

**REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**INVESTIGATION OF WASTE PRODUCTS OF BORON AND
METAKAOLIN UTILIZES IN PORTLAND CEMENT MORTAR**



MIKHAIL MUSHUROV

**MSc. THESIS
DEPARTMENT OF CIVIL ENGINEERING
PROGRAM OF STRUCTURAL ENGINEERING**

**ADVISOR
ASSOC. PROF. DR. ORHAN CANPOLAT**

İSTANBUL, 2018

REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**INVESTIGATION OF WASTE PRODUCTS OF BORON AND
METAKAOLIN UTILIZES IN PORTLAND CEMENT MORTAR**

A thesis submitted by Mikhail Mushurov in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** is approved by the committee on 21.06.2018 in Department of Civil Engineering, Structural Engineering.

Thesis Adviser

Assoc. Prof. Dr. Orhan CANPOLAT
Yildiz Technical University

Approved by the Examining Committee

Assoc. Prof. Dr. Orhan CANPOLAT
Yildiz Technical University

Dr. Lecturer Ahmet Beşer KIZILKANAT
Yildiz Technical University

Assoc. Prof. Dr. Mücteba UYSAL
Istanbul Üniversitesi

ACKNOWLEDGMENTS

First of all, I would like to pay due tribute to my supervisor and his assistants.

I would like to thank the staff of the Civil Engineering department laboratory for providing me with assistance and good advice along my experimental studies. Also, I would like to thank my university for providing me with materials and equipment.

Especially, I would like to thank YTB scholarship organization for giving me a chance to study in Turkey.

TABLE OF CONTENTS

	Page
LIST OF SYMBOLS.....	vii
LIST OF FIGURES.....	viii
LIST OF TABLES	x
ABSTRACT.....	xi
ÖZET.....	xiii
CHAPTER 1	
INTRODUCTION.....	1
1.1 Literature Review	1
1.2 Aim of the Thesis.....	3
1.3 Hypothesis	3
CHAPTER 2	
GENERAL INFORMATION.....	5
2.1 Colemanite Waste Usage in Mortar Production	5
2.2 Metakaolin Usage in Mortar Production.....	5
2.3 Setting Time	6
2.4 Flow Table.....	6
2.5 Compressive Strength	7
2.6 Flexural Strength.....	7
2.7 Unit Weight	8
2.8 Water Absorption.....	8
CHAPTER 3	
MATERIALS AND METHODS.....	9
3.1 Experiments.....	9
3.1.1 Fresh Properties of Mortar	9
3.1.1.1 Flow Table	9
3.1.1.2 Setting Time	12
3.1.2 Hardened Properties of Mortar.....	13

3.1.2.1 Compressive Strength.....	13
3.1.2.2 Flexural Strength.....	14
3.1.2.3 Unit Weight.....	16
3.1.2.4 Water Absorption.....	17
3.2 Pozzolans and Other Fine Minerals.....	18
3.2.1 Introduction.....	18
3.2.2 Classification of Finely Ground Mineral Additives.....	19
3.2.3 Pozzolanic Materials.....	20
3.2.3.1 Definition of Pozzolans.....	20
3.2.3.2 Types of Pozzolanic Materials.....	20
3.2.3.3 Pozzolanic Reaction.....	20
3.2.3.4 Application of Pozzolanic Materials.....	21
3.2.3.5 Test Methods for Natural and Artificial Pozzolans.....	22
3.2.3.6 Conformity of Natural and Artificial Pozzolans.....	22
3.2.4 Mineral Additives as Binding Materials.....	22
3.2.4.1 Liquid Additives.....	22
3.3 Boron.....	23
3.3.1 Introduction.....	23
3.3.2 Boron Products.....	23
3.3.3 Boron Application Spheres.....	24
3.3.4 Boron in Construction Sector.....	25
3.4 Metakaolin.....	26
3.4.1 Introduction.....	26
3.4.2 Metakaolin Products.....	27
3.4.2.1 Origins.....	27
3.4.2.2 Metakaolin Manufacturing.....	27
3.4.2.3 Chemical Composition of Metakaolin.....	27
3.4.3 Application of Metakaolin.....	27
3.4.4 Construction Sector and Metakaolin.....	28
3.5 Material Characteristics.....	28
3.5.1 Used Materials and Their Specifics.....	28
3.5.1.1 Cement.....	28
3.5.1.2 Colemanite.....	29
3.5.1.3 Metakaolin.....	30
3.5.1.4 Polydos TS 14.....	31

3.5.1.5 Fine Aggregates	32
3.5.1.6 Water	32
3.6 Experimental Methods	32
3.6.1 Preparation of Samples.....	32
3.6.2 Experimental Studies	32
3.6.2.1 Performed Experiments	32
3.6.3 Notation.....	34
CHAPTER 4	
RESEARCH FINDINGS AND DISCUSSION.....	36
4.1 Fresh Properties of Mortar	36
4.1.1 Flow Table.....	36
4.1.2 Setting Time	37
4.2 Hardened Properties of Mortar	38
4.2.1 Compressive Strength	38
4.2.2 Flexural Strength.....	44
4.2.3 Unit Weight	50
4.2.4 Water Absorption.....	51
4.2.5 Porosity.....	52
4.3 Effect of Water/Cement Ratio	52
CHAPTER 5	
CONCLUSION AND RECOMMENDATIONS.....	54
5.1 Conclusion.....	54
5.2 Recommendations.....	55
REFERENCES.....	56
CURRICULUM VITAE.....	58

LIST OF SYMBOLS

<i>gr</i>	Gram
<i>kg</i>	Kilogram
<i>rpm</i>	Revolutions per minute
<i>mm</i>	Millimeter
<i>CW</i>	Colemanite Waste
<i>s</i>	Second
\emptyset	Diameter
$^{\circ}\text{C}$	Celsius degree
<i>A</i>	Cross section area
<i>N/s</i>	Newton per second
<i>MPa</i>	Megapascals
<i>%</i>	Percent
<i>min</i>	Minute

LIST OF FIGURES

	Page
Figure 3.1. Mixer pan	9
Figure 3.2. Flow table molding.....	10
Figure 3.3. Flow table spread.....	11
Figure 3.4. Vicat test.....	12
Figure 3.5. Curing cabinet.....	14
Figure 3.6. Curing cabinet temperature adjustment.....	14
Figure 3.7. Compressive strength test.....	14
Figure 3.8. Compressive strength result.....	14
Figure 3.9. Flexural strength test.....	15
Figure 3.10. Flexural strength result.....	15
Figure 3.11. Drying cabinet.....	16
Figure 3.12. Saturation of samples for 72h.....	17
Figure 3.13. Archimedes weight.....	17
Figure 3.14. Obtaining wet weight.....	18
Figure 3.15. Scaling dry samples.....	18
Figure 3.16. Scaling dry samples.....	33
Figure 3.17. Demoulded samples.....	33
Figure 3.18. Decayed samples.....	33
Figure 3.19. Spalled and decayed samples.....	33
Figure 4.1. Compressive strength test results of PC, PCSP, PC5CSP and PC7CSP.....	39
Figure 4.2. Compressive strength test results of PC, PCSP, PC5CSP and PC7CSP.....	40
Figure 4.3. Compressive strength test results of PC, PC20M and PC30M.....	41

Figure 4.4. Compressive strength test results of PC, PC20MSP and PC30MSP.....	42
Figure 4.5. Compressive strength test results of PC, PC5C20M and PC5C20MSP....	43
Figure 4.6. Compressive strength test results of all mixes.....	44
Figure 4.7. Flexural strength test results of PC, PC5C and PC7C.....	45
Figure 4.8. Flexural strength test results of PC, PCSP, PC5CSP and PC7CSP.....	46
Figure 4.9. Flexural strength test results of PC, PC20M and PC30M.....	47
Figure 4.10. Flexural strength test results of PC, PC20MSP and PC30MSP.....	48
Figure 4.11. Flexural strength test results of PC, PC5C20M and PC5C20MSP.....	49
Figure 4.12. Flexural strength test results of all mixes.....	50



LIST OF TABLES

	Page
Table 3.1. Boron application spheres	25
Table 3.2. Chemical and physical properties of cement (CEM I 42,5 R)	29
Table 3.3. Chemical composition of colemanite.....	29
Table 3.4. Chemical composition of metakaolin	30
Table 3.5. Mineralogical composition of metakaolin	30
Table 3.6. PSD analysis.....	31
Table 3.7. Technical properties of polydos TS 14.....	31
Table 3.8. Percentage of materials in the blends.....	34
Table 3.9. Amount of materials in the blends	35
Table 4.1. Flow table results	37
Table 4.2. Flow table results comparison	37
Table 4.3. Setting time table	38
Table 4.4. Unit weight test results (gr/cm ³).....	51
Table 4.5. Water absorption test results (%).....	51
Table 4.6. Porosity test results (%)	52

ABSTRACT

INVESTIGATION OF WASTE PRODUCTS OF BORON AND METAKAOLIN UTILIZES IN PORTLAND CEMENT MORTAR

Mikhail MUSHUROV

Department of Civil Engineering

MSc. Thesis

Advisor: Assoc.Prof.Dr. Orhan CANPOLAT

This study is concerned with an investigation of waste products of boron and metakaolin utilizes in cement mortar. The objective of this paper is to design the most appropriate composition, where colemanite, metakaolin and superplasticizer will take place along with Ordinary Portland cement. The outcome of this study will give us an opportunity to decrease cost of the final product without affecting properties of the construction material and contribute to less CO₂ emission caused by Portland cement manufacturing. Metakaolin produced by Kaolin Endustriyel Mineraller A.S. (Istanbul / Turkey) is a pozzolanic material, but is not a cementitious material itself. By reacting with lime it forms a stable insoluble compound that possesses hydraulic properties. Production of metakaolin releases less CO₂ in the atmosphere comparing to Portland cement clinker, and on the other hand, can partially substitute it. Colemanite waste materials figuring in this study have been provided by Eti Mine Bigadic Boron Inc. (Balıkesir/Turkey). Separate and joint application of 1% superplasticizer solution, colemanite and metakaolin was investigated. Physical and mechanical properties such as compressive and flexural strength, at the age of 2, 7, 28 and 90 days as well as unit weight, water absorption,

porosity, flow table and setting time test were determined and compared with reference mix results. The general trend is the addition of colemanite to the cement mortar impairs compressive strength by up to 43% as well as increases its setting time on 215%. Introduction of 1% superplasticizer mitigates the presence of colemanite and improves the strength of the mortar comparing to reference. Metakaolin facilitates early hardening and with addition of superplasticizer it gains strength up to 12% more than the reference value, although its strength strongly depends on the water-to-cement ratio. Replacement of 25% of the Portland cement by 5% of colemanite and 20% of metakaolin with an addition of 1% super-plasticizer resulted in the almost same characteristics as reference values.

Keywords: Boron, Colemanite, Compressive Strength, Flexural Strength, Metakaolin, Puzzolan, Superplasticizer

ÖZET

PORTLAND ÇİMENTOSU HARCINDA KULLANILAN BOR ATIK ÜRÜNÜ VE METAKAOLİNİN ARAŞTIRILMASI

Mikhail MUSHUROV

İnşaat Mühendisliği Bölümü

M.S. Tezi

Danışman: Doç. Prof. Dr. Orhan CANPOLAT

Bu çalışma, çimento harçlarında kullanılan bor atık ürünleri ve metakaolinin araştırılması ile ilgilidir. Bu çalışmanın amacı, Portland çimentosu (PÇ) ile birlikte kolemanit, metakaolin ve süperakışkanlaştırıcıların yer alacağı en uygun bileşimi tasarlamaktır. Bu çalışmanın sonucu bize, inşaat malzemesinin özelliklerini etkilemeden nihai ürünün maliyetini azaltma ve Portland çimentosu üretiminin neden olduğu daha az CO₂ emisyonuna katkıda bulunma imkanı verecektir. Kaolin Endüstriyel Mineraller A.S. tarafından üretilen metakaolin puzolanik bir malzemedir, fakat tek başına bağlayıcı bir malzeme değildir. Kireçle reaksiyona girerek, hidrolik özelliklere sahip olan stabil çözünmez bir bileşik oluşturur. Metakaolin üretimi, Portland çimentosu klinkerine göre atmosferde daha az CO₂ salgılar ve diğer yandan kısmen yerine ikame edilebilir. Bu çalışmada kullanılan Colemanite atığı Eti Maden Bigadic Boron A.Ş. (Balıkesir/Türkiye) tarafından sağlanmıştır. % 1'lik süperakışlantırıcı çözeltinin kolemanit ve metakaolinle ayrı ayrı ve birlikte kullanımı araştırıldı. 2, 7, 28 ve 90 günlük Basınç ve eğilme dayanımı, fiziksel ve mekanik özelliklerin yanı sıra birim ağırlık, su emme, boşluk yapısı, yayılma tablası ile kıvamı ve priz süresi testleri belirlenmiş ve referans karışım sonuçları ile karşılaştırılmıştır. Genel eğilim kolemanitin tek başına çimento harcına ilavesinin % 43'e

varan oranlarda basınç dayanımını düşürmesi ve %215'in üzerinde erken priz süresini uzatmıştır. Karışıma % 1'lik süperakışkanlaştırıcı ilave ile, kolemanitin basınç mukavemetine olan olumsuz etkisini azaltmış ve referans harç nümunesi ile kıyaslandığında basınç mukavemetini artırmıştır. Metakaolinin PÇ ile ikamesi ve süperakışkanlaştırıcının eklenmesiyle erken sertleşmeyi sağlamış ve dayanımı şahit nümuneden % 12 daha fazla olmuştur. Portland çimentosunun % 5 kolemanit, % 20 metakaolin ile ikamesi ve % 1 süperakışkanlaştırıcı ilavesiyle şahit nümüne değerlerine çok yakın sonuçlar elde edilmiştir.

Anahtar kelimeler: Bor, Kolemanit, Basınç Mukavemeti, Eğilme Mukavemeti, Metakaolin, Puzolan, Süperakışkanlaştırıcı



CHAPTER 1

INTRODUCTION

Boron mine is of the most important ores of the world, its extraction is increasing day by day, and its products are used in the production industries in multiple of applications. The technological development increases the importance of the boron materials. Nowadays, the most important boron compounds are gathered in three main groups. These groups are: Colemanite, Tinkal and Uleksit. In Turkey, there are totally 4 manufactures that can process or refine raw boron ore. Millions of tons of waste products are coming out of these facilities. The primary aim of this research is not only to prevent this waste from being polluting our environment, but to investigate whether use of colemanite waste can bring important features to the cement mortar. Needless to say that mortar and concrete are the mostly used construction materials in the civil and industrial engineering industries.

1.1 Literature Review

Colemanite and tinkal wastes represent themselves the composition of eight oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , SO_3 , Na_2O , K_2O), together with Portland cement and other additives, waste materials can be used in the production of mortar [1].

