

**An Investigation for the Effects of Local Natural
Pozzolans on Some Mechanical Properties of
Concrete**

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ABSTRACT

For a long time, concrete has been used as an important building material. Many research projects are currently carried out on the concrete. Results of these researches show that durability, workability, resistance against fire, corrosion, and aging highly changed and improved in concretes. In concrete production, pozzolan can be used instead of ordinary Portland cement at a specific rate.

In this study, a series of laboratory tests were conducted on various concrete classes (C20, C25, C30, C35) for varying rates of pozzolan (10%, 20%, 30% and 40%) which obtained by TRNC's Karpas region instead of cement. In these experiments, for the various contribution rates of pozzolan in various concrete classes, compressive strength, tensile strength and shrinkage rates for concrete were determined. According to the results of the experiment, by increasing the percentages of pozzolan rates instead of cement in concrete, the compressive, tensile strength and shrinkage decreased. These indicators reveal that used pozzolans are not too active.

Keywords: Natural Pozzolan, Compressive Strength, Tensile Strength, Shrinkage

ÖZ

Uzunca bir zamandır beton önemli bir inşaat malzemesi olarak kullanılmaktadır. Beton üzerine halen birçok araştırma projeleri yapılmaktadır. Yapılan araştırmalarda, betonun mukavameti, dayanıklılığı, işlenebilirliği, yangına karşı dayanıklılığı ve korozyonal karşı direncinin artmış olduğu görülmektedir. Gerek tabii olarak tabiatta bulunan ve gerekse endüstriyel yan ürün olarak ortaya çıkan pozolanlar kullanılarak daha ekonomik beton üretilebilmektedir. Beton üretiminde pozolan Normal Portland Çimentosunun yerine belirli bir oranında kullanılabilir.

.Bu araştırmada, çeşitli beton sınıfları (C20, C25, C30, C35) için değişen oranlarda (%10, %20, %30 ve %40) çimento yerine TRNC’de Karpaz bölgesinden elde edilen tabii pozolan kullanılarak bir dizi laboratuvar deneyi yapılmıştır. Bu deneylerde çeşitli beton sınıfları ve çeşitli pozolan katkı oranları için basınç dayanımları, çekme dayanımları ve büzülme oranları tesbit edilmiştir.

Deney neticelerine göre, betonlara çimento yerine katılan pozolan oranları artarken, beton basınç ve çekme dayanımları ve büzülme oranları azalmaktadır. Bu göstergeler kullanılan pozolanların fazla aktif olmadıklarını ortaya çıkarmaktadır.

Keywords:Doğal Pozolan, Basınç Dayanımı, Çekme Dayanımı, Küçülme

DEDICATION

To My Dear Family and Friends

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LIST OF SYMBOLS AND ABBREVIATIONS

f'_c	Compressive strength of concrete
MPa	Unit for measuring stress or strength which is equal to N/mm^2
Kg	Mass unit equal to Kilograms
C20	Concrete class of 20 according to ASTM code
C25	Concrete class of 25 according to ASTM code
C30	Concrete class of 30 according to ASTM code
C35	Concrete class of 35 according to ASTM code

Chapter 1

INTRODUCTION

1.1 General Introduction

Long time ago, concrete has been used as an important material in construction industry. Different structures such as buildings, dams, bridges, tunnels, offshore structures, towers and special structures are made of concrete. In most cases concrete is supposed to be strengthened against compressive forces. Different researches on various kind of concretes and its containing components in recent years lead us to achieve new kinds of concrete which are durable, have high performance, resistance ability against fire and corrosion adding to its compressive strength. Many researches and experiments in the field of using additives in the concrete mixtures have been performed. It may be interesting that some of the materials that have been observed to be used as additives in the concrete mixture are not valuable and in some cases were found to be polluting materials [1, 2].

On the other hand, the need for energy saving and also saving of energy reservoirs and other commercial effects lead researchers to do extensive efforts for better use of energy reserves. However, the use of natural and synthetic pozzolanic materials with cement not only decreases the cost of cement production but also because of their physical and chemical properties form remarkably an appropriate base for the reform of the properties of concrete [3].

Since early twentieth century, the mixed cements, especially with natural pozzolans, were used to decrease the heat of hydration in massive concrete.

Pozzolan cement includes consumer incentives to improve quality (decrease permeability, decrease vulnerability because of synthesized with Calcium Hydroxide resultant of cement hydration and decrease of cement heating), increase of cement producing volume not only without decrease its quality but also with increase of it, reduce energy consumption and therefore helping to preserve the environment and reduce air pollution [4].

Generally, a natural material with active silica which is an additive for cement is called pozzolan. The properties of pozzolan is mentioned in ASTM C618 as: “a silica or silica alumina material which is not capable of being cemented itself, but can be synthesized with Calcium Hydroxide in presence of water and common heat with powder condition and produces complexes which have properties of being cemented” [5].

The use of pozzolans either naturally or synthesized is not only to decrease the cost of cement production (because of no need any processing and any other cost to be produced as cement clinker), but also to increase durability of concrete in corrosive environments [6]. In addition, other properties of concrete such as rate of strength gaining, heat of hydration and permeability will be affected positively. Some of these effects are because of physical properties of pozzolan particles which are usually finer than Portland cement particles and some others are because of pozzolanic and synthetic properties which are gained in special physical situations.

During mixing cement with water, free lime is not hydrated instantly, but hydration takes a long time in normal situation and this delay between hydration of lime and other parts causes some amount of stresses in concrete and consequently decreases the concrete compression. The natural pozzolans improve resistance of concrete against the attack of groundwater, because replacing some much of cement with pozzolan will make a hardened material that protects concrete against scours and exit of hydrates such as Calcium Aluminate hydrate, Calcium hydroxide and so on. Obviously, decreasing in the damaging factors such as permeability, porosity and expansion will cause concrete quality improvement and enhance more durability.

Furthermore, though in the early age of concrete, the rate of strength increment with the mixture of including pozzolanic cements decreases intensively in comparison with mixtures including pure Portland cements, but at the long run, the strength of concrete produced with pozzolanic cements are equal or even more than those produced with pure Portland cements. Such characteristic is a very effective factor in decrement of hydration heat in early ages and largely decreases the heat cracks in massive concretes which is one of the most important problems in such cases. Therefore in massive concreting such as concrete dams in which long time strength is considered, the use of pozzolanic cements is used widely. Although the use of mixture of cement and pozzolan increases the whole amount of porosity, decreases the volume of pores bigger than 500 Angstrom in diameter which causes permeability in concrete, because hydration products which are formed continuously fill these pores and as a result decreases the concrete permeability [6].

However, in the present research, first of all; a local mine of pozzolan selected to use its material and to be checked if these materials can be used as a cement replacement

material to decrease the save energy of producing cement which is needed for making concrete. After that, the local pozzolan of Karpaz mine was checked chemically and physically to be in range of materials that can be used in concrete mixture. Then, four different class of concretes, C20, C25, C30, and C35, selected to be observed to use this local pozzolan as a cement replacement material in the mix design and to see the effect of this replacement, four different percentage of cement, 10%, 20%, 30%, and 40%, decided to be replaced in mix design.

In this research, we decided to observe three different mechanical properties which are compressive strength, flexural strength, and shrinkage of the concrete to see if they are affected by replacing the cement in the mix design with local pozzolan or not.

The resultants of preparing adequate samples and doing these three groups of experiments on them will be explained in the next chapters though briefly summarized below:

Using of local pozzolan as a cement replacement in the mix design of four different class of concrete with different percentage of mixing affect the compressive strength of concrete somehow that, the more the percentage of cement replacement in the mix design the more the decrement of compressive strength of concrete.

Replacing different percentage of cement in the various classes of concrete causes to decrease in the flexural strength of concrete and this decrement was approximately has a linear proportion to increment in the percentage of cement replacement with local pozzolan in the mix design.

The shrinkage of concrete was also affected by replacing the cement in the mix design of concrete somehow that the more the cement replaced in the mix design with the local pozzolan, the less the shrinkage value of concrete detected.

1.2 Scopes and Objectives

The aim of this research is to observe the effects of using local pozzolan in the mixture of concrete on its mechanical properties. For this purpose, four different classes of concrete which have four different values of strengths; in case of not to use additives in the mixtures used. Also, to show the effect of replacing cement with pozzolan in their mixture with different percentages of their cement replaced with the pozzolan and water cement ratio remained the same to avoid the change in the results. Therefore the results of these experiments compared with each other.

To undertake a comprehensive literature survey on the pozzolans, cements, and fresh and hardened properties of concrete.

- i- To undertake a comprehensive literature survey on the pozzolans, cements, and fresh and hardened properties of concrete.
- ii- To investigate the chemical and physical properties of local pozzolan.
- iii- To investigate the effects of local pozzolan on some of the fresh and hardened concrete properties such as, concrete weight, compressive strength, tensile strength and the value of shrinkage.

1.3 Works Done

1- The first and the most important part of the work done were to search for the concrete additives and specially pozzolans. For this reason, I read primarily some papers and attended the “cement replacement material” course class for better knowledge.

2- The next step was investigating the properties of local pozzolan. This part can be categorized into two parts namely chemical properties and physical properties.

a- The chemical properties of local pozzolan were done in the cement factory laboratory and were all based on the standard of Turkey, TS EN 196-2[7]. In this part all significant components of pozzolan powder were detected and measured.

b- The physical part of controlling pozzolan was measuring the blain of powder and this was performed in the laboratory of civil engineering department.

3- The next part of the work done in this research were making concrete with and without pozzolan to investigate the effect of replacing cement part of the concrete mixture with pozzolan. For this propose:

a- First, the mix design of the concretes without pozzolan was done.

b- In the second step, according to the mixing values, mentioned in a above, and without alter any change but the cement which was replaced with pozzolan, the effect of this replacement was observed.

c- The samples made for this aim can be categorized in three groups of compressive samples, tensile samples, and shrinkage samples. Therefore three groups of tests, compression test, tensile test, and shrinkage were performed for all selected class of concretes and selected percentages of cement replaced with pozzolan.

d- in the last part of this work, the results of all tests gathered together and compared in a manner that effect of replacing different percentages of cement with local pozzolan in each class of concrete for each physical properties were shown. These obtained results will be explained further in the following parts.

1.4 Achievements

1- Participating in the class of “cement replacement materials” course and reading some papers in the field of using pozzolans as cement replacement materials encouraged me to do my Master Thesis in this case and to observe the effect of a special local pozzolan on the concrete properties.

2- To start an observation in the case of effect of this pozzolan as a cement replacement material on the concrete properties, it was necessary to do two distinct group of experiments on chemical and physical properties of concretes including this pozzolan in comparison with the concrete which does not contain this material.

a- The results of testing chemical properties of local pozzolan which were done in the cement factory laboratory and were all based on the standard of Turkey, TS EN 196-2 [7] showed that this local pozzolan is a pozzolan of class N.

b- Controlling the physical properties of pozzolan, including measuring the blain of powder which was made in the laboratory of civil engineering department showed an

amount of at least 2750. It means that in the cases in which pozzolan powder's blain were less than this amount, milling of the powder will be repeated to achieve this value.

3- In the next part of this research, some mechanical properties, such as compressive strength and flexural strength, of concretes including local pozzolan will be observed.

This observation is over different class of concrete, C20, C25, C30, and C35 and for replacing different percentages of cement with pozzolan, 10%, 20%, 30%, and 40% different testing ages.

The results show that the most effect of this pozzolan is as filling role and not to participate in chemical reactions as so increase the compressive strength and flexural strength of the concrete but decrease them because of reduction in the amount of cement used in the concrete mixture. This filling action also causes the concrete to show less shrinkage than the samples without pozzolan. In a brief form it can be said that:

In the case of compressive strength, the more the percentage of replaced cement with local pozzolan in each observed class of concrete, the lesser the achieved compressive strength in the same class of concrete.

For flexural strength, in each class of concrete the more the percentage of replaced cement with local pozzolan in each observed class of concrete, the lesser the achieved flexural strength.

Finally for the shrinkage, for each one of the observed class of concrete, the more the percentage of replaced cement with local pozzolan, the lesser the amount shrinkage.

1.5 Guide to Thesis

In the first chapter of present thesis, I have an introduction of the whole work that contains main problem, the idea of this research to solve this problem, objectives of this research, the works done during this research, and achievements of the observation are offered.

Also, in the second chapter of this thesis, a literature review of previous works done in this category were presented. These works are mainly in the case of effect of using different kinds of pozzolan, either natural or industrial, in the concrete mixture as an additive replaced rather than cement on different properties of concrete.

After that, in the third chapter of present thesis, a chemical view of cement hydration and pozzolanic reactions presented to guide the reader in a way of understanding behaviour of cement and pozzolan in presence of water or generally in the concrete environment. Having this view helps us to have a better ability in following the chain of reactions and effect of using a material in concrete or replacing it with another one.

The fourth chapter of this thesis is an overview of materials used in samples and also the methods used to write mix designs.

All materials containing cement, water, aggregates, and pozzolans should be controlled to be acceptable according to the codes which guide us in making concrete. Not only the quality of all these materials, physically and chemically,

should be in range but also the value of each one should be calculated in each mix. These calculations also have been done according to the codes and explained in the fourth chapter of this thesis.

In the fifth chapter, the method of taking samples and doing tests was described. In this research we mainly had two different kinds of samples, cubes with the size of 150mm and beams with the size of 100*100*450mm. The tests that were done during this work can be listed as:

- Slump test
- Sieve analysis to show the quality of aggregates and also its fineness
- Controlling the moisture of aggregates
- Chemical test of the cement
- Chemical test of the pozzolan
- Blaine test on cement and pozzolan
- Compressive test for cubes
- Bending test for beams to show the tensile strength
- Shrinkage test

In the next chapter of this thesis, results of all compressive, tensile, and shrinkage tests on related samples are presented and explained whether this replacement of cement with pozzolan affect this results or not.

In the last chapter of this thesis, all conclusions of the research presented and according to the ideas of the author some recommendations presented to be followed in the next researches.

Chapter 2

LITRATURE REVIEW

2.1 Introduction

It is not certain exactly when human discovered cement with hydraulic effects. However, it has been told that Romans were fortunate to find hydraulic mortar in volcanic soils in Italy. This volcanic soil had been found around Pozzuoli city near the Naples, so it has been called as Pozzolan. Romans comprehensively had been used pozzolan and lime mortar in their constructions as well as their residential areas buildings located in their empire [10]. Pozzolan could be categorized based on its source in two main groups:

1- Natural Pozzolan is contains Diatoms, Opaline, Chartes, Shales, Tuff and volcanic ashes.

2- Artificial Pozzolan or Industrial Pozzolan, the main source of this is energy installation facilities which use coal as their energy source. Moreover, blast furnaces of steel, copper, nickel, lead, silica and iron alloy become the major sources for industrial pozzolan. Most of these materials could be used in the process of ultimate strength and durability of concrete from Ordinary Portland Cement. Especially, these materials could be alternative superseded for concrete aggregates to increasing ultimate strength and durability of concrete [10].

