RELATIONSHIP BETWEEN COMPRESSIVE AND CHEMICAL COMPOSITIONS OF PORTLAND AND POZZOLANIC CEMENTS

Arın YILMAZ*

Balıkesir University, Faculty of Engineering and Architecture, Department of Civil Engineering, Balıkesir

ABSTRACT

Pozzolans have been used to improve the some properties of concrete and also to reduce the cost of producing cement. Many researchers investigated pozzolanic cements, which were mostly made with kind of artificial or natural pozzolans. While the most recent investigations on pozzolan containing cements study the effect of pozzolan type, replacement amount and fineness, this study was investigated the effect of clinker composition on the properties of pozzolanic cement.

It was aimed to determine the effect of clinker composition on various properties of portland-pozzolan cements. For this purpose, having different chemical compositions five clinker and one natural pozzolan were selected. After ground separately having three Blaine fineness value; such as 3000, 3500, 4000 cm^2/g, portland-pozzolan cements were prepared by using three different replacement amount; 20, 30, and 40%, by weight. Finally, the sixty types of cements were obtained in this study.

Keywords: Clinker; Blended cement; Compressive strength; Mortar

ÖZET

Puzolanlar, betonun bazı özelliklerini geliştirmek ve üretilen çimentonun maliyetini düşürmek için kullanılmıştır. Birçok araştırmacı doğal veya yapay puzolanlar ile üretilen puzolanik çimentoları araştırmıştır. Günümüzde puzolan içeren çimentolar üzerinde yapılan birçok araştırmada puzolan tipinin, miktarının ve inceliğin etkisi incelenirken, bu çalışmada klinker komposizyonunun puzolanik çimento üzerindeki etkisi araştırılmıştır.

Bu çalışmanın amacı, portland-puzolan çimentosunun çeşitli özelliklerine klinker kompozisyonunun etkisinin incelenmesidir. Bu nedenle, farklı kimyasal kompozisyonlara sahip beş adet klinker ve bir adet doğal puzolan seçilmiştir. Klinkerler, 3000, 3500, ve 4000 cm^2/g inceliğe kadar birbirlerinden ayrı olarak öğütüldükten sonra, %20, %30, ve %40 oranlarında doğal puzolanın katılmasıyla portland-puzolan çimentoları oluşturulmuştur. Sonuç olarak, puzolan içermeyen kontrol çimentolarıda dahil olmak üzere altmış çeşit çimento elde edilmiştir.

Anahtar Sözcükler: Klinker, Katkılı çimento, Basınç dayanımı, Harç

1. INTRODUCTION

Pozzolans are siliceous and aluminous materials, which in the presence of moisture and in finely divided form, react with lime at ordinary temperatures to produce cementitious compounds such as calcium silicates hydrates, calcium aluminate hydrates and calcium sulfoaluminate hydrates (1).

Pozzolans are being used for many centuries. Ancient Greeks and Romans firstly used them in combination with lime. Structures built more than 2500 years ago by using natural pozzolans has still remained in very good condition, for example, the Roman aqueducts and water storage tank in Greece. Today, portland cement and pozzolan blends

* ayilmaz@balikesir.edu.tr

containing either natural or artificial pozzolan have been used extensively all over the world. Turkey has also large deposit of natural pozzolans that are mostly used in the production of portland pozzolan cement.

Pozzolanic cements are mixes of portland cement and pozzolan which if dispersed in water and kept under certain conditions, eventually produce solutions unsaturated with calcium hydroxide. Cement and pozzolan show different reaction processes and react at different ages. As is known, the pozzolanic reaction becomes apparent after 7-15 days since mixing occurred (2).

Production of pozzolanic cements are made by two ways; Clinker and pozzolan are ground separately and mixing with after grinding and clinker is ground with pozzolan at the same time (3).

Although more homogeneous cement is obtained by the first method, particle sizes of portland cement and pozzolan differ from each other and are not well controlled. On the other hand, in the second method, problem of homogeneous mixture arises whereas the better particle size distribution is obtained (4).