Multiple artificial and natural pozzolans have been used for a variety of purposes in the production of mortar and concrete from the ancient times. Those materials are not basic constituents of concrete and mortar in the mix, they are called additive materials and used to change various physical, mechanical and durability properties, as well as providing economy and technological advancement [2].

The mineral additives, which have been used in mortar production, have physical properties with similar mineralogical and chemical properties to the Portland cement, the vast majority of the minerals do not have binding capacity. We call the first group as supplementary materials,

and they are changing behaviour of the binder paste by forming number of hydration products due to pozzolanic effect. Thus, mineral additives with high pozzolanic activity can enhance the bond ability at aggregate-binder interface and owing to the improved adhesion the durability of the concrete increases [3].

Some waste materials or by-products, which are very similar to Portland cement by chemical composition and possessing pozzolanic properties, can be used as supplementary materials in cement and concrete production in the construction sector. By using the Portland cement as a main ingredient or by replacing Portland cement with pozzolans totally, both the environmental impact due to the cement manufacturing and cost of the final product can be reduced significantly [2].

Today, products of boron manufacturing are main raw materials of many production industries. It is still possible to explore new areas of its use. With the rapid growth of the industrial consumption, there is a possibility that boron raw can be used as a source of energy production in the near future, this case will give the boron raw a privilege among others materials. Turkey holds approximately 72% the world's known boron reserves and 1.72 million tons of boron is being produced, the world's second largest boron producer is United States [4].

The largest world's boron reserves are located in Turkey, USA, Russian Federation, China, Chile, Peru, Bolivia, and Argentina and Serbia. The Turkey's main borate ore is located in the west of Zonguldak, Turkey-Mersin. In the last year about 780 million tons of boron has been in reserve of Turkey according to Eti BANK. In Eti BANK's official reports data from Emet, Kestelek and Kırka mines was collected. The total reserve of Bigadiç boron mine was added to the new reserves discovered in the ongoing exploration activities, showing the net reserve as 1.029.722.000 tons instead of 765.068.000 tons.

The boron industry develops throughout many production spheres. These are fiber-glass (hardened plastics, automotive parts, airplane industry, sporting goods production), optical fiber-glass (electronic industry), borosilicate glass (auto glasses, washing machine), ceramic industry (hardener and tile coating), soaps and detergents (microbicides and bleach), agriculture (to increase or prevent the development of vegetative factor), metallurgy (melt accelerator, formation of protective slag), nuclear applications and in the other heavy and light industrial sectors [4].

On the contrary, metakaolin is the most widely known and recognised pozzolanic material which can provide to a mortar mix with many valuable characteristics. Metakaolin is produced and available on the construction material market in many different types and chemical

qualities. Its purity is equivalent to the binding capacity or free lime in its chemical composition. Some of pozzolans can also possess reactivity characteristics. Metakaolin is recognised as one of the most valuable addition for cement applications. Generally speaking, 8% - 20% (by weight) of Portland cement can be easily substituted by metakaolin. Resulted mortar will exhibit better mechanical properties, and strong durability against ASR and ACR. The pozzolanic reaction in mortar is usually starting soon after being casted and continues from 7th to 28th day of curing. For the content investigation, metakaolin was subjected to the multiple of analyses in order to determine whether it is complying for the standard application. This experimental program was designed to investigate metakaolin as a partial replacement of cement at 10% and 20% [3].

In order to provide a better plasticity where it is needed, super plasticizer Polydos TS 14 used in proportion of 1% from binder's net weight or 4.5 grams. This chemical also provides high early strength, so it was handy to compensate compressive and flexural strength losses due to replacement of cement especially on early test stages. Before this research, the chemical probably has never been tested before with these types and proportions of supplementary materials.

1.2 Aim of the Thesis

As it was mentioned on the previous pages, colemanite waste is a not an environmentally-friendly material. This material is being thrown out to the nature in exorbitant amounts. Turkey is a world leader in terms of boron refinement, hence large deposits of colemanite is being allocated within the country. In order to recycle these by-products, a proper scientific research is of vital importance. The aim of this thesis is to investigate changes in mechanical and physical behaviour of the mixes where different amounts of supplementary materials used. The planned outcome is to develop a brand new mix, which physical and mechanical properties will correspond with standards.

1.3 Hypothesis

Colemanite produced at different manufactures has different chemical composition. Based on preliminary literature review it is clear that generally application of colemanite will possibly not increase mechanical properties of mortar. Therefore, by using superplasticizer and early hardening enhancement chemical admixture together with metakaolin, we will aim to produce

more sustainable and feasible type of construction material. Along with that, water to cement ratio will also be altered in order to reach desirable properties.



GENERAL INFORMATION

Turkey along with few other countries are having the largest deposits of the boron ore, due to that reason there was not much scientific research done in the world totally. In the literature review part, it is seen that the most of researches are completed in Turkey. Scientific studies on the contribution of boron by-products materials have started actively since 2003. Effects of colemanite waste on mortar physical and mechanical characteristics and other scientific studies are published in material science journals.

2.1 Colemanite Waste Usage in Mortar Production

In the construction sector, when the general costs are examined and compared, price for concrete reflects one of the highest costs, and cement, as its main component, is a pricing factor. Supplementary materials, chemical additives and the most effective curing approaches are used in order to reduce cement ratio of our mix. Considering that manufacturing of colemanite is relatively new process in Turkey, Colemanite waste has no practical engineering application at all. In the cement manufacturing sector, studies on the production of colemanite-containing cements continue due to possibility to decrease the temperature of clinker formation during the manufacturing phase.

2.2 Metakaolin Usage in Mortar Production

Metakaolin is a well-known pozzolanic material, it is obtained by thermal activation of kaolin clays. Use of metakaolin in cement of mortar helps to reduce the cement by almost 30% based on its chemical composition. The important point is addition of metakaolin significantly increases strength of mortar, its resistance to the chemical attacks and other important characteristics. The studies evaluating effect of different types of metakaolin on mortar and concrete are still ongoing due to large variety of types of metakaolin.

2.3 Setting Time

- Gencil et al. reported that colemanite addition prolongs the initial and final setting time of the tested mortar, as a result of experiment conducted with its replacement in cement mortar [5];
- Erdogan et al. (1998) discovered that mix produced with boron, results in delays of setting time [6];
- Targan et al. found that cement paste containing any amount of colemanite shows setting time retardation [7];
- Erdogmus et al. stated that the effect of CW on the initial setting time of the mortar turns in an incredible delay. By adding just 3.5% of colemanite by total binder mass, results in the delay of the initial setting time increased by up to 393% when compared to the reference mix [8];
- Kula et al. discovered that the higher presence of Boron oxide in the colemanite ore brings the stronger negative effect on the mechanical properties of mortar. It also results in higher setting time of the mix and specific surface [1];
- Brooks et al. came across delays in setting time as the share of metakaolin increases, notable that, at 15% metakaolin substitution a significant decrease occurs. Group of researchers explained this phenomenon due to the formation of a denser cementing phase due to increase of water amount [9];
- Moulin et al. reported that the setting time of batches containing metakaolin with water/binder ratio 0.40 is less comparing to the setting time of the control batch. They stated that batches containing metakaolin have strong need of water. Also metakaolin cause thixotropic behaviour, resulted in accelerating effect of Portland cement hydration [10];
- Subaşı and Emiroğlu determined that the reference batch showed the shortest setting time, meanwhile the longest setting time had been exhibited by the 30% metakaolin replaced mixture [11].

2.4 Flow Table

- Mitrovic and Nikolic found that Portland-composite cements containing metakaolin require a larger amount of water and high quality cement to achieve a standard consistency [12];

- G. Batis et al. discovered that the composite cement demand more amount of water than the relatively pure cement which we use in production of the control mortar batch and it is directly attributed to the high fineness and purity of metakaolin [13];
- Mardani-Aghabaglou et al. stated that the flow table values obtained from the mixtures containing either silica fume or metakaolin were the lowest due to the high fineness values of these supplementary materials [14];
- Sevim and Tümen observed consistency reduction as borogypsum content increases [15].

2.5 Compressive Strength

- Kula et al. noted improvement in compressive strength of the samples contained 3% of colemanite. At the early curing ages compressive strength of investigated samples was lower than obtained from testing reference samples [1];
- Sevim and Tümen discovered increases in compressive strength of concretes containing 3% and 5% of borogypsum. These batches showed higher compressive strength comparing to the reference mixes [15];
- Sevinç et al. determined that barite leads to loss of both compressive and flexural strengths on early age due to it is an inactive mineral. The drop in compressive strength is mostly notable at 7th day [16];
- Mutuk and Mesci found that compressive strength of mixes where up to 5% of cement is replaced by boron waste is still high and corresponds with values given in Turkish Standard. Although, compressive strength results of the reference mixes is still higher [17];
- Gencil et al. noted that compressive strength at 28th day decreases significantly with increase of colemanite amount in the mixture [5].

2.6 Flexural Strength

- Sevinç et al. stated that increases and decreases in flexural strength of the colemanite containing samples is similar to compressive strength results [16].

2.7 Unit Weight

- Sevim and Tümen found that addition of colemanite waste to cement has no significant effect on the unit weight of the investigated mixes [15];
- Gencil et al. discovered that depending on mechanical properties of colemanite, notable trend is with increase of colemanite ratio in volume the unit weight of concrete decreases [5].

2.8 Water Absorption

- Sevinç et al. found that addition of colemanite results in reduction of capillary pores development due to contribution of colemanite on microstructure development [16].



MATERIALS AND METHODS

3.1 Experiments

3.1.1 Fresh Properties of Mortar

3.1.1.1 Flow Table

The flow table test is necessary to conduct in order to determine consistency of fresh mortar. The trial amount of cement, colemanite, metakaolin, water and standard sand is used during the mortar preparation stage. All the ingredients are mixed in the blade mixer.

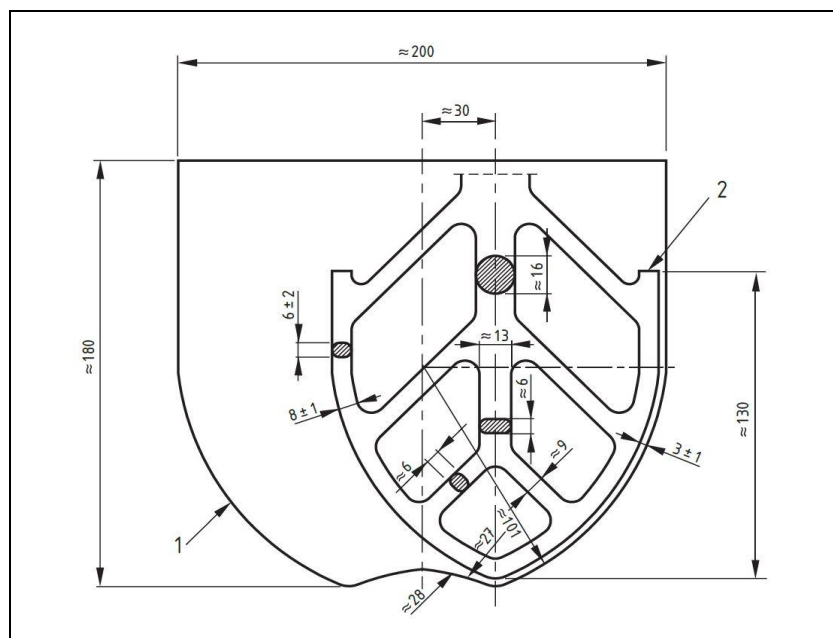


Figure 3.1. Mixer pan

Firstly, for mixtures that do not contain the TS 14 superplasticizer, all mixing water is placed in a bowl. For mixtures contain a superplasticizer, 70% of added water, then the remaining 30% is added after the fine aggregate. The cementitious material, if it is compounded, is first mixed using scrap until it becomes sufficiently uniform. The cement or cementitious compound is added to the water. The mixer should start immediately after cement and water brought in contact and mixes at a slow speed (140 ± 5 rpm) for 30 seconds. The entire amount of sand should be gradually added within following 30 seconds. After all components have added stirring speed, it will change to high speed (285 ± 10 rpm) and mix for 30 seconds. Then the mixer turned off, and the mortar lasts a minute and a half. Within the first 15 seconds from this interval, the mortar that could collect on the sides of the bowl is quickly dumped into the batch. Next mixer should run for one minute at high revolution speed. Mould should be moisturized with water first. Mortar layer of 25 mm is placed in the mould and tamped 20 times with a tamping rod. Then the mould filled completely with mortar and tamp as specified for another 20 times until the mix settle. The excessive amount of mortar should be taken off by a trowel. Take off the mould upwards. Upon that drop the table 25 times in 15s.



Figure 3.2. Flow table molding



Figure 3.3. Flow table spread

Then four measurements of the spread diameter and one mould diameters registered, and result is calculated by equation.

$$Flow = \left[\frac{D_{avg} - D_0}{D_0} \right] * 100 \quad (3.1)$$

Where:

D_0 – Original base diameter;

D_{avg} – Average base diameter.

3.1.1.2 Setting Time

The same steps should be taken in order to prepare a mortar to test for setting time. In this research automatic Vicat test apparatus used to determine setting time of the mortars.

