USING CAPPADOCIA TUFF AS A NATURAL POZZOLAN IN THE CEMENT PRODUCTION

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

MUSTAFA CAN ATAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CIVIL ENGINEERING

SEPTEMBER 2015

Approval of the thesis:

USING CAPPADOCIA TUFF AS A NATURAL POZZOLAN IN THE CEMENT PRODUCTION

submitted by **MUSTAFA CAN ATAN** in partial fulfillment of the requirements for the degree of **Master of Science in Civil Engineering Department, Middle East Technical University** by,

Prof. Dr. Gülbin Dural Ünver
Dean, **Graduate School of Natural and Applied Sciences** ___________________
Prof. Dr. Ahmet Cevdet Yalçıner
Head of Department, **Civil Engineering** ___________________
Assoc. Prof. Dr. Lutfullah Turanlı
Supervisor, **Civil Engineering Department, METU** ___________________

Examining Committee Members:

Assoc. Prof. Dr. Afşin Sarıtaş
Civil Engineering Department, METU ______________________
Assoc. Prof. Dr. Lutfullah Turanlı
Civil Engineering Department, METU ______________________
Assoc. Prof. Dr. Mehmet Baran
Civil Engineering Department, YBU ______________________
Asst. Prof. Dr. Çağla Meral
Civil Engineering Department, METU ______________________
Asst. Prof. Dr. Aslı Akçamete Güngör
Civil Engineering Department, METU ______________________

Date: ______02.09.2015______

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Mustafa Can ATAN

Signature :

ABSTRACT

USING CAPPADOCIA TUFF AS A NATURAL POZZOLAN IN THE CEMENT PRODUCTION

Atan, Mustafa Can

M.S., Department of Civil Engineering

Supervisor: Assoc. Prof. Dr. Lutfullah Turanlı

September 2015, 68 Pages

For the concrete world, it is increasing day by day in importance to use the pozzolans as a cement replacement material or concrete admixture. To be able to use them in this aim, many scientific researchers have been carried out to observe the material's mechanical, physical, and durability characteristics. Moreover, using pozzolan in cement production up to 50%, actually tells that the CO_2 emission is decreased nearly by 50%. Furthermore, whether the pozzolan is natural or a byproduct, the material offers a huge amount of financial benefit by decreasing production cost with having only grinding procedure.

In this study, the natural tuff from Cappadocia Region, Middle Anatolia, was tested as a cement replacement material chemically, mechanically, physically, and for durability. For the tests, one control cement and two blended cements were produced in the laboratory. The materials were intergrinded in this study. At the end of these tests, the observations include 0%, 25% and 50% natural pozzolan replacement with clinker which gives a general idea about the material's efficiency to be used in the cement production with high volume up to 50%.

By means of performance, the cements were tested for fineness, particle size distribution, normal consistency, setting times, autoclave expansions, compressive strength, heat of hydration, and alkali-aggregate reaction in the lights of the related standards in ASTM.

For a given fineness, the material affected autoclave expansion and alkali-aggregate reaction positively. Also the heat of hydration tend to decrease with the increasing pozzolan amount. It is observed that initial and final setting times get longer and water requirement increased. Furthermore, Cappadocia tuff decreased the early strength, however after 90 and 180 days, the strength gaining was quite appearably going on in the Cappadocia tuff blended cements.

Keywords: Natural Pozzolan, Cappadocia Tuff, Blended Cement, Heat of Hydration, Compressive Strength

ÖZ

KAPADOKYA TÜFÜNÜN DOĞAL PUZOLAN OLARAK ÇİMENTO ÜRETİMİNDE KULLANILMASI

Atan, Mustafa Can

Yüksek Lisans Tezi, İnşaat Mühendisliği Bölümü

Tez Yöneticisi: Dr. Lutfullah Turanlı

Eylül 2015, 68 Sayfa

Gün geçtikçe, çimento veya beton katkı malzemesi olarak puzolan kullanımı çimento dünyasında önemini artırmaktadır. Bu doğrultuda puzolan kullanımı için, malzemenin mekanik, fiziksel ve durabilite özeliklerini araştırmak amacıyla, oldukça fazla bilimsel araştırma yapılmaktadır. Ayrıca, %50'ye kadar pozzolan katkılı çimento üretmek, aslında çimento üretiminde ortaya çıkan CO_2 salımını yaklaşık yarıya indirmek anlamına gelmektedir. Daha da fazlası, puzolanın doğal veya yan ürün olması fark etmeksizin, malzeme, sadece öğütme maliyeti sunup üretim maliyetini düşürerek, büyük bir finansal avantaj sunmaktadır.

Bu çalışmada, Orta Anadolu'da bulunan Kapadokya Bölgesi'ne ait doğal tüf, mekanik, fiziksel, ve durabilite özelikleri bakımından, çimento katkı malzemesi olarak test edilmiştir. Deneyler için, laboratuvar şartlarında, bir adet kontrol çimentosu ve iki adet katkılı çimento üretilmiştir. Klinker, alçıtaşı ve puzolan beraber öğütülmüştür. Deneyler sonucunda, %0, %25 ve %50 puzolan katkılı çimentonun, çimento yapımında kullanılabilmesi için gerekli test sonuçları elde edilmiş olup, bu sonuçlar, malzemenin %50ye kadar çimento katkısı olarak kullanılabilirliği hakkında genel bir fikir niteliktedir.

Performans yönünden, çimentolar; incelik, parçacık büyüklüğü dağılımı, normal kıvam, priz süresi, otoklav genleşmesi, basınç dayanımı, hidratasyon ısısı ve alkali-agrega reaktivitesi için, ilgili ASTM standartları yönlendirmesinde test edilmiştir.

Belirli bir incelikte, malzeme otoklav genleşmesini ve alkali-agrega reaksiyonunu azaltmıştır. Bunun yanında, hidratasyon ısısının da artan puzolan miktarıyla azaldığı gözlenmiştir. Yine artan puzolan miktarıyla beraber, su ihtiyacı da artmış, ilk ve son priz süreleri de uzamıştır. Bunun dışında, Kapadokya tüfü katkılı çimentolarda, erken dayanım azalmış, fakat, 90. ve 180. günler sonunda, basınç dayanımının fark edilir şekilde artmaya devam ettiği gözlenmiştir.

Anahtar Kelimeler: Doğal Puzolan, Kapadokya Tüfü, Katkılı Çimento, Hidratasyon Isısı, Basınç Dayanımı

To My Namesake Grandfather Mustafa ATAN,

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Dr. Lutfullah TURANLI for his perfect assistance guidance, recommendations, and support throughout this research and preparation of this thesis.

Sincere thanks are due to my friends, Burak Bulut, Osman Göksu, Barış Kaya, Burhan Aleessa Alam, Meltem Tangüler. Thanks are also extended to the staff of the laboratory, Cuma YILDIRIM and İsmail TEKİN for their help during the experimental study.

Due to their financial and technical contribution and for offering the occasion to improve my engineering skills, I am thankful to my principal TML İnşaat family.

Finally, I am grateful to my family for endless patience, encouragement, support, and confidence in me throughout my life.

TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

LIST OF ABBREVATRIONS

ASTM	American Society for Testing and Materials
TS	Turkish Standards
C0	Cement Produced with 0% Cappadocia Tuff
C25	Cement Produced with 25% Cappadocia Tuff
C50	Cement Produced with 50% Cappadocia Tuff

CHAPTER 1

INTRODUCTION

1.1. General

Pozzolans are siliceous or siliceous and aluminous materials which have little or no cementitious properties by themselves, but in finely divided form, and in the presence of moisture they react with calcium hydroxide to form compounds which have cementitious value. [1]

Pozzolans have been used as a binding material for different construction purposes since the ancient times. The paste was generally the lime-pozzolan mortar.

After cement production introduced, although they lose their importance as building material, because of offering many advantages when compared to portland cement, they went on to be used both as a cement replacement material and as a concrete admixture. These benefits for fresh and hardened concrete are; lowered heat of hydration, decreased permeability, increased resistance to chemical attacks, and decreased freeze-thaw effect.

Another important factor for preferring pozzolan in cement or concrete is the production cost. Most generally, pozzolans are cheaper to be used in cement as producing portland cement from the clinker requires more energy than that of the pozzolan replaced cements. This makes portland-pozzolan cement more feasible than portland cement depending on the construction needs, and while the feasibility is one of the most important factors to be concerned, this gives very high importance to pozzolans as all the production over the world aim to decrease the production cost.

From the ecological point of view, also pozzolanic cements offer some advantages by decreasing the clinker amount. During portland cement production, for every ton of cement produced, one ton of CO_2 is released to the atmosphere. About half of this emission is related with limestone calcinations, and the rest is fossil fuel combustion. [2] When the amount of cement produced over the world considered, it can be commented that, every decrease in the clinker amount in the cement is going to give our ecosystem some more credits for the future.

To be able to use pozzolans in hydraulic cements, the material should satisfy some standard specifications. According to ASTM, the main specification for this study, there is no amount limitation for pozzolans. As long as the material should satisfy the performance criteria for ASTM C 1157 [3], the blended cement is acceptable. For Turkey, TS 1244 [4] puts an upper limit for pozzolans to be used in blended cements as 55% by mass.

In the Cappadocia Region, Central Anatolia, there is a huge amount of volcanic tuff reserve which is able to be used as pozzolan. Until nowadays, N. Ertek [5] studied the material to produce white cement, and by means of cement production, there has been no other study using Cappadocia Tuff. The material is widely used for brick production. Introducing this material as a cement replacement material is going to mean introducing a natural pozzolan that is going to save energy and decrease cost while offering several technical advantages for concrete durability. This is the main aim of this study.

1.2. Object and Scope

The object of this study is to investigate the effect of blending clinker, with up to 50% Cappadocia Tuff by weight, on the physical and mechanical properties of cements. For these observations, three types of cements were produced: Control cement from clinker and gypsum, C25 from 25% natural tuff replacement with clinker, and C50 from 50% natural tuff replacement with clinker by weight.

The cements include 4% gypsum by clinker's weight, and C0, C25 and C50 have nearly 3500, 400, and 4500 cm^2/g Blaine finenesses respectively.

All types of cements were tested for specific gravity, Blaine fineness, 45µ wet sieving, particle size distribution, normal consistency, initial and final setting times, autoclave expansion, heat of hydration, alkali-aggregate reactivity under the physical tests topic. The mechanical tests were compressive strength tests up to 180 days (3, 7, 14, 28, 56, 90, 180 days) for all three types, as well. Also chemistry of the gypsum, natural tuff, and clinker were investigated by X-Ray diffraction method.

CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1. Portland Cements

Portland cement is a hydraulic binder that is produced by pulverizing clinker and gypsum. The ingredients of clinker are generally hydraulic calcium silicates and they contain one or more forms of calcium sulfate which is added while intergrinding. [6]

'Hydraulic cement' refers to a reactive powder material, reactive with water, and at the end of this reaction, product is a binder material that is insoluble with water.

Portland cement produced from lime and clayey materials those are burned in the 'rotary kilns' and interground with a small amount of gypsum. At the end of grinding, the product is portland cement. [7]

The name 'portland' actually did not specify a cement type and it is just a trade name. However, by the time, it refers to a group of cements those are in the similar chemical and physical characteristics. Some different portland cement are also produced by some deserved property modifications. [8]

2.1.1. Oxide Compositions of Portland Cements

For portland cements, mainly for clinker, there are four major oxides: Lime (CaO), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). These four majors constitute about 95% of the clinker. Other six minor impurities constituting about 5% are magnesia, sodium oxide, potassium oxide, titania, phosphorous and manganese oxides. [7]

For a usual portland cement, the composition of oxides in it shown in Table 2.1. In this table, the oxides are shown by a capital letter in the shorthand notation. Also for the carbon and sulfur oxides, which have more important role in cement chemistry, the shorthand symbols have a line over them. (C & S) Then, gypsum is shown as CSH_2, and calcium carbonate is shown as CC in shorthand notation. [8]

Table 2.1. Typical Oxide Composition of an Ordinary Portland Cement [8]

Oxide	Shorthand Notation	Common Name	Weight Percent
CaO	C	Lime	63%
SiO2	S	Silica	22%
Al2O3	A	Alumina	6%
Fe2O3	F	Ferric Oxide	2,5%
MgO	M	Magnesia	2,6%
K2O	K	Alkali	0,6%
Na_2O	N	Alkali	0,3%
SO_3	S	Sulfur Oxide	2%
CO_2	C	Carbon Dioxide	-
H_2O	H	Water	-

2.1.2. Compound Composition of Portland Cements

According to Le Chatelier's research, given in Table 2.2., for the portland cements, there are four compounds those can be called as major compounds. [7]

Table 2.2. Major Constituents of Portland Cements [7]

Name	Composition	Symbol	Mineral Name
Tricalcium silicate	$3CaO.SiO_2$	C_3S	Alite
Dicalcium silicate	$2CaO.SiO_2$	C_2S	Belite
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	-
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	Celite

Shown in Table 2.2., alite and belite are seen in about 75-80% of the portland cement structure. In internal structure, these silicates have separated SiO_4 and then connected by calcium ions.

These names of the minerals, shown in Table 2.2., are originated by Torneborn [1897]. Since the clinker minerals do not have a pure compound composition and have some impurities in them, those are able to affect the properties of the cements, it is better to name these compounds by their mineral name. As an example, alite and belite have alumina, magnesia, and other oxides in them. [7]

2.1.3.Minor Constituents of Portland Cements

When the constituents of portland cement called minor, this tells that the 'minors' are existing in low percentages. It does not tell they are in lower importance for the portland cement. For instance, magnesia is a minor for portland cement, and if the cement contains it about 5%, and especially if it is in crystal form, it affect the soundness of the cement. The effect is very similar to the that of free lime for the cement, it decreases the soundness. Also, as another example, alkali can react with the silicates in the paste, and this reaction generally ends with the expansion and relatively cracking in the concrete or paste until the older ages.

At the very first times, the calcium sulfate compounds were being used to calibrate the setting time in the cement. Nowadays, they are also being used for the calibration of early-day-strength of the paste, and drying shrinkage. [8]

2.1.4. Hydration of Portland Cement

The term 'hydration' for the portland cement is actually the result of number of chemical reactions of the constituents of the cement. These reactions occur with the meeting of the water and the constituents. Starting from first meeting of the water and cement until the late hardening period, these reactions go on, and this process is called the hydration of the portland cement.

For the hardening, the constituents of cement have number of reactions with the water starting from just after the mixing with the water for hardening of the paste or concrete. After the hydration, reaction with the water, there are new products called 'hydration products'. All of the reactions including hydration are described by the rate of reaction and heat of hydration. The cement chemistry also interesting in the affect of the products, mainly whether they are affecting strength of the paste or not. At the end of many researches, the main responsibility of the constituents are described as can be followed in the Table 2.3. [8]

In hydration on other reactions, it is assumed that every reaction go on independently from one another. The constituents are assumed to be separate from each other, actually this means they are pure, however, this is not actually completely true, but the interaction ratio is a reasonable generally, and this assumption is acceptable for almost every portland cement reaction procedures.