The reaction of pozzolans with calcium hydroxide under moist conditions is called pozzolanic reaction. The lime-pozzolan reaction can occur in portland pozzolan cement when the lime is produced by the hydration of βC_2S and C_3S minerals in the cement. This reaction begins in the first few hours of hydration, but the effects of the pozzolanic reaction take place more slowly. The mechanism of the lime-pozzolan reaction in porland pozzolan cement are not understood completely. The simple explanation of reaction can be given as follow(5,6,7);

$$2(Al_2O_3.2SiO_2) + 7Ca(OH)_2 \rightarrow 3CaO.2SiO_2.H_2O + 2(2CaO.Al_2O_3.SiO_2.H_2O) \quad (1)$$

$$(\text{Pozzolan} + \text{Hydrated Lime} \rightarrow 3CS_2H + 2C_2ASH)$$

Vast amount of research on pozzolans in cement and concrete have led to the following general conclusions related with the properties of cementitious systems containing pozzolans(8,9,10,11):

Decrease;

- Permeability
- Thermal volume change
- Heat of hydration
- Segregation and bleeding

Increase;

- Freezing-thawing and chemical resistance
- Long term strength
- Workability of fresh concrete

In addition to these use of pozzolans can provide a major economic benefit such as;

Decrease;

- the cost of product
- energy consumption

In portland pozzolan mixtures the amount of portland cement replaced by pozzolan depends not only on the physical and chemical properties of the pozzolan but also on the characteristics of the portland cement such as chemical composition of the clinker and fineness (6,7,12).

This research was carried out to investigate the effect of clinker composition on the properties of pozzolanic cement by using five different clinkers and one natural pozzolan having different amounts of pozzolan and different fineness values.

2. EXPERIMENTAL STUDY

2.1 Materials

Five clinkers were chosen from seventeen types of clinkers with respect to to their C_3S/C_2S ratios. A natural pozzolan, which have a light green colour and porous structure, was used. The chemical compositions and material properties of clinkers and pozzolan were provided in Table 1.

Table 1. The chemical and material properties of clinkers and pozzolan

	CLINKER A (%)	CLINKER C (%)	CLINKER D (%)	CLINKER N (%)	CLINKER S (%)	POZZOLAN (%)
SiO_2	19,46	20,46	20,46	20,87	19,72	64,29
Al_2O_3	6,01	6	4,52	6,24	6,12	11,55
Fe_2O_3	3,57	3,44	3,57	2,65	3,22	2,97
CaO	65,16	65,32	66,38	65,01	64,69	7,63
MgO	2,14	1,78	2,01	1,48	3,24	0,2
SO_3	1,42	1,02	1,39	1,26	0,63	0,5
K_2O	0,81	0,81	0,68	1,03	0,7	2,98
N_2O	0,08	0,17	0,16	0,64	0,33	1,26
Free CaO	0,15	0,31	0,68	0,49	0,13	-
Loss on Ignition	1,17	0,85	0,75	0,65	1,06	7,47
C_3S	71,23	63,88	76,45	58,29	67,18	-
C_2S	2,07	10,48	1.00	15,87	5,86	-
C_3A	9,89	10,08	5,94	12,05	10,77	-
C_4AF	10,86	10,47	10,86	8,06	9,80	-
C_3S/C_2S	34.48	6.10	76.65	3.67	11.46	-
Specific Surface (cm^2/g)	3051 3589 4051	3043 3499 4023	3004 3512 4043	3031 3504 4153	3043 3487 4034	3010 3540 4100
Specific Gravity	3,16	3,15	3,15	3,16	3,16	2,32

2.2 Preparation of Materials

There is no specifications or test methods to determine the grindability of raw materials. Many types of grinding machines were developed to grind the clinkers such as; ball mill, tube mill, rod mill. In this study, the ball type grinder was used. The clinkers, pozzolan and gypsum were ground separately up to three different Blaine fineness values; 3000, 3500, 4000 cm^2/g. After grinding, clinkers were mixed with the natural pozzolan in there different amount; 20%, 30% and 40% by weight replacement. The gypsum was used %4 by weight in the production of all cements. Finally, 45 Portland pozzolan cement and 15 Portland cement were obtained for this investigation.