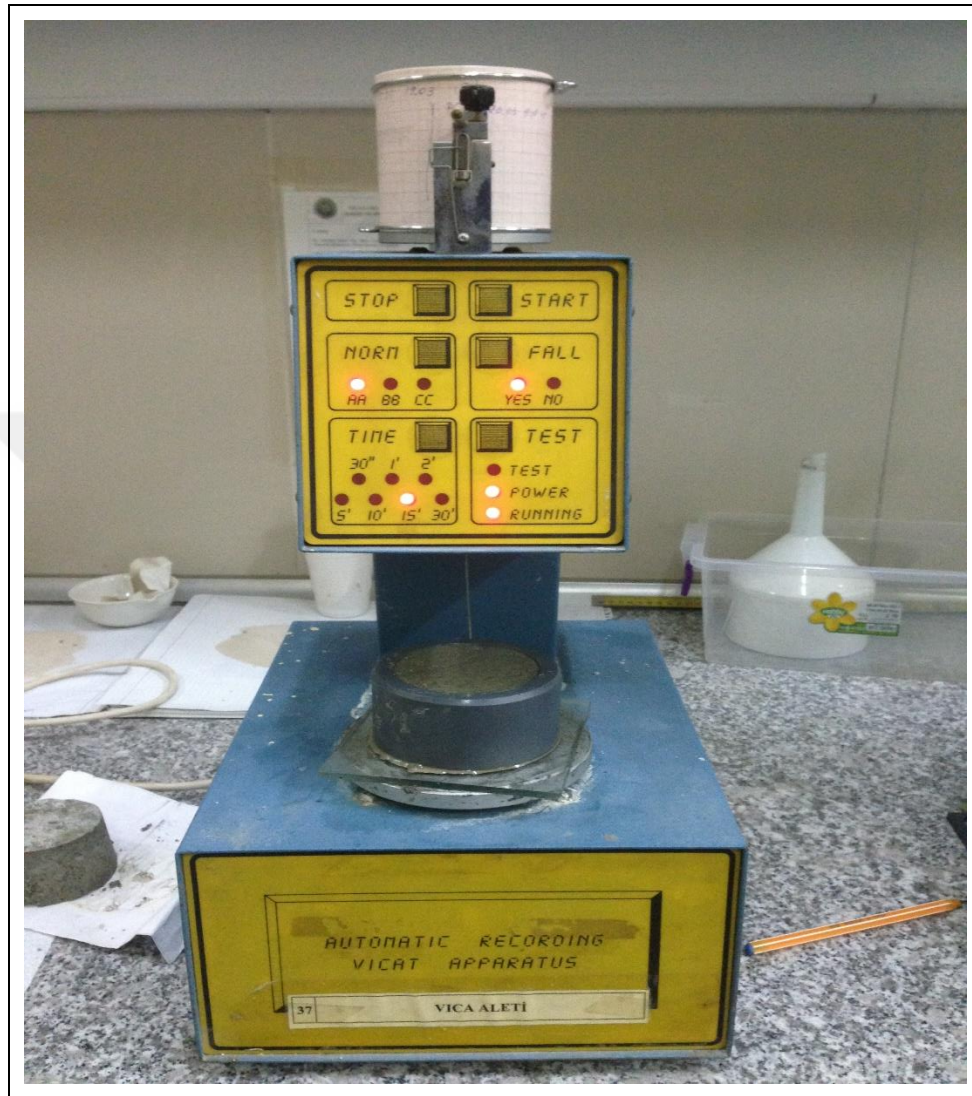


Figure 3.4. Vicat test

According to ASTM C807-13 [18] the needle of $\varnothing 1.3$ penetrates the specimen every 15 minutes. We use four recordings,

H – time in minutes of first penetration less than 10 mm;

E – time in minutes of last penetration greater than 10 mm;

C – measure of penetration at Time E;

D – measure of penetration at Time H.

Then, setting time is computed by formula:

$$\text{Setting Time} = \frac{(H - E)}{(C - D)} * (C - 10) + H \quad (3.2)$$

3.1.2 Hardened Properties of Mortar

3.1.2.1 Compressive Strength

Samples to test for compressive strength were prepared in the same manner as for the rest of the tests. The mortar is casted in moulds, kept in 20°C environment for 24 hours. After, specimens demoulded and kept in separate boxes under the water for 2 days, 7 days, 28 days and 90 days at $20^{\circ}C \pm 1^{\circ}C$. At the specified day and time certain samples taken out of water and covered with damp cloth until tested.

Size of the samples is 40×40×160 mm. After completing flexural test two pieces $A = 1600 \text{ mm}^2$ subjected to compressive strength analysis.

Compressive strength R_c is calculated in megapascals by equation 3.3:

$$R_c = \frac{F_c}{1600} \quad (3.3)$$

Where:

R_c – Compressive strength in megapascals;

F_c – The maximum load in newtons;

1600 – The cross section area of the sample.



Figure 3.5. Curing cabinet



Figure 3.6. Curing cabinet temperature adjustment

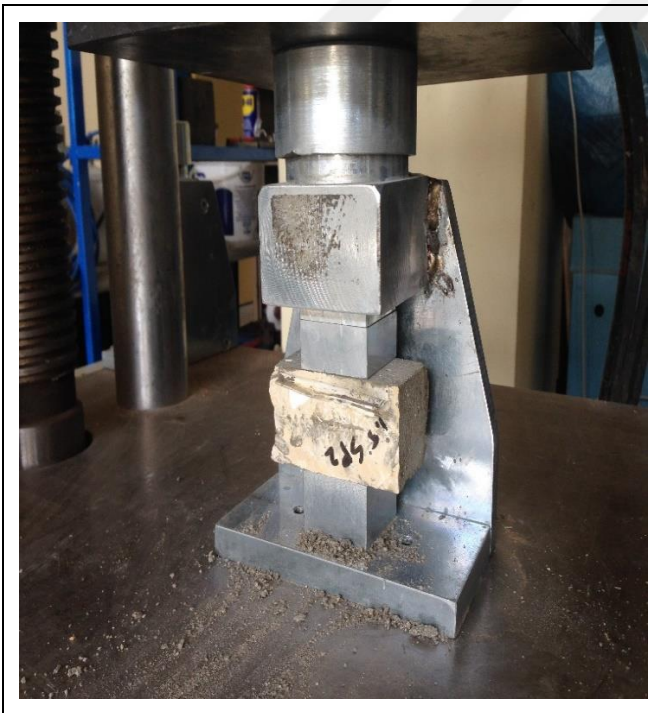


Figure 3.7. Compressive strength test

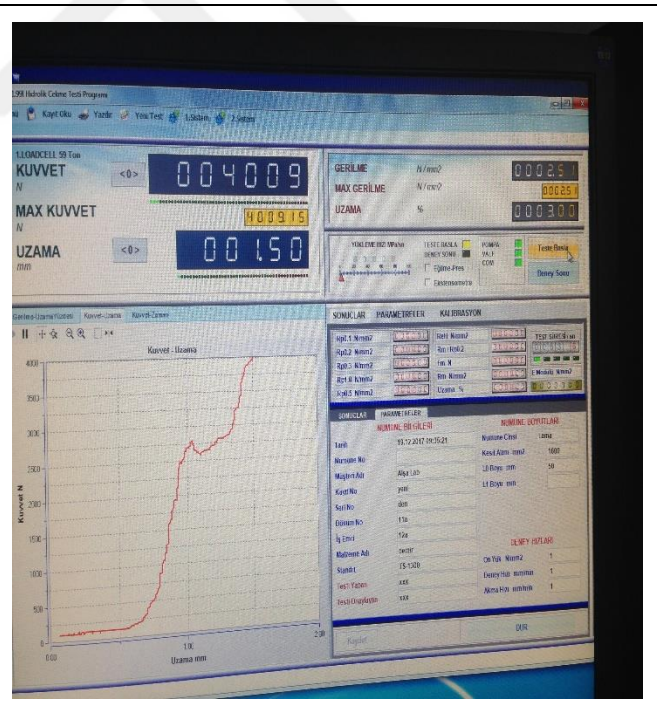


Figure 3.8. Compressive strength result

3.1.2.2 Flexural Strength

For the flexural test, at the required day and time specimen is taken from the water, and kept wrapped in cloth until the test commencement. The three-point loading method applied on the samples. Load applies by roller vertically on the top surface and increases smoothly at the rate of $50 \pm 10 \text{ N/s}$ until sample breaks.

The strength R_f is calculated by formula 3.4 in megapascals:

$$R_f = \frac{1.5 \times F_f \times l}{b^3} \quad (3.4)$$

Where:

R_f – Flexural strength in MPa;

F_f – Load applied in Newtons;

b – Side of the square section of the prism in millimetres;

l – The distance between support rollers in millimetres.



Figure 3.9. Flexural strength test

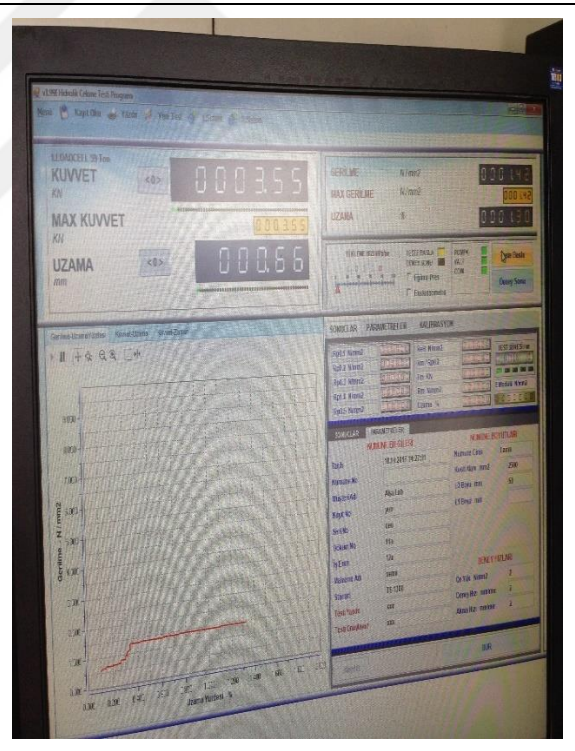


Figure 3.10. Flexural strength result

3.1.2.3 Unit Weight

In order to estimate unit weight of the obtained samples, three parameters need to be scaled. Dry weight, saturated weight and Archimedes weight. Dry weight is obtained by keeping the samples in the oven for 24 hours at the temperature of 105 °C.



Figure 3.11. Drying cabinet

Then, samples immersed in water for 72 hours at the room temperature. After 72 hours, saturated weight is scaled. Archimedes weight is the weight of the sample under the water. These three value give us unit weight value which is designed by the equation 3.5 below:

$$Unit\ weight = \frac{Dry\ weight}{Dry\ weight - Archimedes\ weight} \quad (3.5)$$



Figure 3.12. Saturation of samples for 72h



Figure 3.13. Archimedes weight

3.1.2.4 Water Absorption

In order to find water absorption value, we need two scales the dry weight of the samples and the water saturated weight of the samples. Dry weight is obtained by scaling after keeping the samples in the oven for 24 hours at 105°C. Water saturated weight is obtained by scaling after keeping the samples in the water reservoir for 72 hours at the room temperature. Water absorption is calculated by formula 3.6:

$$\text{Water absorption} = \left(\frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \right) * 100 \quad (3.6)$$

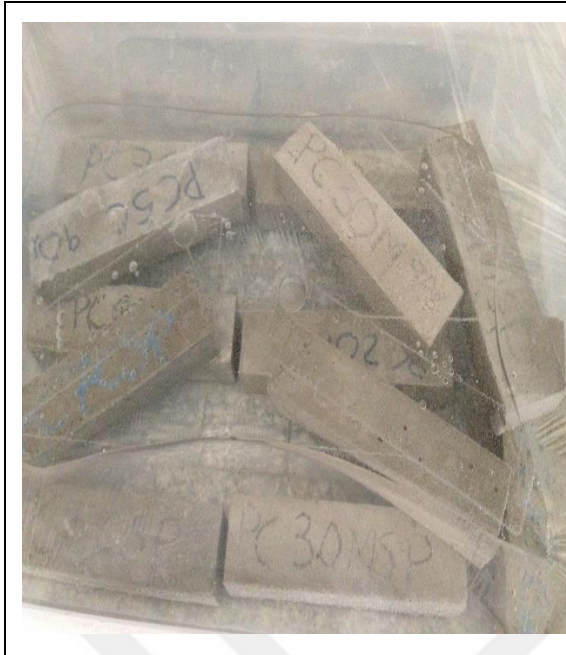


Figure 3.14. Obtaining wet weight



Figure 3.15. Scaling dry samples

3.2 Pozzolans and Other Fine Minerals

3.2.1 Introduction

Mineral additives and other components are being extra finely ground and added to the mortar or concrete before or during the mixing stage. In the world, there are very many materials used as mineral additives. For example:

1. Waste or industrial by-products, such as finely-grained ashes from power generating coal-burning power plants. Also those could be the slags obtained from the production of iron and other metals;
2. Natural materials such as volcanic tuff, volcanic glass, diatomaceous earth and various rock powders;
3. Heat-treated natural materials such as baked clay and shale;
4. Bonding materials such as natural cement and water lime;
5. By-products from chemical refinery plants.

The mineral additives are milled as fine as normal Portland cement and used as a powder substance. These additives are changing the main properties of the concrete or mortar mix. Such as, increasing its workability by forming dough with Portland cement paste during its hydration process. Mineral admixtures are used in mortars and concrete production; they are replacing

some amount of cement or fine aggregates [19].

Mineral additives can affect many properties of fresh and hardened mortar. Properties such as mixing ratios, water/cement ratio, setting time characteristics, workability are the properties that can be affected by the addition of mineral components.

For solidified concrete, the rate of strength recovery, final strength, water permeability, durability, frost resistance, sulfate attack resistance, alkali-silica reaction, resistance to carbonation and thermal cracks are the properties that can be highly improved or impaired by the addition of mineral additives.

The effect of the mineral components over the concrete properties is not dependent solely on their physical and chemical properties. Usually, the production of extra finely ground mineral admixtures is not expensive. Thus, the use of mineral admixtures provides considerable financial savings in concrete and mortar production. The use of industrial wastes in very large volumes by partial replacement of Portland cement will also help to conserve energy and the natural resources.

The annual production of industrial by-product wastes such as slag and colemanite waste from fly ash and iron production at coal-fired power plants is very high. For example, it is estimated that the amount of fly ash is being collected in the world starting from the 1990s is more than 500,000,000 tons per year. These by-product volumes, which are very large, turn to the various environmental issues. The use of industrial byproducts or waste materials from refineries, as a suitable mineral additive will not only improve the engineering properties of concrete, but also contribute to the reduction of environmental problems.

3.2.2 Classification of Finely Ground Mineral Additives

Finely-ground mineral admixtures can be classified under three general types:

1. Pozzolanic materials or materials with additional binding properties but mainly pozzolanic;
2. Materials with binding properties;
3. Others.

Mineral additives which are commonly used for concrete and mortar production are usually pozzolanic. Sometimes these pozzolanic materials have pozzolanic properties as well as binding properties. The use of mineral additives with binding properties is comparatively less than the use of pozzolanic materials. For this reason, the discussion in the following sections will generally cover pozzolanic materials in the first group of the classification above.

3.2.3 Pozzolanic Materials

3.2.3.1 Definition of Pozzolans

In compliance with ASTM C 618 [20], pozzolans are siliceous or silicic and aluminous materials, with small or no binding characteristic. When finely ground and present in humid environment at the normal ambient temperature, as a result of chemical reaction, calcium hydroxide forms a component with a binding property. In addition to the main oxides, silica and alumina, the chemical structure of pozzolans includes iron oxide, calcium oxide (CaO), alkali and carbon. The quantities of these substances vary according to the natural source.

Fly ash obtained from power the power generating plants by burning of dusted carmine. Silica fume is produced as a by-product from the production of silicon metal or alloys. Volcanic ash, pumices, clay and shales, the ashes obtained from the burning of the rice husk (paddy). These all are known as pozzolanic materials.

Some fly ash obtained from the burning of lignite or clays demonstrate cementitious binding properties in coupe with pozzolanic properties. Rapidly cooled and finely grained slag obtained from the iron production also acts like a pozzolanic material in addition to its binding properties. The high amount of silica, alumina, calcium oxide and ferrum oxide in their chemical composition is the reason why these materials are showing binding properties.

2000 years ago, the ancient Romans coined the word “pozzolana” defining the chemical reaction between the volcanic soils of Pizoli in Italy and the hydraulic binder in the mixture of pyrethrum.