2.1.1 Natural Pozzolan

Natural pozzolans have volcanic base. Most of the time, this material could be found in the areas that have latest volcanic activities. Serale [11] put this, pozzolans formed under the effect of exploding blow out volcanic activity. Although, intense eruptions of melting lava through the atmosphere lead to form vitreous materials as well as slight eruptions are the major cause of volcanic ashes, which less likely combine with the lime. The point that should have noticed is that in both situations the chemical components of these materials are the same.

For centuries, Porphyry's of natural pozzolan was used in the Vesuvius city in Italy, which located near Pozzuoli as well as Naples and Rome. These pozzolan's first used in the lime mortar and afterwards used in Portland cement's concrete. Sersale [11] claims that in 1977 in Italy the pozzolan cement production was almost 15 million tons. There is probability that as well as the natural pozzolan's they also use industrial pozzolan's. However, there is no doubt about this fact that most of these productions contained by natural pozzolan's. Although, Lea [12] believes that these porphyry's also used in Romania as well as the Russia. The first time that pozzolan's used, as a comprehensive material in United States was in the period of 1910 to 1912 to build the Los Angles channel. In this project more than one hundred thousand tons of pozzolan's had been used.

Afterwards, in projects like dam, bridges and other enormous constructions Americans used natural pozzolan's in the west coast of United States, which (natural pozzolans) could be found in those areas. For decades in the concrete structures Japanese's used pozzolan combinations in their projects, which used mostly in marine structure. During recent years, pozzolan's combination become interesting

additional features for concrete structures especially in under develop countries because of their expansion projects.

Moreover, in the Northern-Cyprus there are great pozzolan supplements in Karpaz area. This is a huge opportunity to use these local supplements. Not only as economical advantage but also as a quality measurement to be used in the structures construction of North Cyprus projects. These advantages could be considered as well as the technical advantage that could be possible within the researches that have the potential to improve the knowledge of using pozzolans in concrete structures.

2.1.2 Industrial Pozzolan

2.1.2.1 Rice Husk Ashes

Rice husk ashes have almost 80% organic material and 20% mineral material [13]. In process of burning the rice husk, the 18% of original weight converted to rice husk ashes. The most important feature of rice husk ashes is the amorphous silica in the special overall level [14]. Therefore, there is a possibility to use this combination as cement replacement additive feature to the pozzolan concrete. This replacement leads to increase the concrete strength in the offshore structures against the various mineral components of seawater. The components of seawater are the main cause of the porosity in the concrete structure. So, the pozzolan components also used in other corrosive environments [15].

Despite of 21 million tons production of the rice husk, the usage of this component in the concrete is much less than expectations. In the developed countries that used the technology of giant rice mill, gathering and burning the rice husks become a problem. Ecologically, these processes become harmful for human environment, so

these rice husk leave on the ground without any useful purpose. These problems become an active base on the academics research, due to find an ecological and technological solution to use rice husk, especially in United States [14].

2.1.2.2 Micro Silica

Micro silica consumption as an additional material in the process of producing concrete with high strength in present years has becomes a common fact as simple practical method to produce variety of concretes [16]. The researches on this subject show that among all additional pozzolan materials, micro silica is a suitable choice to provide high strength concretes. The main reasons of this suitability are the particulate and fragmented nature of silica, which is, contain by 90% with amorphous silica (non-crystalline) [17]. The main difference between the micro silica and ordinary pozzolans is that the pozzolanic action amount of micro silica particles is very faster than that of other pozzolan particles [18]. It has been suggested that consuming micro silica, which used in the process of providing concrete with high strength: firstly, have the 85% of micro silica dioxide, secondly, it should have a sphere particles as well as non-crystalline particles [19]. Generally, the positive effect of micro silica on the mechanical strength of concrete caused by two major mechanism:

1- Pozzolanic activity

2- High fineness and filing effect

High pozzolanic activities decrease the calcium hydroxide which is produced in the process of cement's hydration. This process increases the productivity rate of cement gel in cement paste. High plasticity in this case becomes the main cause of filing the

porous between cement particles and cement gel [20]. Until now there is no precise estimation on the role of micro silica in the process of concrete strength. However, this issue should be noticed that this role could be effected by mechanical and chemical features of the micro silica that used in the concrete as well as cement quality, proportion of water to the cement and the method that used to provide the concrete [21]. ASTM C1240 standard tries to explain the method of silica soot Usage as an additional feature in concrete, mortar and grout [22].

Micro silica or silica soot provides as a collateral production of industrial Ferro silicon which achieved beside the gas from electric arc furnace. To avoid any harm to the environment especially for animals and crops, it has been suggested the used filters for providing gas. This attribute helps the separation process of micro silica from the other gases. The deposition of the rest of the material, which are waste, is the other important issue in this process. Afterwards the silica soot which gathered through the filters have been mixed with the water. This mixture makes the possibility that you can transport this mixture through piping system.

First time in 1947, Norway, researchers understood the fact that micro silica (active silica) has a combination potentiality with lime. Since then researchers start to use micro silica in the concrete samples. Moreover, from 1950 the benefits of micro silica have been a proven fact and the usage of micro silica in concrete combination become popular.

Researches show that if micro silica combined with cement, active silica particulars combined with calcium hydroxide, which produce during the hydration of cement, and produce hydride calcium silica. This chemical reactions lead to decline the

vulnerability of concrete as well as increasing the strength of it. This mechanism makes a possibility to declining the consuming cement. As well as, particulars fulfill the porous of cement gel. This means diffusion and permeability of chloride declined. In other words, not only micro silica is detected as pozzolans with pozzolanic behavior but also it acts like isolation and decline the diffusion effect of cement gel.

The silica particulars diagonal that attached to the filters measured 0.1 micron as an average. These particulars have a high specific surface, which increased the combination ability. If the particulars increased, the specific surface will be decreased compared to the volume, so the combination ability decline. For example, the combination rates of particulars with high diagonals in the first levels are not noticeable. So their combination could be finalized during the hydration. This means particulars trapped in the cement gel [23].

2.1.2.3 Nano Silica

Nano-technology is the ability of observe and experience in the atomic, molecular, and ultra-molecular size, i.e. 1 to 100 nanometer, with the aim of produce and changing in the structure of atoms and molecules. Decreasing the size of particles to the range of nanometer will increase the specific surface and the effect of surface behaviors will be increase. Therefore, it can be said that ability of reaction in materials at range of nanometer increases intensively which can improve the properties of pozzolanic additives. Generally, nanoparticles, on one hand have the role of filling the little pores in cement paste (especially in pores among aggregates and cement paste) and on the other hand can make some changes in hydration of cement paste [24].

One of the most famous nanoparticles in the field of concrete technology is nano silica or amorphous nano silica (SiO_2) [25]. Nano silica having extensive amount of amorphous silica (more than 99%) and very little particles (1nm to 50nm) has a better function than micro silica. According to low rate of strengthening in early age of concretes containing pozzolans, it seems that using of nano silica can remove this problem. During hydration of Portland cement, a large amount of pozzolanic reaction of nano silica causes calcium hydroxide crystals (which results from cement hydration) to change to the hydrated calcium silicate (C-S-H) [26].

2.2 Pozzolanic Classification According to the Codes

Nowadays, each material which reacts with lime and in presence of water, sets, and strengthened and also its strength increases is called pozzolan. Pozzolanic materials set is increasing, but their resource, chemical complex, and mineralogy is very different. Sersale[11] and Massazza[27] believe that using “additive mineral” is more correct than “pozzolan”. However, additive minerals can be classified as natural pozzolans, calcinated clay, shale, fly ash, silica soot, and remained ash of burning herbs. The first classification of natural pozzolans was proposed by Mielenz et al [28]. They classified pozzolans to six groups according to their activity. The earliest classification of pozzolans by Massazza[27], classifies them to three groups according to their resource.

ASTM C618[5] introduces pozzolan as “a silica or alumina silica material which is not able to be cemented or is less able to be, but with the shape of very little particles in presence of humidity at common temperature chemically reacts with calcium hydroxide and produces complexes with cement properties”.

Since the properties of pozzolans can extensively vary, there should be some tests to accept them before use. ASTM C618 introduces natural pozzolans and fly ash as additive materials in concrete. The procedure of sampling and testing of fly ash is presented in ASTM C311 [30]. Suitable pozzolans for using in concrete due to ASTM C618 [5] are classified as type N, type F, type C, and type S.

2.3 Concrete Properties Made by Pozzolanic Portland Cement

2.3.1 Introduction

Generally, pozzolan reacts with lime. In other words, lime can be either straightly as a mixture of pozzolan and lime or as a subsidiary product of portland cement hydration. For mixture of lime and pozzolan, presence of pozzolan will make hydraulic properties for the mixture, i.e. decreases setting time, increases the strength, and intensively increases durability of concrete [3].

Lime and pozzolan react in the mixture of pozzolanic portland cement, because lime is the product of hydration of C_3S and C_2S in cement, though it is probable that many of strengthened concrete's properties change due to adding pozzolanic materials. Some of these effects are according to physical factors such as fineness of pozzolan particles, shape of particles, and so on. The effect on strength and permeability of strengthened concrete, resistance against thermal cracks, reaction between silica and alkaline, and sulfate attacks are some of the signs of pozzolanic cements.

Pozzolans are sometimes used to decrease the internal temperature of concrete.

Some of the pozzolans are used to neutralize or decrease the expansive ability of concretes due to alkaline reacts of particles. Whenever using of active particles in

concrete is inescapable, the cement with low alkaline property or standard pozzolan due to ASTM C441 [31] can be used to avoid expansion.

In pozzolanic concrete, many of the concrete properties are affected by pozzolans that will be introduced flowingly.

2.3.2 Compressive Strength

It is clear that lime and pozzolan reaction in the mixture of pozzolanic portland, because lime is the product of C_3S and C_2S hydration. There are some signs that these reactions between pozzolan and portland cement starts in early setting time. Strength growing in pozzolanic portland cement at the beginning for a specific pozzolan is related to the amount of replaced cement with pozzolan. In many countries, it is allowed to replace up to 40% of hydraulic cement with pozzolan with the condition of reaching needed compressive strength [20]. In this research, the replaced amount of cement with pozzolan is up to 40%.

Strength growing is a function of process of filling the pores. This filling is with the products of hydration. Some researchers such as Mehta [32] have previously done works in the case of effects of using pozzolan in different percentages on concrete strength. In one part of this present research, the effect of using pozzolan on the strength of concrete was observed.

Using micro silica is observed by some researchers such as Loland and Hustad [33]. These researches show that portland cement replacement with silica soot in concrete can improve compressive strength. Of course using silica soot with plasticizer or super plasticizer will be more effective.

2.3.3 Heat of Hydration

Totally, the hydration heat in early age concretes with portland cement is more than concrete with pozzolanic portland cement, but pozzolanic reaction is also exothermic. As Davis [34] says, “total released heat during hydration is basically more than reckoned heat for just using cement”. He also mentioned that these properties in mass concrete like dams is suitable, because released heat should be controlled before concreting one block on another. Davis proposed to increase replaced amount of cement with pozzolan to achieve 50% less released heat amount. Mather [35] also has done experiences in this category which show intense hydration heat decrement by using more pozzolan. Masazza [36] also shows that the more portland cement replacement with pozzolan will causes more decrement of released hydration heat.

2.3.4 Porosity and Permeability

Mather [37] and Davis [38] proved that using pozzolans in concrete mixtures with low cement amount is very effective on decrement of permeability and this decrement is related to ability of pozzolan to react. Increasing pozzolan value, the reaction of lime and pozzolan will continue and pore's volume decreases. On the other, hand bigger pores (with the size of more than 500 Angstrom) effect strength, permeability, and as a result durability of the concrete. Mehta [39] shows a direct relation between concrete permeability and the volume of pores with the size of more than 500 Angstrom for the mixtures of cement and Santorin soil. Davis [34] says that using suitable pozzolan in dam concretes with low cement amount can achieve such low permeability ratio which is not accessible in any other way.

2.3.5 Elasticity

In general condition, concrete properties such as modulus of elasticity and creep is affect by concrete strength, aggregates' modulus and their volume in unit volume of concrete, environment's relative humidity, temperature, cement type, and stress value. Obviously, concrete containing natural pozzolanic portland cement with low strength in early age have less modulus of elasticity and more creep than non-pozzolanic concrete.

Abdun and Nur [40] realized that concrete modulus of elasticity, made up of fly ash, in early age will be low and during passing time will be increased. Naturally, concretes which contain fly ash have more modulus of elasticity than the one which do not have fly ash. Ghosh and Timusk [41] observed concrete containing fly ash with the age of 28 days. They have concluded that for all strength values, modulus of elasticity of concrete with and without pozzolan are approximately equal.

Lane and Best [42] have seen in their experiments that concretes made up of pozzolanic cement in early age have less modulus of elasticity than concrete with non-pozzolanic cement and in the age of 90 days this relation will be changed somehow that the modulus of elasticity of concrete with pozzolanic cement will be more than that of concrete with non-pozzolanic cement.

2.3.6 Concrete Workability

Workability is one of the significant properties of concrete paste that is basically related to adhesive. Davis et al [38] show that pozzolanic portland cement need more water to gain same workability than normal portland cement. Though, it is obvious that increasing cement replacement with pozzolan and also increasing pozzolan fineness will increase water need, but Tuthill and Cordon [43] show that these bad

effects can be removed by using plasticizers and super plasticizers which decrease water amount used in concrete mix. Wallace and Ore [44] presented some results of using additives such as water reducer and retarder in pozzolanic portland concretes. They observed water reducer effect and show that strength and durability are improved. Also conclude that changes due to expansion in water environment, shrinkage due to drying, and permeability is not affect intensively by using retarders and water reducer.

2.3.7 Primary and Final Setting of Pozzolanic Portland Cement

Primary and final setting of pozzolanic portland cement is affect by the value of replaced normal portland cement, fineness and ability of pozzolan to react. Davis et al [38] show that replacing 20% of cement with pozzolan, setting time is approximately is the same of normal Portland Cement.

Process of strengthening for concretes containing micro silica is more than common concretes and concretes containing mineral pozzolans. On the other hand, pozzolanic activity of nano silica is very faster than that of other available pozzolans [26]. Rate of strengthening for concretes containing rice husk in early age is less than that of older ages of concrete and by increasing concrete's age rate of strengthening for concretes containing rice husk increases. Therefore pozzolanic reaction of rice husk soot increases during the time and causes the increment of concrete strength [14].

2.3.8 Effect of Chloride Ion on Concrete

Chlorides may be in fresh concrete due to additives or because of polluted materials and in strengthened concrete may be due to external resources such as salts and sea water, but however just some of the chloride ions will be exist. Therefore, capacity of concrete for limiting chlorides is like resistance against chloride permeability.