Table 2.3. Characteristics of Hydration of the Cement Compounds [8]

Compounds	**Reaction Rate**	**Amount of Heat Liberated**	**Contribution to Cement**	
			Strength	**Heat Liberated**
C_3S	Moderate	Moderate	High	High
C_2S	Slow	Low	Low initially, high later	Low
$C_3A + CSH_2$	Fast	Very High	Low	Very High
$C_4AF + CSH_2$	Moderate	Moderate	Low	Moderate

The hydration of tricalcium silicate and dicalcium silicate to form calcium hydroxide are given in Equation 2.1. and Equation 2.2.

$$\underset{\text{tricalcium silicate}}{2C_3S} + \underset{\text{water}}{6H} \rightarrow \underset{\text{C-S-H}}{C_3S_2H_3} + \underset{\text{calcium hydroxide}}{3CH} \tag{2.1.}$$

$$\underset{\text{dicalcium silicate}}{2C_2S} + \underset{\text{water}}{4H} \rightarrow \underset{\text{C-S-H}}{C_3S_2H_3} + \underset{\text{calcium hydroxide}}{CH} \tag{2.2.}$$

After these reactions, the main product is calcium silicate hydrate. The chemical formula can be different as the composition of the C-S-H gel can differ. It was also called tobermorite gel. It is generally in non-crystal form. On the other hand, the calcium hydroxide is a crystalline material.

As given in Equation 2.3., tricalcium aluminate reacts with the sulfates coming from gypsum and the product is ettringite.

$$\underset{\text{tricalcium aluminate}}{C_3A} + \underset{\text{gypsum}}{3CSH_2} + \underset{\text{water}}{26H} \rightarrow \underset{\text{ettringite}}{C_6AS_3H_{32}} \tag{2.3.}$$

Ettringite is mainly calcium sulfoaluminate hydrate that is a product of the reaction just when the sulfate occurs in the system. The hydration products depending on the C-S-H to tricalcium aluminate ratio are given in Table 2.4.

Table 2.4. Formation of Hydration Products from C_3A [8]

CSH_2/C_3A Molar Ratio	**Hydration Products Formed**
3.0	Ettringite
3-1	Ettringite + monosulfoaluminate
1	Monosulfoaluminate
< 1	Monosulfoaluminate solid solution
0	Hydrogarnet

If there is not any non-consumed sulfate in the system, tricalcium aluminate reactions occur as shown in Equation 2.4.

$$2C_3A + C_6AS_3H_{32} + 4H \rightarrow 3C_4ASH_{12} \tag{2.4.}$$

This time the product is monosulfoaluminate. Sometimes, this reaction occur before the reaction of the ettringite. For this to happen, tricalcium aluminate should react faster than the sulfates coming from the gypsum. Both Equation 2.3. and 2.4. are exothermic reactions.

When there is monosulfoaluminate meet with more sulfate, as shown in Equation 2.5., there can be a reaction which has ettringite as product. This is generally seen when the cement is exposed to sulfate by any source.

$$C_4ASH_{12} + 2CSH_2 + 16H \rightarrow C_6AS_3H_{32} \tag{2.5.}$$

The reason why gypsum is added to the clinker while grinding is the rapid reaction of the tricalcium aluminate with hydrogen shown in Equation 2.6. This is a very fast reaction ends with flash set, and with an appropriate amount of gypsum addition, 'Flash Set' can be prevented.

$$C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8 \qquad (2.6.)$$

Furthermore, these products are not stable and they form hydrogarnet as shown in Equation 2.7.

$$C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H \qquad (2.7.)$$

In the case of celite, the first main effect is having slower reaction. Celite does not react as fast as to have flash set, moreover, gypsum gets the reaction slower than that of tricalcium aluminate. The second difference is, with the longer time, the heat generation during the reaction is lower. Also, as the iron content is increased, the speed gets lower. In Equation 2.8. and Equation 2.9. celite reactions are shown chemically. [8]

$$C_4AF + 3CSH_2 + 21H \rightarrow C_6(A,F)S_3H_{32} + (A,F)H_3 \qquad (2.8.)$$

$$C_4AF + C_6(A,F)S_3H_{32} + 7H \rightarrow 3C_4(A,F)SH_{12} + (A,F)H_3 \qquad (2.9.)$$

2.1.5. Fineness of Portland Cement

Fineness of a portland cement is related with how much or long it is grinded and the degree of the fineness tells how small the particles are. It is one of the most important characteristics of the portland cement to be able to classify. While fineness increases, the early strength increases, bleeding decreases, and expansions due to autoclave decrease. Especially, from the strength point of view, until 1950's, the finer cements were deserved more. However, other than increasing the cost of the cement, some disadvantages such as; shrinkage, alkali-aggregate reactivity, water requirement, and storability proved that having finer cement does not mean having the best cement always, and there should be an optimal fineness depending on the usage area of the cement and the needs of users. [8]

2.2. Pozzolanic Materials

A pozzolan is a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. [9]

Pozzolans were started to be used as a hydraulic binding material at 300 B.C. The Ancient Rome citizens found the binding property of the pozzolans. The material was the volcanic tuff coming from explosion of Vesuvius Mountain, near the Italian city 'Pozzuoli'. The name pozzolan comes from that Italian city. [10]

Reaction of a pozzolan in the cement is shown in Equation 2.10.

$$\underset{\text{calcium hydroxide}}{CH} + \underset{\text{silica}}{S} + \underset{\text{water}}{H} \rightarrow \underset{\text{calcium silicate hydrate}}{C\text{-}S\text{-}H} \qquad (2.10.)$$

The reaction of pozzolan occurs with calcium hydroxide and at the end of the reaction, the product is C-S-H gel. It can react with CH in the lime if directly mixed. However, in the4 case of blending with portland cement, the reaction is between pozzolan and the calcium hydroxide, that is a product of the portland cement reaction. By this way, C-S-H gel amount in the system increases, and this is the main effect of the pozzolan on the portland cement. [8]

There are several mainly known and used pozzolans. Volcanic ashes, tuffs, glasses, clays, diatomic earths are the main naturally derived ones. There are also artificial ones such as fly ash, that is gained from the chimneys of the power plants using coal, silica fume, a byproduct of silicon production, and rice husk ash. All these materials are widely used in the pozzolanic cement production.

As an artificial pozzolan, fly ashes show high pozzolanic activity. Especially sub-bituminous coal and lignite, rather than having high pozzolanic activity, have a little cementitious behavior. Another artificial pozzolan that is a byproduct of iron production, also has the same pozzolanic and cementitious property. The reason for these two materials' high pozzolanic property is having high calcium oxide in them.

In chemistry, alumina-silicates in pozzolans are reacting with the calcium hydroxide. This calcium hydroxide can be in the lime, or it can be the product of portland cement reaction. The rate of reaction of pozzolan with calcium hydroxide is basically called pozzolanic activity and a material should satisfy some tests to prove that is over some pozzolanic activity limit to be able to be called as a pozzolan.

For pozzolans, ASTM C 311 [11] is the test method to decide the activity level. By this method, strength activity index is decided, and with comparing compressive strengths of the control and test specimens, the material is expected to satisfy some limit for being called as a pozzolan by strength activity index. [12]

As mentioned before, pozzolans are binder materials. But to have binding effect, the first way is mixing them with calcium hydroxide. This method was widely used in ancient times and the usage are is limited with generally pavement or some similar applications. Secondly, they can be ground with clinker to have portland pozzolan cement. In this method, pozzolan react with the calcium hydroxide that is a product of cement reaction with C-S-H gel. After this hydration product, with the pozzolan and CH reaction, the C-S-H amount in the system increases and the binding property directly increases, moreover, porosity decreases. The last usage type is adding them directly to the concrete before pouring. This is the most widely usage way for the pozzolans nowadays. [12]

2.2.1. Types and Classification of Pozzolanic Materials

There are two main groups for pozzolan: natural pozzolans and artificial pozzolans. Natural pozzolans are obtained naturally and volcanic ash, volcanic tuff, clays and shale, diatomic earths are some examples of natural ones. Artificial pozzolans are the by-products of industry and fly ash, silica fume, granulated blast furnace slag are examples to artificial pozzolans.

In practice, artificial pozzolans are generally used as concrete admixture while the natural ones are widely used for producing portland pozzolan cement in the grinding procedure. The natural ones are rarely being used as admixture, as well.

Although natural pozzolans cannot be classified according to specifications, they are generally classified according to some researches. One of these is made by Mienlez and the results are given in Table 2.5. [12]

Table 2.5. Classification of Natural Pozzolans [12]

Activity Type	Essential Active Constituents
1	Volcanic glass
2	Opal
3a	Kaolinite-type clay
3b	Montmorillonite-type clay
3c	Illite-type clay
4	Zeolites
5	Hydrated oxides of aluminum
6	Non-pozzolans

As a sub-title, natural pozzolans can be divided into two groups: Volcanic ones is the one group, and thermally treated clays, shale, diatomic earths is the second group. The reason why these groups can be formed is that volcanic materials (tuff, ash, trass) can be used as pozzolan without any treatment, in other words, in the natural form, they are pozzolan. On the other hand, clay, shale, and diatomic earth generally have to be treated thermally to be able to be used as pozzolan, for increasing their pozzolanic activity. Therefore, the first group includes more active pozzolans.

Volcanic eruptions resulting in the eruption of magma is the way how the natural pozzolans, from volcanic origin, are formed in the nature. They are composed of alumina silicates. After coming up to ground surface, magma gets cooled rapidly with the high temperature difference, and because of this difference, the structure is amorphous and disordered. Moreover, having dissolved gases in the structure, after those gases leave the system, these materials are generally porous that is related with high surface area also. Thanks to the two properties, having alumina silicates and being porous, the reaction with calcium ions and pozzolans in the presence of water easily happens. If the magma eruption is violent, the material has high pozzolanic activity and these are glassy materials. If the eruption is less violent, the materials have less pozzolanic activity. These are ash type materials.

In Bacali,- Italy, Shirasu - Japan, Santorin-Greece, the pozzolans are examples of widely known glassy materials. These regions' natural pozzolans have disordered structure and include alumina silicate glass, and have high pozzolanic activity.

As example to less active natural pozzolans, Segni Latium-Italy and Rheinland - Germany pozzolans can be introduced. This type includes tuffs and trasses, and the chemical composition reserves augite, apatite, biotite, hauynite, nosean, magnetite, muscovite, hematite, cristobalite, kaolinite, illnite, mica, and hornblend. [12] Chemical and mineralogical composition of natural pozzolans are given in Table 2.6. [14]

From clay and shale point of view, because of having crystal structure in natural form, to be able to have pozzolanic activity, the materials should be treated thermally up to 700-900°C. After this calcinations procedure, crystal structure leaves its place to amorphous and disordered structure, and the materials get high pozzolanic activity. The activity depends on the duration and the temperature of the calcinations. According to researches, illite and montmorillonite have optimum conditions to be calcined at about 800°C for one hour, while those of kaolinite are 700°C and one hour. [12]

For diatomic earths, the ingredients are opline or hydrated silica. These two come from skeletons and diatoms, and can be seen up to 94%. As activity, diatomic earths are over qualified, however, because of high water requirement, low strength, and low durability, they are not widely used in practice. [12] A microporous texture which leads high water requirement is given in Figure 2.1. [16]

Table 2.6. The Typical Chemical and Mineralogical Analysis of Some Natural Pozzolans [14]

Pozzolan	**Percentage (%)**						**Ignition loss (%)**	**Estimated non-crystalline matter (%)**	**Major Crystalline Materials**
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Alkalies**			
Santorin earth	65.1	14.5	5.5	3.0	1.1	6.5	3.5	65 - 70	Quartz, plagioclase
Rheinish trass	53.0	16.0	6.0	7.0	3.0	6.0	-	50 - 60	Quartz, feldspar, analcite
Phonolite	55.7	20.2	2.0	4.2	1.1	10.8	3.6	-	Orthoclase, albite, pyroxene, calcite
Roman tuff	44.7	18.9	10.1	10.3	4.4	6.7	4.4	-	Herschellite, chabazite, phillipsite
Neapoliten glass	54.5	18.3	4.0	7.4	1.0	11.0	3.1	50 - 70	Quartz, feldspar
Opaline shale	65.4	10.1	4.2	4.6	2.7	1.4	6.3	-	-
Diatomite	86.0	2.3	1.8	-	0.6	0.4	5.2	-	-
Rhyolite pumicite	65.7	15.9	2.5	3.4	1.3	6.9	3.4	-	-
Jalisco pumice	68.7	14.8	2.3	-	0.5	9.3	5.6	90	Sanidine

Figure 2.1. Scanning Electron Micrograph Showing the Microporous Nature of Diatomic Earth [16]

2.3. Hydration Between Portland Cement and Pozzolans

The chemical reaction between portland cement and pozzolans, actually goes on between the alkalies of cement and the oxides of the pozzolans. After the reaction between the calcium hydroxide (product of cement reaction) and pozzolan, calcium silicate hydrate gel is added to the system other than calcium silicate hydrate gel coming from the cement hydration. Calcium hydroxide amount change in the system whem pozzolan added to the cement is shown in Figure 2.2. [14]

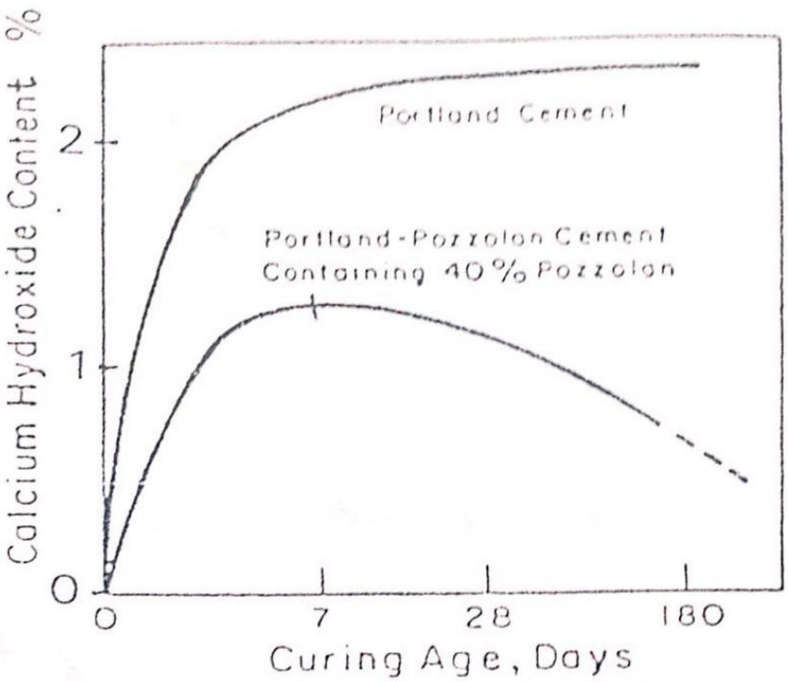


Figure 2.2. Change in Calcium Hydroxide Content of Portland Cement and Portland Pozzolan Cement Pastes [14]

According to ACI Committee Report [14], it is observed that, if SiO_2/R_2O_3 ratio is higher in the pozzolan, the paste or the concrete is stronger for sulfate attack by pozzolans' decreasing free calcium hydroxide. [14]

Also pozzolanic reaction has beneficial effects on the physical properties of the paste. There is more calcium silicate hydrate introduced to the system, and the system gets less porous when cement is blended with pozzolan. Researches on Santorin Earth confirmed that, pozzolan blended cements are better for physical durability and mechanical strength, rather than the pastes chemical properties. [14,15]

According to Massaza [18]; there are four main types of crystalline hydrates as result of the reaction between lime and pozzolan: The first one is C-S-H gel, second one is hexagonal calcium aluminate hydrate, third hydrate is gehlenite, and the last one is ettringite.