3.2.3.2 Types of Pozzolanic Materials

Pozzolans are generally grouped as follows:

- a) Natural Pozzolans - naturally occurring materials such as volcanic ashes, glass, tuffs, heated clay and shales, diatomaceous composites;
- b) Artificial Pozzolans - Industrial by-products such as fly ash, silica fume and finely-grained slag [21].

3.2.3.3 Pozzolanic Reaction

Finely ground pozzolanic materials are reacting at the normal temperatures when calcium hydroxide is occurring in the humid or wet environment.

The main chemical product of the lime pozzolanic reaction is called calcium-silica-hydrat. The

materials other than $C - S - H$ in the lime pozzolanic reaction, this reaction also brings in hydrated gehlenite, calcium carboaluminate, calcium alumina monosulphate and etrengittir [6]. As a result, a chemical compound possessing hydraulic binding properties is being developed. In a humid environment, the chemical reaction between the finely ground pozzolanic silica and calcium hydroxide can be expressed as: $CH + S + H \rightarrow C - S - H$ (calcium silicate hydrate). This reaction is going slowly. In the cementitious compound, $C = CaO, H = H_2O, S = SiO_2$, when this chemical reaction occurs $C - S - H$ is formed and this substance has binding property.

3.2.3.4 Application of Pozzolanic Materials

Pozzolanic materials are used in three different ways in order to benefit cement mix with a better binding properties:

- a) Directly - Mixing with Calcium Hydroxide;
- b) Contributing to the production of pozzolanic cement (such as pozzolanic Portland cement) – admixing pozzolanic material to Portland cement clinker is happening at the manufacturing stage;
- c) Direct addition to the concrete or mortar mixture - by adding it as a blended component during mixing or before the mixing operation.

Direct mixing of the pozzolans with calcium hydroxide is not a common practice. However, this method had been widely used in ancient times. As an exaxmple of its application, the construction of road sub-grades or sub-bases as well as many other applications. The lime pozzolan admixture is still used. On the other hand, the second and third options are widely used.

Puzolan materials reacting with calcium hydroxide, this chemical reaction occurs during the hydration of calcium-silicate in Portland cement. Pozollanic materials can be used either directly in Portland cement or as an supplementary to the concrete or mortar at the mix preparation stage. As known, the hydration of $C3S$ and $C2S$, which are the compounds of Portland cement, results in the formation of calcium hydroxide $C - S - H$ gels. The finely ground pozzolanic materials are reacting with the calcium hydroxide that precipitates as a result of the hydration of Portland cement. As a result of this reaction, an additional $C - S - H$ component appears, which is providing the better binding property.

3.2.3.5 Test Methods for Natural and Artificial Pozzolans

American standard ASTM C 311 [22] includes tests to be carried out for natural pozzolans and fly ash in Portland cement concrete. Also, this standard provides steps how to carry out the sampling.

Similar to ASTM C311 is published in Turkish Standard TS 25 [23] for natural pozzolans, fly ashes and pozzolanic admixtures.

3.2.3.6 Conformity of Natural and Artificial Pozzolans

Reactions of pozzolans with calcium hydroxide is strongly depend on chemical and physical properties of pozzolanic materials. The use of natural and artificial pozzolanic is described in the ASTM C 618 [20]. This include the chemical and physical properties that must be met so that these materials can be used effectively.

Binding materials are the materials that hold ability to develop hydration gel after being mixed with water. Types of the widely used binding materials as mineral admixtures for concrete and mortar are water lime, slag cement, calcined lime mixed with thermal activated lime.

3.2.4 Mineral Additives as Binding Materials

3.2.4.1 Liquid Additives

Polydos TS 14 is a new generation super plasticizing admixture to cement and concrete, which provides mix better workability and allows to use relatively less water. It is used as for in-situ mixes as well as precast. According to the usage manual, it is recommended to admix 0.6-2.0 kg per 100 kg of binder. The binder, in this case, is a cement based compound. In order to estimate required amount of super plasticizer prior test mixes have been made and its most reasonable value is 1% of binder by mass. The chemical component is diluted in 30% of the water and added to the mix next to sand. Use of Polydos TS 14 provides considerable increase in early and final strength of mix, reduces water/cement ratio, allows for achieving smooth pore-free surface.

3.3 Boron

3.3.1 Introduction

Boron is a stable isotope, with periodic number 5, its atomic weight is 10.81, represented by symbol B, located in the periodic table IIIA group; B10 (19.8%) and B11 (80.2%) is an intermetallic element. By nature, it is never in the free form. On average, in the Earth's crust is 10 ppm of boron contain and 4.6 ppm of boron in the seas. It is known that there are about 230 kinds of boron minerals in the soil [24].

Boron compounds possess different properties, by having various metals or non-metal elements in its chemical composition. It makes it possible to be used in many industrial spheres. Boron behaves like a non-metallic compound, but in contrast to pure boron, its appearance and optical properties are similar to diamond and almost as hard as it [24]. Borates, which are main family of boron are Tinkal, Colemanite and Ulexit. At the same time, these are the most common boron compounds in nature.

3.3.2 Boron Products

Refined borates obtained by chemical reaction of the raw borates refining. These reactions are borax pentahydrate, decahydrate borax, anhydrous borax and boric acid. The products of boron are elementary boron, boron carbide, boron nitride, boron halides, inorganic borates, fluoroborates, boric acid esters, boron hydrides, organic boron compounds and boron-nitrogen compounds.

In addition, there is a table arranged in relation to the application areas of these products:

- Sodium borohydride;
- Zinc borate;
- Boron trichloride;
- The boron trifluoride;
- Trimethyborate;
- Fluoboricacid products are included.

Apart from this, there is no definition of the mostly manufactured type of boron as an end product in Turkey. The common products of turkish manufacturing are boron carbide, boron nitride, zinc borate and boron based products, for example, fiberglass [25].

The derivatives of the boron are listed below:

- Pure boron;
- Boron halides;
- Inorganic borates;
- Fluoroborates;
- Boric acid esters;
- Refractory boron compounds.

Boron application spheres will be presented in more detail in this section in Table 1. Boron minerals and their compounds are used in a wide variety of industries to produce multiple different materials and products. There are the main areas of its application:

- Glass Industry;
 - Borosilicate glass;
 - Insulating glass fiber;
 - Textile glass fiber;
 - Alumina borosilicate glass;
 - Optical fibers;
 - Glass ceramics.
- Enamel and Glaze;
- Fire resistant materials;
 - Cellulosic insulation materials;
 - Plastics;
 - Textiles.
- Soap and detergents (as a whitener and rinse aid);
- Paper clay (as Whitener);
- Fertilizers and agricultural chemicals;
- Metallurgical;
- Magnetic materials;
- Nuclear applications;
- Other applications.

3.3.3 Boron Application Spheres

Products of boron refineries are finding lots of application as in civil use, as well as in industrial use. In the Table 1, boron types and suitable application fields are listed:

Table 3.1. Boron application spheres

Material	Application Fields
<i>Calcium borate mineral (coliform)</i>	Textile glass and fiber boron alloys. Metallurgical flux
<i>Sodium borate minerals (ulexite and probertite)</i>	Glass fiber and borosilicate glass.
<i>Boric acid</i>	Antiseptics, boron alloys, nuclear industry, fire resistant materials, nylon, photography, textile, fertilizer, enamel and glaze, sorts of catalysts, glass and fiberglass.
<i>Anhydrous borax</i>	Fertilizer, glass, fiberglass, metallurgical flux, enamel and glaze and fire resistant material.
<i>Sodium perborate</i>	Detergents and bleach, disinfectants and textile finishing.
<i>Sodium metaborate</i>	Adhesives, detergent, plant killer, photography and textile finishing.
<i>Sodium pentaborate</i>	Fire resistant material and fertilizers.
<i>Borax decahydrate, Borax pentahydrate</i>	Adhesives, cement, corrosion inhibitors, medicine and cosmetics, electrolytic refining, fire resistant material, glass, fiberglass, plant killer, insect killer, skin powder and textile finishing.

3.3.4 Boron in Construction Sector

Boron products are also widely used in the construction sector. Boron contributes with valuable qualities in various construction materials:

1. Preventing the wear and abrasion of the material;
2. The protective effect against stains and bleach;
3. Resistance to water absorption;
4. Heat and flame resistance;
5. It provides properties like thermal and sound insulation.

One of the areas where boron is used is the construction sector, or more precisely the cement manufacturing sector. It is known that during the clinker production phase B_2O_3 contributes to energy savings by decreasing the burning temperature. In addition, boron products are widely used in the production of roofing, and building insulation materials. In the recent years, there has been a significant increase in the consumption of the roofing materials called shingles. Cellulosic insulation materials obtained by mixing recycled paper with boric acid, provide sound and heat isolation properties especially for wooden structures, because they have considerable consumption of energy [25].

A significant part of the world boron consumption is in the ceramic industry. Raw and refined boron products are used as additives for the production of glaze and frit. Boron is used to increase the mechanical strength and abrasion resistance, as well as to protect the surface against chemically aggressive compounds. It is also used to decrease the thermal expansion coefficient and to facilitate the cohesion between the glaze and the clay [25].

The glass and fiber glass industry is one of the most important fields of boron minerals and boron products application. Around 40% of the boron consumed in the world is used in the glass industry. This makes boron as very important material in terms of glass production. It is used as a strong flux to reduce the temperature and thus to facilitate melting. In addition, to control the balance between temperature, viscosity and surface tension. Also, to provide optimum fiber glass formation, increase surface hardness and durability, and to inhibit devitrification [24].

Colemanite waste is an industrial waste of boron refinery. The process of concentration of colemanite by ETİ Mine Bigadic Boron Works., which is located in Bigadic. It has a light grey color and is used after being milled. As a result of grinding, the final material is thinner than cement.

3.4 Metakaolin

3.4.1 Introduction

The metakaolin is a reactive aluminosilicate pozzolan obtained after milling purified burned kaolin or kaolinite clay at a certain temperature range. Due to its specific properties that complement mechanical characteristics of mortar and concrete, metakaolin is widely used in the construction sector. In this study metakaolin processed at Kaolin Endustriyel Mineraller

A.S (Istanbul/ Turkey) is used, and its chemical composition and other characteristics are described in the further chapters.

3.4.2 Metakaolin Products

3.4.2.1 Origins

Metakaolin is a final product of kaolin clays manufacturing. Kaolinite mineral leaves hygroscopic water below 200 °C when heated in ceramic making. At 500-600 °C, it releases the relative water in the chemical form, transforming into metakaolinite.

3.4.2.2 Metakaolin Manufacturing

At the high temperatures above 900 °C, metakaolin undergoes a wide variety of transformation reactions to form crystalline compounds. As a result of this reaction, free silica compound is formed. Metakaolin is also may be combined with calcium hydroxide for hydrate formation. Use of this material contributes to the improvement of mortar and concrete properties. The reaction capacity of metakaolin is mainly dependent on the mineral content, raw kaolin source and manufacturing conditions.

Metakaolin reacts with calcium hydroxide very quickly. In the 1980s, lots of research has been done on the formation of glass fiber and fiber reinforced compounds by using metakaolin in cement matrices. In the 1990s, the use of metakaolin in concrete and mortars has become widespread. As a result of the research carried out at that time, many properties of concrete have been improved.

3.4.2.3 Chemical Composition of Metakaolin

From the chemical perspective, the basic components of metakaolin are SiO_2 and Al_2O_3 species. However, Fe_2O_3 , TiO_2 , Na_2O and K_2O are also found in small quantities. The most important components that are providing benefits are mostly related to SiO_2 and Al_2O_3 content in chemical composition of metakaolin.

3.4.3 Application of Metakaolin

The strength properties concrete and mortar are directly depending on the type, shape, size and distribution of the hydration products of the material. Until now, the reaction mechanism draws

attention to pozzolanic activity. Also, the changes that are occurring in these materials resulting from the addition of metakaolin to Portland cement have been examined in a numerous of publications [24].

The first result of using metakaolin as a partial replacement of Portland cement was demonstrated in the construction of the Jupia dam in Brazil in 1962. The purpose of metakaolin use was to increase the durability of the concrete. Since then, there has been a remarkable increase in the use of metakaolin in cement and concrete. Today, addition of metakaolin in Portland cement, mortar and concrete helps to produce high performance concrete and mortars. The important part of this research on metakaolin is to determine the optimum amount of metakaolin suitable for use with colemanite [12].

3.4.4 Construction Sector and Metakaolin

Since metakaolin is a highly reactive pozzolan, its application improves durability of mortar and concrete. Metakaolin is not a cementitious material itself, but reacting with lime at normal temperature and presence of water it forms stable insoluble compound that possesses hydraulic properties. It improves strength, durability, early age behaviour and contributes to sustainability due to lower processing temperatures comparing to cement manufacture [11].

3.5 Material Characteristics

3.5.1 Used Materials and Their Specifics

In this study several materials are taking place. These materials are Portland cement CEM I 45.2 R, colemanite waste, metakaolin, super-plasticizer, Rilem sand and potable tap water. The supplementary characteristic of these materials is presenting in numerous of tables along this chapter.

3.5.1.1 Cement

The cement used in this study is CEM I 42,5 R Portland cement, manufactured by Adana Cement Industry. All necessary measures were taken to keep and use only the fresh cement. The cement is kept in special protective containers so that it does not show agglomeration with moisture. Chemical and physical properties of cement (CEM I 42,5 R) are given in Table 2.

Table 3.2. Chemical and physical properties of cement (CEM I 42,5 R)

Chemical Compounds	Results (%)
SiO ₂	19.55
Al ₂ O ₃	5.31
Fe ₂ O ₃	4.15
Mg ₂ O ₃	0.06
CaO	62.30
MgO	3.14
SO ₃	2.55
Na ₂ O	0.36
K ₂ O	0.88
Na ₂ O + 0.658K ₂ O	0.94
Insoluble Residue	0.42
Free CaO	0.31
L. O. I	1.73

3.5.1.2 Colemanite

In this study dried and ground boron from Eti Mine Bigadic Boron Works (Balikesir, Turkey) is used. The grinding process was carried out at ready-mixed concrete plants. The Blaine fineness value of KA is 4140 cm²/gr and the density is 2.43 gr/cm³. Chemical composition of colemanite is given in Table 3.