2.3 Test Methods

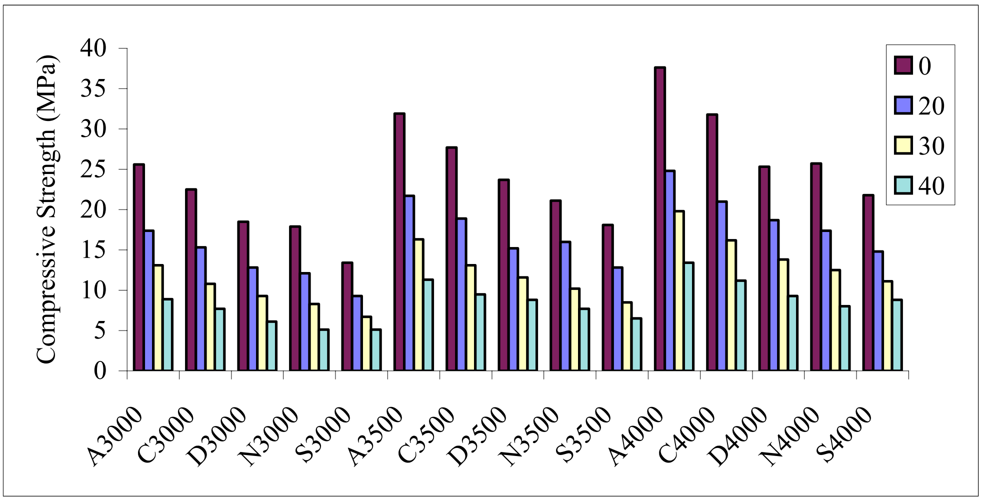
The composition of the mortar specimen mixes was 1:2:6 (water/cement/standard sand). After mixing, the mixture were cast into 40*40*160 mm steel mold prism and were put into the chamber which were set at 100% humidity and 20±2°C temperature. Steel molds were removed after 24 h and specimens were cured in the water with 20±2°C temperature. Flexural and compressive strength tests were applied at the test ages of 2, 7, 28 and 90 days. First, the flexural test with one-point loading was applied to the center of the specimen. The broken parts were used for compressive strength test. The experimental results of six identical specimens were averaged.

3. RESULTS AND DISCUSSION

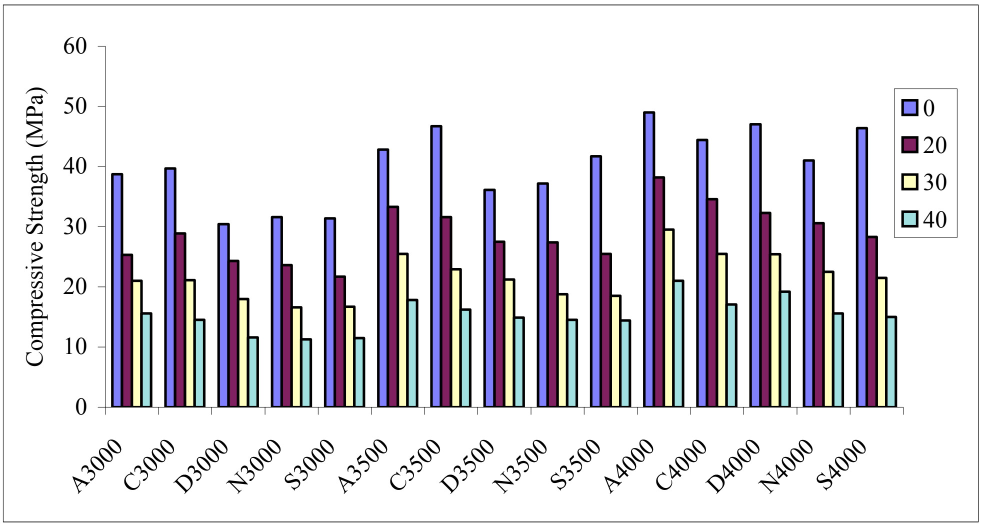
The compressive strength values of mortar were given in Table 2. The replacement amount has an important role for the strength development of pozzolanic cement at specified ages. Therefore, the relationship between pozzolan content and strength development were taken into consideration and represented in Figure 1. As shown in Figure 1(a) and (b), early strength decreases with increasing pozzolan content for each type clinker and every Blaine fineness values. At later ages, in Figure 1(c) and (d), the same one was observed, but the differences between pure cement and pozzolanic cement was less than the early ages. Percent decrease in strength was not proportional with the pozzolan content of the cements.