2.4. Pozzolanic Cements and Portland Pozzolan Cements

The difference between pozzolanic cement and the portland pozzolan cement is basically the pozzolan amount. If the pozzolan amount is sufficient for all the free lime in the system to react, it is called pozzolanic cement. If the pozzolan amount is insufficient to react with all the free lime, it is called portland pozzolan cement. [18]

According to Malhotra V.M. [17]; low basicity when the lime amount in the cement is, increased mechanical strength with respect to other cements, decreased heat of hydration are the main three properties of portland pozzolan cements.

2.5. Standard Specifications for Blended Cements

According to the standards, blended cements should satisfy some different limits as all the cements do. For many countries, blended cement standards exist. For instance, according to TS 12144 [4], pozzolanic cement may maximum have 55% pozzolan by mass while according to ASTM C 595 [19], that ratio is 40% by mass. Also ASTM C 595 prescribes to ASTM C 1157 [3] some performance tests. Therefore, if the product satisfies ASTM C 1157, it is acceptable for usage. According to ASTM C 1157, hydraulic cement types are shown in Table 2.7., performance specifications are shown in table 2.9., and the strength range limits of Table 2.9. is given in Table 2.8.

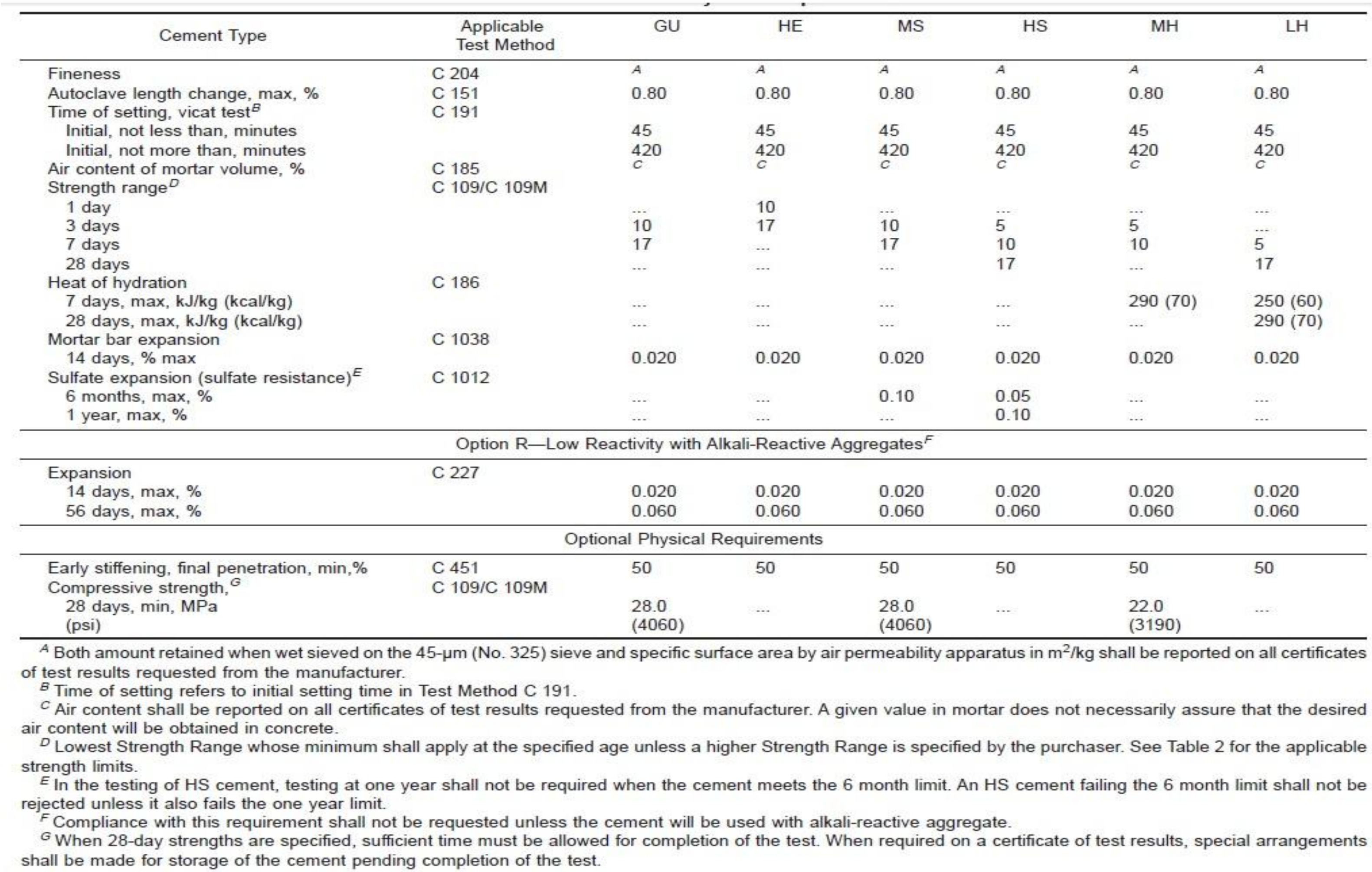
Table 2.7. Types of Hydraulic Cements According to ASTM C 1157

Cement Type	**Description**
Type GU	Hydraulic cement for general construction
Type HE	High early strength
Type MS	Moderate sulfate resistance
Type HS	High sulfate resistance
Type MH	Moderate heat of hydration
Type LH	Low heat of Hydration

Table 2.8. Strength Range Limits Specified in Table 2.9.

Strength Range	5	10	17	25	35	45
Compressive Strength, min, MPa (psi)	5 (725)	10 (1450)	17 (2465)	25 (3625)	35 (5075)	45 (6525)
Compressive Strength, max, MPa (psi)	15 (2175)	20 (2900)	30 (4350)	40 (5800)	60 (8700)	-

Table 2.9. Performance Specifications in ASTM C 1157



Cement Type	Applicable Test Method	GU	HE	MS	HS	MH	LH
Fineness	C 204	[A]	[A]	[A]	[A]	[A]	[A]
Autoclave length change, max, %	C 151	0.80	0.80	0.80	0.80	0.80	0.80
Time of setting, vicat test[B]	C 191						
Initial, not less than, minutes		45	45	45	45	45	45
Initial, not more than, minutes		420	420	420	420	420	420
Air content of mortar volume, %	C 185	[C]	[C]	[C]	[C]	[C]	[C]
Strength range[D]	C 109/C 109M						
1 day		...	10	...	...	...	...
3 days		10	17	10	5	5	...
7 days		17	...	17	10	10	5
28 days		...	...	...	17	...	17
Heat of hydration	C 186						
7 days, max, kJ/kg (kcal/kg)		...	...	...	...	290 (70)	250 (60)
28 days, max, kJ/kg (kcal/kg)		...	...	...	...	...	290 (70)
Mortar bar expansion	C 1038						
14 days, % max		0.020	0.020	0.020	0.020	0.020	0.020
Sulfate expansion (sulfate resistance)[E]	C 1012						
6 months, max, %		...	...	0.10	0.05	...	...
1 year, max, %		...	...	...	0.10	...	...
Option R—Low Reactivity with Alkali-Reactive Aggregates[F]							
Expansion	C 227						
14 days, max, %		0.020	0.020	0.020	0.020	0.020	0.020
56 days, max, %		0.060	0.060	0.060	0.060	0.060	0.060
Optional Physical Requirements							
Early stiffening, final penetration, min,%	C 451	50	50	50	50	50	50
Compressive strength,[G]	C 109/C 109M						
28 days, min, MPa (psi)		28.0 (4060)	...	28.0 (4060)	...	22.0 (3190)	...

[A] Both amount retained when wet sieved on the 45-µm (No. 325) sieve and specific surface area by air permeability apparatus in m^2/kg shall be reported on all certificates of test results requested from the manufacturer.

[B] Time of setting refers to initial setting time in Test Method C 191.

[C] Air content shall be reported on all certificates of test results requested from the manufacturer. A given value in mortar does not necessarily assure that the desired air content will be obtained in concrete.

[D] Lowest Strength Range whose minimum shall apply at the specified age unless a higher Strength Range is specified by the purchaser. See Table 2 for the applicable strength limits.

[E] In the testing of HS cement, testing at one year shall not be required when the cement meets the 6 month limit. An HS cement failing the 6 month limit shall not be rejected unless it also fails the one year limit.

[F] Compliance with this requirement shall not be requested unless the cement will be used with alkali-reactive aggregate.

[G] When 28-day strengths are specified, sufficient time must be allowed for completion of the test. When required on a certificate of test results, special arrangements shall be made for storage of the cement pending completion of the test.

CHAPTER 3

REVIEW OF RESEARCH ON THE POZZOLANIC AND HIGH VOLUME POZZOLANIC CEMENTS

Use of pozzolans as a cement replacement material is increasing day by day. The most important factor for this increase is, aim of decreasing the energy for production. Also, instead of using ordinary portland cement, blended cements with pozzolan require some advantages: lower heat generation, higher ultimate strength, and better long term durability. [21]

Another advantage of using pozzolan as a cement replacement material is that, especially the natural ones, do not affect ecosystem negatively as the ordinary portland cement production pollute the environment.

For every ton of portland cement production, one ton of CO_2 raises to the atmosphere. If the clinker amount in the blended cement decreased to 50%, it means that, half of the cement raw material will be produced only with grinding procedure, and the CO_2 emission will be decreased to almost 50%, and this is very important for ecosystem, even almost ecology is one of the most important topics to be preserved. [20]

3.1. Chemical and Physical Properties of Portland-Pozzolan Cements

Differing from cement, pozzolans do not react with water, they react with CH, that is a byproduct of cement-water reaction, and this is called pozzolanic reaction. The first difference is the speed of the reaction. The pozzolanic reaction is slower and taking a longer time, so, the heat liberation is less and wider in the time. The second difference is, again instead of lime producing cement reaction, this reaction is lime consuming, which is increasing the durability to acid attack. The last difference is pore size distribution. The reaction goes on after even cement reaction finished, and the products are better to fill capillary pores when compared to cement reaction products, so, the strength and impermeability of the system increases. [14]

3.2. Result on Microstructure of Hydrated Cement with Natural Pozzolan

In literature pozzolan replacement effects on microstructure of cement paste is studied many times. 0, 10, 20, and 30 % pozzolan replacement with cement effect on microstructure is studied by Mehta [21]. These studies were including pore size distribution, x-ray diffraction analysis, free $Ca(OH)_2$ determination, and scanning microscopy of the cement pastes. As shown in Figure 3.1.(a) and 3.1.(b), at the end of 28 days, some piece of the paste is covered with aggregating $Ca(OH)_2$ crystals. However, in Figure 3.1.(c) and 3.1.(d)., it is clearly seen that, at the end of 1 year period, the $Ca(OH)_2$ aggregation is decreasing with increasing pozzolan amount in the cement. Also, the result of scanning microscopy in Figure 3.2. tells the indirect proportionality of the pozzolan and $Ca(OH)_2$.

From the point of view of pore size distribution, especially in long term up to 1 year, it is observed that, with 10, 20, 30% pozzolan replacement, the pore sizes were decreased. The results are same in the water permeability tests. Results are shown in Table 3.1. and Figure 3.3. [21]

According to ACI committee report [14] and Mehta's study [21], instead of chemical symptoms, physical symptoms of pozzolanic reaction, for example pore refinement, is more important to have a chemically and mechanically more durable cement paste.

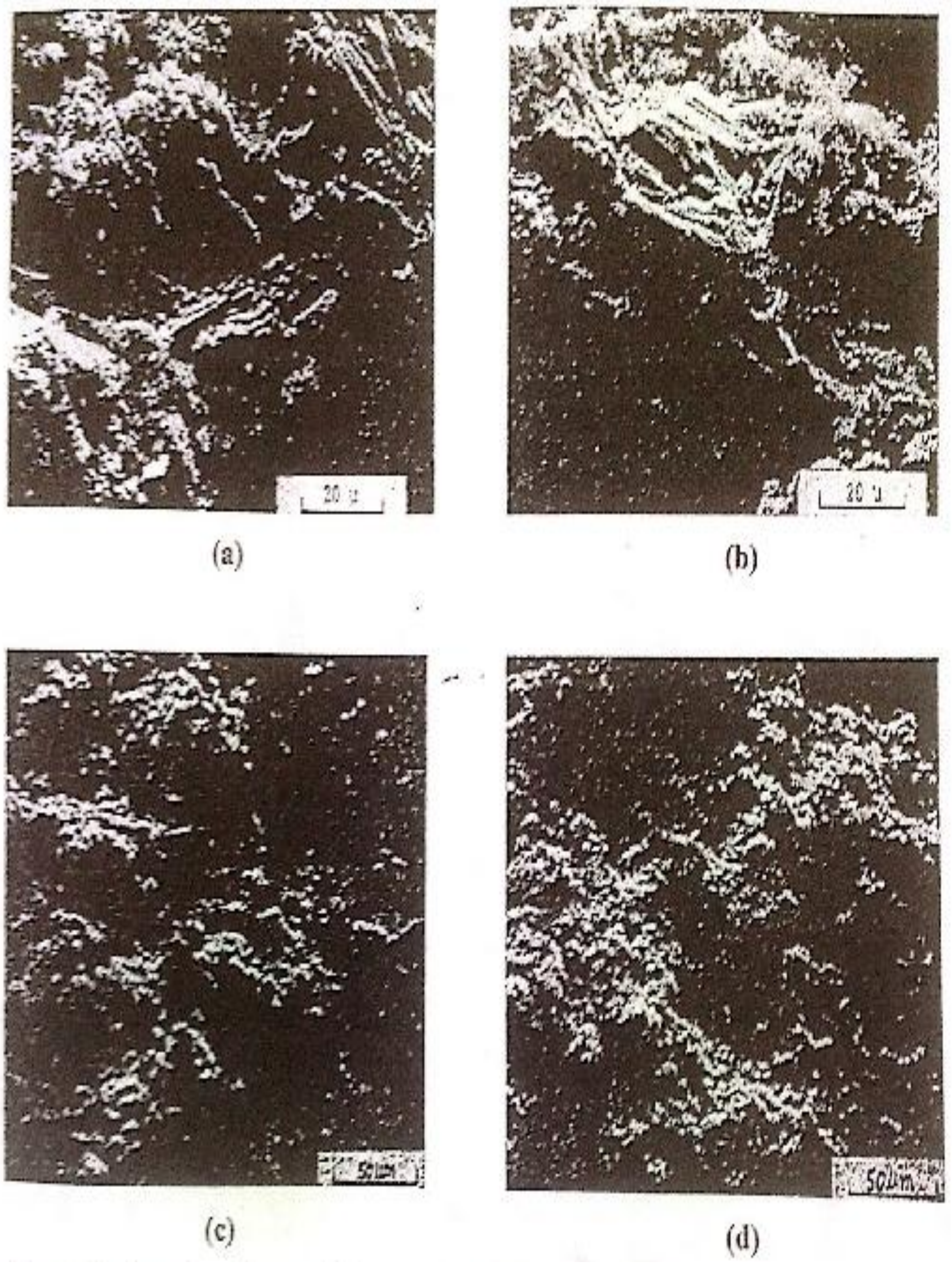


Figure 3.1. Scanning Electron Microcopies of Hydrated Cement Pastes [21]

