressive strength and the sample age of the concrete is studied in Figure 1.

3. RESULTS AND DISCUSSION

This study was designed to investigate the effects of potassium sulphate salt on the mechanical properties of colemanite concentrator waste blended Portland cement. The specific conclusion can be drawn from the results of this study:

1. When the grinding times of cement mixes are investigated , it is clearly found out that grinding time for the cement consisting colemanite concentrator waste is quite short than the necessary time for grinding of PC. It is obvious that by using additive materials, we can profit from the energy.
2. Specific gravity, Specific surface and volume expansion values of additive cements are with in the accaptable range of TS. Specific gravity values of the mixtures containing cement additive materials are less than the PC's. This result is because the higher specific gravity of clinker than the additive materials.
3. Setting time values of the cements with additive materials are suitable with the TS values.
4. The compressive strength of the cement mortars at the age of 2,7,28 days are in accordance with Turkish Standards. The compressive strength of KKAKC-1 at the curing time of 2 and 7 days are less than its compressive strength of the other ages. From these results, we can say that, compressive strength of the cements containing colemanite concentrator waste is increasing by the time.
5. The compressive strength values of the cements with K2SO4 are higher than the compressive strength of KKAKC-1 at the age of 2 and 7 days, but less than KKAKC-1 and PC at the curing time of 28 days. The concrete, PSKKAKC-4, including 0,75 wt% K2SO4, has higher compressive strength than PC and other additive cements at the age of 2 and 7 days. From these results, it is clearly seen that alkali sulphate salts increase the compressive strength in the early ages (at the age of 2 and 7 days). By this effect of alkali sulphate salts, it is possible to increase the compressive strength values of colemanite concentrator waste blended cements, at the early ages.

Table 1. Kinds and the codes of produced cements

Kind of Cement	Code of Cement
Portland Cement	PC
3 wt % Colemanite waste blended cement	KKAKC

Table 2. Kinds and the codes of blended cement mortars

Kind of Cement Mortar	Code of Cement Mortar
Portland Cement Mortar	PC
Colemanite waste blended cement mortar	KKAKC-1
0,25 wt % K_2SO_4 blended cement Mortar	PSKKAKC-2
0,50 wt % K_2SO_4 blended cement Mortar	PSKKAKC-3
0,75 wt % K2SO4 blended cement Mortar	PSKKAKC-4
1,00 wt % K2SO4 blended cement Mortar	PSKKAKC-5 >

Table 3. Chemical Analysis of Clinker and Gypsum

Components	Clinker (%)	Gypsum(%)
SİO2	21	0,94
Al2O3	4,49	0,54
Fe_2O_3	4039	0,37
CaO	65,79	32,46
MgO	1,92	1,71
SO_3	0,84	42,56
Na_2O+K_2O	0,80	0,70
B2O3	-	-

Table 4. Physical Analysis of Produced Cements

Cement	wt % Fineness			Grinding Time (min)	Spesific Surface (cm^2/g)	Spesific Gravity g/cm^3
	32n	*90\i*	200u			
KKAKC	27	1,5	-	150	3290	3,13
PC	27	1,5	-	155	3100	3,20
TS 10156	-	<14,0	<1,0	-	>2800	-
TS26	-	<14,0	<1,0	-	>2800	-

Table 5. Experiments Done To Cements Mixtures

Cement	% Water	Setting Time (h:min)		Volume Expantion (mm)		
		Initial	Final	Cold (mm)	Hot (mm)	Total (mm)
KKAKC	25	2:00	3:40	1	1	2
PC	25	2:00	3:10	1	1	2
TS 10156	-	>1:00	<10:00	-	-	<10
TS26	-	>1:00	<10:00	-	-	<10

Table 6. Compressive Strength

Cement	2 Days (N/mm^2)	7 Days (N/mm^2)	28 Days (N/mm^2)
KKAKC-1	15,9	30,6	44,7
PSKKAKC-2	18,8	30,8	42,2
PSKKAKC-3	22,5	34,1	41,8
PSKKAKC-4	24,1	34,2	40,8
PSKKAKC-5	23	33,2	36,2
PC	19,7	32,9	46,9
TS 10156	>10	>21	>32,5
TS 26	>10	>21	>32,5

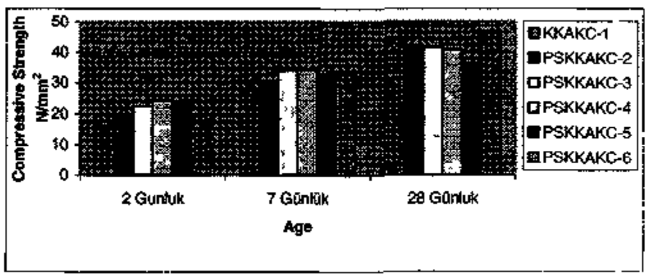

Figure 1. Relationship between Compressive Strength & Sample Age

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