Table 2. Compressive strength values of mortars (MPa)

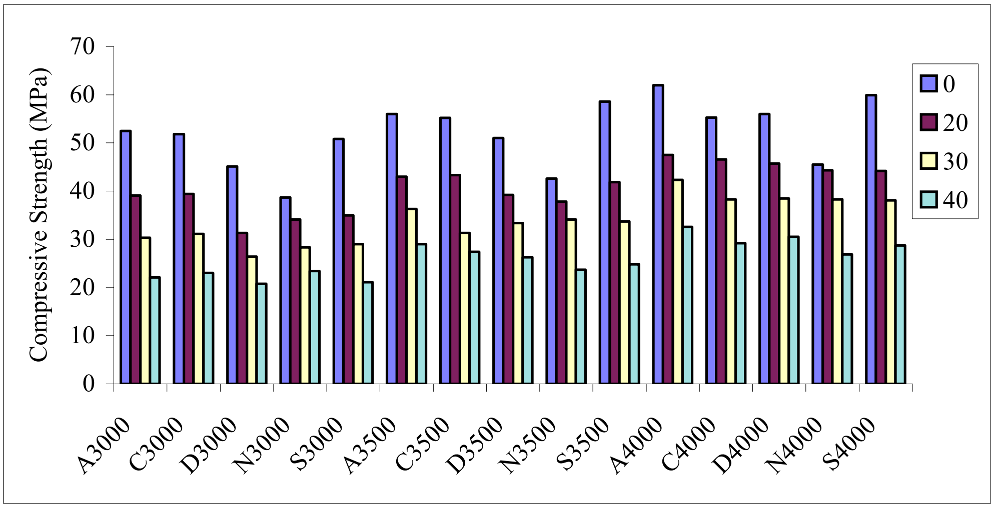
CEMENT TYPE	T I M E	2 DAYS			7 DAYS			14 DAYS			90 DAYS		
	%	BLAINE (cm^2/g)			BLAINE (cm^2/g)			BLAINE (cm^2/g)			BLAINE (cm^2/g)		
		3000	3500	4000	3000	3500	4000	3000	3500	4000	3000	3500	4000
A	0	25.6	31.9	37.6	38.7	42.8	49	52.5	56	62	57.2	60.6	64.3
	20	17.4	21.7	24.8	25.3	33.3	38.2	39.1	43	47.5	46	49.5	53.1
	30	13.1	16.3	19.8	21	25.5	29.5	30.3	36.3	42.3	36.5	42.1	47.4
	40	8.9	11.3	13.4	15.6	17.8	21	22.1	29	32.6	25.7	28.8	35.9
C	0	22.5	27.7	31.8	39.7	46.7	4.4	51.8	55.2	55.3	56.2	63.9	64.2
	20	15.3	18.9	21	28.9	31.6	34.6	39.4	43.3	46.6	51.7	52.2	59.1
	30	10.8	13.1	16.2	21.1	22.9	25.5	31.1	31.3	38.3	42.3	44.1	45.5
	40	7.7	9.5	11.2	14.5	16.2	17.1	23	27.4	29.2	29	30.1	33.7
D	0	18.5	23.7	25.3	30.4	36.1	47	45.1	51	56	49.2	56	58
	20	12.8	15.2	18.7	24.3	27.5	32.3	31.1	39.2	45.7	42.1	47.5	51.3
	30	6.3	11.6	13.8	18	21.2	25.4	26.4	33.4	38.5	33.5	38.9	43.9
	40	6.1	8.8	9.3	11.6	14.9	19.2	20.8	26.3	30.5	23.8	24.4	30.6
N	0	17.9	21.1	25.7	31.6	37.2	41	38.7	42.6	45.5	38.6	44	49.9
	20	12.1	16	17.4	23.6	27.4	30.6	34.1	37.8	44.3	39.5	42.2	47.3
	30	8.3	10.2	12.5	16.6	18.8	22.5	28.3	34.1	38.3	30.7	34.2	43.8
	40	5.1	7.7	8	11.3	14.5	15.6	23.4	23.7	26.9	21.6	28.4	31.8
S	0	13.4	18.1	21.8	31.4	41.7	46.4	50.8	58.6	59.9	53.1	62.1	63.8
	20	9.3	12.8	14.8	21.7	25.5	28.3	35	41.9	44.2	45.5	45.8	51.3
	30	6.7	8.5	11.1	16.7	18.5	21.5	29	33.7	38.1	29	37.1	40.7
	40	5.1	6.5	8.8	11.5	14.4	15	21.1	24.8	28.7	22.4	28.9	30.1