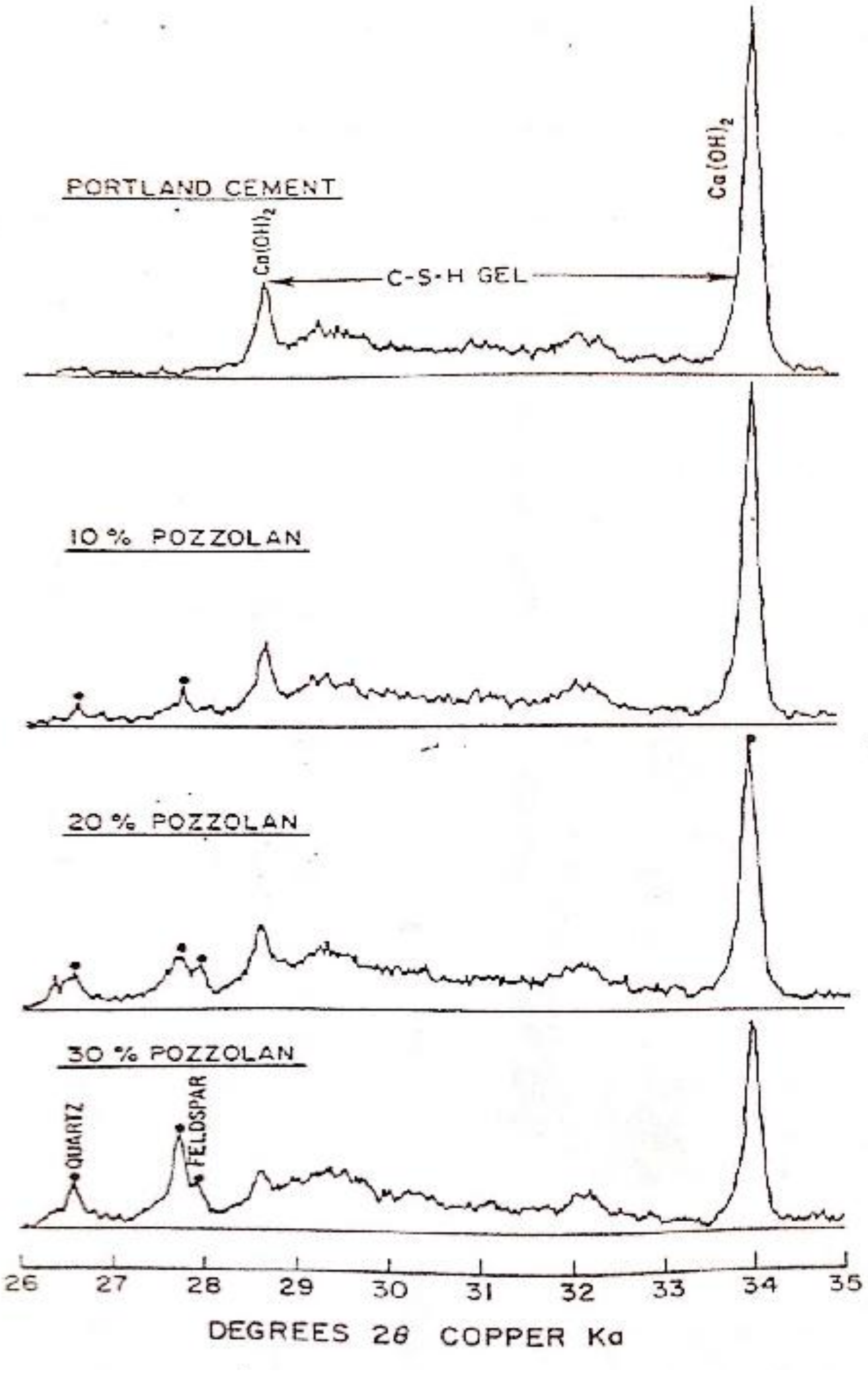


Figure 3.2. X-Ray Diffraction Analysis of Hydrated Cement Paste [21]

Table 3.1. Relative Depth of Penetrations of Water into Hydrated Cement Pastes [21]

Hydration Age (Days)	Depth of Penetration (mm)			
	Portland Cement	10% Pozzolan	20% Pozzolan	30% Pozzolan
28	26	24	25	25
90	25	23	23	22
360	25	23	18	15

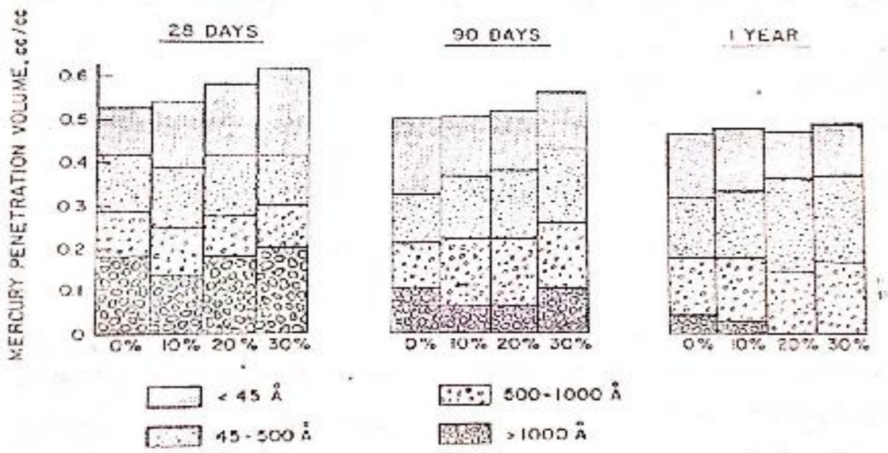


Figure 3.3. Pore Size Distribution of Hydrated Cement Pastes [21]

3.3. Influence of Pozzolan Addition on Properties of Cement Containing Natural Pozzolan

3.3.l. Grindability

There is an interaction between clinker and natural pozzolan in the intergrinding procedure. The grindability is not the weighted average of these two materials' grindability in intergrinding procedure. [22]

At the end of Erdogdu’s study [23], it is observed that; when natural pozzolan and clinker intergrinded, because of pozzolan’s easily grindable structure, the fineness of pozzolan is getting very high when compared to clinker, and the result is non-uniform and hard-controllable particle size distribution.

There is a comparison study of intergrinding and separate grinding of pozzolan and clinker in the literature. The study is interesting in strength and particle size distribution of the materials. With the same energy consumption, it is observed that, the materials do not have the same particle size distribution. From the compressive strength point of view, the intergrinded blended cement has higher strength than that of the separately grinded ones at the same fineness level. However, by the time, the difference among the separately and intergrinded ones decrease. [24]

3.3.2. Normal Consistency, Setting Time, Autoclave Expansion, Heat of Hydration

With 15, 25, and 35% replacement with clinker, effect of natural pozzolan on the cement paste is studied by Shannag and Yeginobali. [25] The study was both intergrinding and separately grinding. Natural pozzolan replacement with clinker, initial setting time of the paste gets longer. Also the final setting is prolonged, but, the effect on the final set is lower as can be seen in Figure 3.4. Autoclave expansion ratio is decreased as well with pozzolan addiction, is shown in Figure 3.4. As can be seen in Figure 3.5. and 3.7., the heat of hydration value is lover in pozzolanic cement. Also, Ramachandran [26] tells that, especially in mass concrete, the heat can go up to 50°C in 2 to5 days, and pozzolans decrease this value. The flow is also lower in pozzolanic cements. In Figure 3.6., it can be seen that, pozzolan increases the water requirement of the cement.

3.3.3. Compressive Strength of the Mortars

Mehta [21] studied the natural pozzolan addiction effect on the compressive strength of the mortars. As Figure 3.8. shows, in the long term, (up to 1 year), even 30% pozzolan added cement gains the same strength with the 0% pozzolan added cement.

According to Massaza [17], especially in early ages, compressive strength of the cement is lower when pozzolan added. When the time passes, the strength of blended cement more rapidly increase, gives a maximum, and then a slight decrease is seen. This procedure is affected by chemical and physical characteristic of the pozzolan and curing. In Figure 3.9., the effect can be seen.

Also, Turanlı states that, [27], the compressive strength level is directly proportional with heat of hydration value and $Ca(OH)_2$ produced. Figure 3.10. and 3.11. show the heat of hydration and $Ca(OH)_2$ – strength relationship, respectively.

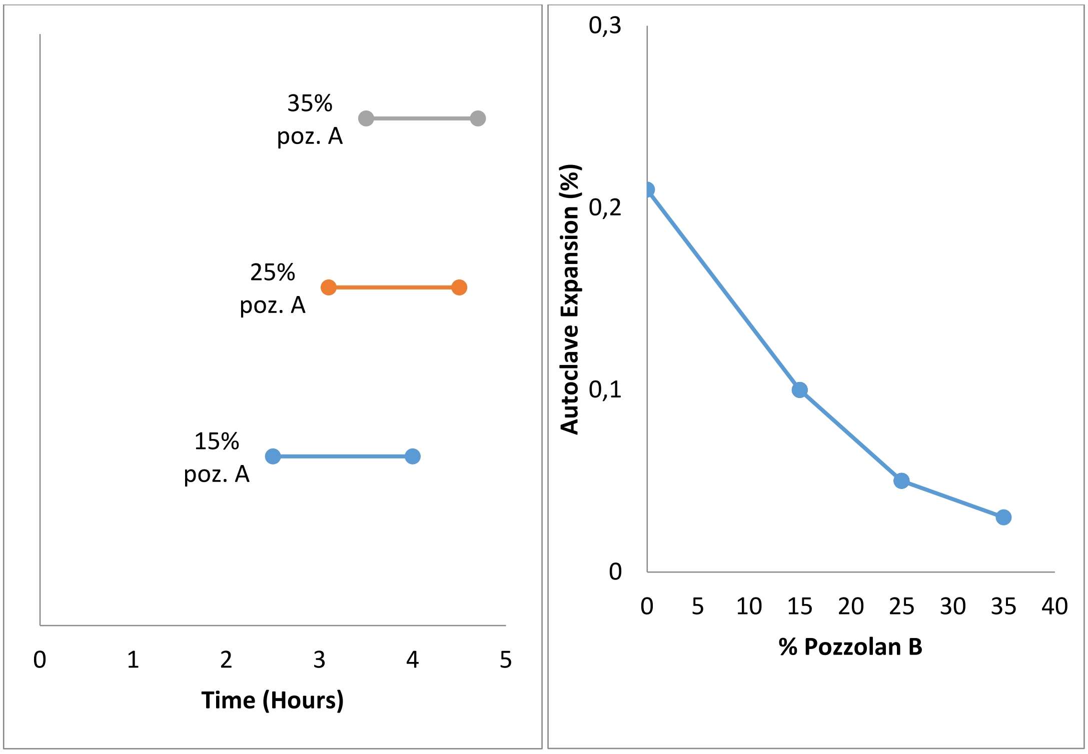


Figure 3.4. Setting Times and Soundness of Pozzolanic Cements [25]

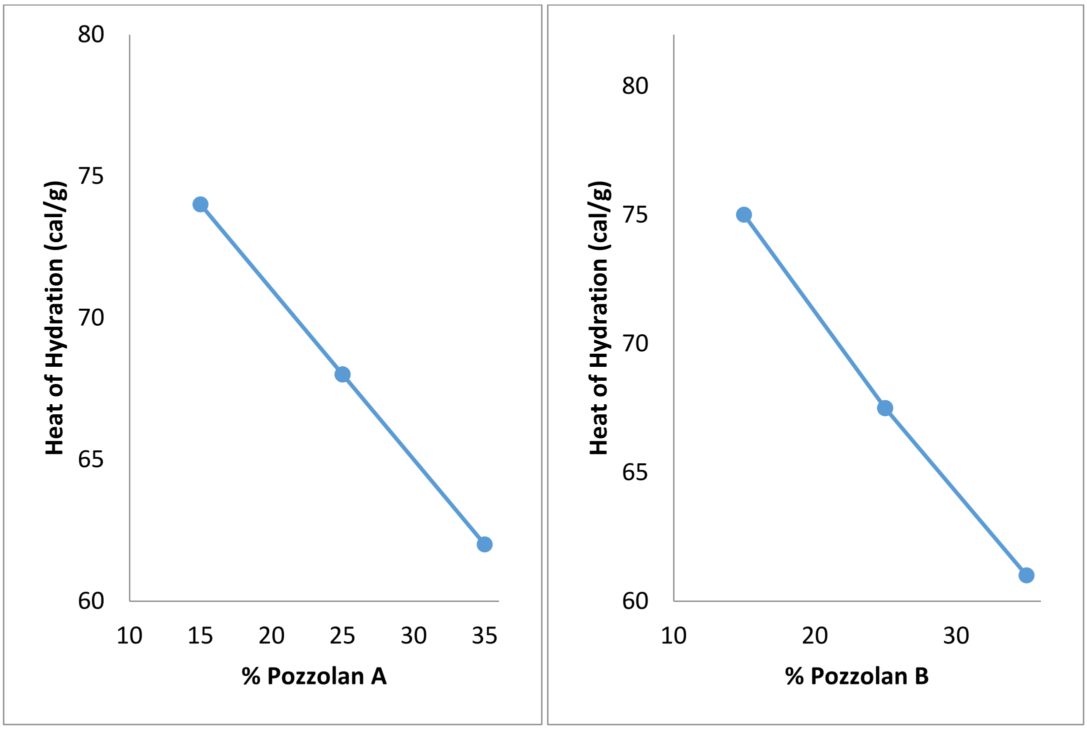


Figure 3.5. Effect of the Pozzolan on Heat of Hydration of Pozzolanic Portland Cements [25]