The high ability of pozzolanic concrete in limiting chloride ions' movement could be due to produce sheets, in long term, and can ban the steel corrosion. These steels usually are not covered in chloride environment [45].

Fisher et al [46] observed permeating of chloride to the concrete containing silica soot from sea water. They realized that using silica soot as an additive decreases permeating chloride in concrete intensively.

According to the function of micro silica due to the type of used cement, replacement of 6% to 10% of cement with micro silica in concrete causes the decrement of concrete permeability and the distribution of chloride ion. The decrement of internal humidity in concrete and also increment of electric resistance in armed concrete is due to the filling pores by products of micro silica function. As a result the probability of making corrosive cell for steel bars and concrete fracture will decrease valuably [23]. Nowadays, the advice of most of the engineers in the field of construction is to use silica soot with super plasticizer, because scientific experiments show that existence of silica soot with the weight of 7% in respect to cement in concrete stop permeating chloride significantly [45].

2.3.9 Steel Corrosion and Carbonation

One of the effective and significant factors in construction of concrete structures is the steel bars. Steel corrosion in concrete is an electro-chemical process and will the resultant of corrosive cell in place of steel bars. In this process, present humidity in concrete acts such an electrolyte and eases the ion transfer. When steel bars firstly touch cement paste, their surface particles in the water environment, start to react with oxygen. Hydrated Ferro-Oxide produced by this reaction in alkaline environment of cement paste which has a PH of more than 13, is non-soluble and

covers the steel bars as a resistant film and barricade the continue of this reaction, thus a passive situation will be caused and resists the steel bars from being more stained and corroded. Now if materials such as chlorides and carbon-dioxide gas (CO_2) permeate the concrete decrease the PH of liquid inside the pores, this resistant film on steel bars start to be solved in that liquid. Then, little by little, the passive form of the steel bars will disappear and staining will start again. It is clear that the more amount of humidity inside concrete the more electric transferring will accelerate the corrosion [23].

In recent years many researches in the field of using pozzolanic portland cement in making concretes have been done. There is a negligible amount of knowledge about corrosion rate in natural pozzolanic concretes available. Most of the researchers believe that the reaction between lime and pozzolan decreases concrete pH, but release of alkaline may increase the pH again. Battler [47] believes that this decrement is not so much that can be dangerous for resistant oxide layer of steel bars.

Carbera, Cusens, and Ramezaniapour [48] show in a research that pozzolanic mortars made up of trass gained from Baluchestan of Iran and silica soot carbonated faster than the ones with the additive of rice husk.

In the case of micro silica function, due to the type of used cement, using micro silica for 6% to 10% of whole weight of cement causes the decrement of concrete permeability and the ability of chloride ion distribution. Also the internal humidity of cement paste because of filling pores with the products of micro-silica function will decrease and electric resistant will increase and as a result the probability of making corrosive cell of steel bars and concrete fracture will decrease valuably [23].

2.3.10 Durability

Durability and stability of concrete against environmental aggressive factors around concrete is very important. Generally, such factors including solution of sulfates especially sodium sulfate, potassium sulfate, calcium sulfate, magnesium sulfate, chlorides, and alkaline are often present in soil and water naturally. Concrete permeability has a basic importance for permeating bad chemical materials such as acids and sulfates. Since the pozzolanic reaction of mineral additives have the ability to proof the porosity and decreases concrete permeability, will make valuable improvement in chemical durability of concretes containing such materials. Additives are approximately able to use calcium hydroxide in hydrated cement paste and thus it is excellent to improve concrete strength against sulfate attack [45].

2.3.10.1 Sulfate Attack and the Advantage of Using Pozzolan

Concrete damage due to sulfate attack can be affected by cement amount, cement type, and mineral additives. It is known that solid salts don't attack concrete, but when they are in solution form, can react with strengthened cement paste. All components of strengthened cement paste will be attacked with sulfate solutions. During this attack, sulfates react with calcium hydroxide and hydrated calcium aluminate. Generally, reactions between strengthened cement paste and sulfate ions can be classified to three groups due to their significance:

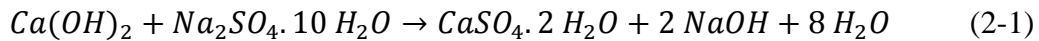
- a- Production of sulfur-aluminates including mono sulfate and ettringite

- b- Production gypsum

- c- Other reactions which will accelerate with sulfated concrete

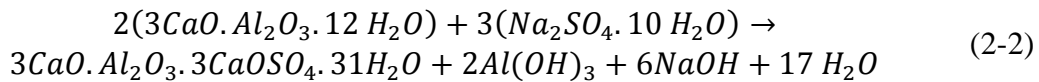
The volume of these reactions is valuably more than replaced complex volumes somehow that reaction with sulfates causes the concrete to expansion and rapture of concrete [49].

Sodium sulfate can react with calcium hydroxide as bellow:

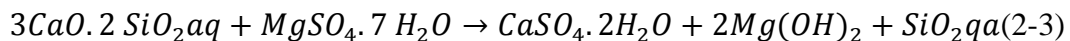


Flow waters can solve sodium hydroxide completely and bring it out, but if sodium hydroxide (Na(OH)) concentrated, the equality situation will result and just a part of SO₃ will sediment as gypsum.

The reaction with hydrated calcium aluminate can be written as bellow [50]:



The resultant of above reaction, $3CaO \cdot Al_2O_3 \cdot 3CaOSO_4 \cdot 31H_2O$, is called ettringite. On the other hand magnesium sulfate attacks to hydrated calcium silicate, calcium hydroxide, and hydrated calcium aluminate and the related reaction is as bellow:



Due to very low ability of solution of magnesium hydroxide, Mg(OH)₂, this reaction will continue up to end, somehow in some conditions magnesium sulfate's attack is more intense than other sulfates [51].

Sulfate attack will increase by increasing the density of solution. Attack rate to the concrete in addition to sulfate density is depending on process of eliminated sulfate replacement due to cement reaction. Thus, in approximation of sulfate attack, the way of underground water movement should be recognized too.

Replacement of portland cement with pozzolan causes better condition in the case of sulfate attack. First step of sulfate attack is expansive reaction between sulfate ions and calcium hydroxide. Pozzolan reacts with calcium hydroxide and as a result reduces the expansion amount. Like alkali reaction of silica due to sulfate attack, enough pozzolan should be added to control the expansion. Conclusions of trass experiments by Lea [12] shows that 20% replacement of portland cement with pozzolan has a negligible improvement in the required time to gain 0.1% expansion but 40% replacement of portland cement with pozzolan causes a valuable improvement. Mehta [32] by using Santorin soil shows that replacement of 10% does not cause effective control in concrete expansion although replacement of 20% and 30% is very effective.

The second effect of pozzolan is reduction of C_3A in cement. Thus, the more replacement causes the presence of less amount of C_3A in mixture. The main reason of expansion in portland cement due to sulfate attack is a reaction which makes the transformation of aluminum mono-sulfate to ettringite possible. Turriziani and Rio [52] believe that profusion of hydrated calcium silicate and also less amount of the ratio of CaO in respect to SiO_2 in comparison with the same ratio in portland cement paste causes the ability of hydrated calcium silicate in saving lime and decreases the problem of its flow out.

The third beneficial effect of pozzolan is decrement of concrete permeability. Pozzolan decreases the rate at which sulfate solution penetrates inside the concrete. Putting concrete in the environment of sulfate solution causes strength decrement and this reduction is due to sulfate ion density and also due to concrete properties.

According to Massaza and Costa [53], calcium hydroxide in hydrated pozzolanic cements not only presents lowly, but also is confined with C-S-H gel. This condition is not suitable for producing ettringite which is generally the reason of expansion and crack. On the other hand, permeability of cement paste increases the saving factor of hydrated lime which hardened the permeation of ions inside concrete.

In another research by Mehta [54], effect of replacement with the value of 10%, 20%, and 30% with Santorin soil on the sulfate resistance of portland cement of type I with two different research methods is observed. He realized that sulfate attack is remarkably low in the mortars with 20% and 30% pozzolanic cements.

2.3.10.2 Silica and Cement Alkali Reaction and Advantage of Pozzolan Reaction

Some of aggregates have a special kind of silica which reacts with the alkalis present in the cement paste. The product of this reaction is expansive and causes deep cracks in concrete. The shape of passive silica can be blurred or not. This reaction starts with attack of alkalis inside the cement to the aggregates silica. These alkalis which participate in the reaction are hydroxides produced from Na_2O and K_2O . The signs of injury of concrete due to reaction of concrete's alkali with non-blurred silica of aggregate are expansion, crack, exit of Sodium silicate and potassium silicate from pores and cracks, production of hard particles at the concrete surface, and protrusions. The size of cracks increases during the time and finally causes the failure of concrete member. The mechanism of this attack is similar to sulfate attack,

because just some of concrete components participate in this reaction. There is a difference between this attack and sulfate attack which is the place of it. Sulfate attack occurs in cement but this attack is in aggregates. Generally, type of active materials, value of active materials, value of alkali in cement, water value in the mixture, and permeability of hardened cement paste affect the reaction of alkalis with aggregates. To reduce the reaction of alkali silica with cement, either the value of alkali in cement should be limited or special type of cement which stops harmful reaction between aggregates and alkalis should be used.

ASTM C441 [31] specifies controlling alkali reactions of aggregates using mineral additives. Mehta [39] showed that for increasing the replacement of cement in the mortar with Santorin soil, the expansion decreases.

Davis [34] says that effect of a specific pozzolan on expansion control of alkali silica is depend on react ability of that pozzolan and this factor can specify the value of cement replacement, i.e. silica soot is more reactive than rhyolite, though to control the alkali silica expansion, it is less used.

2.3.11 Shrinkage Based on Dehydration

Saturated cement paste, during being in a common environment will not have constant size due to dehydration of C-S-H gel partially in unsaturated environment. Indeed the strain due to shrinkage is imputed to the outflow of absorbed water and water flow from hydrated cement paste. The subsidiary reason of shrinkage based on dehydration is flow and outflow of the water in capillary spaces (with the size of more little than 50nm) in hydrated cement paste due to hydrostatic tension.

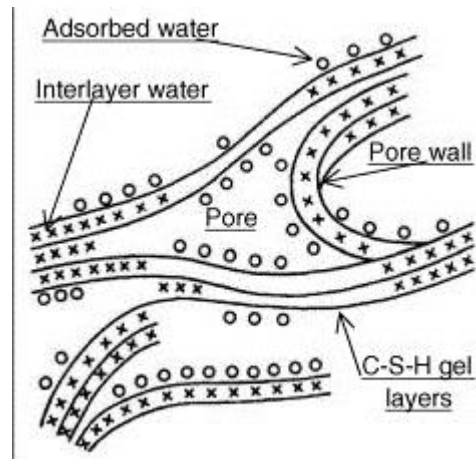


Figure 1. Different waters in C-S-H [55]

Practically, replacement of humidity in hydrated cement paste, which is basically controlling shrinkage strain of concrete, is effected by multiple factors simultaneously. The relation among these factors is very complicated and is not so easy to be studied. Some of these factors are mentioned and discussed in beneath.

2.3.11.1 Materials and Their Amount in Mixture

The main resource of transformation based on concrete moisture is hydrated cement paste. Therefore, many efforts in the case of finding relation between shrinkage based on dehydration and the volume of hydrated cement paste are done. This volume is measured from amount of used cement and hydration degree. Although shrinkage based on dehydration is a function of cement paste amount, there is no straight relation available. This is due to restrict of transformation. Factors such as grading of aggregates, the maximum size of aggregates, shape and texture of aggregates are also effective on the shrinkage amount. Most of researchers believe that aggregate's modulus of elasticity is the most important factor in this case and the others affect the shrinkage indirectly, i.e. either with effect on compressibility of the concrete mix or with effect on the amount of aggregates.

The effect of aggregate's properties and specially, modulus of elasticity during 23 years of concrete age is proved in a research by Troxell [56]. He shows in this research that concrete shrinkage is increased up to 2.5 times more by replacing aggregates with the ones that have less modulus of elasticity.

2.3.11.2 Time and Humidity

Drainage of absorbed water and confined water in the little pores (smaller than 50 nanometer) by capillary of hydrated cement paste to the bigger pore or to the outside of the sample is a time dependent process which will occur during a long time.

2.3.11.3 Shape of Concrete Member

Because of resistance against water extension from concrete environment, its rate is depend on the length which should be passed with the water from inside to surface and this is the water that exits during shrinkage. In a constant related humidity, the shape and size of the concrete sample will affect the amount of shrinkage. Often the size and shape of sample are shown with a number known as effective thickness or theoretical thickness. This parameter is equal to the ratio of area over the half-perimeter of the surface that is in contact with atmosphere [6].

2.3.11.4 Pozzolans

Pozzolans cause the little pores' in cement hydration products to be grown. Since shrinkage in concrete is based on confined water in pores with the size of 3nm to 20nm, concretes with additive, which make more little pores, show usually more shrinkage. Additives will cause better distribution of non-hydrated cement particles in concrete, such as plasticizers, improve the situation of pores in hydration productions.

2.3.12 Concrete Expansion

2.3.12.1 Expansive Reactions

The chemical reactions which produce expansive productions can be somehow harmful for the system. Expansion may be non-destructive primarily, but increment of internal stresses finally shows itself by closing the expansion joints, displacement of structure's different points, cracking, and flaking the concrete surface. These four events are related to chemical expansive reactions: sulfate attack, alkaline aggregates' attack, postponed hydration of free CaO and MgO, and steel corrosion in concrete.

2.3.12.2 Sulfate Attack Base Expansion

Decrement of concrete quality by chemical reacting of hydrated Portland cement and sulfate ions from an external resource is known which can be occurred in two completely different types. The items that can cause the system to follow which type of corrosion processes are the density and the resource of present sulfate ion in the water either in touch with the concrete or is used in the concrete mix. The sulfate attack can be detected as concrete expansion. When concrete cracks, its permeability is increased and the water is penetrated in concrete more easily, therefore corrosion process will accelerated. Sometime this expansion will cause significant structural problems such as building's wall displacements by slab expansion. Sulfate attack also can cause continues decrement of strength.

Chapter 3

CEMENT HYDRATION AND POZZOLANIC REACTION

3.1 Introduction

Detecting pozzolanic activity is the base of estimate and quantitatively use of pozzolan. That is why several researches are done in this category.

3.2 Cement Hydration

3.2.1 Non-hydrated Portland Cement

Non-hydrated Portland cement is a grey powder which its particles have sharp angles with the size of 1 through 50 Micron. Cement is gained from milling clinker mixed with little amount of Calcium Sulfate. Clinker is a non-homogenous mixture of several minerals which are produced of syntheses of Calcium Oxide, Silica Oxide, Aluminum, and Iron in high temperature. The main complexes of cement clinker (in normal Portland cement) are C_3S (45% to 60% by weight), C_2S (15% to 30% by weight), C_3A (6% to 12% by weight), and C_4AF (6% to 8% by weight) in which S, C, A, F, and H are respectively the abbreviations of SiO_2 , CaO , Al_2O_3 , Fe_2O_3 , and H_2O [58].