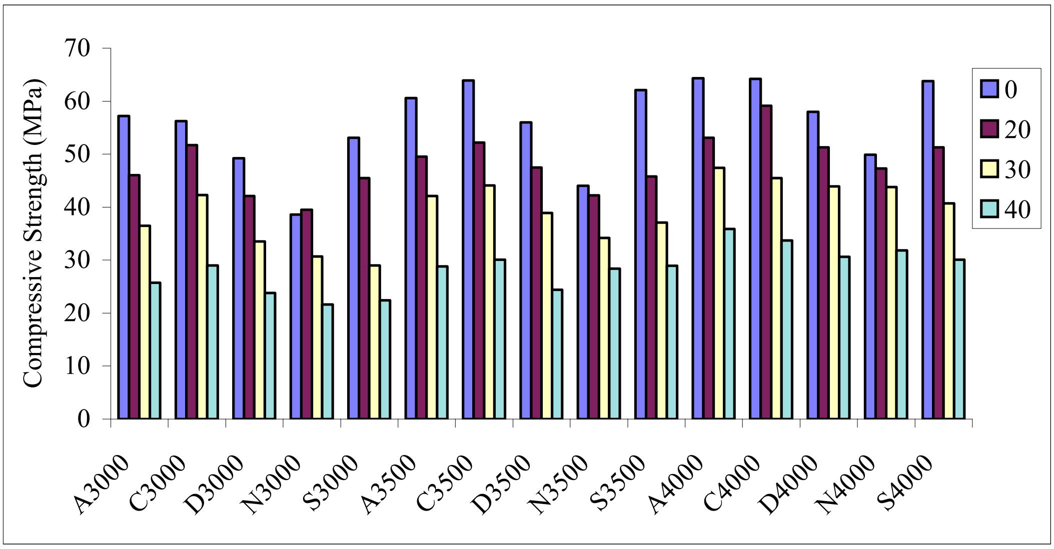
(a) 2 days



(b) 7 days



(c) 28 days



(d) 90 days

Figure 1. Strength pozzolan content relationship for cements

The strength of cements was directly related to the amount of C_3S, C_2S and C_3A. It was necessary to note the unexpected behavior of cement D that had the highest C_3S (76.45 %) content. Cement D was expected to show highest early strength (2 and 7 days), however, it did not. The reason for this behavior would be the cooling state of this clinker. Rapid cooling would result in high amount of amorphous material, which consequently reduces the binding property.

Table 3. The correlation coefficients between various chemical parameters and compressive strength of cements.

Parameters	2 DAYS			7 DAYS			28 DAYS			90 DAYS		
	Blaine (cm^2/g)			Blaine (cm^2/g)			Blaine (cm^2/g)			Blaine (cm^2/g)		
	3000	3500	4000	3000	3500	4000	3000	3500	4000	3000	3500	4000
C_3S	0.83	0.84	0.83	0.85	0.87	0.93	0.86	0.90	0.92	0.82	0.86	0.85
C_3A	0.53	0.53	0.56	0.64	0.65	0.57	0.67	0.61	0.56	0.53	0.55	0.57
C_3S+C_3A	0.86	0.87	0.87	0.90	0.92	0.97	-	-	-	-	-	-
% Finer 45μm	0.98	0.95	0.92	0.96	0.98	0.96	0.90	0.95	0.95	0.90	0.95	0.94
C_2S	-	-	-	-	-	-	0.17	0.07	0.02	0.07	0.07	0.1
C_2S+ C_4AF	-	-	-	-	-	-	0.51	0.42	0.37	0.41	0.42	0.44
C_4AF	-	-	-	-	-	-	0.90	0.92	0.93	0.90	0.92	0.89