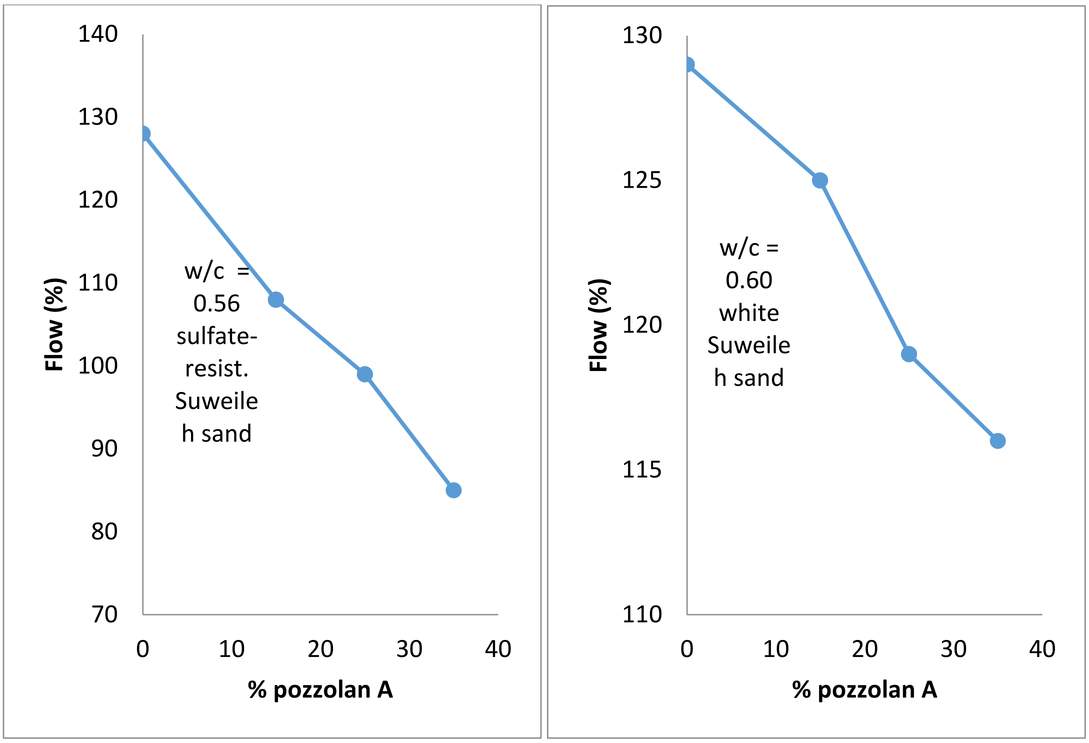


Figure 3.6. Effect of Pozzolan Content on the Flow of Mortars [25]

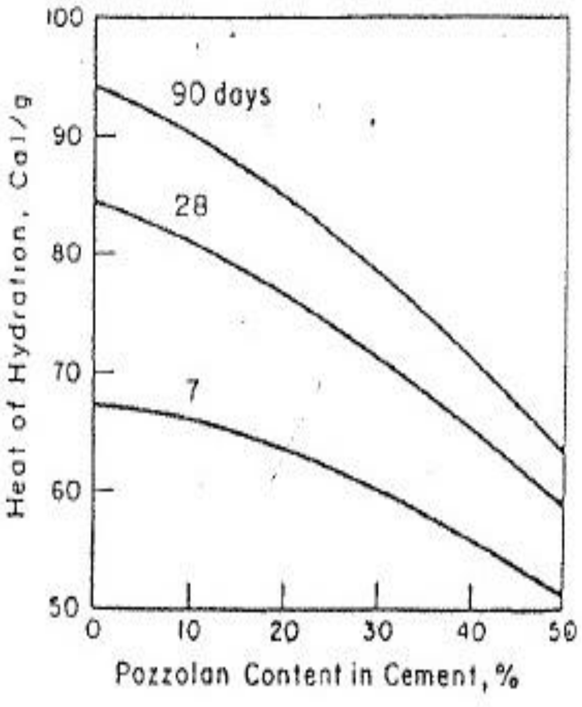
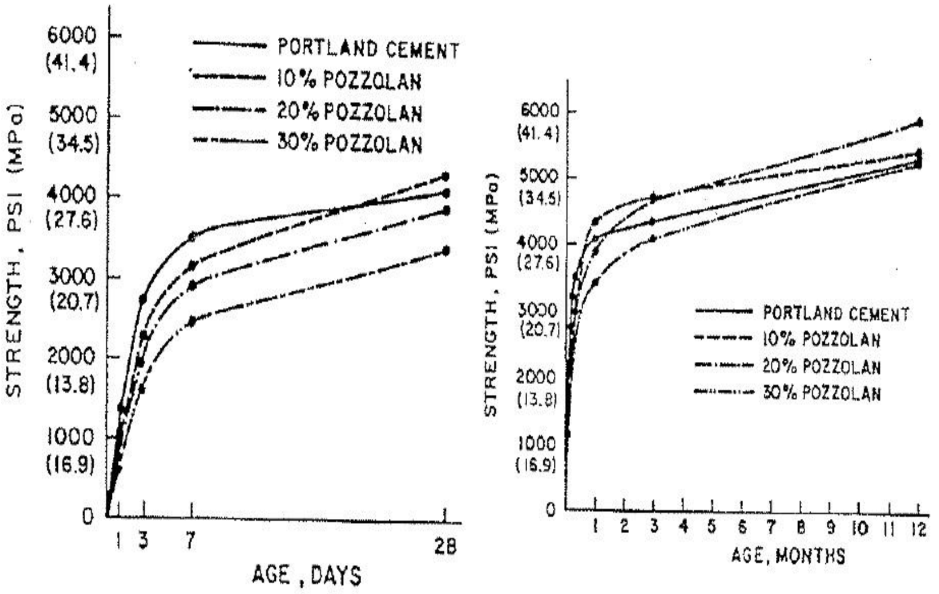


Figure 3.7. Effect of Pozzolan Content on the Heat of Hydration of Pozzolanic Cements [25]



Compressive Strengths up to 28 Days

Compressive Strengths up to 12 Months

Figure 3.8. Compressive Strengths up to 28 Days and 12 Months [21]

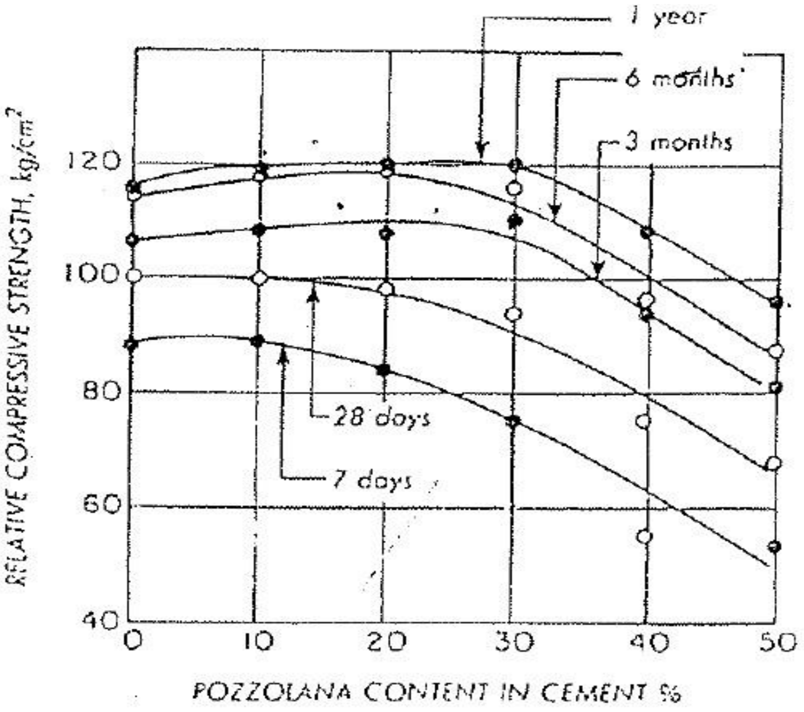


Figure 3.9. Effect of Pozzolan Content on the Compressive Strength of Portland-Pozzolan Cements [17]

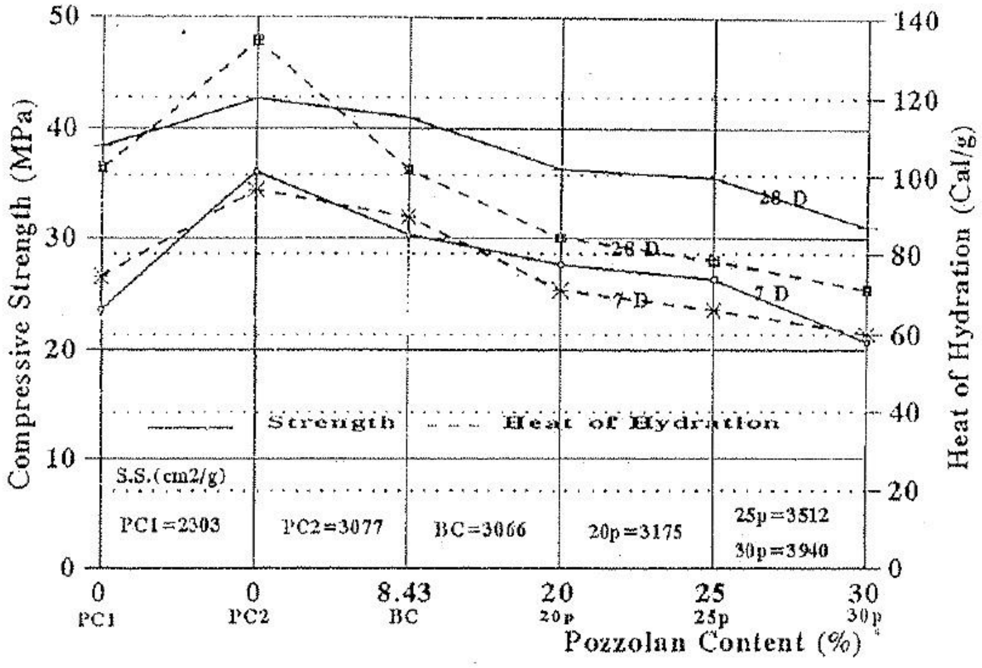


Figure 3.10. Compressive Strengths and Heat of Hydrations of Portland Pozzolan Cements with Different Pozzolan Contents [27]

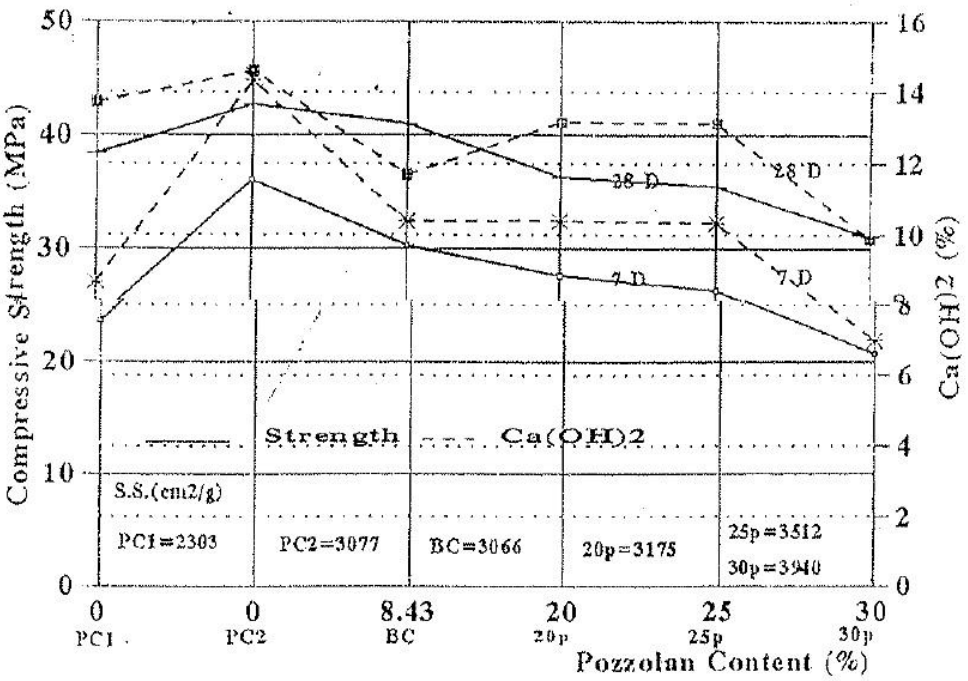


Figure 3.11. Compressive Strengths and $Ca(OH)_2$ Content of Portland Pozzolan Cements with Different Pozzolan Contents [27]

3.3.4. Durability

According to Mehta [21], when natural pozzolan is replaced with cement, alkali-silica reaction is decreased. As can be seen in Figure 3.12., when pozzolan added, expansions caused by alkali-aggregate reaction is decreased.

From the sulfate resistance point of view, Mehta [21] interest in mortar prism expansion and the loss of compressive strength of the cylinders when exposed to sulfate solution. In the study, when 10, 20, 30% cement replaced, there was a decrease in the sulfate effect on the mortar that is directly proportional with the pozzolan ratio as can be seen in the Table 3.2. and Table 3.3. Mehta also states that, there is less uncombined $Ca(OH)_2$ in the paste, there is less ettringite having less C_3A, and when the permeability is reduced with better pore refinement of the pozzolan, the sulfate attack risk is lower when pozzolan replaced with cement.