Table 3.3. Chemical composition of colemanite

Chemical	Amount %
B ₂ O ₃	40.05±0.5
CaO	27.00±1.0
SiO ₂	4.00-6.00
SO ₄	0.60
As	35
Fe ₂ O ₃	0.08
Al ₂ O ₃	0.40
MgO	3.00
SrO	1.50
Na ₂ O	0.50
L.O.I	25.00
Moisture	1.00
Bulk Density	1.00

3.5.1.3 Metakaolin

Metakaolin prefabricated at Kaolin Endustriyel Mineraller A.S (Istanbul/ Turkey) is used in this study. Its chemical composition is given in the Table 4, mineralogical composition in the Table 5 and PSD analysis in the Table 6:

Table 3.4. Chemical composition of metakaolin

Chemical	Amount %
SiO ₂	56.10
Al ₂ O ₃	40.23
Fe ₂ O ₃	0.85
SO ₄	0.55
CaO	0.19
MgO	0.16
K ₂ O	0.51
Na ₂ O	0.24
L.O.I	1.10

Table 3.5. Mineralogical composition of metakaolin

Mineralogical Composition/ XRD Siemens D 500/, %	quartz ~ 8
	mica ~ 4
	kaolinite – traces
	amorphous phase ~ 87
	others ~ 1

Table 3.6. PSD analysis

PSD – Sedigraph 5120, %	Amount %
< 45 µm	99.3
< 32 µm	99.0
<20 µm	96.9
<10 µm	89.1
<7 µm	81.1
<5 µm	71.9
<2 µm	45.8
<1 µm	18.4
D50, µm	2395
Pozzolanic Index/Chapelle test	1359

3.5.1.4 Polydos TS 14

Super plasticizing agent Polydos TS 14 is used in this study. In the official document recommended dosage of the chemical compound is varying between 0.6 to 2.0 kg per 100 kg of binder. In order to estimate optimal amount of additive, preliminary studies have been conducted. It is found that by adding 2% and 1.5% of TS 14 by mass, the setting time of the mix prolong too much. After obtaining the results, it was observed that the most optimal amount of Polydos TS 14 is 1% by the mass of binder, or 4.5 grams. Table 7 provides with technical properties of the used chemical.

Table 3.7. Technical properties of polydos TS 14

Technical Properties	Description
Chemical Contents	Polycarboxylate based
Apperance-Colour	Brown liquid
Density	1.05±0.02 kg/l
pH Value	4.5±1
Cloride Content (CI)	< %0.1
Alkali Content	< % 4
Freezing Point	-4 °C

3.5.1.5 Fine Aggregates

Standard Rilem sand has been used during the mix preparation, it has been produced by Trakya Cement Factory. This sand satisfies regulations stated in TSE EN 196-1 [26]. Sand is packed in airtight pockets each weight is 1350g.

3.5.1.6 Water

Tap water has been used for preparation of the mixes and for storage of the hardened samples. This is a normal potable water without any deviations from the chemical standards.

3.6 Experimental Methods

3.6.1 Preparation of Samples

Samples prepared in compliance with BS EN 196-1 [26]. 12 different mix proportions have been prepared. For some mixes water/binder ration is less or more than 0.5 due to some mixes getting too stiff or loose. In this study amount of colemanite is 3%, 5% or 7%. Amount of metakaolin is 10% or 20%. Amount of chemical additive is always 1% out of weight of the binder.

Samples were immersed in water on the second day of curing, and kept in it at $20\pm 2^{\circ}\text{C}$.

3.6.2 Experimental Studies

3.6.2.1 Performed Experiments

- 1) Preparation stage: obtaining the most appropriate chemical composition for the samples. Firstly, amount of colemanite used was 10%, 20% and 30%. These mixes decayed (Picture 15-18) at the curing stage, their setting time was extremely high. Then, colemanite percentage has been decreased to 7% and 5%;



Figure 3.16. Scaling dry samples



Figure 3.17. Demoulded samples



Figure 3.18. Decayed samples



Figure 3.19. Spalled and decayed samples

- 2) Flow table test: all mixes were tested in order to estimate workability parameters;
- 3) Setting time test: all mixes were tested in order to estimate the initial and final setting time;
- 4) Determination of compressive strength: mixes were tested at 2nd, 7th, 28th and 90th days;
- 5) Determination of flexural strength: mixes were tested at 2nd, 7th, 28th and 90th days;
- 6) Determination of unit weight of the samples;
- 7) Determination of water absorption characteristics.

3.6.3 Notation

The following notations will be used when the results obtained from the experiments are shown in the charts.

The PC means Portland Cement 42.5R. The C letters refer to Colemanite. The M letter refers to Metakaolin. The SP denotes addition of Polydos TS 14 at the amount of 1%. The sample properties that the mixture names are given in Table 3.10. Table 8 and Table 9 shows the amount and percentage of materials used in the blends.

Table 3.8. Percentage of materials in the blends

Mix ID	Cement	Sand	Colemanite	Metakaolin	Water	TS 14 (SP)
	%	%	%	%	w/c ratio	%
<i>PC</i>	100	100	0	0	0.5	0
<i>PC5C</i>	95	100	5	0	0.5	0
<i>PC7C</i>	93	100	7	0	0.5	0
<i>PCSP</i>	100	100	0	0	0.4	1
<i>PC5CSP</i>	95	100	5	0	0.4	1
<i>PC7CSP</i>	93	100	7	0	0.4	1
<i>PC20M</i>	80	100	0	20	0.5	0
<i>PC30M</i>	70	100	0	30	0.6	0
<i>PC20MSP</i>	80	100	0	20	0.5	1
<i>PC30MSP</i>	70	100	0	30	0.5	1
<i>PC5C20M</i>	75	100	5	20	0.5	0
<i>PC5C20MSP</i>	75	100	5	20	0.5	1

Table 3.9. Amount of materials in the blends

Mix ID	Cement	Sand	Colemanite	Metakaolin	Water	TS 14 (SP)
	(g)	(g)	(g)	(g)	(g)	(g)
<i>PC</i>	450	1350	0	0	225	0
<i>PC5C</i>	428	1350	22.5	0	225	0
<i>PC7C</i>	419	1350	31.5	0	225	0
<i>PCSP</i>	450	1350	0	0	203	4.5
<i>PC5CSP</i>	428	1350	22.5	0	203	4.5
<i>PC7CSP</i>	419	1350	31.5	0	203	4.5
<i>PC20M</i>	360	1350	0	90	225	0
<i>PC30M</i>	315	1350	0	135	270	0
<i>PC20MSP</i>	360	1350	0	90	225	4.5
<i>PC30MSP</i>	315	1350	0	135	225	4.5
<i>PC5C20M</i>	338	1350	22.5	90	225	0
<i>PC5C20MSP</i>	293	1350	22.5	90	225	4.5

The specimens used for flexural test are 40x40x160mm prisms, after flexural test conducted, two chunks 40x40x80mm tested for compressive strength. In this study 144 prisms were prepared for testing.

RESEARCH FINDINGS AND DISCUSSION

4.1 Fresh Properties of Mortar

4.1.1 Flow Table

Results from testing mortar at the flow table gave us insight on spreading properties of the batches. As it is seen from Table 10, all the batches are behaving differently. Nearly same result to PC batch demonstrate PC7CSP, PC20MSP, PC5C20MSP batches. Experiment shows that addition of colemanite reduces spreading of mortar. In case of addition of 1% super plasticizer TS 14 to all of the batches lower amounts of water took place, due to this reason the obtained spread is comparatively low. Metakaolin affected spreading characteristic significantly, water/cement ratio increased to 0.6 in order to facilitate flow and compact the mortar easily. The mix PC5C20MSP has shown very good result close to PC which is taken as a reference.

Table 4.1. Flow table results

Name	D_1 (cm)	D_2 (cm)	D_3 (cm)	D_4 (cm)	D_{avg} (cm)	D_0 (cm)	RES (%)
<i>PC</i>	17.5	18	18	17.5	17.75	10	77.5
<i>PC5C</i>	12.5	12	12.5	12	12.25	10	22.5
<i>PC7C</i>	15.5	16	15.5	16	15.75	10	57.5
<i>PCSP</i>	15	15.5	15.5	15.5	15.375	10	53.75
<i>PC5CSP</i>	15	15	15.5	15.5	15.25	10	52.5
<i>PC7CSP</i>	17.5	17.5	17.5	17.5	17.5	10	75
<i>PC20M</i>	12.5	12	12	12.5	12.25	10	22.5
<i>PC30M</i>	16.5	16	16	16	16.125	10	61.25
<i>PC20MSP</i>	17.5	17.5	18	18.5	17.875	10	78.75
<i>PC30MSP</i>	15.5	15.5	15	15	15.25	10	52.5
<i>PC5C20M</i>	12	11.5	12	12	11.875	10	18.75
<i>PC5C20MSP</i>	16.5	17	17	16.5	16.75	10	67.5

More precise data provided in Table 11, flow table results are compared with plain Portland cement mortar flow result, which is 17.75 cm spread. Water/cement ratio of PC5C20MSP is the same as PC or 0.5.

Table 4.2. Flow table results comparison

Name	Comparing to PC
<i>PC</i>	100.00%
<i>PC5C</i>	69.01%
<i>PC7C</i>	88.73%
<i>PCSP</i>	86.62%
<i>PC5CSP</i>	85.92%
<i>PC7CSP</i>	98.59%
<i>PC20M</i>	69.01%
<i>PC30M</i>	90.85%
<i>PC20MSP</i>	100.70%
<i>PC30MSP</i>	85.92%
<i>PC5C20M</i>	66.90%
<i>PC5C20MSP</i>	94.37%

4.1.2 Setting Time

Setting time data of the mortar mixes is provided in the Table 12. From this table it is clear that colemanite prolong setting time of the mix. In case of PC7CSP setting time took 16 hours. The PC5C20MSP batch showed setting time result which is three times longer than the reference

mix. Application of metakaolin shortens setting time of the mortar, but it makes mix sticky and not appropriate for mixing and placement.

Table 4.3. Setting time table

Name	H (min)	E (min)	C (mm)	D (mm)	Result (min)
<i>PC</i>	<i>170</i>	<i>185</i>	<i>14</i>	<i>6</i>	<i>177.50</i>
<i>PC5C</i>	<i>350</i>	<i>365</i>	<i>15</i>	<i>6</i>	<i>356.67</i>
<i>PC7C</i>	<i>545</i>	<i>590</i>	<i>12</i>	<i>5</i>	<i>577.14</i>
<i>PCSP</i>	<i>225</i>	<i>235</i>	<i>14</i>	<i>6</i>	<i>230.00</i>
<i>PC5CSP</i>	<i>500</i>	<i>545</i>	<i>13</i>	<i>5</i>	<i>528.13</i>
<i>PC7CSP</i>	<i>920</i>	<i>980</i>	<i>13</i>	<i>4</i>	<i>960.00</i>
<i>PC20M</i>	<i>115</i>	<i>125</i>	<i>13</i>	<i>5</i>	<i>121.25</i>
<i>PC30M</i>	<i>200</i>	<i>215</i>	<i>15</i>	<i>6</i>	<i>206.67</i>
<i>PC20MSP</i>	<i>275</i>	<i>290</i>	<i>11</i>	<i>5</i>	<i>287.50</i>
<i>PC30MSP</i>	<i>215</i>	<i>225</i>	<i>13</i>	<i>7</i>	<i>220.00</i>
<i>PC5C20M</i>	<i>245</i>	<i>300</i>	<i>15</i>	<i>7</i>	<i>265.63</i>
<i>PC5C20MSP</i>	<i>510</i>	<i>535</i>	<i>14</i>	<i>6</i>	<i>522.50</i>

4.2 Hardened Properties of Mortar

4.2.1 Compressive Strength

For the better comparison compressive strength results were grouped according to the admixture used. The reason behind it is to demonstrate how different components are affecting or enhancing compressive strength property. In each group reference mix PC is figuring, colored in light blue. Figure 2 shows us effect of colemanite on mortar compressive strength.

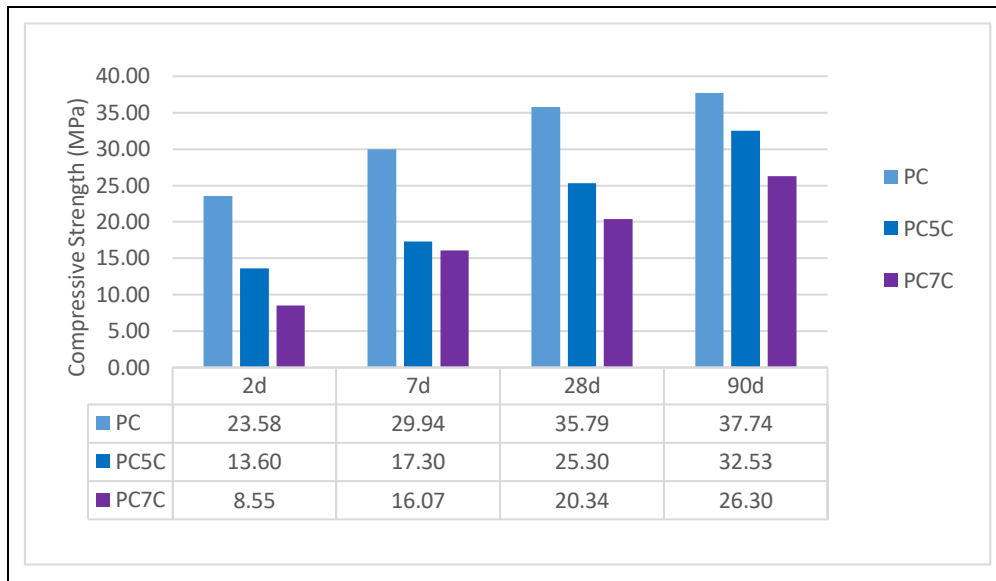


Figure 4.1. Compressive strength test results of PC, PCSP, PC5CSP and PC7CSP

Addition of 5% colemanite by mass, or 22.5 gram, decreases compressive strength at the 7th day of testing on 40%, for 7% substitution strength decreases on 46%. Addition of 5% decreases compressive strength on almost 30% at 28th day of curing. Increase of colemanite proportion to 7% deteriorate compressive strength on 43.16%. This conclude that this particular colemanite shall be used in the amounts less than 5%. This occurs due to high calcium content of the figuring colemanite. In some of the previous researches, investigated colemanite had more silica and alumina in its chemical composition. The result of 90th day test shows the same tendency, PC5C mix is still almost 14% less than compressive strength of the reference mix. PC7C achieved 26.3MPa compressive strength at 90th day of curing, which is approximately 31% lower than attained by PC mix.

Figure 3 shows us results of 1% Polydos TS 14 addition together with the same proportions of colemanite. Investigated colemanite demonstrated setting time retarder characteristics, the mix PC7CSP was not ready for demolding and immersing to the water for the further curing after 24 hours of normal curing. Its curing was extended for another 24 hours, but it was still not enough for compressive strength test due to non-solidification.