Since different types of clinkers having different compositions and fineness were used, the relationship between C_3S, C_3A, C_3S+ C_3A, C_2S, C_4AF, C_2S+ C_4AF, and fineness (% finer than 45μm) and strength of cements produced were investigated for specified ages and three different fineness values, respectively. Considering all 20 types of the cements produced for each Blaine fineness value, good correlations were found between these parameters stated above and compressive strengths at specified ages. These correlation coefficients and related parameters were listed in Table 3.

A linear regression involving the related parameters stated above and the pozzolan content have revealed the equations for specified ages and Blaine fineness value. These equations and correlation coefficients are given in Table 4.

Table 4. General equations between various parameters and compressive strength at specified ages and fineness.

BLAINE (cm^2/g)		DAY	EQUATION	R
	3000	2	0.07*C_3S+0.5*C_3A+1.13*(% Finer 45μm)-0.09*(% POZ.)-73.3	0.986
		7	-0.06*C_3S+0.41*C_3A+1.07*(% Finer 45μm)-0.24*(% POZ.)-43.9	0.990
		28	-0.05*(C_3S/C_2S)+0.91*C_3A+3.8*C_4AF+0.1*(% Finer 45μm)-0.14*(% POZ.)-4.8	0.983
		90	-0.15*(C_3S/C_2S)-0.78*C_3A+4.7*C_4AF+0.48*(% Finer 45μm)-0.12*(% POZ.)-17.9	0.944
	3500	2	1.43*C_3S-4.6*C_3A-23.2*C_4AF+7.5*(% Finer 45μm)+0.07*(% POZ.)-385.2	0.993
		7	0.06*(C_3S/C_2S)-0.14*C_3A-3.6*C_4AF+2.45*(% Finer 45μm)-0.27*(% POZ.)-115.7	0.990
		28	-0.002*(C_3S/C_2S)+2.9*C_3A+8.7*C_4AF-1.48*(% Finer 45μm)+0.04*(% POZ.) +55	0.978
		90	-0.15*(C_3S/C_2S)-0.62*C_3A+5.9*C_4AF-0.16*(% Finer 45μm)-0.22*(% POZ.)+23	0.965
	4000	2	-1.8*C_3S+7.5*C_3A+34.6*C_4AF-11.8*(% Finer 45μm)-0.66*(% POZ.)+703	0.994
		7	-0.63*C_3S+4.2*C_3A+18.3*C_4AF-6.3*(% Finer 45μm)-0.58*(% POZ.)+383.5	0.991
		28	0.007*(C_3S/C_2S)+2.9*C_3A+9.75*C_4AF-2.74*(% Finer 45μm)-0.12*(% POZ.)+157	0.970
		90	-0.04*(C_3S/C_2S)+0.43*C_3A+3.7*C_4AF+0.49*(% Finer 45μm)-0.12*(% POZ.)-18.6	0.944

Finally, the general equation for compressive strength was obtained by using (C_3S/C_2S), C_3A, C_4AF, time, Blaine fineness or % finer than 45μm, pozzolan content parameters. Therefore, these equations and correlation coefficient were written as follow;

$$\sigma = 0.003*(C_3S/C_2S) + 1.36*C_3A + 4.23*C_4AF + 0.25*\text{Time} + 0.008*\text{Blaine Fineness} - 0.03*\text{Pozzolan Content} - 46.8 \quad (R=0.885) \tag{2}$$

Or,

$$\sigma = 0.014*(C_3S/C_2S) + 0.86*C_3A + 1.95*C_4AF + 0.25*\text{Time} + 0.85*(\%\ \text{Finer } 45\mu m) - 0.06*\text{Pozzolan Content} - 59.3 \quad (R=0.886) \tag{3}$$

This formula indicated that for pozzolanic cements, other things being constant increasing pozzolan content decreases strength whereas increasing (C_3S/C_2S) and fineness increase the strength. However, it was difficult to say the same thing for C_3A and C_4AF in these equations, although it was seemed that they had a certain effect which might be due to the independence of the relative proportions of the major compounds in the cement.