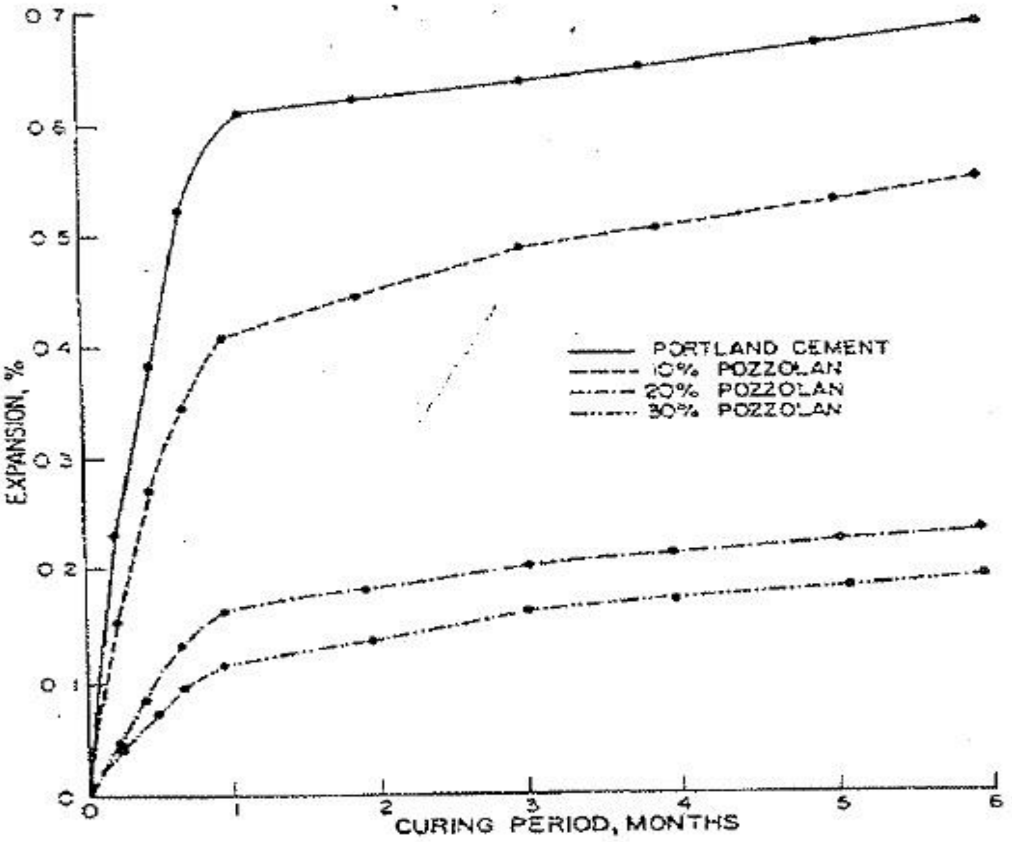


Figure 3.12. Alkali-Silica Expansion of Cements Tested [21]

Table3.2. Expansion of Mortar Prisms in Sulfate Solution, % [21]

Cement Type	4 Weeks	8 Weeks	12 Weeks	25 Weeks
Portland Cement	0.004	0.034	0.212	0.520
10% Pozzolan	0.006	0.018	0.071	0.285
20% Pozzolan	0.007	0.010	0.048	0.072
30% Pozzolan	0.006	0.008	0.027	0.050

Table 3.3. Compressive Strength Loss of Cement Paste Cylinders in Sulfate Solution Head at Constant pH [21]

Cement Type	Strength Before Immersion, Mpa	Strength After 28 Days Immersion, Mpa	Strength Loss
Portland Cement	18.0	6.1	65%
10% Pozzolan	18.5	9.5	49%
20% Pozzolan	16.1	12.9	20%
30% Pozzolan	15.2	12.8	16%

3.4 High Volume Pozzolanic Cements

As pozzolans are being used worldwide as a cement replacement material, the cements including natural pozzolan should satisfy some restrictions. For Turkey, according to Turkish Standard number 12144 [4], the maximum pozzolan in the cement can be 55% by weight. For American Standards, according to ASTM C 595, this weight ratio is 40%. On the other hand, according to ASTM C 1157 [3], for performance based cements, there is no restriction for the blending amount (percentage) of the pozzolan.

CHAPTER 4

EXPERIMENTAL STUDY

4.1. Experimental Program

In this study, three types of cements are produced. The first one is; control cement that is ground from clinker and gypsum only, 96:4 mass rate respectively. The second one is ground with 25% natural tuff by weight, and the third and last one has 50% natural tuff by weight.

The Fineness of cements are increasing directly proportionally with the pozzolan rate in it, so, the grinding times are selected for a decided fineness of the cements.

All the materials are ground together, in other words, intergrinding type is decided for the grinding step.

Table 4.1. Cements Produced in the Study with Their Designations and Descriptions

Designation	**Description**	**Grinding Time (mins)**
C0	Blended Cement with No Tuff	115
C25	Blended Cement with 25% Tuff	175
C50	Blended Cement with 50% Tuff	190

Experimental program of the study was divided into three main parts:

i) Chemical analysis of the three types of cements;
  - Using XRF method, chemical ingredients of C0, C25, and C50 are decided. Using the same method, also, clinker, gypsum, and natural tuff were chemically analyzed.

ii) Physical analysis of the three types of cements;
  - Fineness (Both Blaine and 45µ wet)
  - Specific Gravity
  - Particle Size Distribution
  - Normal Consistency
  - Setting Time
  - Alkali-Aggregate Reaction
  - Autoclave Expansion
  - Heat of Hydration
  - Initial and final Setting Times

iii) Mechanical tests of the three cements;
  - 3, 7, 14, 28, 56, 90, 180 days compressive strengths of the cement mortars

4.2. Materials

4.2.1. Portland Cement Clinker and Gypsum

The clinker and gypsum are obtained from Votorantim Ankara Cement Factory. Their chemical composition are given in the Table 4.2.

4.2.2. Natural Pozzolans

The pozzolan tested was natural tuff taken from Cappadocia region that is generally used for brick production. The chemical composition is shown in Table 4.2. These chemical analysis are observed by Middle East Technical University Central Laboratory. Before grinding, pozzolans are oven dried at 100°C

Table 4.2. Chemical Compositions of the Materials Used

Component	Clinker (mass %)	Gypsum (mass %)	Pozzolan (mass %)
CaO	64,40	39,20	2,45
SiO_2	17,60	5,96	58,60
CO_2	5,53	6,05	7,71
Al_2O_3	4,35	1,82	12,60
Fe_2O_3	3,52	0,97	2,55
MgO	1,85	0,88	0,87
SO_3	1,15	43,10	1,40
K_2O	0,76	0,31	3,46
Na_2O	0,54	-	3,25
TiO_2	0,26	0,10	0,25
P_2O_5	0,07	-	0,05
SrO	0,05	1,59	0,02
B_2O_3	-	-	5,91
Cr_2O_3	-	-	0,01
MnO	-	-	0,09
ZnO	-	-	0,01
As_2O_3	-	-	0,00
ZrO_2	-	-	0,01
Nb_2O_5	-	-	0,00
BaO	-	-	0,03
Rb_2O	-	-	0,01

4.3. Production of the Cements

The tests were performed in Middle East Technical University Civil Engineering Materials of Construction Laboratory. A laboratory grinding mill is used for grinding. It is 450mm in length, 420mm in diameter. There are 15 50mm, 62 40mm, 174 29mm balls, and 160 22mm in diameter and 27mm in length, 210 16mm in diameter 20mm in length cylinders in it. The optimum weight for a material with S.G.≈3.2 is 8kg for this machine.

The mass ratios of clinker and gypsum are 96:4 respectively. In the production of C25 and C50 the cement and gypsum ratios are kept same, and the pozzolan added out of this ratio by mass.

The grinding procedure aimed to gain a specific surface area and the material was tested until reading that fineness. The fineness values were increasing while pozzolan amount increases. For C0, 3500 cm^2/gr; C25 4000 cm^2/gr; C50 4500 cm^2/gr were minimum fineness values of the cements.

The chemical composition of C0, C25, and C50 are given in Table 4.3.

Table 4.3. Chemical Compositions of the Cements

Component	C0 (mass%)	C25 (mass%)	C50 (mass%)
CaO	61,10	38,90	25,60
SiO_2	16,40	36,20	48,00
CO_2	7,15	5,00	4,05
Al_2O_3	4,10	8,08	10,40
Fe_2O_3	3,29	2,97	3,03
MgO	1,75	1,21	1,11
SO_3	4,34	3,19	1,64
K_2O	0,76	1,99	2,77
Na_2O	0,52	2,05	2,84
TiO_2	0,26	0,24	0,26
P_2O_5	0,07	0,05	0,05
SrO	0,12	0,09	0,05
MnO	0,05	-	-
ZrO_2	-	0,01	0,01
Rb_2O	-	-	0,01

4.4. Testing Pozzolans, Cements, Cement Pastes, and Mortars

The tests were performed in Middle East Technical University Civil Engineering Materials of Construction Laboratory. The base standards used in these tests were ASTM. The related standard numbers are given in the sections.

4.4.1. Tests Performed on the Natural Pozzolans

In this study, cement, gypsum and, pozzolan are ground together, so, important number of tests are applied to cement instead of raw materials. However, chemical composition, specific gravity, strength activity tests are applied to natural pozzolan. For chemical analysis, X-Ray Fluorescence Spectrometry Method (XRF) is used. Strength activity according to ASTM C311 is needed for the material to be called as a 'pozzolan'. And also for the specific gravity determination, again an American standard, ASTM C188 is performed.

The tests related to pozzolans are listed in Table 4.4.

Table 4.4. Tests Performed to Natural Pozzolans

Test	**Test Type**
Chemical Composition	X-Ray Fluorescence Spectrometry Method
Specific Gravity	ASTM C188
Strength Activity	ASTM C311

4.4.2. Tests Performed on Cements

For all three types of cements in this study, five tests were carried out. Chemical composition, and specific gravity tests were the same as those of the pozzolans. Out of these two, two fineness and a particle size distribution tests were carried out. The first fineness test was the 'Fineness by Blaine Apparatus Tests' according to ASTM. This test is helping to determine the fineness by air permeability of dry cements.

The second fineness test was using wet sieving method. Again according to ASTM, ASTM C430; 'Standard Test Method for Fineness of Hydraulic Cement by the 45μm (No. 325) Sieve', fineness is tested second time.

The third test of the cement different than pozzolans was the particle size distribution test. For all types of cements, by laser diffraction method, particle size distribution was determined. In this test, the material sizes are determined by laser light passing through an appropriate liquid which has the material (cement) in it, and with help of a computer software, determining the particle size distribution of the material. The tests related to cement are listed in Table 4.5.

Table 4.5. Tests Performed on Cements

Test	**Test Type**
Chemical Composition	X-Ray Fluorescence Spectrometry Method
Specific Gravity	ASTM C188
Fineness by Blaine Apparatus	ASTM C204
Fineness by 45µ Sieve	ASTM C430
Particle Size Distribution	Laser Diffraction

4.4.3. Tests Performed on Cement Pastes

Same as cement tests, for all three types of cement pastes, several tests were implemented. These were normal consistency, setting time, heat of hydration, and autoclave expansion tests.

Normal consistency test was applied according to ASTM C187 'Standard Test Method for Normal Consistency of Hydraulic Cement'. By this method, the appropriate water amount for cement pastes were decided.

Setting time procedure is followed according to ASTM C191 'Time of Setting of Hydraulic Cement by Vicat Needle'. Using ASTM C187 water amount, the initial and final setting times of the cement pastes are observed.

For autoclave expansion, the test need is coming from the high SO_3 amount in the cement. During the production of the cement, all of the clinker is not grinded smaller than 850µm sieve. This was because of the gypsum amount of the cement. After a desirable fineness, the cement was not grinded any more, and 15.75%, 7.14%, 4.25% of the material (actually clinker) was retained 850µm sieve at C0, C25, C50 cements, respectively. So, the clinker amount decreased by above ratios while gypsum amount staying same, moreover, the desired 96:4 clinker to gypsum ratio increased. After this situation, it is needed to test autoclave expansion to observe the expansion due to CaO and/or MgO. This test is carried on according to ASTM C151, 'Autoclave Expansion of Hydraulic Cement'.

For heat of hydration, until 28 days, observation is made. Using a computer software, the heat values of cement hydration is gained for every 45-50 seconds, and the difference between the cement types by the point of view of heat exerted, is observed 28 days long.

The test related to cement pastes are listed in Table 4.6.

Table 4.6. Tests Performed on Cement Pastes

Test	**Test Type**
Normal Consistency	ASTM C187
Setting Time	ASTM C191
Autoclave Expansion	ASTM C151
Heat of Hydration	-----

4.4.4. Tests Performed on Cement Mortars

There were two observations needed to be made for the cement mortars. Compressive strength and alkali-aggregate reactivity tests were carried out for three types of mortars. Both of the tests were made according to American standards for mortars.

The first test was compressive strength test, that was one of the most important and deterministic test for the cement because the cements are classified according to their compressive strength, and as long as the strength increases, the usability of the cement increases. According to ASTM C109, 'Compressive Strength Test for Cement Mortars', 3, 7, 14, 28, 56, 90, 135, 180 days strength of the cements were observed. In this procedure, the flow (water need) of the cement mortars were decided by ASTM standards with the guidance of C109.

The second test was 'Alkali Silica Reactivity Test for Cements' with code ASTM C1260. In this test, the cements were observed until 56 days for expansion amounts with using a reactive aggregate in the mortar.

The tests related to cement mortars are listed in Table 4.7.

Table 4.7. Tests Performed on Cement Mortars

Test	**Test Type**
Compressive Strength	ASTM C109
Alkali-Aggregate Reactivity	ASTM C1260

CHAPTER 5

TEST RESULTS AND DISCUSSIONS

5.1. Strength Activity Index of Pozzolans

According to ASTM C 311, to be called as pozzolan, a material should satisfy strength activity index parameters, so, the first test applied to material was strength activity. At the end of 7 and 28 days, the compressive strength of mortars those have 20% natural tuff in them, are tested and compared to the control cubes, without any pozzolan in it, and the results are given in Table 5.1.

Table 5.1. Strength Activity Index of Natural Pozzolan

Blaine Fineness (cm^2/gr)	**Flow (%)**	**Strength Activity Index (%)**	
		7 Days	**28 Days**
3967	104	80	82

According to ASTM, strength activity after 7 and 28 days, should be at least 75%. Also according to Turkish Standards, the ratio is 70%. The pozzolan, as shown in Table 5.1., satisfied the requirements of both standards, and received the name of pozzolan after strength activity test. Also, it was observed that the ratio increased by the time passes.

5.2. Specific Gravity, Fineness, and Particle Size Distribution of Cements

Specific gravity of the cements were differing inversely with the tuff amount in it. In this study, as mentioned before, there were three types of cements with 0%, 25%, and 50% pozzolan by mass.

Fineness was controlled by the grinding time of the cements. Moreover, while the ingredients of the cements changes, it was observed that, the grinding time for the same fineness is changing. Grinding time versus Blaine Fineness curves are given in Figure 5.1. The 45µ fineness values could be called as a 'step' for deciding the fineness of the cements in this study, and they were used in Blaine Fineness procedure. The values are given in Table 5.2.

For the fineness determination, three methods were followed. The first one was 'Blaine Fineness Test' according to ASTM C 204. The surface area values of a unit volume of materials with a specific grinding time recorded for all three types of cements. Also, 45µ sieve passing amounts were tested for all cements after fineness was reached at the expected values. This was because of that the standards are interesting in the 45µ passing amounts of the cements. These values are also given in Table 5.2.

For the fineness, the last test was particle size distribution and this was performed with the help of laser diffraction method. The particle size distribution values and the particle size distribution curves are available in Figure 5.2.

Table 5.2. Physical Properties of the Cements

Cement Type	Specific Gravity	Blaine Fineness (cm^2/gr)	Passing 45 µm (%)
C0	3,12	3620	74
C25	2,87	4060	78
C50	2,66	4545	84

As can be followed from Table 5.2., while pozzolan added with increasing percentages by mass to the cements, the weight of the cements decreased. The aim in this study was increasing the surface area by the clinker decreases, so, the cements tested had 500cm^2/gr more surface area for every 25% increase in natural tuff mass. Also, the material amount passing from 45µm sieve increased while the Blaine Fineness increases, by this values, it is seen that, cements produced were finer with decreasing clinker as it was aimed at the beginning of the study.