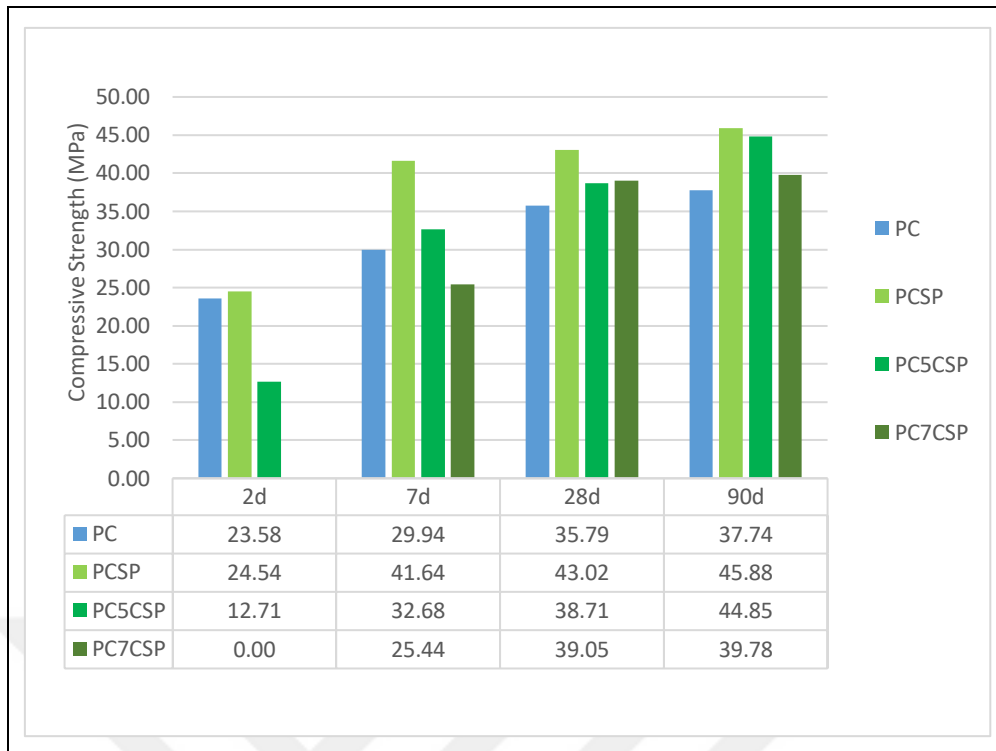


Figure 4.2. Compressive strength test results of PC, PCSP, PC5CSP and PC7CSP

Addition of 5% colemanite and 1% of super plasticizer resulted in 4% increase of PCSP in comparison with result shown by reference mix at 2nd day. PC5CSP demonstrated 46% decrease at 2nd day, PC7CSP did not get hard enough to take part in the testing, its result is failure. On the 7th day PCSP showed 39% increase, PC5CSP gained 9.1% more strength than PC, PC7CSP reached 25.44MPa or 15% less than control mix. At 28th day, PC5CSP resulted in 8% increase in compressive strength, comparing to the reference mix. PC7CSP demonstrated the result close to PC5C, the difference between two is 0.3%.

For 90th day compressive strength of PC5CSP is close to PCSP, and 21.5% higher than reference mix PC. Based on this data, 5% of colemanite selected for the further mix preparations.

Compressive strength results over the amount of metakaolin in the mix are provided on Figure 4. Metakaolin is a pozzolanic material which augmenting all hard properties, including compressive strength. The pozzolanic reaction gives better result on long-time curing perspective.

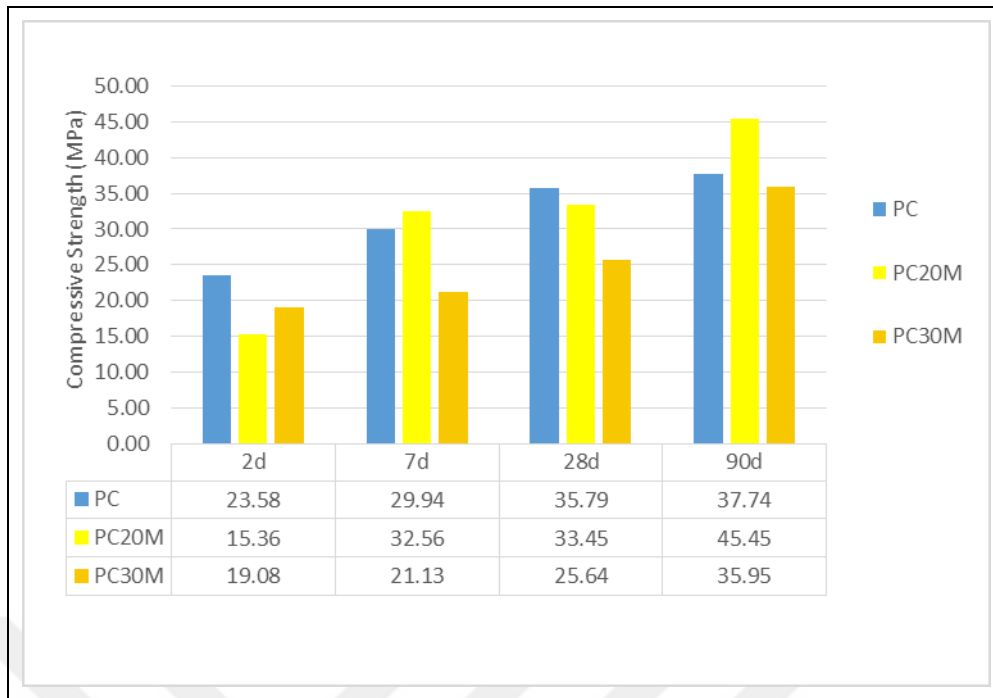


Figure 4.3. Compressive strength test results of PC, PC20M and PC30M

On the 2nd day of curing results of both PC20M and PC30M are lower than reference values, but PC30M gained 24% more strength after this early period. The picture changes at 7th day, here PC20M reach 32.56MPa or 8.75% more than reference value. At the same time PC30M gained just 21.13MPa or almost 30% less than PC value.

On the 28th day of curing, compressive strength result of PC20M is close to the reference mix result or 6.5% less. Compressive strength result demonstrated by PC30M on 28th day of curing is 28.35% lower than PC result. On 90th day compressive strength of PC20M raised 20.42% higher than shown by PC at the same curing age. At the same time, the PC30M sample developed strength close to the reference at 28th day.

On the 90th day PC20M dominating among the three mixes, its result reach 45.45MPa or 20.5% higher than PC. PC30M developed strength close to the reference value at 90th day.

Addition of 1% by mass of super plasticizer TS 14 to the same PC20M and PC30M mixes gives us controversial results. As seen from Figure 5, 2nd and 7th days are showing familiar trend, gap between compressive strength of PC, PC20MSP and PC30MSP is decreasing, but the compressive strength of PC batch is still the highest at these dates. At the 28th day of curing both mixes exceeded compressive strength value demonstrated by the reference mix. For

PC20MSP it is 37.72 MPa or 5.39% more than obtained by reference mix, and for PC30MSP developed compressive strength is 39.94 MPa or 11.6% higher than PC.

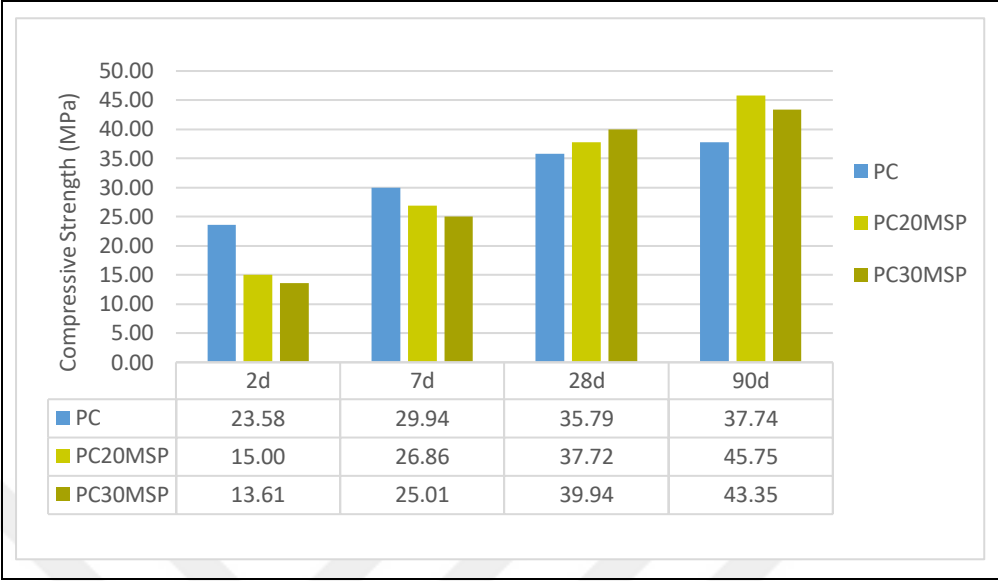


Figure 4.4. Compressive strength test results of PC, PC20MSP and PC30MSP

This trend changes on 90th day, where test results are 45.75 MPa and 43.35 MPa correspondingly. Based on the obtained data, it’s been decided to use 20% of metakaolin by the gross binder mass in the further research.

In order to decrease part of cement in the mix, but remain its strength high, 25% of the Portland cement was replaced with 20% of metakaolin and 5% of the colemanite. One of these two mixes also contained 1% of Polydos TS14.

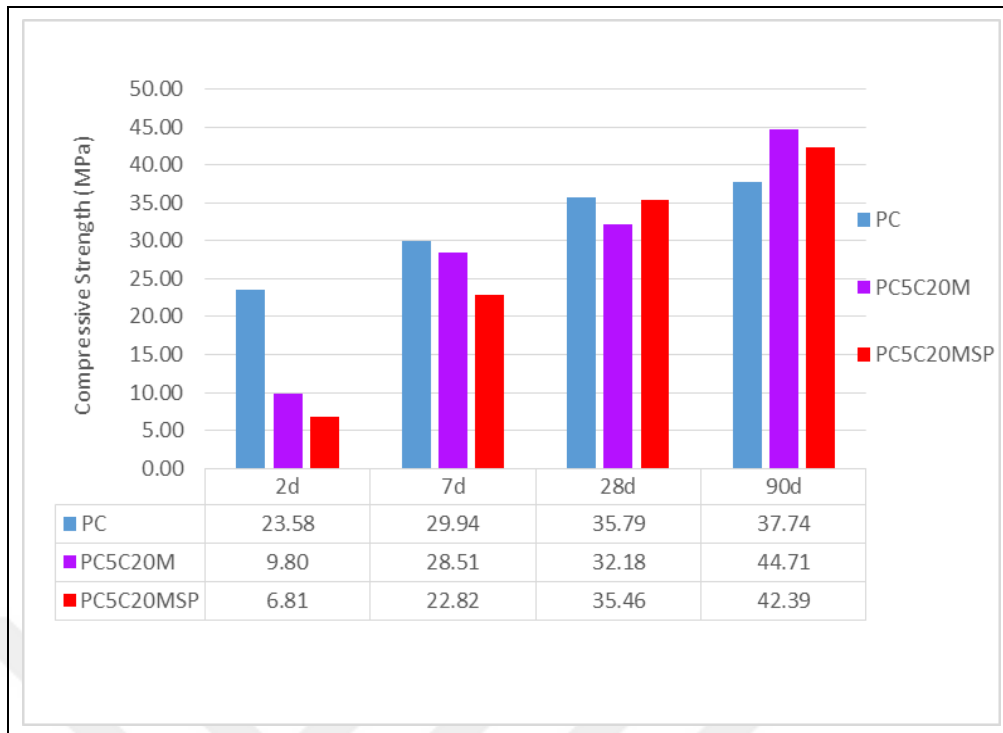


Figure 4.5. Compressive strength test results of PC, PC5C20M and PC5C20MSP

From Figure 6, on the 2nd day both experimental mixes demonstrated weak in comparison to the reference mix. PC5C20M yield 9.8MPa or 58.5% less than PC, PC5C20MSP get 6.81MPa or 71% less than PC.

Five days later, compressive strength were closer to each other. PC5C20M demonstrated 4.7% less than PC, PC5C20MSP gave 22.82MPa or 23.7% less than PC.

28th day mix PC5C20MSP was nearly the same as plain PC compressive strength. At the same time, PC5C20M performed 10% weaker than reference. On 90th day, PC5C20MSP developed 12.32% more strength than PC, but PC5C20M gave 18.46% higher strength than PC mix.

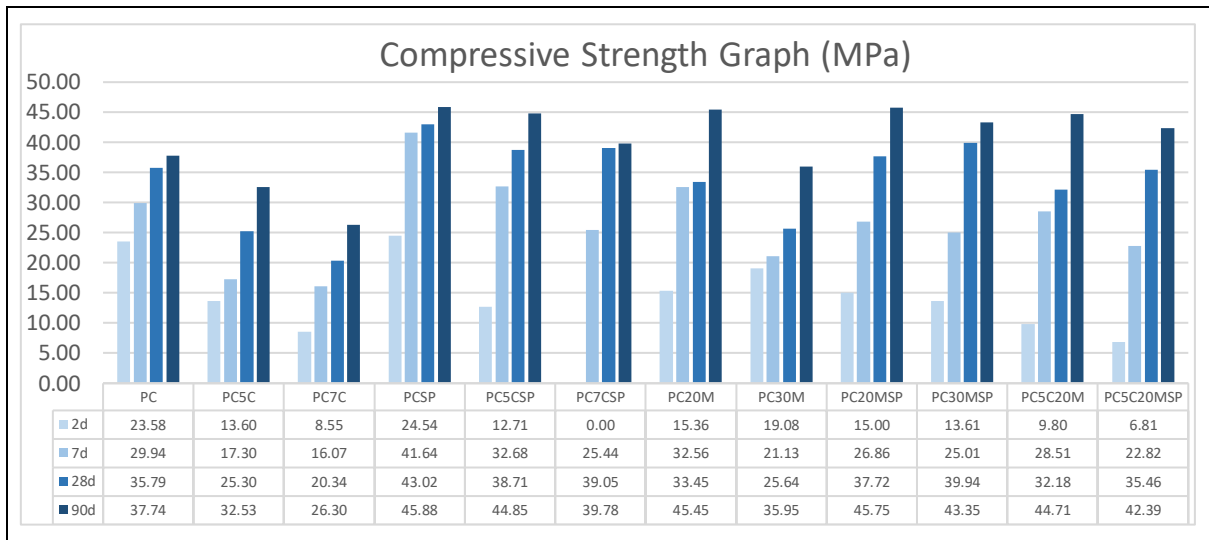


Figure 4.6. Compressive strength test results of all mixes

Figure 7 provides us with combined compressive strength results, based on that, PC5C20MSP has shown the best performance.

4.2.2 Flexural Strength

Flexural strength was measured at 2nd, 7th, 28th and 90th days. Each result represents interpolated value of 3 measurements. For the better distinction each table contain result of plain Portland cement as a reference value, colored in light blue.

On the Figure 8 flexural strength of plain Portland cement mix compared with mixes where 5% and 7% of cement replaced with colemanite. General trend is colemanite badly effects on flexural strength of the mortar. On the 7th day negative difference between tested PC, PC5C and PC7C is 25% and 40%. On 28th day 5% of colemanite addition turned in 23% decrease of flexural strength. Addition of 7% or 31.5 gram of colemanite turned in 24% of loss in flexural strength. In other words, flexural strength dropped from 8.03MPa to 6.19 MPa and 6.13 MPa correspondingly.