3.2.2 Hydration Reactions

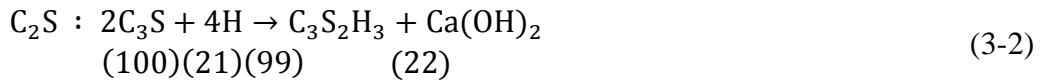
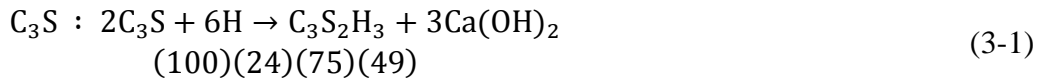
Combination of water with the components of cement is called hydration. The product of this combination is at first a paste with physical formability and then hardened during time passed. During hydration and hardening of cement paste, some changes and synthesis are done which can be listed as bellow:

- a- Chemical processes, especially hydration reactions and combination of water with cement components.
- b- Reactions related to the solution of cement components and their crystalline and producing new gel-like and crystalline components which is due to formation of water saturated cement components.
- c- Produce of new surface attractions among mutual hydrated surfaces and finally making the hydraulic connections among cement components.

Hydration, like many other chemical reactions is exothermic. The exothermal heat is called to the heat amount, which is resulted from hydration of each gram of cement. The temperature in which reactions are done has an intensive effect on produced heat. Also this produced heat is related to the cement components and is equal to the summation of produced heat by each one of the components [57].

Silicates (C_3S and C_2S) are the main and important components of cement and the strength of hydrated cement is related to them. C_3S hardened rapidly and the primary strength of the cement is because of that. Generally, the more the primary strength of concrete made up of Portland cement, the more the percentage of C_3S in that. C_2S hardened slowly and mostly participates in the strength of elder than 7 days [58].

Reaction of C_3S with water results micro crystalline, $C_3S_2H_3$, and crystalline Calcium Hydroxide, $Ca(OH)_2$. C_2S Also results similar complexes, but the produced lime is less than that of C_3S . Hydrated Calcium Silicates are called C-S-H which was known as Tobermorite gel. The reaction can be summarized as bellow [57]:



The values in parentheses show the weight of each component and according to these values, both silicates need the same value of water to react with. Though C_3S approximately produces two times more $\text{Ca}(\text{OH})_2$ than C_2S .

C_3A makes a huge amount of heat during first couple days of hardening. Also this component participates in gaining primary strengthening. The cement with the less percentage of this component is more resistant against soils and water including sulfates than the one which has more percentage of C_3A . In other words, C_3A is not beneficial in cement and has no act in the strength of cement but a little in the primary one and after hardening the cement, will produce Ettringite under sulfate attack which causes its failure and corruption. The reaction of pure C_3A with water has a very high rate and this rate is controlled with adding gypsum. Anyway, setting of C_3A is faster than Calcium Silicate and is as bellow:



The weight value written in parentheses shows that reaction of C_3A needs more water than Silicates. C_4AF decreases the temperature of clinker, therefore cooperates in cement produce. C_4AF is approximately passive and participates in strengthening and heating a little. This component produces Calcium ferrite sulfosuccinates and sulfosuccinates calcium aluminate by reacting with gypsum and cement. When all of

the sulfates participate in complex, the remaining C_4AF reacts with water and hydrated calcium aluminate will results [59].

3.2.3 Solids in Hydrated Paste

Types, values and properties of four different phases of hydrated cement paste are mentioned bellow:

3.2.3.1 Hydrated Calcium Silicate

The hydrated calcium silicate phase, which is called C-S-H, constitutes about 50% to 60% of total volume of fully hydrated cement paste, so it is the most important solid part of paste in characterizing its properties. Because the ratio of the components in hydrated calcium silicate is not exactly known, it is named as C-S-H in which the ratio of C/S is between 1.5 and 2 and its chemical water is very different. The structure of C-S-H is varying from weak fiber-like crystals to coherent networks. Because of its colloidal form and also tending to be clustered, C-S-H blurs just can be detected by accurate electronic microscope. The blur internal structure of C-S-H is still unknown. Previously it was thought that its blurs are like Tobermorite mineral material hence it was sometimes called as Tobermorite gel [58].

3.2.3.2 Calcium Hydroxide

About 20% to 25% by volume of the solid part of hydrated paste is formed with hydrated Calcium blurs. Calcium hydroxide, against C-S-H, has a known formulation of $Ca(OH)_2$, but the structure of these blurs which is usually plate-like is a function of available volume in the paste, hydration heat, and impurities in the paste. Because of lower specific surface of Calcium hydroxide in comparison with C-S-H, its role in strength is lower also [57]. The existence of valuable amount of calcium hydroxide in hydrated cement paste has inappropriate effect on chemical durability against acids, because of more solubility in comparison with C-S-H [58].

3.2.3.3 Calcium Aluminate Sulfate

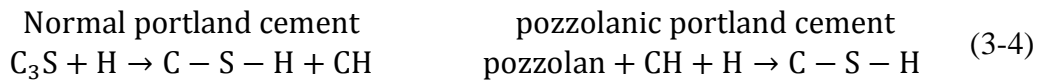
About 15% to 20% by volume of solid part in hydrated paste is formed with calcium aluminate sulfate. Therefore, it has less effect in properties and structure of this paste. In the process of cement hydration, the ionic ratio of sulfate over aluminium oxide is somehow that like $C_6AS_3-H_{32}$ or ettringite which are acerate blurs. Finally in cement paste ettringite will deform to hexagonal plate shape blurs of C_4AS-H_{18} . The existence of mono-sulfate hydrate in concrete made up of Portland cement will make it vulnerable against sulfate attacks. It should be mentioned that both ettringite and sulfate contain Iron oxide which can be replaced with aluminium oxide in crystal structure [58].

3.2.3.4 Non-hydrated Clinker Particles

There will be some much of non-hydrated clinker particles in hydrated cement paste structure due to the level of cement hydration, non-hydrated cement particles which can be exist even long time after hydration. In new cements, the clinker particles are about 1 to 50 micron size. During the process of hydration, first the fine particles and then bigger particles will be solved. Because of limited exist volume among particles, the resultants of reactions tend to be crystalline about clinker particles and cover them. In long term, because of lack of existing volume, the clinker particle's hydration will produce compacted hydrated results which form the main shape of hydrated clinker particles [58].

3.3 Pozzolanic Reaction and the Importance

The comparison between Normal Portland cement and pozzolanic Portland cement can be helpful in knowing the difference of their behaviour about the reaction of C-S-H production.



The reaction between pozzolan and calcium hydroxide is called pozzolanic reaction. The importance of pozzolanic cements is mostly because of three reasons. First, this reaction is slow though the rate of heating and strengthening will be slow. Second, this reaction use lime instead of producing lime which has important effect on the resistance of hydrated paste against acidic environments. Third, observing the distribution of pores in hydrated cements shows that the products of this reaction are very effective in filling large capillary areas though improves the strength and permeability of the system.

3.4 Pozzolanic Reaction's Origin

One theory is based on assuming the existence of zeolites in pozzolans as reason of reaction between pozzolan and lime. It means that there are some known zeolite minerals which tend to attract lime with the mechanism of ion replacement. According to Dron theory [11] the pozzolanic reaction can be explained due to solubility of feldspar shape materials in lime solution. He realized that the four-side units of silica are in a situation in these materials that oxide ions present in all four sides, though the oxide ion will change to hydroxide ion on surface.



This reaction will cause silica to enter lime solution and react with calcium ions and produce non-solved hydrated calcium silicate. Therefore, exiting one unit of silica from surface causes the other silica unit to be in contact with solution and the mechanism will repeat. It is mentioned in Dron theory that this mechanism will

happen in pyroclastic Pozzolans easier than other kinds because of weaker internal connections in four sides silica blurs and in zeolite pozzolans because of porosities and permeation of lime solution inside, it will happen more rapid.

Takemoto and Uchikawa [60] understood that in very alkaline solution of lime, pozzolanic particles are attacked with protons. Therefore the surface will have negative charge and attracts Ca^{2+} and causes the pozzolan alkaline solved in liquid phase and Ca^{2+} in surface of particle will react with silica and alumina and form a layer which thickened during time. Osmotic pressure due to difference of density between inside and outsides caused this to be broken. As a result, the properties of concentration of hydrated calcium aluminate and hydrated calcium silicates causes the hydrated calcium aluminate to settle outside of pozzolan whereas hydrated calcium silicates stay on the surface of pozzolans.

3.5 Pozzolan's Structure

Generally, the structure of pozzolan is transparent alumina silicate having some part, which is remained in soot, or material left over from burning organic materials and mostly in the shape of very fine particles to the particles with the size of 1^{mm} can be seen. The remained ash has the properties of pozzolan and has the ability of reaction against calcium hydroxide and also has a good ability to form like Portland cement.

The chemical analysis of pozzolan shows that non-homogeneity of its quality is related to the value of calcium oxide. More than 45% of calcium oxide (CaO) is accessible in waterways or lava flow and the significant point is the value of calcium oxide which is less than 10% in most of the cases [58].

Generally, pozzolans contain 50% to 70% silica (SiO_2), 20% to 35% alumina (Al_2O_3), 3% to 10% hematite (Fe_2O_3), 2% to 7% lime (CaO), 1% to 7% magnesium oxide (MgO), and 1% to 5% potassium oxide (K_2O). The detrimental parts of pozzolans are organic materials and clays which have inverse effect on pozzolanic cement paste's strength and stop it to set.

3.6 Effective Factors on Pozzolanic Reactions

Costa and Massaza [61] in a research on Italian pozzolans show that it is probable that the compressive strength of mortar is related to the value of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ in long term but the primary strength (in 7 days) and its react with lime is mostly related with special surface. The finer size of the particles causes them to have more pozzolanic reactions. Chatterjee and Lahiri [62] show that there is no general relation between reactions of pozzolans which is measured with strength of mortars and their special surface. They show for some special pozzolans that the strength increases with increasing of fineness, even though this increment was very small.

3.7 Pozzolanic Reaction Measurement

There are three types of tests to measure the pozzolanic reactions: Chemical, physical and mechanical. The relation among methods used in the test of these three groups is weak [63]. Yet Price insists that mechanical test is the best way of measuring pozzolans [64]. The mechanical method is mentioned in many codes. The American standard of ASTM C618-73 [5] for natural pozzolans and virtual pozzolans of fly ash presents two indexes which are related to detecting the pozzolanic reaction when lime is used. In the case of mixtures with pozzolanic Portland cements the pozzolanic reaction index is presented as the ratio of mortar's compression of pozzolan-cement in respect to that of control mixture of pure cement.

Chapter 4

EXPERIMENTAL STUDY

4.1 Introduction

One of the effective factors in using concrete is the suitable selection of its components. It is clear that without suitable selection of concrete materials, its main characteristics will never be achieved. Therefore knowing the physical and chemical properties of the materials are necessary. Each kind of change in used materials during production of laboratory samples will cause errors and make it hard to do an overall and exact judge. To avoid this in this project, first needed material prepared and stored in a convenient location to use materials with constant physical and chemical properties during the work. In this chapter, first the properties of used material in producing concretes and mortars explained and then their mix designs are expressed.

4.2 Used Cement

The used cement in this research is normal portland cement. Because of changes of the properties in produced cement of each factory, all amount of needed cement was prepared at once which was from same producing line of the factory and without any additives. Because the blain of this cement was 2750 and remained amount over sieve #170 was 3.2, it can be said that the physical quality of this cement is according to ASTM C150 [65]. Also to show if the chemical quality of cement is acceptable, table-1 is prepared based on test methods of TS EN 196-2 [7] and compared with the acceptable values mentioned in the ASTM C150 [65].

Table 1- Chemical properties of used cement and allowable range of ASTM C160

Complexes of cement	Percentage	Standard percentage	Result of comparison with
LOI (500 C)	0.61	0.3	Not good
LOI (975 C)	2.28	---	---
Insoluble reduce %	0.57	0.75	In range
SO ₃ %	3.26	3.5	In range
SiO ₂ %	19.61	---	---
CaO %	59.55	---	---
MgO %	2.82	6	In range
Fe ₂ O ₃ %	2.99	---	---
Al ₂ O ₃ %	5.02	---	---
Limestone %	3.34	---	---
Gypsum %	5.22	---	---
Slag %	3.36	---	---

According to the table-1, all chemical properties of used cement in this research are compared with the acceptable ranges of ASTM C150 and they are all in range.

4.3 Used Pozzolan

4.3.1 Pozzolanic Activity

The pozzolanic activity is a measure for the degree of reaction over time or the reaction rate between a pozzolan and Ca²⁺ or Ca(OH)₂ in the presence of water.

The rate of the pozzolanic reaction is dependent on the intrinsic characteristics of the pozzolan such as the specific surface area, the chemical composition and the active phase content.

Physical surface adsorption is not considered as being part of the pozzolanic activity, because no irreversible molecular bonds are formed in the process.

4.3.2 Particle Properties

Prolonged grinding results in an increased pozzolanic activity by creating a larger specific surface area available for reaction. Moreover, grinding also creates crystallographic defects at and below the particle surface. The dissolution rate of the strained or partially disconnected silicate moieties is strongly enhanced. Even materials which are commonly not regarded to behave as a pozzolan, such as quartz, can become reactive once ground below a certain critical particle diameter.

4.3.3 Composition

The overall chemical composition of a pozzolan is considered as one of the parameters governing long term performance (e.g. compressive strength) of the blended cement binder, ASTM C618 prescribes that a pozzolan should contain $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70 \text{ wt.}\%$. In case of a one phase material such as blast-furnace slags the overall chemical composition can be considered as meaningful parameter, for multi-phase materials only a correlation between the pozzolanic activity and the chemistry of the active phases can be sought

Many pozzolans consist of a heterogeneous mixture of phases of different pozzolanic activity. Obviously, the content in reactive phases is an important property determining the overall reactivity. In general, the pozzolanic activity of phases thermodynamically stable at ambient conditions is low when compared to on an equal specific surface basis to less thermodynamically stable phase assemblages. Volcanic ash deposits containing large amounts of volcanic glass or zeolites are more reactive than quartz sands or detrital clay minerals. In this respect, the thermodynamic driving force behind the pozzolanic reaction serves as a rough

indicator of the potential reactivity of a (alumino-)silicate material. Similarly, materials showing structural disorder such as glasses show higher pozzolanic activities than crystalline ordered compounds.