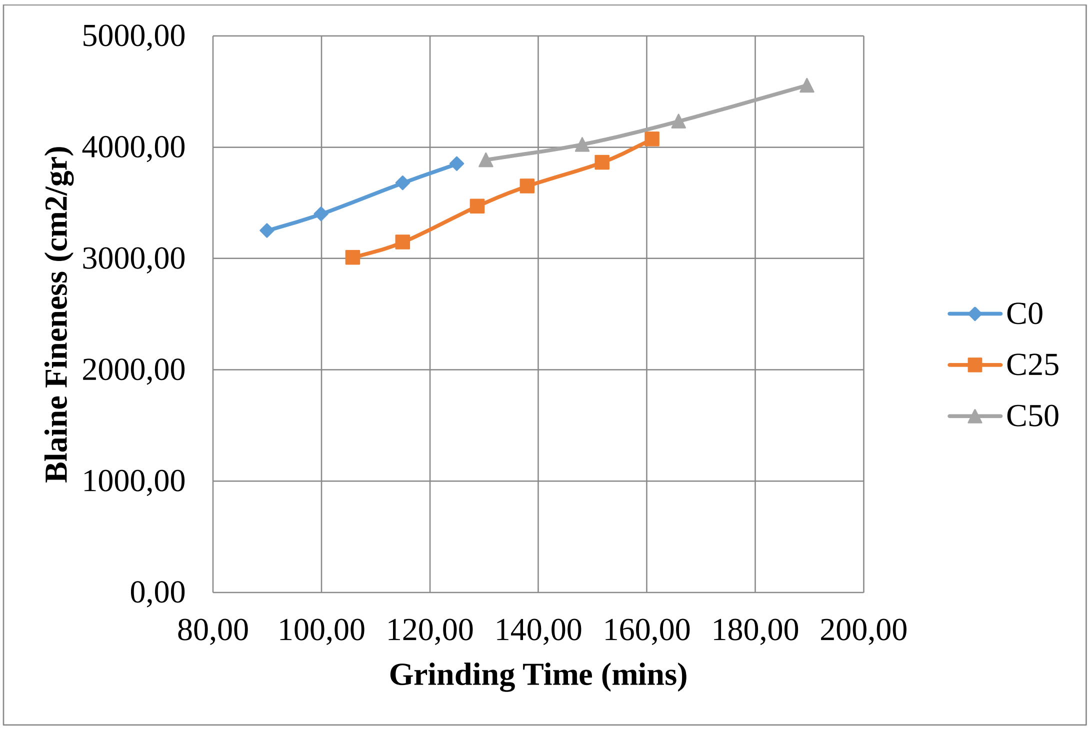


Figure 5.1. Effect of Grinding Time on the Blaine Fineness

From Figure 5.1., it is observed that, the grinding time decreases for the increasing clinker ratio. This graph shows that, the material is not being ground easily, and an increase in the energy while the grinding procedure is expected with knowing Figure 5.1.

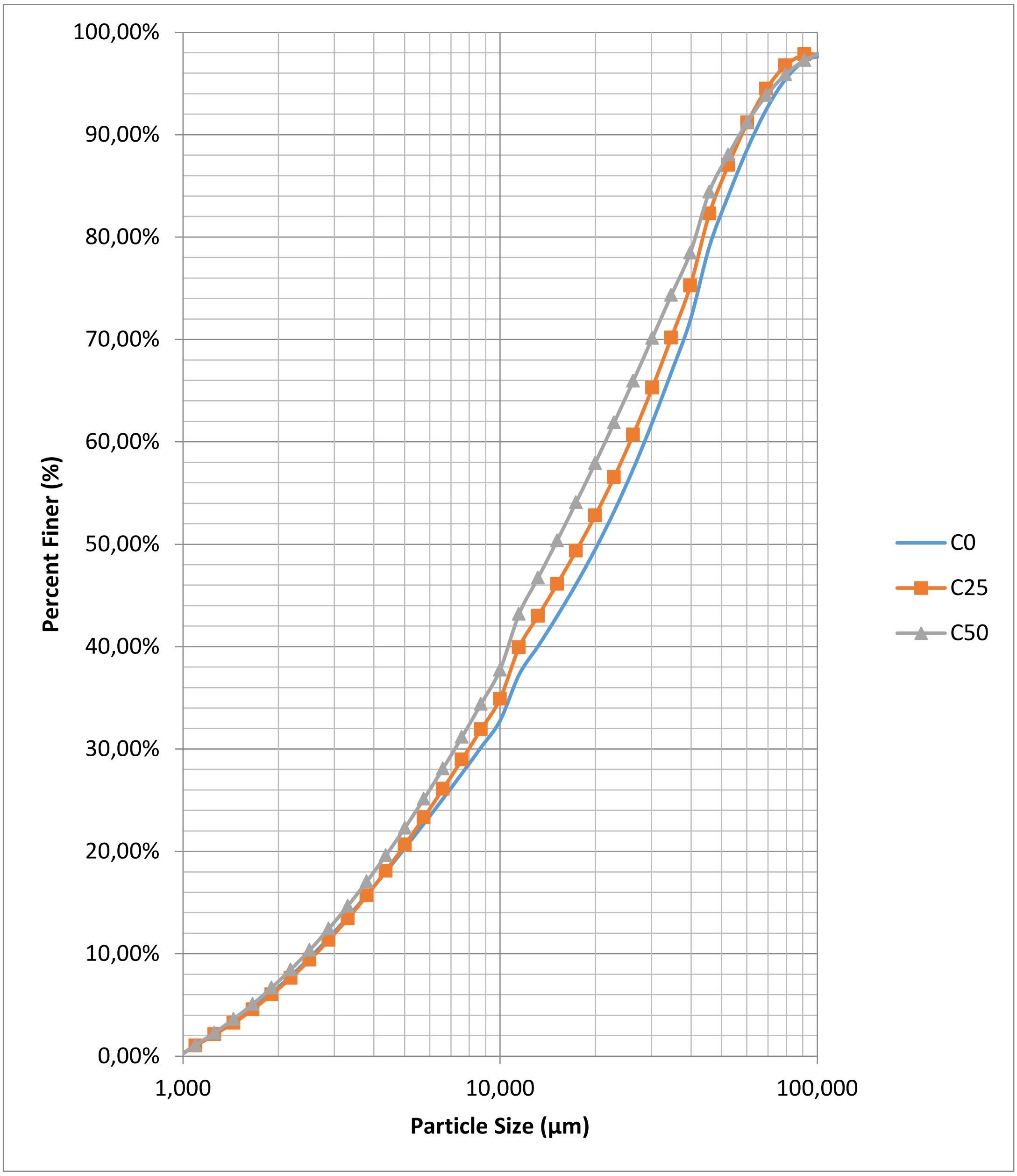


Figure 5.2. Comparison of Particle Size Distribution of Cements Produced

5.3. Normal Consistency, Setting Time, Autoclave Expansion, and Heat of Hydration of Cement Pastes

There were four tests applied to cement pastes. The first one was setting time, which is restricted by the standards, and actually a characteristic specialty of the cement. It was decided by vicat machine according to ASTM C191 for all three types of cements.

The second was, on the lights of ASTM C187, normal consistency. Again another character of cements, water requirement for getting normal consistency is tested.

Autoclave expansion was another method to test cements in this study. ASTM C151 was the guide for the test, and the expansion amount under a certain pressure and high temperature recorded.

The hydration heat values were also recorded for three cement types. At the end of 7 and 28 days, cumulative heat exerted was recorded with the help of a computer software. The cumulative heat flow observations up to 28 days. In this study, a TAM air (Thermometric AB, Sweden) calorimeter, an 8-channel isothermal micro-calorimeter with precision of ±20 μW, was used for heat flow measurements during the hydration of the pastes. The total paste amount was 6 grams, and the w/c ratios were same as the w/c for the normal consistency of the cements. The cumulative normalized heat flow values of the pastes are given in Figure 5.3.

Results of all the tests performed on cement pastes are given in the Table 5.3. and the effect of natural tuff addiction and differences are discussed after the results.

Table 5.3. Test Results Performed on Cement Pastes

Cement Type	Blaine Fineness (cm^2/gr)	Setting Times (mins)		w/c for Normal Consistency	Autoclave Expansion (%)	Cum. Heat of Hydration (cal/g-paste)	
		Initial	Final			7 days	28 days
C0	3620	125	190	0,23	0,150	45	48
C25	4060	198	240	0,27	-0,306	39	46
C50	4546	217	302	0,30	-0,400	32	37

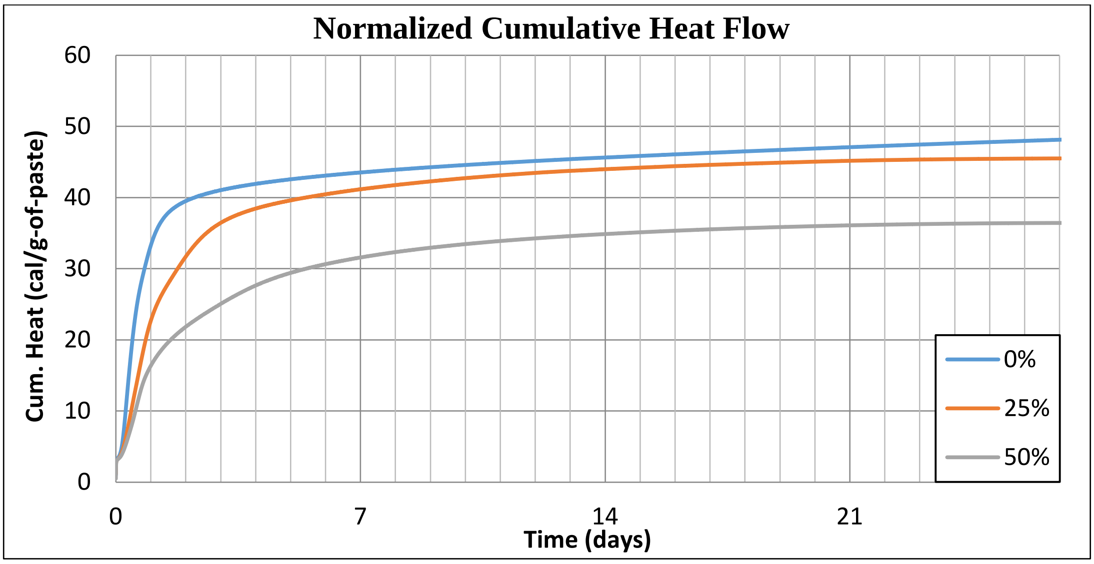


Figure 5.3. Normalized Cumulative Heat Flow of the Cements Up to 28 Days

According to the results, first of all, with the increasing fineness and pozzolan amount, it can be said that the water requirement for the normal consistency increases. Also the w/c ratio is increasing while the specific gravity of the cement decreases. The ratio is increasing up to 30% when natural tuff amount is at half weight in the cement.

Also again according to the test results, pozzolan amount affects the setting time. When the cement has natural tuff in it, the setting times, both initial and final ones, go further. With the 25% increases in the tuff amount, for the initial setting, it is observed that, the time increases by 50% and 70% respectively. In the final setting, again respectively, the ratios are 25% and 60%.

Under autoclave test conditions, C0 elongated by 1.5%. However, the pozzolanic cements C25 and C50 shortened.

The results of the last cement paste test, heat of hydration, is differing again within the cement types. While the pozzolan increases, the heat values decrease. Between C0 and C25, at 7 days, there is 15 percent decrease, and, between C0 and C50, the decrease is about 30%.

When it is 28 days, C0 and C25 difference is 8% negatively, and C0-C50 difference is about 25% again on the negative side.

5.4. Compressive Strength and Alkali-Aggregate Reactivity of Cement Mortars

In this study, ASTM C109 was the guide for the mechanical test of cements. The flow limit is selected as 1.05 and the w/c ratios were selected in that way. All three types of cements were tested for compressive strength with their own proper water ratio. At the end of 3, 7, 14, 28, 56, 90, and 180 days, the compressive strength of C0, C25, and C50 were recorded. In Table 5.4 the compressive strength values are given, and in Figure 5.4., there are graphs of the compressive strength values of the cement mortars.

Table 5.4. Compressive Strength of the Cement Types

Cement Type	**Blaine Fineness (cm^2/gr)**	**Compressive Strength (MPa)**						
		3 days	**7 days**	**14 days**	**28 days**	**56 days**	**90 days**	**180 days**
C0	3620	25	32	40	47	53	54	55
C25	4060	16	24	28	32	36	41	44
C50	4546	11	14	18	23	26	28	38

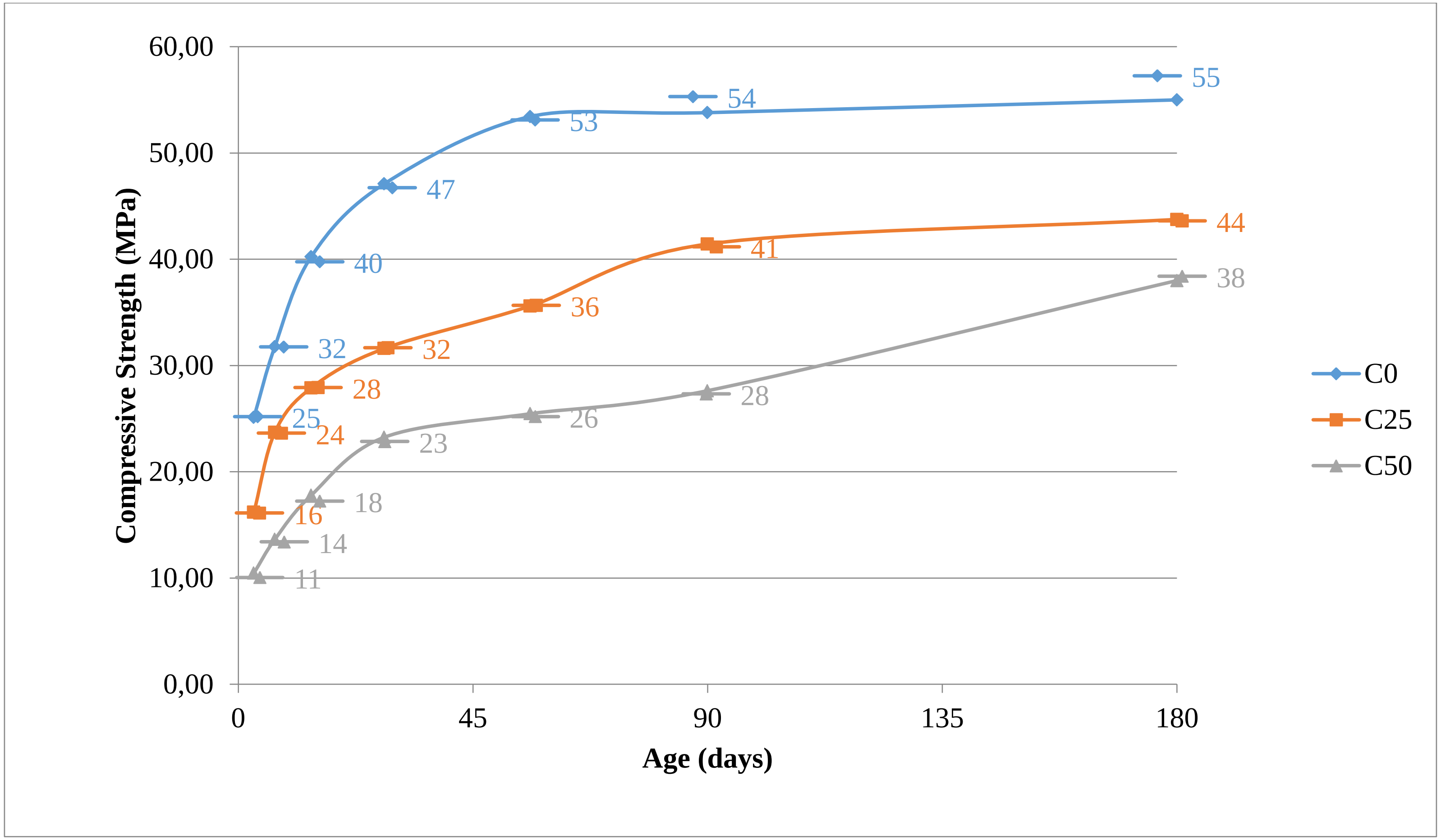


Figure 5.4. Comparison of Compressive Strengths of C0, C25, and C50

As can be followed from Table 5.4. and Figure 5.3., while the pozzolan amount in the cement decreased, it was observed that, the compressive strength of the mortar increased. There is a correlation between the strength values until 56 days, and with the increasing strength with respect to less pozzolan added ones, C50 broke down the correlation with increasing its strength until 180 days. When C25 and C0 compared, it was again observed, pozzolan addiction decrease the early strength, and, helps cement to gain strength after 56 days.