A comparison of the test data and the calculated values from equations (2) and (3) were shown in Figures 2 and 3. The figures were indicated a good correlation between the experimental data and proposed equations.

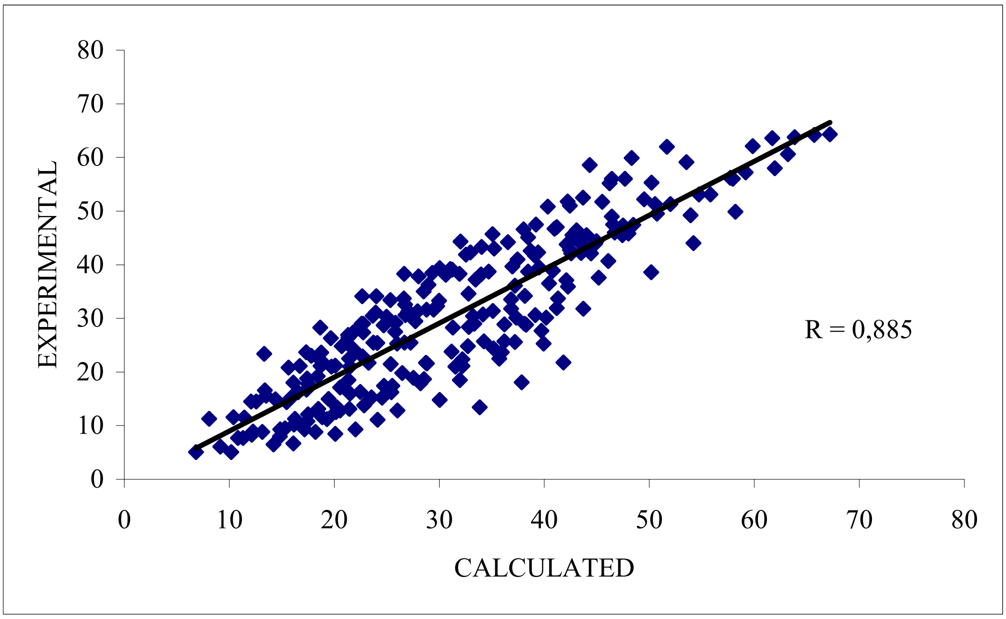


Figure 2. The relationship between the experimental data and proposed equation (2)