4.3.4 Reaction Conditions

The rate of the pozzolanic reaction can also be controlled by external factors such as the mix proportions, the amount of water or space available for the formation and growth of hydration products and the temperature of reaction. Therefore, typical blended cement mix design properties such as the replacement ratio of pozzolan for Portland cement, the water to binder ratio and the curing conditions strongly affect the reactivity of the added pozzolan.

4.3.5 Local Pozzolan Properties

The used pozzolan was obtained locally in Karpaz and ground in the laboratory of the Civil Engineering Department of EMU by the author of this thesis and sieved due to ASTM-C618 which allows up to 34% to be remained on the 45 micron sieve [29].

According to the table-2, all chemical properties of used pozzolan in this research are compared with the acceptable ranges of ASTM C618 and they are all in range.

Table 2- Chemical properties of used pozzolan

Complexes of cement	Percentage		Class N acceptable ranges	Compare result
LOI (500 C)	3.07		Max 10	In range
LOI (975 C)	9.42		---	---
Insoluble reduce %	49.9		---	---
SO ₃ %	0.09		Max 4	In range
MgO %	11.51		---	---
CaO %	8.93		---	---
SiO ₂ %	63.12	Total% 74.88	Min 70	In range
Fe ₂ O ₃ %	5.71			
Al ₂ O ₃ %	6.05			

4.4 Used Aggregates

The course and fine aggregates used in all mixtures were obtained from quarries from Beşparmak mountains which were prepared all together from the beginning of the work to avoid from changes of the quality during the tests. Sieve analysis for fine and coarse aggregates was done according to ASTM D422 [66].

Bellow figures show the sieve cumulative graphs of used fine and coarse aggregate in comparison with allowable range due to ASTM C33 [67].

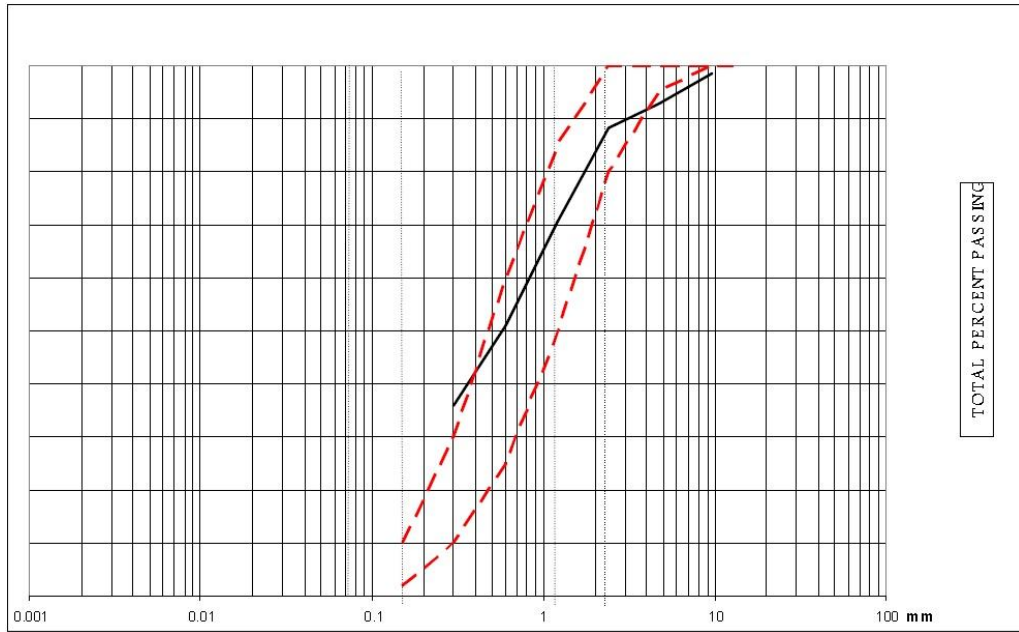


Figure1. Sieve cumulative graph of fine aggregates

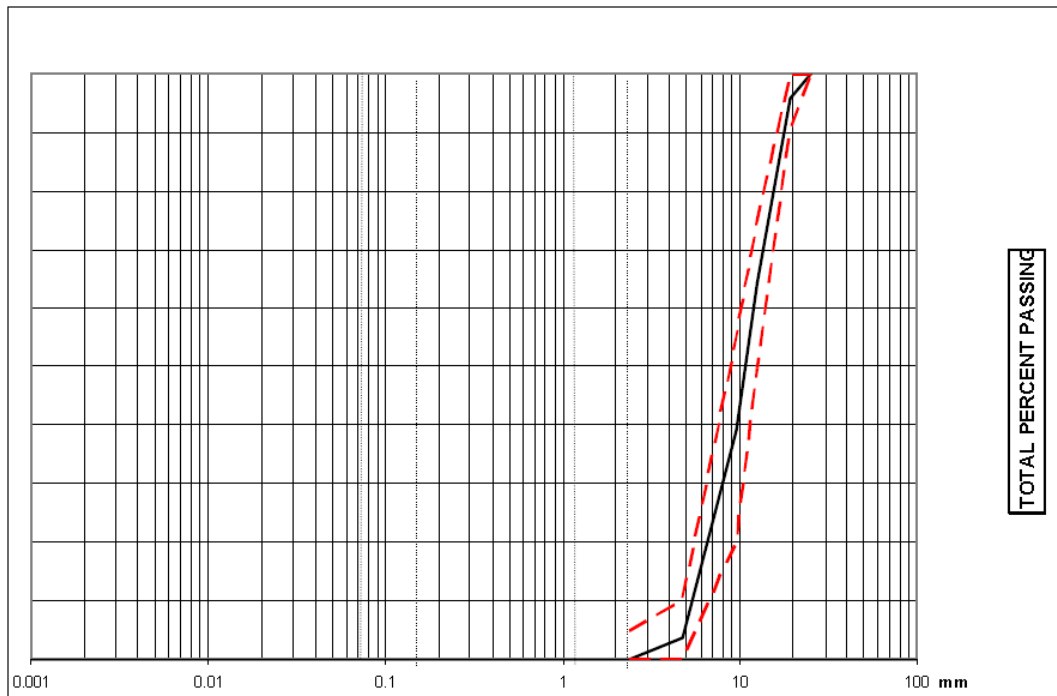


Figure2. Sieve cumulative graph of coarse aggregates

4.5 Mix Design Calculations

To calculate the mix design based on ACI211 it is necessary to know the properties of used aggregates. These properties can be classified as the ones based on coarse

aggregate and the ones based on fine aggregate. For fine aggregate the properties which have to be known are real density of fine aggregate, water absorption's percentage of fine aggregate, wetness's percentage of fine aggregate, and fineness modulus of fine aggregate. The properties which are necessary to be measured for coarse aggregates are density of compacted coarse aggregate, maximum nominal size of coarse aggregate's particles, real density of coarse aggregate, water absorption's percentage of coarse aggregate, and wetness's percentage of coarse aggregate.

Used fine aggregate's properties in this research that its sieve graph presented in figure 2 are measured and presented as table 3:

Table 3- physical properties of fine aggregate

Title of property	value
Specific gravity	2.63
Fineness modulus	2.25
SSD absorption %	0.86
Void %	36.2
Unit weight (Kg/m ³)	1690

The properties of used coarse aggregate which has the mentioned sieve graph presented in figure 3 are as presented in table 4:

Table 4- physical properties of coarse aggregate

Title of property	Value
Specific gravity	2.61
Fineness modulus	6.61
SSD absorption %	1.12
Void %	39.6
Unit weight (Kg/m ³)	1615

After knowing all these, using tables and guidelines of ACI211 mix design of the concrete can be done.

4.5.1 Slump

If the slump of the concrete is not ordered at the beginning, according to the structure type, this value can be taken from Table (6-3-1) in ACI211 [8] that in this research it is assumed to be 75 millimeter.

4.5.2 Fineness Modulus of Fine Aggregate

According to ASTM C125 [68], the fineness modulus of both fine aggregate and coarse aggregate can be calculated by dividing cumulative remained percentages of some special sieves over 100. This special group of sieves is including #100, #50, #30, #16, #8, #4, 9.5mm, 19mm, 37.5mm, 75mm, and 150mm. The more value of the fineness modulus the more the size of the aggregates.

4.5.3 Water and Cement Values

In the present research, four different class of concrete have been observed. These different classes of concrete were C20, C25, C30, and C35. This naming is according

to the compressive 28-day strength of the concrete. For the Cn class of concrete, the assumed value of compressive 28-day strength is n (MPa), i.e. in the C20 class of concrete, the compressive 28-day strength is equal to 20(MPa).

Water content of the mix design can be drawn up from the Table 3.2.2.2 of ACI 211.1 [8] due to the slump value, 75^{mm} or 3ⁱⁿ, the type of concrete if it is air-entrained or not that in this research supposed to be non-air-entrained, and the maximum size of aggregate which have been assumed as 20^{mm} or 3/4ⁱⁿ. The proposed value of water content for all these assumptions is 340(Kg) for 1(m³) of mix. According to the Table 3.2.2.3(a) of the ACI 211.1 [8], the water cement ratio of mix design for four class of concrete of C20, C25, C30, and C35 are 0.609, 0.534, 0.473, and 0.424 respectively. Therefore, cement value of each mix design can be calculated from above values:

Table 5- water and cement value of each concrete mix design based on ACI 211

Concrete Class	Water amount (from table 3.2.2.2) (Kg)	Water cement ratio (from table 3.2.2.3(a))	Cement amount (Kg)
C20	170	0.609	279
C25	170	0.534	318
C30	170	0.473	359
C35	170	0.424	400

Chapter 5

SAMPLING AND TESTING

5.1 Introduction

Most of the tests on the hardened concrete are about measuring the strength[3]. These tests can generally be classified in two groups as destructive and non-destructive tests. Destructive tests are such as compression test, flexural strength test, and Brazilian tensile test. Using non-destructive tests such as Schmidt hammer, penetration strength test, ultrasonic test, and so on. This can show the variation of sample properties during its life time. There are some other tests to show the durability of concrete which still have no standards and many researchers are working on it. Generally, tests which have done in this research are as bellow:

- 1- Compressive strength of concrete cube samples with four different classes of C20, C25, C30, and C35 and four different percentages of pozzolan (10%, 20%, 30%, and 40%) as cement replacement in various ages of 7, 14, 21, and 28 days.
- 2- Flexural strength test of the samples with four different classes of C20, C25, C30, and C35 and four different percentages of pozzolan (10%, 20%, 30%, and 40%) as an additive in various ages of 7, 14, 21, and 28 days.
- 3- Shrinkage test for all different class of concrete observed in this research, C20, C25, C30, and C35, and for all four values of the percentage which have

been assumed as pozzolan to be replaced in the mixture instead of cement during its curing up to the age of 28 days.

5.2 Sampling in Laboratory

For concrete sampling there should be some facilities available:

- Molds and needed tools for their installing and uninstalling should be all from the material that don't react with concrete and also don't absorb its water. Mold should remain in the same shape and size during their service and also have to not to leak the concrete's wetness.



Figure3. Plastic cube molds



Figure4. Steel molds for beams

- The mixer should be suitable for the considered slump of the concrete. In this research type of mixer used to make all samples is cylindrical with the ability of rotating horizontally for mixing and vertically for evacuating.



Figure5. Used mixer in the laboratory

- Air compressor should be as powerful as to bring out the samples from plastic molds.

- The vibrator should have appropriate size and power to be able to handle the samples and shake them well. The type of vibrator which is used in this research is a table vibrator. In such type of vibrators, there is an inclined mass is attached on the shaft of an electric motor and the inclination of the mass causes the desk to vibrate not only vertically, but also horizontally.



Figure6. Table vibrator

The procedure of making concrete is as bellow:

- Before starting the concrete to be made, all aggregates, cement, pozzolan, and water should be measured and be prepared according to calculated mix design. If we don't prepare all these materials before starting to mix them together, it may take time during mix procedure and causes cement to start its primary setting and causes the samples to not to show proper results.
- One of the other works that before preparing the fresh concrete is to lubricate all molds which are going to be used. Because if we do not lubricate them the samples cannot be demoulded properly and be used for the research. This

lubrication should be somehow that let the sample be demoulded easily and also should not be so much to let the lubricating oil to affect the concrete and react with it. The moulds, which should be made ready in this research, were in two different sizes of cube 150*150*150 millimeter, and prismatic mold of the size 100*100*450 millimeter.

- Also before starting mixer to rotate, all coarse aggregates with a part of water should be put inside. This part of the water is usually about one third of whole amount of calculated water in mix design. This part is needed to be mixed shortly, about 1 minute.
- As it is mentioned in previous part, after 1 minute of mixing of coarse aggregate with one third of whole amount of calculated water in mix design, fine aggregate, cement, and another one third of calculated water in mix design was added to the mix inside the mixer and let to be mixed for about 2 minutes.
- Then in the next step the remained amount of water which is last one third of calculated water in the mix design, should be added to the mix in the mixer and let it mix for about 2 minutes more. According to this explained procedure, mixing is about 5 minutes long.
- Usually the first mix of each time of using the mixer is not usable, because there may be some segregation occurred and a part of cement gel is remained after discharge of mixer inside. Therefore to avoid the error caused by this reason, the first mix of each time of using the mixer can be taken out.

- After that, the mixed concretes should be put inside the molds at least in three layers and after putting of each layer inside the mold, it should be settled using vibration.
- The effective vibrator is somehow that cause the casted concrete surface to become stretch for each layer of concrete put inside the mold. The extra vibration can cause segregation and less than this amount cannot be able to settle the concrete inside the mold properly and will not bring containing air of concrete out. Concrete of each sample was put inside the mold in three layers and each layer was vibrated about 30^s to be sure that all amount of air content is taken out.
- After shaking the molded concrete well by vibrator, an amount of concrete should be added to the overall part and distributed by trowel. There can be added 2~3mm more and after stretching the extra amount can be removed.
- Before casting concrete that should be done before primary setting time of the cement, slump test of the mix should be done as it will be explained in the part 5.4.

5.3 Curing

The concrete curing conditions should be based on ASTM C31/C31 M-96 [69]. The water reservoir in which samples are cured (according to ASTM C511 [70]) should be made by the resistant materials against corrosion and be put in a room with controlled temperature of 23 degree (centigrade). To avoid solving the lime part of samples (lime part of cement) the water in the reservoir is better to be saturated with Ca(OH)_2 [3].

After molding the concrete and making top part of the molded concrete stretched, samples remained in the temperature of 16 to 27 degrees of centigrade and avoid the environment from decrement of wetness and temperature in the curing room (about 24 hours).



Figure7. Curing room

After completing primarily curing, samples should be demolded by helping air compressor for plastic molds and by uninstalling steel molds using their special tools and also they should be put inside the water reservoir at most in half an hour after demolding in a fully sunk position.

Concrete curing can be done in the steam environment or also with the high air pressure. These situations can accelerate the strengthening of concrete and cause it to become strengthened sooner than usual.