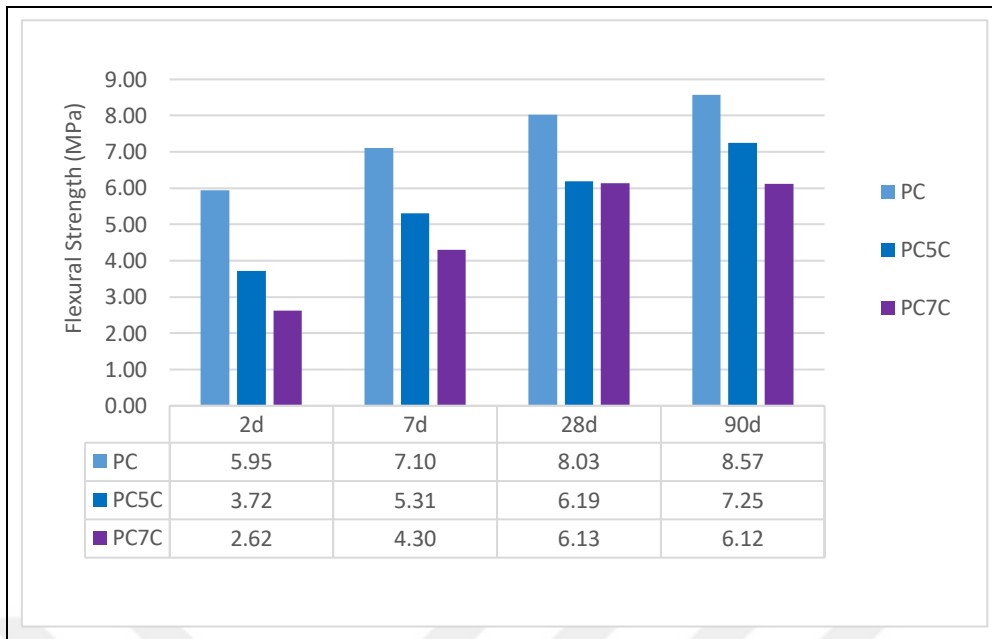


Figure 4.7. Flexural strength test results of PC, PC5C and PC7C

On the 90th day the difference in flexural strength between PC, PC5C and PC7C become more clear. At that specified period, 5% of colemanite supplementary resulted in 15.4% decrease, 7% has shown almost 28.6% decrease in the flexural strength.

Negative effect of colemanite supplementary on flexural strength has been amortized by addition of 1% by mass super plasticizer Polydos TS 14. As a result, on the 7th day of curing strength of PCSP reached 9.45 MPa or exceeded value of PC on more than 33%. Comparing to PC, PC5CSP and PC7CSP showed 5.5% and 1% increase in flexural strength at 7th day.

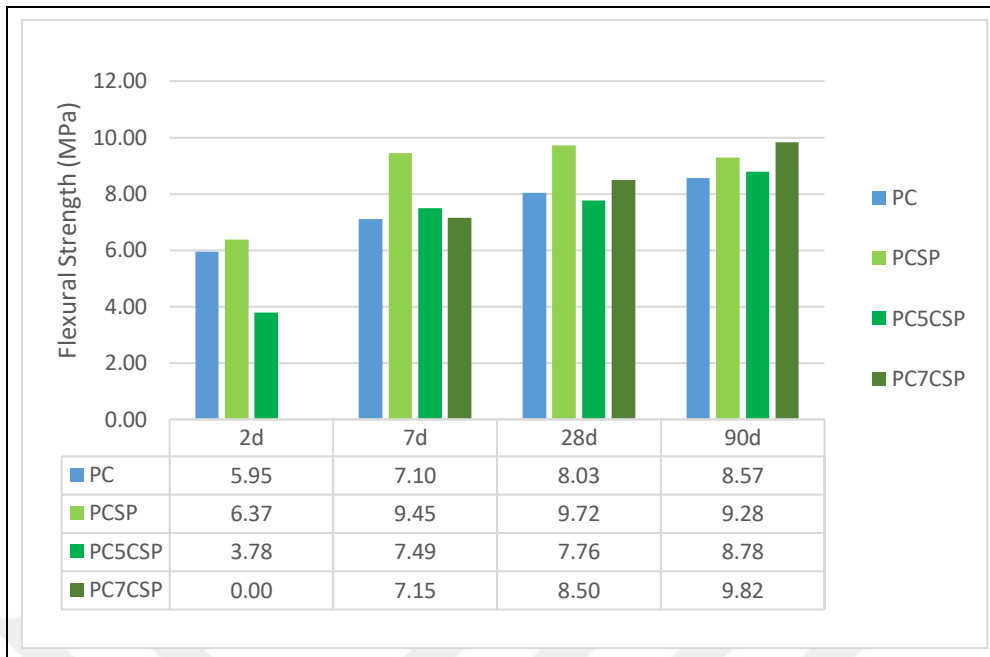


Figure 4.8. Flexural strength test results of PC, PCSP, PC5CSP and PC7CSP

As it can be seen for Figure 9, at the 28th day, PCSP still dominating in terms of flexural strength result, its measure is 9.72 MPa or 21% higher than PC. PC5CSP and PC7CP gained 7.76 MPa and 8.5 MPa, which is relatively 3.36% lower and 5.85% higher than reference.

On the 90th day results are more close to each other, all of the samples demonstrated results higher than PC. Even though PC7CSP showed better performance in this set, obtained data made us believe that we shall not exceed 5% margin for colemanite amount.

In order to assess effect of metakaolin presence on the flexural strength, let us refer to Figure 10. At the beginning of the curing, flexural strength of PC20M and PC30M is almost same, but still slightly less than reference value.

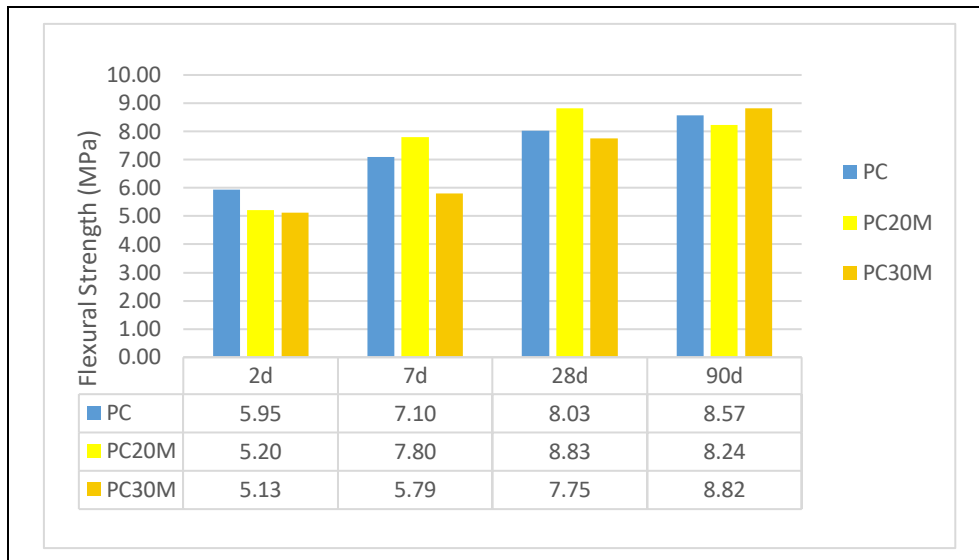


Figure 4.9. Flexural strength test results of PC, PC20M and PC30M

On the 7th day of the curing flexural strength of PC20M is nearly 10% higher than PC, PC30M gain 5.79MPa or 18.45% lower than the reference value. On the 28th day, difference between PC and PC20M remains the same, although PC30M show just 3.85% lower result than PC. On 90th day PC30M gained the highest average result of this trinity or 8.82 MPa.

On the Figure 11, represented flexural strength results of PC, PC20MSP and PC30MSP. As it seen from the graph, on the 2nd day PC showed the best performance. At the 7th day of curing, PC20MSP gained 7.67 MPa, PC30MSP gained 6.37 MPa comparing to 7.10 MPa of PC. The most important 28th day showed that the leader of these three is PC30MSP, a mix that contain 135g of metakaolin, 315g of cement, 4.5g of TS14, and 225g of water. Its result is 9.27 MPa. The result of PC20MSP is also higher than PC, 8.71MPa.

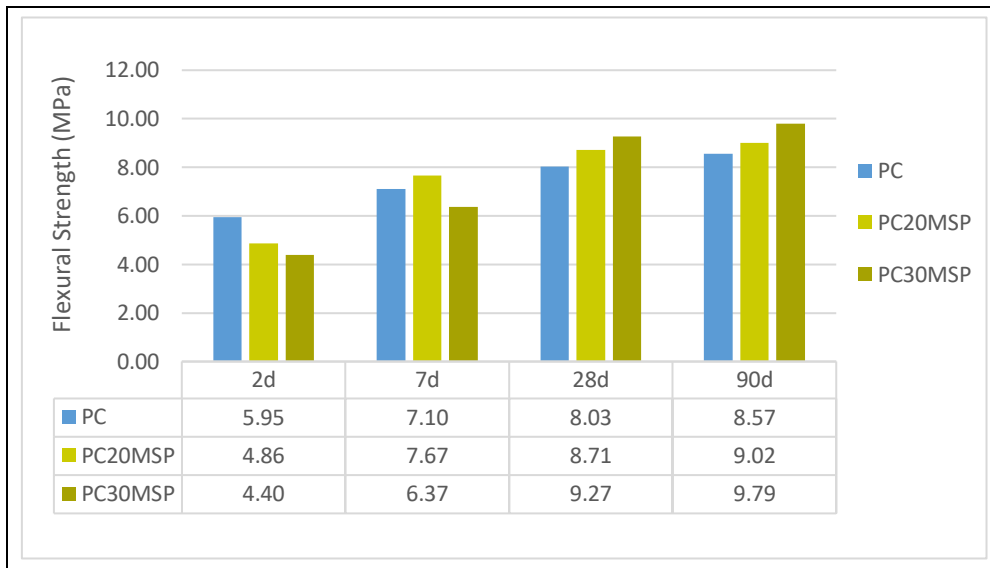


Figure 4.10. Flexural strength test results of PC, PC20MSP and PC30MSP

At 90th day PC30MSP show the highest flexural strength result and still keeping the leading position of three mixes, gaining over 14% comparing to PC mix. PC20MSP has shown 9.02MPa or 5% higher than PC.

Considering the data collected, PC5C20M and PC5C20MSP were selected for the further investigation.

Notable that on the 2nd and 7th days, PC5C20M and PC5C20MSP could not outperform reference mix. As can be seen from Figure 12, on the 2nd day difference between PC and two is around 55% and 61% negatively.

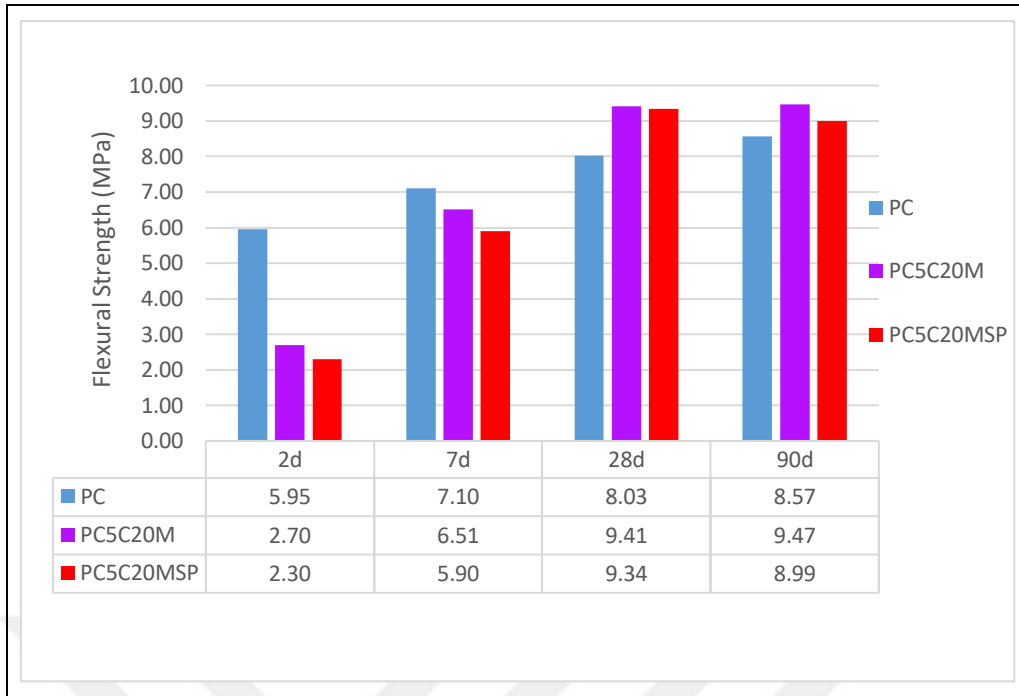


Figure 4.11. Flexural strength test results of PC, PC5C20M and PC5C20MSP

On the 7th day, PC show 7.10 MPa and difference among the rest become much more less, or 6.51 MPa and 5.9 MPa which makes 8.3% and 17% negatively. The 28th day result shows great improvement in the performance of both PC5C20M and PC5C20MSP mixes. PC5C20M gained 9.41MPa which is only less than PCSP mix. PC5C20MSP show 9.34 MPa which is the third highest flexural strength result.

The 90th day flexural test shows that PC5C20M is holding the top position out of these tree samples, its value is 9.47 MPa or 10.5% higher than flexural strength of PC at 90th day.