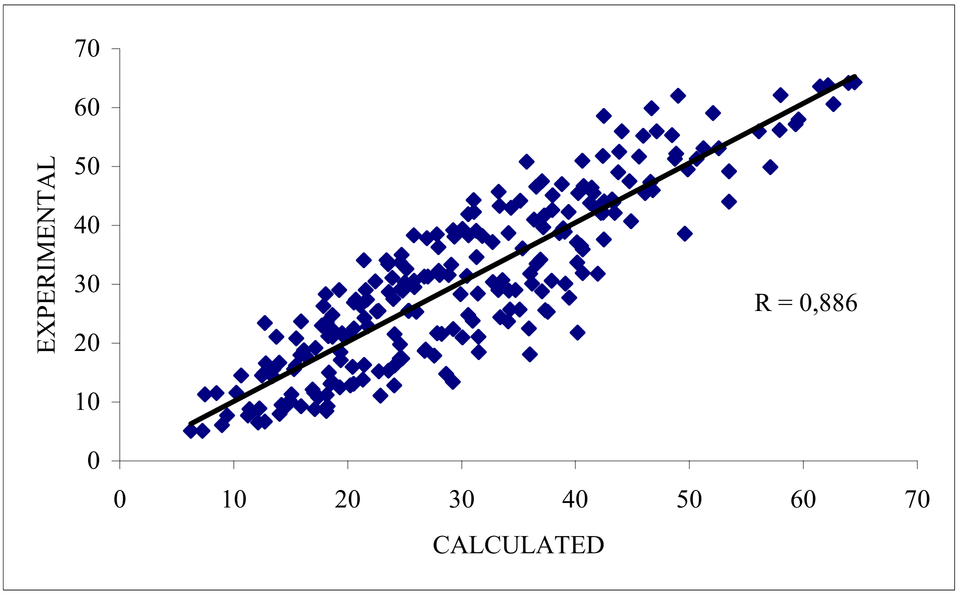


Figure 3. The relationship between the experimental data and proposed equation (3)

4. CONCLUSIONS AND RECOMENDATIONS

The study on pozzolanic cement produced by using natural or artificial pozzolan was performed by many scientists for many years. The following conclusions appear to be justified form this study:

1. Early strength was found to be inversely proportional to the amount of pozzolan used. The difference between the strength of portland cement and pozzolan incorporated cements decreases with time.

2. Cement strength was found to be a function of amount of major compounds, pozzolan content, fineness and time. Two linear equations were proposed in terms of C_3S/C_2S, C_3A, C_4AF, time and fineness to estimate the strength of cements. The calculated values of the strength were found to be in good relation with the experimental values obtained.

The use of the pozzolan in the production of pozzolanic cement was very wide throughout the world. Up to now, the effect of pozzolan on the various properties of pozzolanic cement was investigated by many researches. In this study, the effect of chemical compositions of clinker, before grinding, on the properties of pozzolanic cement were evaluated by using one type of natural pozzolan and five different clinkers. The followings were recommended for the future study on this subject:

1. For full understanding of the effect of the chemical composition of clinkers on the various properties of pozzolanic cement, the major compound of clinkers such as C_3S, C_2S, C_3A, and C_4AF could be produced in laboratory conditions. Therefore, the effect of each compound could be observed separately by taking each one of them with varying percent whereas the others had fixed amount.

2. Using more than five commercial cement and type of pozzolans could extend this study.

REFERENCES

[1] ACI Material Journal Title No. 91-M42 "Proposed Report: Use of Natural Pozzolans in Concrete" Reported by ACI Committee 232, July-August, (1994).

[2] Massazza, F., "Pozzolanic Cements", Cement and Concrete Composites V.15, (1993), 185-214.

[3] Ghosh, S. N., "Cement and Concrete Science and Technology Progress in Cement and Concrete" Part 1, Volume 1, ABI Books Ltd., New Delhi, 1992.

[4] Erdoğdu K., "Effect of Pozzolanic Additions on Grindability and Some Mechanical Properties of Pozzolanic Cements of Different Fineness Values" , A Master Thesis in the Department of Civil Engineering, METU, 1996.

[5] Neville, A. M., “Properties of Concrete” , Longman Scientific and Technical, Singapore, 1993.

[6] Lea, F. M., “The Chemistry of Cement and Concrete”, Edward Arnold (Publishers) Ltd., London, 1970.

[7] Swamy, R. N., “Cement Replacement Materials” , Surrey University Press, 1986.

[8] Shannag, M. J. and Yeğinobalı A., ”Properties of Pastes, Mortars and Concrete Containing Natural Pozzolan”, Cement and Concrete Research V.25, pp. 647-657, 1995.

[9] ACI Material Journal Title No. 84-M34 “Ground Granulated Blast-Furnace Slag as a Cementitious Constituent in Concrete”, Reported by ACI Committee 226, July-August 1987.

[10] ACI Material Journal Title No. 84-M18 “Silica Fume in Concrete”, Reported by ACI Committee 226, March-April 1987.

[11] Mehta, P. K., “Pozzolanic and Cementitious By -Product in Concrete- Another Look”, Silica Fume, Slag and Natural Pozzolan in Concrete Proc. 3rd International Conference, 1989, Trondheim, Norway.

[12] Massazza, F., “Principal Paper, Chemistry of Pozzolanic Additions and Mixed Cements”, Proc. 6th International Congress on the Chemistry of Cements, Moscow, September (1974) .