Using of both steam and air high pressure together is more effective in accelerating the strengthening process of concrete than only using steam curing.

5.4 Slump Test

5.4.1 Terms and Accessories

This method is used for concrete pastes with maximum aggregate size of 38mm and based on ASTM C143/C143M-98 [71]. Slump apparatus is a steel frustum mold. This mold has two arms at both sides and is open at both two ends. Upper open circle diameter is 4in (102mm) and the lower one is 8in (203mm). This apparatus is 12in (305mm) height. The other part of slump apparatus is a compacting rod with the length of 24in (60cm) and the diameter of 5.8in(16mm) which has a dome end.

5.4.2 Test Method

First the clean frustum mold should be put vertically on the steel plate somehow that its bigger end touches that and fresh concrete poured inside the mold in three layers and each layer should be compacted with 25 times hitting of the mentioned rod in the apparatus part. Each layer should fill one third of the mold.

Hitting should be done all around the surface of each layer. For the first layer, it is necessary to do the hitting partially inclined and partially vertical at the middle. The second and third layer hitting should be in a manner that the rod penetrate all the same layer and also transpire in the bellow layer a little. The third layer should be somehow that be heap shape over the mold and if it is necessary should be added also during hitting. Then, after compacting, the overall part of the mold should be stretched and the mold should be held up immediately and slowly by using its two arms and the concrete should be left to lie down over the plate. Now, concrete slump which is equal to the amount of distance between mold height and concrete heap on the plate should be measured. All slump values of sample were in the range of 60 to 80^{mm} and this value is acceptable because the assumed value of slump at the beginning of mix design was 75mm.

5.5 Compression Test

Concrete compression test based on ASTM C140-13 [9] which is published for cylindrical samples can be modified for cube samples using the formula which will be presented later on in the part 5.5.2.

5.5.1 Compression Test Method

In this test, two surfaces of the sample which are not the upper surface during molding and were touched with lateral sides of the mold should be put at the center of hydraulic jack. One of the plates in this jack is fixed and the other one is moving. The moving plate is connected to the system over a core and this will make the plate able to be regulated with the surface of the concrete if there is any inclination.



Figure8. Compression test apparatus

5.5.2 Specified Compressive Strength of the Concrete

The specified compressive strength of the concrete in the age of 28 days which is shown with the symbol of f'_c , is the compressive strength of a cylinder of concrete with diameter of 150mm and height of 300mm[8]. If there is any difference between

these values and real ones, the results can be modified with beneath formulas[72]. To convert the compression of the cubic samples with the length of 150mm to the cylindrical ones, using the beneath formula is advised.

$$f'_c = \left(0.76 + 0.21 \log \left(\frac{f_{cu}}{19.6}\right)\right) f_{cu} \quad (5-1)$$

In the above formula all values of cylindrical strength, f'_c , and cubical strength, f_{cu} , are in MPa.

The used molds in this research to achieve compressive strength are cubes with the size of 150mm.

5.6 Flexural Strength of Concrete

5.6.1 Test Method

The method of applying two point loads on a beam with simply supports is used to measure flexural strength of concrete. Loading should be without any inclination and the extension loads should intersect to the axes of the beam. The distance between point load and support should not be less than depth of the beam. The length of sample should be at least three times more than its depth. This test is based on ASTM C78-94 [73].

The sample should be put in the apparatus somehow that all loadings including supports and point loads applied to the surfaces which were in contact with mold during molding.



Figure9. Bending test apparatus

The primary load that can be applied immediately is at most 50% of sample's rupture load and since that much of the load the rate of load should be regulated to not to force the sample's end point's stress to be increased more than 10 Kg/cm^2 during each minutes of loading [9,75].

5.6.2 Calculation of Flexural Strength in Concrete Samples

Free body diagram of concrete sample under loading is shown in figure11.

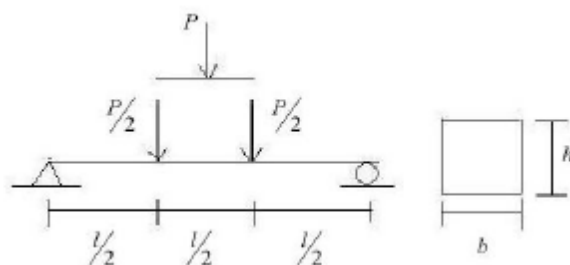


Figure10. Free body diagram of flexural strength measurement test

The formula of calculating maximum stress that can cause the sample to be cracked is as bellow:

$$\sigma = \frac{M.c}{I} \quad (5-2)$$

in which, M is the moment of maximum load that causes the sample to start crack, c is the distance between end lower point of the section and its neutral axes, and I is moment of inertia of the section. Though if c is assumed to be $h/2$, above formula will change to:

$$\left. \begin{array}{l} M = \frac{P}{2} \times \frac{l}{3} \\ c = \frac{h}{2} \\ I = \frac{b h^3}{12} \end{array} \right\} \Rightarrow \sigma = \frac{\left(\frac{Pl}{6}\right)\left(\frac{h}{2}\right)}{\left(\frac{b h^3}{12}\right)} = \frac{Pl}{b h^2} \quad (5-3)$$

but experimentally, this may not occur that c can be assumed to be $h/2$.

The properties of ASTM C78-94 [73] with the subject of “the standard method of measuring the flexural strength of beam with three point loads” says that if the crack occurs in between middle one-third of the beam’s length, the rupture modulus of the beam is calculated as bellow [73]:

$$R = Pl/b h^2 \quad (5-4)$$

in which, R is the rupture modulus with the unit of Kg/cm^2 , P is the maximum applied load to the sample at the time of rupture with the unit of Kg, l is the length of

sample in between two supports with the unit of cm, b is the width of sample with the unit of cm, and h is the height of sample with the unit of cm. on the other hand, the sample's weight is not included in the above calculations.

This code also mentions that if crack occurs out of the area in between two applied point loads to the beam, and restrictedly with the distance of not less than 5% of whole beam length from support, the flexural strength of the sample is calculated as bellow [73]:

$$R = 3 P a / b h^2 \quad (5-5)$$

in which, a is the distance between crack and the nearest support with the unit of cm. This distance is measured along longitudinal axes and on the beneath surface of the beam. If the crack is out of distance between two point loads and also is more far from nearest support than 5% of beam's length, the test should be repeated [73].

5.7 Shrinkage of Concrete

To show the effect of using this pozzolan on concrete shrinkage, on all four class of concrete, C20, C25, C30, and C35 which are used in this research and for to situation of without pozzolan and with 20% of cement replaced with pozzolan, shrinkage test is done. For each test, a cube with the size of 100*100*450mm was made.

All samples after demolding remained at the laboratory's environment (was not put in the water) for couple of hours to lose surface moisture. Then two flakes of the apparatus will be attached to the sample surface and the distance between these two flakes was measured with an index. After that all samples were remained for a while to be sure about the strength of the glue which attached the flakes to them. Therefore,

all samples were put inside the water and the distance between two flakes was recorded.



Figure11. Shrinkage test apparatus

The process of recording distance between two flakes and comparing new distance with original ones was done for all samples during 28 days regularly.

Chapter 6

RESULTS AND DISCUSSIONS

6.1 Introduction

In this part of the research results are the compressive strength tests, tension tests, and shrinkage tests presented and are classified based on percentage of replaced cement with pozzolan and age of curing in each.

6.2 Results of Compression Tests

In the following part the results of compression experiments on the samples of types C20, C25, C30, and C35 for different percentage of replaced cement with pozzolan are shown. Also the weight of each sample is presented to have a better view of these samples.

In Table 6, the weight of each sample (in Kg) and compressive strength of each samples (in MPa), tested in different ages of 7 days, 14 days, 21 days, and 28 days with different values of 0% (pure cement), 10%, 20%, 30%, and 40% replaced cement with pozzolan gained from the same mine mentioned in chapter 4. As it is presented in this table, for each age of the sample more than one sample is tested to avoid errors caused by different resources.

In the Tables 7, 8, and 9, the presented information of Table 6, but for the concretes in the different classes of C25, C30, and C35 are presented.

Table 6- weight and compressive strength of C20 samples

Testing age	0% replacement		10% replacement		20% replacement		30% replacement		40% replacement	
	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)
7	2354	24.15	2311	22.05	2279	17.73	2330	13.38	2329	9.96
7	2341	24.73	2298	22.05	2308	16.80	2308	13.57	2350	9.65
14	2218	27.18	2293	26.37	2273	21.23	2319	16.68	2339	12.88
14	2287	28.35	2299	26.37	2299	20.65	2305	16.45	2307	12.68
21	2295	30.21	2320	27.88	2311	23.33	2279	17.50	2280	14.43
21	2338	29.63	2316	27.53	2283	22.98	2253	17.50	2290	14.85
28	2360	31.85	2316	29.40	2327	23.92	2356	19.13	2319	15.22
28	2320	31.96	2335	28.47	2284	24.73	2293	18.90	2296	15.26
28	2311	30.33	2304	26.48	2311	26.72	2344	19.02	2252	14.10

Table 7- weight and compressive strength of C25 samples

Testing age	0% replacement		10% replacement		20% replacement		30% replacement		40% replacement	
	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)
7	2231	26.25	2359	24.38	2357	20.77	2304	14.96	2284	12.25
7	2213	26.95	2345	23.45	2364	20.88	2314	15.77	2319	12.44
14	2285	30.45	2277	25.43	2293	24.97	2345	19.60	2314	16.05
14	2222	30.80	2301	27.88	2370	25.20	2323	20.30	2321	16.00
21	2247	29.18	2290	30.10	2336	27.42	2323	21.58	2335	17.38
21	2276	32.55	2327	33.00	2341	27.77	2341	21.70	2354	17.59
28	2257	33.83	2314	31.26	2293	29.05	2344	23.80	2356	19.37
28	2233	33.01	2323	30.91	2335	29.51	2342	22.87	2344	19.48
28	2315	33.95	2311	30.68	2267	28.82	2344	23.92	2317	18.55

Table 8- weight and compressive strength of C30 samples

Testing age	0% replacement		10% replacement		20% replacement		30% replacement		40% replacement	
	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)	Weight (Kg/m ³)	comp. (MPa)
7	2356	30.56	2329	27.07	2357	22.87	2324	17.38	2320	12.04
7	2363	29.63	2370	27.18	2327	22.75	2299	18.20	2338	13.11
14	2335	33.25	2332	32.20	2348	27.07	2332	22.52	2345	17.03
14	2339	32.78	2329	31.85	2330	27.42	2359	22.28	2308	16.10
21	2379	34.30	2314	33.71	2341	31.61	2324	24.62	2317	18.55
21	2338	35.23	2341	32.55	2335	30.45	2329	24.36	2293	17.27
28	2367	37.56	2323	34.30	2359	32.43	2332	24.27	2324	19.83
28	2339	35.11	2370	34.88	2350	31.96	2370	24.50	2361	21.35
28	2348	34.41	2359	35.35	2376	32.20	2356	24.76	2351	21.93

Table 9- weight and compressive strength of C35 samples

Testing age	0% replacement		10% replacement		20% replacement		30% replacement		40% replacement	
	weight	comp.	weight	comp.	weight	comp.	weight	comp.	weight	comp.
7	2364	31.73	2341	31.38	2360	28.82	2360	22.75	2350	17.73
7	2356	32.90	2370	31.38	2333	29.75	2356	21.93	2347	17.03
14	2298	36.98	2342	36.28	2350	31.73	2347	25.90	2370	21.47
14	2353	36.63	2324	34.88	2385	30.10	2366	28.00	2335	20.65
21	2319	37.33	2396	38.85	2363	33.71	2341	31.15	2347	24.30
21	2293	39.20	2381	38.38	2369	37.68	2329	29.86	2370	23.38
28	2323	39.20	2354	38.73	2388	36.75	2364	31.50	2375	24.62
28	2400	37.68	2366	40.95	2319	38.03	2353	32.08	2344	25.20
28	2396	40.48	2364	38.26	2366	36.86	2388	31.73	2404	25.43

To have a better view of changes of compressive strength in concretes with different percentage of cement replacement with pozzolan, for concretes in different classes of C20, C25, C30, and C35 in different ages of 7 days, 14 days, 21 days, and 28 days data presented in the Tables 6 through 9 are shown graphically in Figures 13 through 16.

In the Figure 13, compression of different classes of concretes, which have been observed in this research, (C20, C25, C30, and C35) in the age of 7 days curing, were shown each one with an independent line and different marks. In this graph the compressive strength is shown versus percentage of replaced cement with local pozzolan. The 0% value of cement replaced with pozzolan has the meaning of control mix design's results, without pozzolan. In the Figures 14, 15, and 16 the same information of Figure 13 but in different ages of curing 14, 21, 28 days respectively are presented.

As it is clear in the graph presented Figure 13, the effect of increasing the value of replaced cement with pozzolan is approximately linear reduction of compressive strength related to the percentage of replacing cement with pozzolan on 7 days of curing. Also in all other graphs shown in the Figures 14, 15, and 16 similar results achieved.

Other researchers mostly say that using pozzolan improve the compressive strength in long time. All of compressive strength test were done up to 28 days curing in this research. Because using pozzolan reduces the rate of strengthening may show the results of the compression with pozzolan less than the ones without pozzolan. May be it is better to compare the strength of concretes with pozzolan on the later ages of

curing with the compression of concrete without pozzolan and the concretes containing pozzolan may show more compressive strength in long life age than non-pozzolanic concretes.