At the end of 28 days, C0 gained about 45MPa, C25 gained about 32.5 MPa, and C50 gained about 25 MPa strength. When it is 180 days, C0 reached 55MPa while C25 reached 44MPa and C50 reached 38MPa. These values tell that, with up to 50% pozzolan addiction to the cement by mass, strength gaining between 28 and 180 days can be increased from 20% to 50%.

To sum up, it is observed from the compressive test, while the clinker ratio in the cement is decreased using natural tuff, strength gaining still goes on after 56 days with much higher ratio, and early strength is decreasing with pozzolan addiction.

The last test for cements was alkali-silica reactivity test. This was performed according to ASTM C1260. In the guidance of ASTM, the potential of cements to react with aggregates, will cause expansion, was tested under high temperature conditions until 28 days. The expansion amount are given in Table 5.5.

Table 5.5. Alkali-Silica Expansions of Cement Mortars

Cement Type	**Blaine Fineness (cm^2/gr)**	**Alkali-Silica Expansions (%)**				
		3 days	**7 days**	**14 days**	**21 days**	**28 days**
C0	3620	0,024%	0,154%	0,340%	0,614%	0,957%
C25	4060	0,007%	0,010%	0,035%	0,045%	0,042%
C50	4546	0,014%	0,007%	0,024%	0,017%	0,017%

At the end of test results of alkali-silica reactivity, it was seen that, the clinker and aggregate selected were reactive. For intergrinded cements (clinker-pozzolan), the expansions did not reach 1/1000 ratios in one month. C25 and C50 cements decreased the expansion amounts and, the expansion ratios were almost 2 to 1 respectively. In 14 days, C25 expanded 0.024%, C50 expanded 0.035% In 28 days, C25 and C50 expanded 0.042% and 0.017% relatively.

However, C0 expansion ratio at the end of 14 days was 0.34% which is about 10 times that of C25. In 28 days, C0's expansion ratio increased up to 1%.

Under 80°C, C0 expansion started to result in cracks on the sample after 7 days. These were visible cracks those confirming the alkali-silica expansions. On the other hand, over C25 and C50, there were no cracks observed within 28 days. While the natural tuff amount in the intergrinded clinker increased, the result was, elimination of alkali silica expansion cracks, in other words, elimination of expansion due to alkali-silica reactivity.

CHAPTER 6

CONCLUSIONS

According to the results of the studies and the tests performed, the following comments can be called as conclusions for Cappadocia tuff for usage as natural pozzolan in blended cements:

1. The material satisfies ASTM C 311 requirements with gaining over 80% strength of the control paste. Furthermore, the tuff of Cappadocia can be called as a pozzolan.

2. The intergrinding procedure needs longer time to get the same fineness level with the increasing pozzolan amount in the blended cements. This tells that the material is ground harder than clinker.

3. C25, and C50 elongates the initial and the final setting times. The increase in the grinding time increasing with the increasing Blaine Fineness increases.

4. Water requirement of the cement is increasing with the increasing pozzolan content. To be able to have normal consistency, pozzolanic cement requires more water.
5. Autoclave expansion decreased with the increasing pozzolan amount with using Cappadocia tuff.

6. Heat liberation during the hydration is decreased with using this material. Especially in C50, there is a sharp decrease in hydration heat. The heat generation value observed between 7 and 28 day is increasing. Thus, it can be concluded that, heat generation occur in a wider time.

7. Expansions due to alkali-aggregate reactivity are decreased to very ignorable values with using this pozzolan.

8. For C0, C25, and C50, were tested nearly 3500, 4000, and 4500 cm^2/g Blaine finenesses, respectively. While C0 reached 42.5 MPa, C25 reached 32.5 MPa and continued to strength gaining more rapidly than C0 does after 28 days. For C50, especially after 90 days, strength gaining goes on, and the strength values get nearer to those of C0 and C25. This increase shows that, C50 is also acceptable for special purposes requiring late strength gaining.

CHAPTER 7

RECOMMENDATIONS

In this study, production of blended cements with Cappadocia tuff, a natural pozzolan, up to 50% is investigated by means of physical and mechanical properties. At the end of the studies performed for this thesis, the following recommendations can be made:

1. While intergrinding the cement and the pozzolan, after the deserved fineness is reached, cement retained on the 850µm sieve was not used while the laboratory tests. However, actually it is observed that the material retained was only clinker, and all the pozzolan and gypsum were smaller than 850µm. This caused the SO_3 amount to be higher than the standard specifications for cement, 3%. But this did not affect the test results because this study aims to compare the three types of cements. In the further studies, this noon-ground material should be considered.

2. This material proved that, when blended with clinker, the heat of hydration decreases and the heat is released in wider time. This is very important for mass concrete applications to be able to avoid the cracks caused thermally. Especially for the possible mass concrete applications, such as dam, will be carried out near to Cappadocia Region, this material is strongly recommended to be used.

3. For durability and/or sulfate attack conditions, this material is recommended also. With having less permeable concrete, the system is protected more, and the durability of the concrete is increased.

4. The most important recommendation is that, with using this natural material in the cement production, CO_2 emission to the atmosphere is decreased and while the environmental projects are one of the most important topics worldwide nowadays, this material's being called as another environmentally friendly material is in very high importance. Moreover, instead of producing clinker and grinding after, just grinding cost of this material without any production procedure (just oven-dry), when replaced with clinker, offers a very big financial advantage.

5. In this study, clinker and gypsum were ground together, which is called intergrinding method. In another study, they can be ground separately and mixed after to be able to see the effect of the separate grinding on the cements.

REFERENCES

1. Mehta, P.K. (1987). "Natural pozzolans: Supplementary cementing materials in concrete". *CANMET Special Publication* **86**: 1–33.

2. V.M. Malhotra, Role of Supplementary Cementing Materials in Reducing Greenhouse Gas Emissions, CANMET Report MTL 98-30 (OP-J), CANMET, Ottawa, Canada, 1998 (Quoted from reference No.20).

3. ASTM C 1157, "Standard Performance Specifications for Hydraulic Cements", American Society for Testing Materials, 2011.

4. TS 12144, "Pozzolanic Cements", Turkish Standards Institute, Ankara, 1997.

5. N. Ertek, F.Öner, Mineralogy, geochemistry of altered tuff from Cappadocia (Central Anatolia) and its use as potential raw material for the manufacturing of white cement, Applied Clay Science, 2008.

6. ASTM C 150, "Specifications for Portland Cement", American Society for Testing Materials, 2015.

7. Popovics, S., "Concrete Materials: Properties, Specifications and Testing", Second Edition, Noyes Publications, USA, 1992.

8. Mindess,S., Young, J.F., "Concrete", Prentice-Hall, New Jersey, 1981.

9. ASTM C 618, "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete", American Society for Testing and Materials, 2012.

10. Vitruvius, Pollio, Ten Books on Architecture, Translated by Ingrid D. Rowland, Cambridge University Press, Cambridge, United Kingdom, 1999.

11. ASTM C 311, "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete", American Society for Testing and Materials, 2013.

12. Erdoğan, T.Y., Admixture for Concrete, Middle East Technical University, Ankara, 1997.

13. Mielenz, R.C., Witte, L.P. and Glantz, O.J., "Effect of Calcination on Natural Pozzolans", Symposium on Use of Pozzolanic Materials in Mortars and Concrete, STP-99, pp. 43-91, 1950 (Quoted from reference No. 12).

14. ACI Committee Report, "Proposed Report: Use of Natural Pozzolans in Concrete", ACI Materials Journal, Vol. 91, No. 4, pp. 410-426, 1994.

15. Mehta, P.K., "Natural Pozzolans", Supplementary Cementing Materials for Concrete, CANMET-SP-86-8E, Canadian Government Publishing Center, Supply and Service, Ottawa, Canada, 1987 (Quoted from reference No. 14).

16. Malhotra, V.M. Mehta, P.K., "Pozzolanic and Cementitious Materials", Gordon and Breach Publishers, Ottawa, Canada, 1996.

17. Massaza, F., "Chemistry of Pozzolanic Addition and Mixed Cements", 6th International Congress on the Chemistry of Cements, Moscow, 1974.

18. Massaza, F., Pozzolanic Cement Seminar, Ankara, 1989.

19. ASTM C 595, " Standard Specification for Blended Hydraulic Cements", American Society for Testing and Materials, 2015.

20. Bouzoubaa, N., Zhang, M.H., Bilodeau, A., Malhotra, V.M., "Laboratory Produced High-Volume Fly Ash Blended Cements: Physical Properties and Compressive Strength of Mortars", Cement and Concrete Research Vol. 28, pp. 1555-1569, 1998.

21. Mehta P.K., "Studies on Blended Cements Containing Santorin Earth", Cement and Concrete Research, Vol. 11, pp. 507-518, 1981.

22. Hosten, C., Avsar, C., "Grindability of Mixtures of Cement, Clinker, and Trass", Cement and Concrete Research, Vol. 28, No.11, pp. 1519-1524,1998.

23. Erdogdu, K., "Effect of Pozzolanic Additions on Grindability and Some Mechanical Properties of Pozzolanic Cements of Different Fineness Values", Master of Science Thesis, Middle East Technical University, 1996.

24. Erdogdu, K., Tokyay, M., Türker, P., "Comparison of Intergrinding and Separate Grinding for the Production of Natural Pozzolan and GBFS-incorporated Blended Cements", Cement and Concrete Research, Vol. 29, pp. 743-746, 1999.

25. Shannag, M.J., Yeginobali, A., "Properties of Pastes, Mortars, and Concretes Containing Natural Pozzolan", Cement and Concrete Research, Vol. 25, pp. 647-657, 1995.

26. Ramachandran, V.S.," Concrete Admixtures Handbook", Noyes Publication, New Jersey, USA, 1995.

27. Turanlı, L., "Effects of Natural Pozzolan Addition on the Portland-Pozzolan Cements and the Concretes Made with Those Cements", Ph.D. Thesis, Middle East Technical University, Ankara, 1995.

28. Uzal, B., Turanlı, L., "Studies on Blended Cements Containing a High Volume of Natural Pozzolans", Cement and Concrete Research, Vol. 33, pp. 1777-1781, 2003.

29. Turanlı, L., Uzal, B., Bektas, F., "Effect of Large Amounts of Natural Pozzolan Addition on Properties of Blended Cements", Cement and Concrete Research, Vol. 35, pp. 1106-1111, 2005.

30. Uzal, B., Turanli, L., Yücel, H., Göncüoğlu, M.C., Çulfaz, A., "Pozzolanic Activity of Clinoptilolite: A Comparative Study with Silica Fume, Fly Ash and a Non-Zeolitic Natural Pozzolan", Cement and Concrete Research, Vol. 40, pp. 398-404, 2010.

31. ASTM C 109, " Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)", American Society for Testing and Materials, 2013.

32. ASTM C 151, " Standard Test Method for Autoclave Expansion of Hydraulic Cement", American Society for Testing and Materials, 2015.

33. ASTM C 187, " Standard Test Method for Amount of Water Required for Normal Consistency of Hydraulic Cement Paste", American Society for Testing and Materials, 2011.

34. ASTM C 188, "Standard Test Method for Density of Hydraulic Cement", American Society for Testing and Materials, 2014.

35. ASTM C 191, " Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle", American Society for Testing and Materials, 2013.

36. ASTM C 204, "Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus", American Society for Testing and Materials, 2011.

37. ASTM C 430, "Standard Test Method for Fineness of Hydraulic Cement by the 45-μm (No. 325) Sieve", American Society for Testing and Materials, 2008.

38. ASTM C 1260, "Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)", American Society for Testing and Materials, 2014.

39. Turanlı, L., Uzal, B., Bektas, F., "Effect of Material Characteristics on the Properties of Blended Cements Containing High Volumes of Natural Pozzolans", Cement and Concrete Research, Vol. 34, pp. 2277-2282, 2004.

40. Uzal, B., "Effects of High Volume Natural Pozzolan Addition on the Properties of Pozzolanic Cements", Master of Science Thesis, Middle East Technical University, 2002."

41. Najimi, M., Sobhani, J., Ahmadi, B., Shekarchi, M., "An Experimental Study on Durability Properties of Concrete Containing Zeolite as a Highly Reactive Natural Pozzolan", Construction and Building Materials, Vol. 35, pp. 1023-1033, 2012.

42. Turanlı, L., Meral, C., Sassani, A., Emwas, A., "The Alumino-Silicate Chain Structure of C-S-H Phase in High-Volume Volcanic Natural Pozzolan-Portland Cement Blended Systems", 34th Cement and Concrete Science Conference, Sheffield, 2014.

43. Tydlitát, V., Zákoutský, J., Černý, R., "Early-Stage Hydration-Heat Development in Blended Cements Containing Natural Zeolite Studied by Isothermal Calorimetry", Thermochimica Acta, Vol. 582, pp. 53-58, 2014.