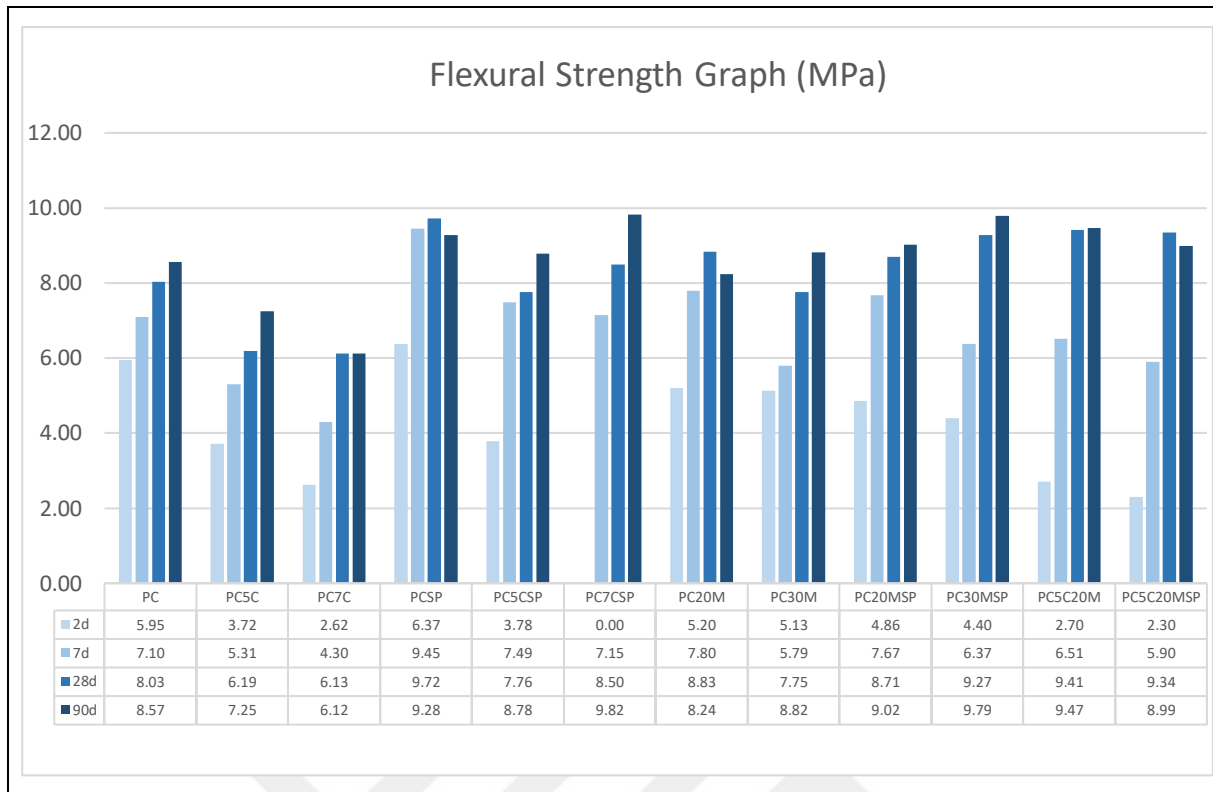


Figure 4.12. Flexural strength test results of all mixes

Based on the results obtained, and demonstrated on the Figure 13, PC5C20M and PC5C20MSP have shown high results comparing to the rest of the tested batches.

4.2.3 Unit Weight

On the Table 13 Unit Weight test results are given. Based on the values obtained, PC5C20MSP is the lightest sample out of 12 tested samples. Its result is 2.298 gr/cm³ or 3.5% lighter than PC unit weight. PC5C20M show 2.384 gr/cm³ which is an average result. The heaviest batch is PC7C with 2.435 gr/cm³ or 2.2% heavier than PC.

Table 4.4. Unit weight test results (gr/cm³)

Name	Unit Weight (gr/cm³)
<i>PC</i>	2.382
<i>PC5C</i>	2.395
<i>PC7C</i>	2.435
<i>PCSP</i>	2.426
<i>PC5CSP</i>	2.390
<i>PC7CSP</i>	2.398
<i>PC20M</i>	2.362
<i>PC30M</i>	2.301
<i>PC20MSP</i>	2.363
<i>PC30MSP</i>	2.306
<i>PC5C20M</i>	2.384
<i>PC5C20MSP</i>	2.298

4.2.4 Water Absorption

The water absorption test results are given in the Table 14 the values of absorption are provided as a percentile change between dry weight and wet weight. Taking in consideration the PC water absorption value of 6.525% as a reference, PC5C20M and PC5C20MSP are showing result close to each other, 5.692% and 5.505%, or approximately 14% less than PC.

The least value belongs to PC30MSP which is 3.147% or 51.7% lower than PC. The highest water absorption value shown by PC7C mix, which is 7.894% or 21% more than PC.

Table 4.5. Water absorption test results (%)

Name	Water Abs. (%)
<i>PC</i>	6.525
<i>PC5C</i>	7.504
<i>PC7C</i>	7.894
<i>PCSP</i>	5.167
<i>PC5CSP</i>	5.703
<i>PC7CSP</i>	5.257
<i>PC20M</i>	6.231
<i>PC30M</i>	5.849
<i>PC20MSP</i>	4.949
<i>PC30MSP</i>	3.417
<i>PC5C20M</i>	5.692
<i>PC5C20MSP</i>	5.505

4.2.5 Porosity

Porosity results are given in percent, it represents ratio between dry weight, wet weight and Archimedes weight. In the Table 15, porosity test results are showing us that results of PC5C20M and PC5C20MSP are close to each other, but still less than PC value on 14.5%. Reference value is 13.454%.

The most porous batch is PC7C with value of 16.121% or around 20% more than value of the reference batch. The least porous material is PC30MSP with 7.304% porosity which is 45.7% less than PC porosity result.

Table 4.6. Porosity test results (%)

Name	Porosity (%)
<i>PC</i>	13.454
<i>PC5C</i>	15.236
<i>PC7C</i>	16.121
<i>PCSP</i>	11.140
<i>PC5CSP</i>	11.994
<i>PC7CSP</i>	11.194
<i>PC20M</i>	12.828
<i>PC30M</i>	11.864
<i>PC20MSP</i>	10.470
<i>PC30MSP</i>	7.304
<i>PC5C20M</i>	11.949
<i>PC5C20MSP</i>	11.230

4.3 Effect of Water/Cement Ratio

In order to estimate required amount of water, experimental batches were prepared. In those batches water/cement ratio was changing within 0.4-0.6 margins. It has been noticed that with decrease of water the mix is getting more sound. Although, some mixes were too stiff for mixing and compaction, in these cases water ratio has been increased. In this work, three types of water-to-cement ratios were used:

- High (0.6);
- Normal (0.5);
- Low (0.4).

High water/cement ratio takes place in PC30M mix only, it equals to 0.6 or 270 grams. On the preliminary test, 0.5 or 225 gram of water was not sufficient to provide good mixing and compaction. Normal water/cement ratio takes place in PC, PC5C, PC7C, PC20M, PC20MSP, PC30MSP, PC5C20M and PC5C20MSP. Fresh properties of these mixes were within acceptable margins.

Low water/cement ratio used for PCSP, PC5CSP and PC7CSP mixes due to extreme fluidity in case of 0.5 or 225 gram of water applied.



CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

1. Flow table test results show decrease in fresh mortar workability of the mixes containing 5% and 7% of colemanite waste only. Addition of TS 14 improves workability characteristic of these mixes;
2. Mixes containing 20% and 30% of metakaolin only, show low workability characteristics, addition of super plasticizer fixed this problem;
3. Addition of colemanite only retarding the setting time of the mortar, in case of 7% substitution only setting time has been extended on 215%. Furthermore, addition of 1% TS 14 prolonged setting time to 16 hours;
4. Metakaolin facilitates early hardening, but it strongly depends on water/cement ratio. Addition of 1% TS 14 doubled setting time of PC5C20MSP to 522 min;
5. Addition of colemanite only, reduces compressive and flexural strength of the mortar;
6. Use of 20% of metakaolin only, helps mortar to gain strength close to reference. In case of super plasticizer applied, both compressive and flexural strength improving significantly;
7. Addition of Polydos TS 14 to the mixes containing colemanite improved both strength exceeding the reference characteristics;
8. PC5C20M and PC5C20MSP both demonstrated high strength at 28th day of curing and especially on the long curing perspective;
9. Flexural strength of the tested batches resembles compressive strength in terms of gaining and losing strength;
10. Increase in colemanite amount leads to proportional increase in unit weight, porosity and water absorption characteristics;

11. Use of Polydos TS 14 decreases porosity value of the hardened mixes. This happens due to increase of workability of the fresh mortar;
12. Water absorption is decreases with introduction of super plasticizer;
13. PC5C20MSP demonstrated results very close to Ordinary Portland cement results. Only notable difference is extended setting time from 177.5 min to 522.5 min. The rest of the results are either equal or showing even better performance.

5.2 Recommendations

1. According to the results obtained from compressive and flexural strength colemanite shall not be used in the mortar only. If included, then chemical like TS 14 shall be applied too;
2. Super plasticizer amount shall not exceed 1% out of the binder mass, in order to provide mix with reasonable setting time;
3. Metakaolin amount shall not exceed 30%, if it is, then water/cement ratio need to be increased too;
4. Raw materials from different sources may behave and react different, so this study shall not be referenced is an ultimate;
5. Due to the large gap in metakaolin amount, further study need to carried out in order to assess metakaolin effect in more detail;
6. Additional study may be carried out in order to include experiments that have not taken place in this study (freeze-thawing, sulphate and acid attack, alkali silica reaction tests, hydration heat measurement).

REFERENCES

-
- [1] Kula, I., Olgun, A., Erdogan, and Y., Sevinc, V. (2000), "Effects of Colemanite Waste, Cool Bottom Ash, and Fly Ash on the Properties of Cement", *Cement and Concrete Research*, 31:491-494.
- [2] Sevim, U.K. (2003), "Afşin-Elbistan Termik Santrali Uçucu Külünün Beton ve Çimento Katkısı Olarak Kullanılabilirliğinin Çimento Hamuru ve Harçların Üzerinde Yapılan Deneylerle Araştırılması", (Doktora Tezi) Çukurova Üniversitesi, Adana.
- [3] Özturan, T. (1991), "Beton Üretiminde Uçucu Kül Kullanımının İrdelenmesi. Türkiye İnşaat Mühendisliği XI. Teknik Kongresi Bildiriler Kitabı", *TBMMO İnşaat Mühendisleri Odası*, 5:149-158.
- [4] Özdemir, M. and Öztürk, N.U., (2003), "Utilization of Clay Wastes Containing Boron as Cement Additives", *Cement & Concrete Research*, 33:1659-1661.
- [5] Gencel, O., Brostow, W., Ozel, C. and Filiz, M. (2010), "An Investigation on the Concrete Properties Containing Colemanite", *International Journal of Physical Science*, 5(3):216-225.
- [6] Erdoğan, Y., Zeybek, M.S. and Demirbaş, A. (1998), "Cement Mixes Containing Colemanite from Concentrator Wastes", *Cement & Concrete Research*, 28(4):605-609.
- [7] Targan, Ş., Olgun, A. Erdoğan, Y. and Sevinç, V. (2002), "Influence of Natural Pozzolan, Colemanite Ore Waste, Bottom Ash, and Fly Ash on the Properties of Portland Cement", *Cement & Concrete Research*, 33:1175-1182.
- [8] Erdogmus, E., Erdogan, Gencel, O., Targan, S. and Avciata, U., (2012), "Influence of Colemanite Admixture on Portland Cement Durability", *Advances in Cement Research*, 24(3):155-164.
- [9] Brooks, J.J., Johari, M.A.M., and Mazloom, M. (2000), "Effect of Admixtures on the Setting Times of High-Strength Concrete", *Cement and Concrete Composites*, 22(4):293-301.
- [10] Moulin, E., Blanc, P. and Sorrentino, D. (2001), "Influence of Key Cement Chemical Parameters on the Properties of Metakaolin Blended Cements", *Cement and Concrete Composites*, 23(6):463-469.

- [11] Subaşı, A. and Emiroğlu, M. (2015), “Effect of Metakaolin Substitution on Physical, Mechanical and Hydration Process of White Portland Cement”, *Construction and Building Materials*, 95:257–268.
- [12] Mitrovic, A. and Nikolic, D. (2012), “Properties of Portland-Composite Cements with Metakaolin: Commercial and Manufactured by Thermal Activation of Serbian Kaolin Clay” *MATEC Web of Conferences*, 2:1-7.
- [13] Batis, G., Pantazopoulou, P., Tsivilis, S. and Badogiannis, E., (2005), “The effect of metakaolin on the corrosion behavior of cement mortars”, *Cement & Concrete Composites*, 27:125–130.
- [14] Mardani-Aghabaglou, A., Gözde Sezer I. and Ramyar, K. (2014), “Comparison of Fly Ash, Silica Fume and Metakaolin from Mechanical Properties and Durability Performance of Mortar Mixtures View Point”, *Construction and Building Materials*, 70:17-25.
- [15] Sevim, U. and Tümen, Y. (2013), “Strength and Fresh Properties of Borogypsum Concrete”, *Construction and Building Materials*, 48:342–347.
- [16] Sevinç, A., Durgun, M. and Eken, M. A. (2017), “Taguchi Approach for Investigating the Engineering Properties of Concretes Incorporating Batite, Colemanite, Basaltic Pumice and Grounf Blast Funace Slag”, *Construction and Building Materials*, 135:343–351.
- [17] Mutuk, T. and Mesci, B. (2014), “Analysis of Mechanical Properties of Cement Containing Boron Waste and Rice Husk Ash Using Full Factorial Design”, *Journal of Cleaner Production*, 69:128-132.
- [18] ASTM C807-13, “Standard Test Method for Time of Setting of Hydraulic Cement Mortar by Modified Vicat Needle”.
- [19] Erdoğan, Y., Genc, H. and Demirbas, A. (1992), “Utilization of Borogypsum for Cement”, *Cement & Concrete Research*, 22:841–844.
- [20] ASTM C 618, “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete”.
- [21] Erdoğan, T. and Erdogan, E. (2014), “Basic Materials of Construction”, METU Press, 4:346.
- [22] ASTM C311, “Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete”.
- [23] TS 25, “Natural Pozzolan (Trass) for Use in Cement and Concrete - Definitions, Requirements and Conformity Criteria”.
- [24] Badogiannis, E., Kakali, G., Dimopoulou, G., Chaniotakis, E. and Tsivilis, S. (2005), “Metakaolin as a Main Cement Constituent: Exploitation of Poor Greek Kaolins”, *Cement & Concrete Composites*, 27(2):197–203.
- [25] Mitrovic, A., F. (2005), Bor. Ulusal Bor Araştırma Enstitüsü, Ankara BAÜ Fen Bil. Enst. Derg., Ankara.
- [26] BS EN 196-1, “Determination of Strength”.

CURRICULUM VITAE

PERSONAL INFORMATION

Name Surname : Mikhail MUSHUROV
Date of birth and place : 05.10.1992 Russian Federation, Sochi
Foreign Languages : English, Turkish
E-mail : mushurov.m.s@gmail.com

EDUCATION

Degree	Department	University	Date of Graduation
Master			
Undergraduate	Civil Engineering	Voronezh State University of Architecture and Civil Engineering	2015
Undergraduate	Foreign Languages	Voronezh State University of Architecture and Civil Engineering	2015

WORK EXPERIENCE

Year	Corporation/Institute	Enrollment
2017	Ltd. "Nika Proje"	Planning Engineer
2013	Ltd. "Firma ViS"	Civil Engineer

PUBLISHERMENTS

Papers

1. **Mushurov M.**, Canpolat O., Uysal M., Al-Mashhadani M.M., Aygörmez Y., "Investigation of Waste Products of Boron and Metakaolin Utilizes", Journal of Sustainable Construction Materials and Technologies, vol.3, pp.212-220, 2018. (DOI: 10.29187/jscmt.2018.22)