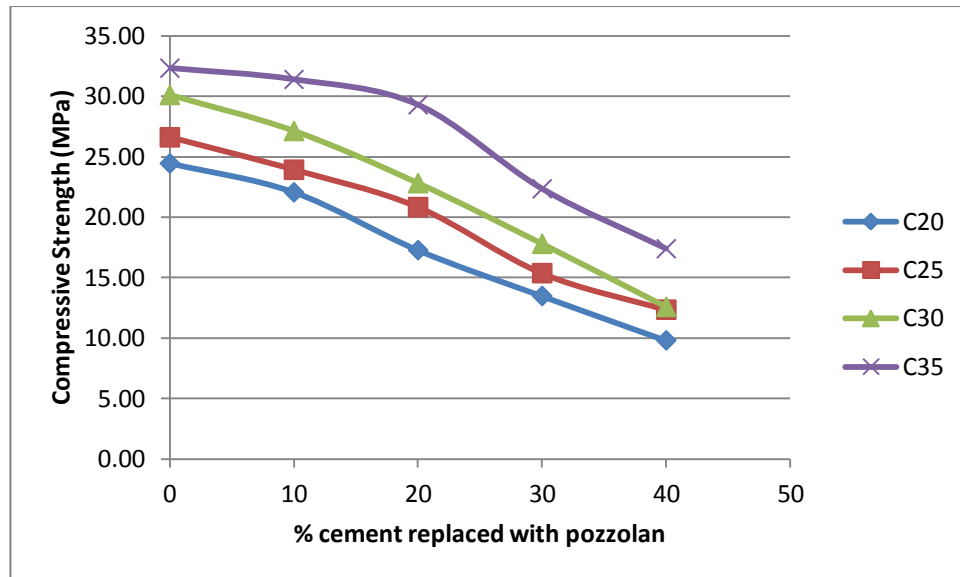


Figure12. Compressive strength of concretes with 7 days curing age

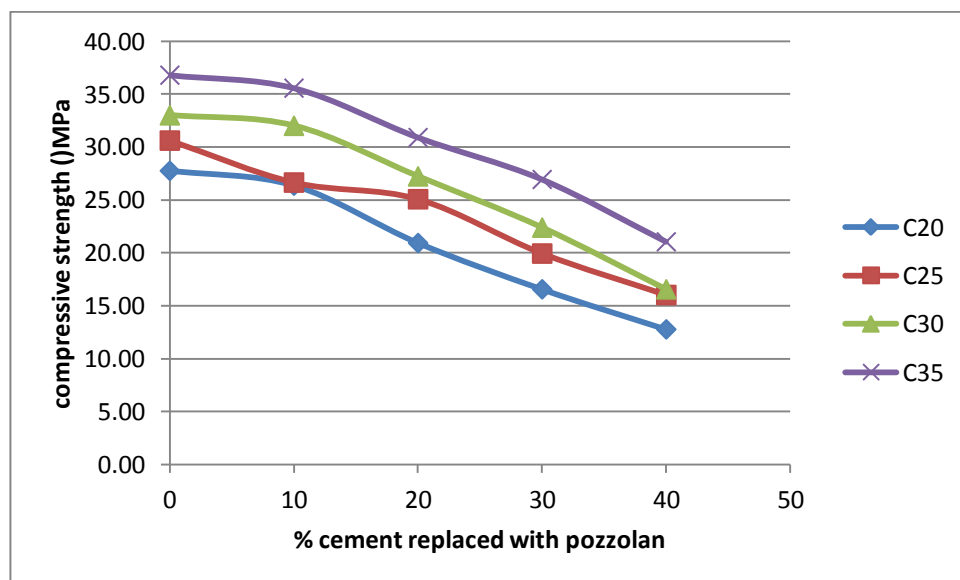


Figure13. Compressive strength of concretes with 14 days curing age

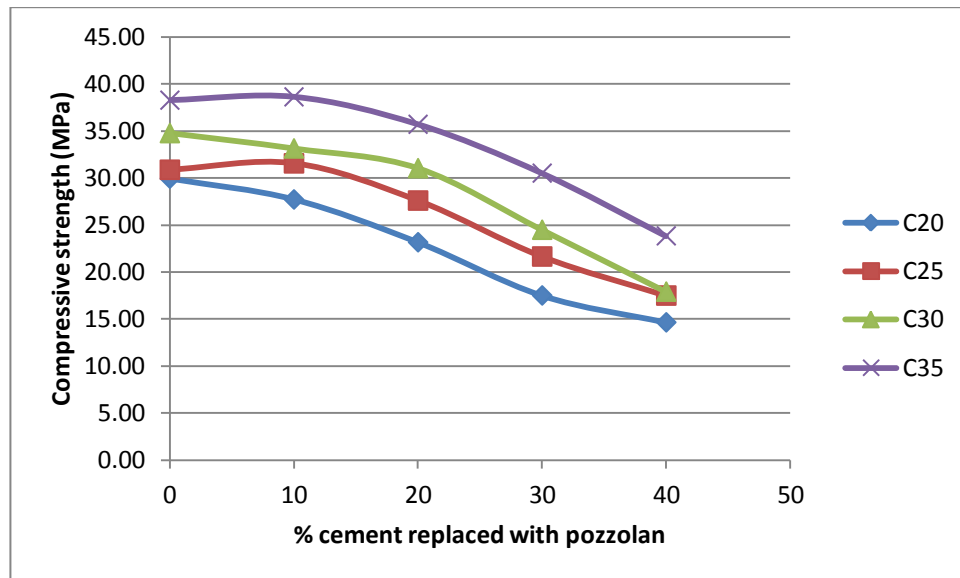


Figure14. Compressive strength of concretes with 21 days curing age

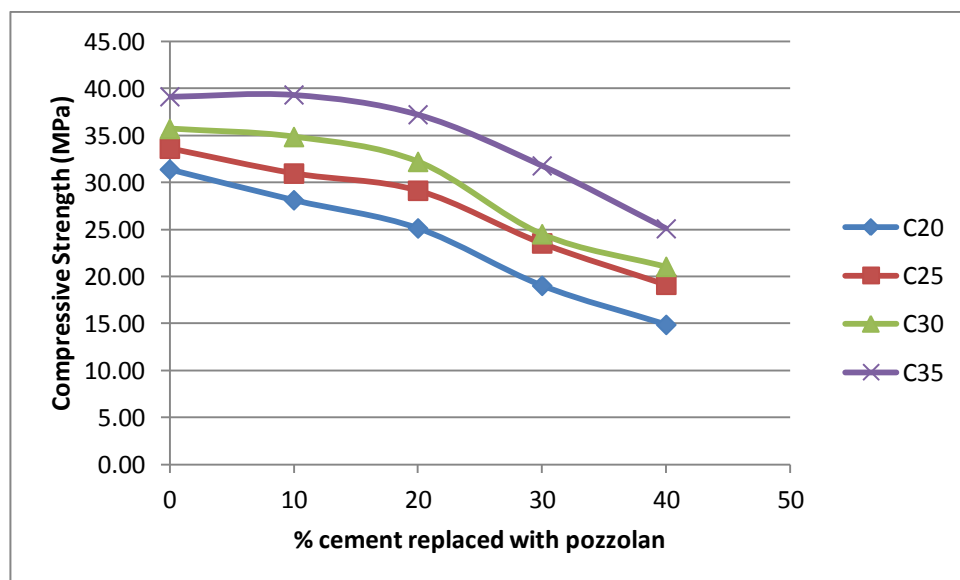


Figure15. Compressive strength of concretes with 28 days curing age

In the Table 6, compressive strength of samples class C20 is presented. The difference between flexural strength for the concrete with 10% of cement replaced with local pozzolan, on each curing age of concrete, with compressive strength of control mix is about 10% of control mix compressive strength. This difference for 20% of cement replaced with local pozzolan is about 25% of compressive strength of control mix

and also this value for the concretes with 30% and 40% of cement replaced with local pozzolan are respectively 31% and 43% of compressive strength of control mix. These results are similarly repeated for the concretes of other observed classes, C25, C30, and C35 respectively in the Tables 7, 8, and 9.

In previous works done in the case of mechanical properties of concretes with cement replaced with pozzolans, it is mentioned that the effect of using pozzolan is increasing the compressive strength of concrete in long life. But here we can see that this result is in reverse side, that is; there is a meaningful decrement of compressive strength by increment of the percentage of cement replaced with local pozzolan. It means that this special pozzolan's effect is mostly filling role than participating in chemical reactions and helping the concrete system to have more compressive strength.

6.2 Results of Tension Tests

In this part, the results of tension experiments on the samples of types C20, C25, C30, and C35 for different percentage of replaced cement with pozzolan are shown.

In the Table 10, the tensile strength of samples, tested in the ages of 7 days curing with different values of 0% (pure cement), 10%, 20%, 30%, and 40% replaced cement with pozzolan for different classes of concrete are presented. It means that the first column of this table is the percentage of replaced cement with pozzolan and first row of this table shows the class of concrete which has been observed.

After that, the result of tensile strength in the samples with the ages of 14 days, 21 days, and 28 days respectively presented in the Tables 11, 12, and 13 with different values of replaced cement with local pozzolan for various classes of concrete.

To show these results presented in the tables 10 through 13, Figures 17 through 20 are prepared respectively.

In the graph presented in Figure 17, tensile strength of each class of concrete which has been observed in this research shown with a different line and point mark and each one of these independent lines are the graph of tensile strength of concrete with proper class (either C20 or C25 or C30 or C35) versus percentage of replaced amount of cement with local pozzolan.

In the Figures 18, 19, and 20, similar information of Figure 17 but respectively for the samples with the curing ages of 14 days, 21 days, and 28 days are presented. The graphs shown in the Figures 17 through 20, show an approximate linear dependence between increment of the percentage of cement replaced with local pozzolan and reduction of tensile strength in each sample. As it was mentioned in the case of compression; using of pozzolan in the mix design of concretes reduces the rate of strengthening. And that is why comparing the results of the concretes with and without pozzolan on the same ages of curing show reduction of strength in the concretes with pozzolan and also the more the pozzolan used in the mix design the less the strength at the same age. As other researchers mentioned [3] the long term effect of using pozzolan in the concrete mix design is increment of strength. Therefore to have a better view of the effect of using pozzolan on the strength of concrete, both compression and tension, there should be a comparison between strength of concretes with the different ages, that is; the strength of concrete without pozzolan at 7 days age of curing shouldn't be compared with the strength of concrete with 10% replaced cement with pozzolan at the same age of curing, but with the later age of curing.

Table 10- Flexural strength of samples with 7 days age of curing in MPa

		Concrete class			
		C20	C25	C30	C35
Replaced percentage of cement with local pozzolan	0	2.39	2.61	2.96	3.18
	10	2.16	2.34	2.67	3.09
	20	1.79	2.15	2.35	2.54
	30	1.42	1.60	1.85	2.30
	40	0.97	1.22	1.44	1.72

Table 11- Flexural strength of samples with 14 days age of curing in MPa

		Concrete class			
		C20	C25	C30	C35
Replaced percentage of cement with local pozzolan	0	2.74	3.03	3.27	3.65
	10	2.62	2.85	3.18	3.54
	20	2.08	2.50	2.71	3.08
	30	1.74	2.07	2.32	2.77
	40	1.36	1.62	1.73	2.18

Table 12- Flexural strength of samples with 21 days age of curing in MPa

		Concrete class			
		C20	C25	C30	C35
Replaced percentage of cement with local pozzolan	0	2.94	3.04	3.43	3.83
	10	2.72	3.11	3.27	3.86
	20	2.38	2.83	3.17	3.57
	30	1.82	2.23	2.52	3.05
	40	1.45	1.73	1.78	2.38

Table 13- Flexural strength of samples with 28 days age of curing in MPa

		Concrete class			
		C20	C25	C30	C35
Replaced percentage of cement with local pozzolan	0	3.10	3.33	3.54	3.91
	10	2.79	3.08	3.46	3.93
	20	2.50	2.90	3.21	3.72
	30	1.98	2.43	2.73	3.18
	40	1.56	1.99	2.18	2.51

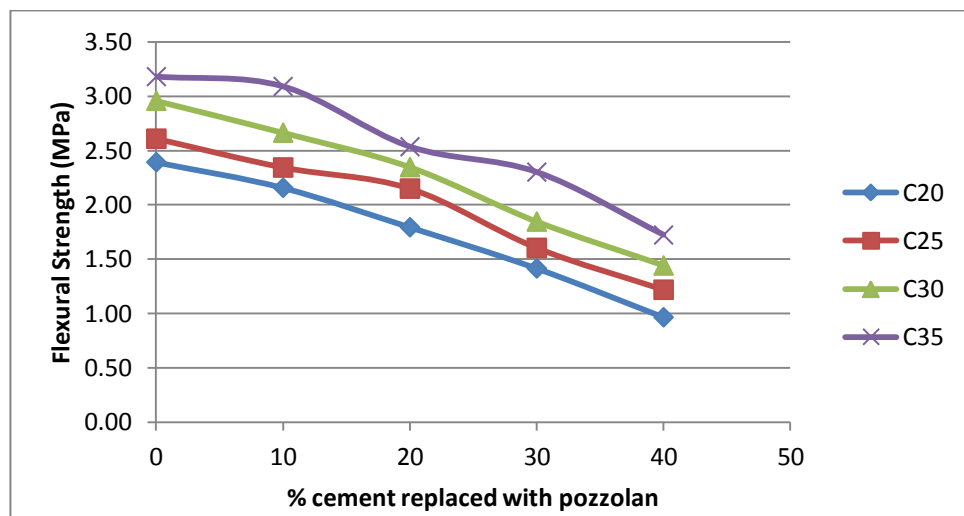


Figure16. Flexural strength of concretes with 7 days curing age

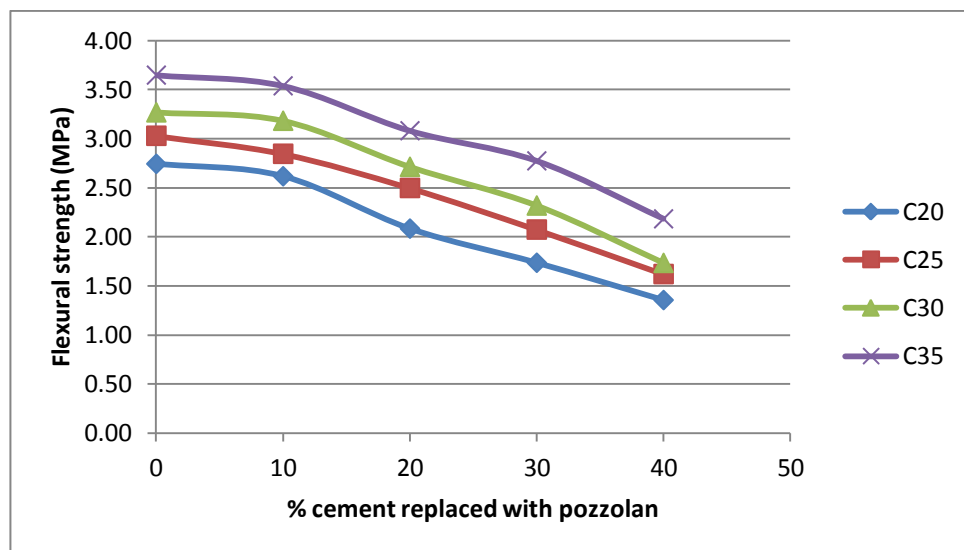


Figure17. Flexural strength of concretes with 14 days curing age

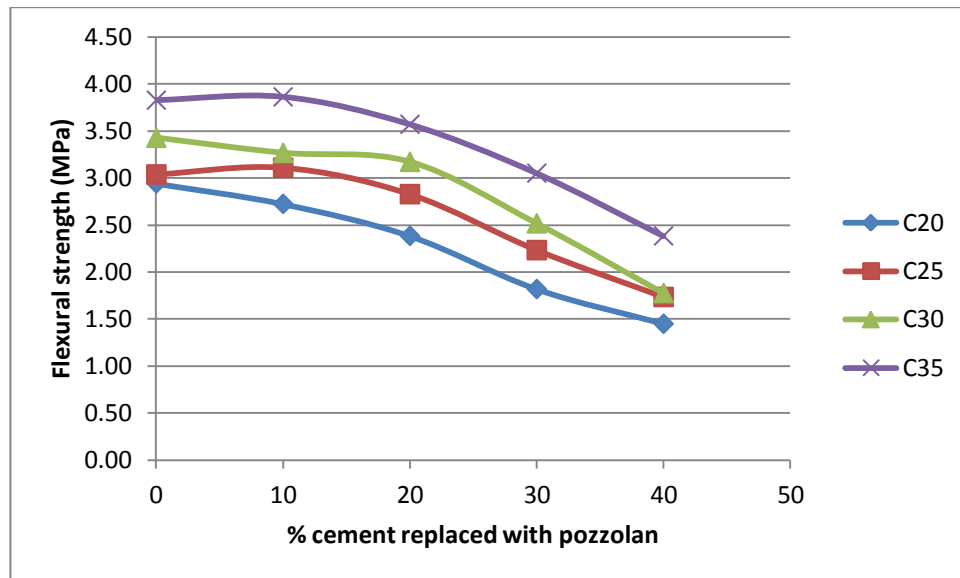


Figure18. Flexural strength of concretes with 21 days curing age

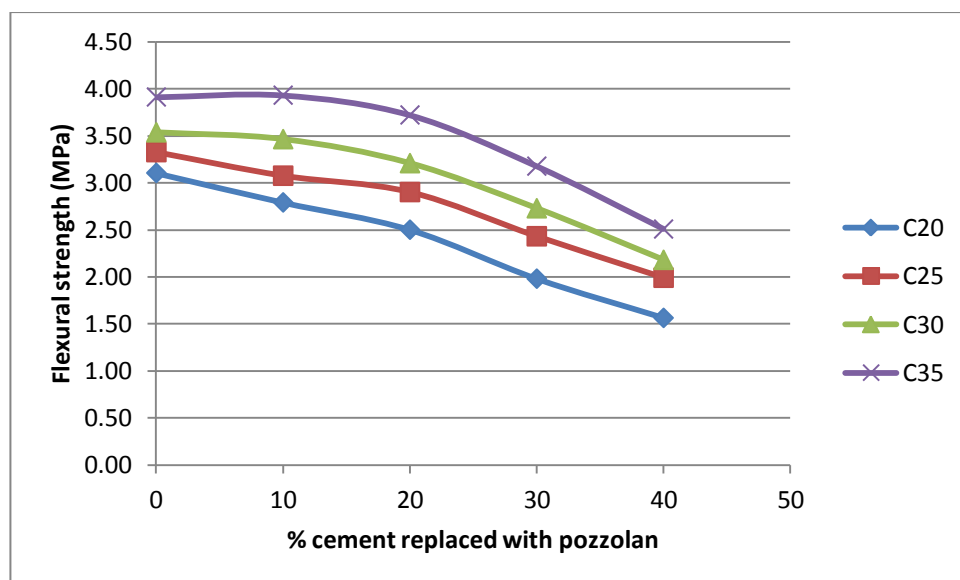


Figure19. Flexural strength of concretes with 28 days curing age

In the Table 10, flexural strength of samples with 7 days age of curing is presented. The different between flexural strength for the concrete with 10% of cement replaced with local pozzolan, on each observed class of concrete, with flexural strength of control mix is about 10% of control mix flexural strength. This difference for 20% of cement replaced with local pozzolan is about 22% of flexural strength of control mix

and also this value for the concretes with 30% and 40% of cement replaced with local pozzolan are respectively 40% and 55% of flexural strength of control mix. These results are similarly repeated for the concretes with the curing age of 14 days, 21 days, and 28 day respectively in the Tables 11, 12, and 13.

The results of experiments show a meaningful reduction in the flexural strength of concrete by increasing the value of used pozzolan in mix design. Most of the researchers mentioned in their works that if pozzolan participate in the chemical reactions of concrete, can change flexural strength of concrete positively and improve it. Since in this research, there is a reduction of flexural strength for the samples with replaced cement with local pozzolan and this reduction increased with the amount of percentage of replaced cement in the mix design with local pozzolan it can be said that the most role of this pozzolan in the concrete is filling role and this role of local pozzolan of Karpaz in the concrete is more than its chemical react.

6.3 Results of Shrinkage Tests

As it is mentioned before, type of shrinkage which is sighted is drying shrinkage. Since there is no specific way to distinguish different types of shrinkage from each other, using standard method of measuring shrinkage lead us to measure just drying one.

As it can be seen in bellow graphs, all amounts of shrinkages in the samples are affected by different values of cement replaced with pozzolan in all concrete classes. By increasing the value of cement replaced with pozzolan, shrinkage decreases and also as it was expected increasing the strength of concrete decreases the amount of shrinkage.

But as it is clear, the rate of shrinkage in different classes of concrete and different ages of curing is not affected so much by using various amounts of pozzolan replaced instead of cement.

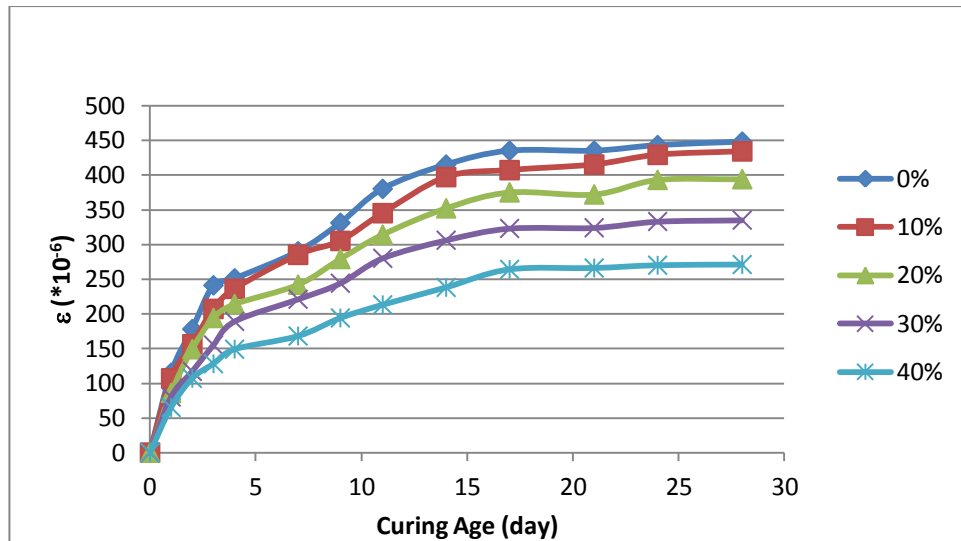


Figure20. Shrinkage VS age for C20 concrete

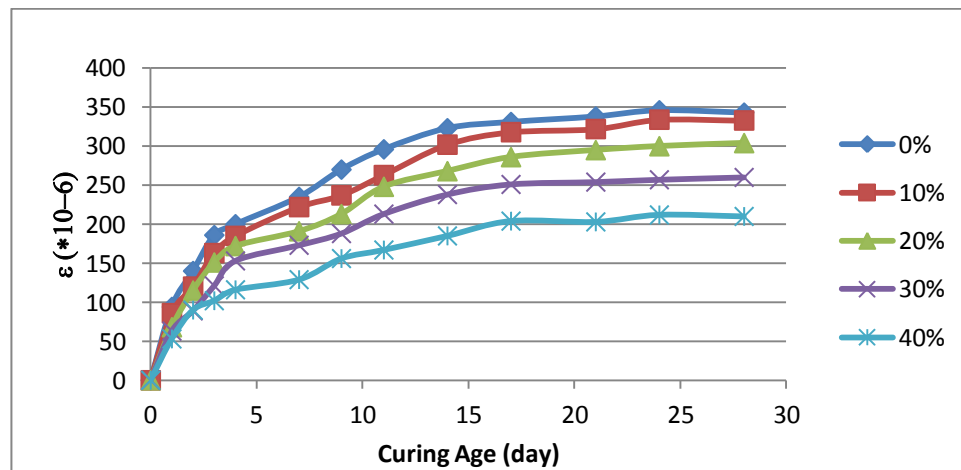


Figure21. Shrinkage VS age for C25 concrete

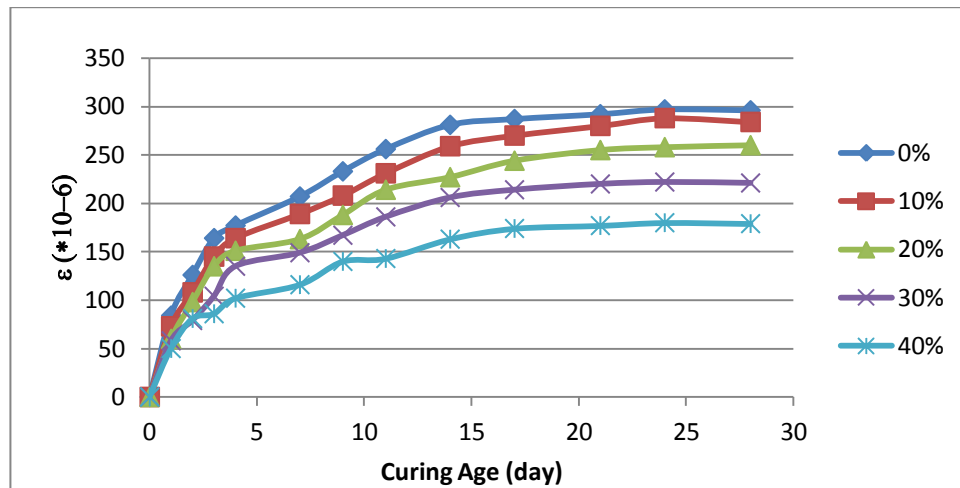


Figure22. Shrinkage VS age for C30 concrete

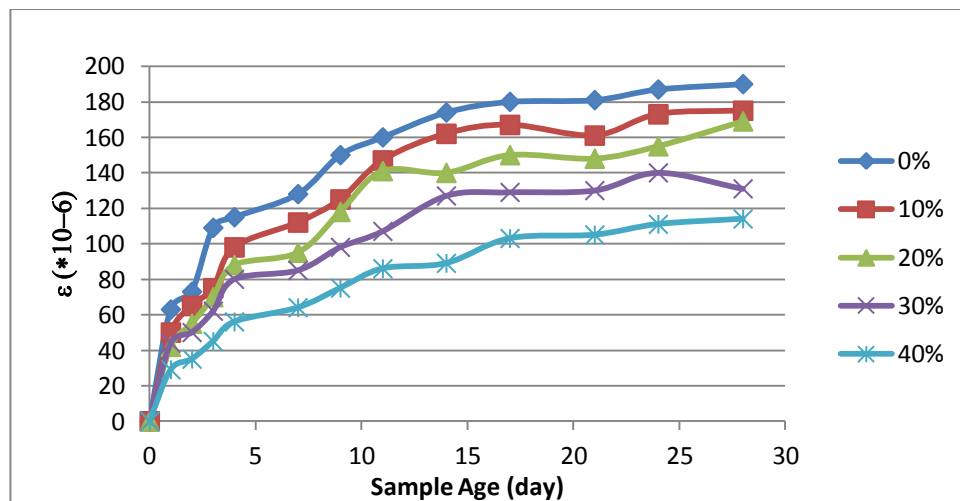


Figure23. Shrinkage VS age for C35 concrete

In Figure 21, the shrinkage test results of samples made based on C20 mix design are presented. On each curing age of the samples in which shrinkage test was done, the difference between results of samples with 10% of cement replaced with local pozzolan and control sample is less than 8 percent of shrinkage value, but for the samples with 18% of cement replaced with local pozzolan, this difference is about 20 percent of shrinkage value. Also the difference between shrinkage of concrete with 30% and 40% of cement replaced with local pozzolan and control sample on each

age of curing are respectively about 27% and 40% of shrinkage value of control sample.

As it was explained and also can be seen in the graphs of Figures 21 through 24, the more the cement replaced with pozzolan in the mixture of concrete, the more the reduction of shrinkage value and the relationship between increment of percentage of cement replaced with local pozzolan and decrement of shrinkage value is approximately linear.

This is the same result that other researchers mentioned in their works before [3,4]. It happens due to filling role of pozzolan in the matrix of concrete and also partially caused by chemical reactions between pozzolan water as a cement replacement particle. But in this case as mentioned before, the most effect of pozzolan is because of its filling act.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In the present research, four different classes of concrete, C20, C25, C30, and C35, which have 20 MPa, 25 MPa, 30 MPa, and 35 MPa of compression respectively at the time that there is no pozzolan in their mixture are used. For all of these different concrete classes, five different percentage of replacing cement with local pozzolan, 0% (without any pozzolan as a control sample), 10%, 20%, 30%, and 40%, selected to be tested. For all above mix designs, samples tested on the curing age of 7 days, 14 days, 21 days, and 28 days. The effect of using local pozzolan in the mix design of concrete on compression, bending tensile strength, and shrinkage was observed and bellow results achieved:

- 1- In the case of compression it can be said that compression of concrete on specific age of curing with the same mix design (same values of slump, water, aggregates, and water cement ratio) has a relation with the value of replaced cement with local pozzolan.
- 2- The relationship between value of replaced cement in the concrete mixture with local pozzolan and compression of samples at the same age of curing is approximately linear as shown in the related detailed data and graphs.

- 3- The more the cement replaced with the local pozzolan in a specific mix design, the less the compression at the same age of curing.
- 4- In the case of flexural strength it can be said that bending tensile strength of concrete on a specific age of curing with the same mix design (same values of slump, water, aggregates, and water cement ratio) has a relation with the value of replaced cement with local pozzolan.
- 5- The relationship between value of replaced cement in the concrete mixture with the local pozzolan and bending tensile strength of samples at the same age of curing is approximately linear as shown in the related detailed data and graphs.
- 6- The more the cement replaced with the local pozzolan in a specific mix design, the less the bending tensile strength of samples at the same age of curing.
- 7- In the case of shrinkage it can be said that there is a relationship between shrinkage amount of concrete, on a specific age and constant mix design (same values of slump, water, aggregates, and water cement ratio), and the value of replaced cement with local pozzolan.
- 8- The more the value of cement replaced with the local pozzolan in a constant mix design, the less the value of shrinkage at the same age of concrete sample.

7.2 Recommendations

1. Since in this research, just a special water cement ratio is observed, it is recommended to do another research with the same cement replacement percentages and also different water cement ratios to see the effect of water cement ratio also.
2. In the present research, the mix was include cement, pozzolan, water, and aggregate, and there were no observation in the case of using micro silica or nano silica to see their effect in the presence of pozzolan in the concrete mix.
3. Because the only type of cement which was used in the present research mix designs was type I, it is recommended to use different types of cement (i.e. type II, III, IV, and V) with this pozzolan and observe its effect of the mechanical properties of concrete.
4. Observe the results of experiments for the curing age of older than 28 days.

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