

**B. M. MÖREL**

**INVESTIGATION OF THE EFFECTS OF TEMPERATURE ON PHYSICAL  
AND MECHANICAL PROPERTIES OF MONOLITHIC REFRACTORY  
MADE WITH POZZOLANIC MATERIALS**

**BAYRAM MURAT MÖREL**

**METU**

**2005**

**OCTOBER 2005**

**INVESTIGATION OF THE EFFECTS OF TEMPERATURE ON PHYSICAL  
AND MECHANICAL PROPERTIES OF MONOLITHIC REFRACTORY  
MADE WITH POZZOLANIC MATERIALS**

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

**BY**

**BAYRAM MURAT MÖREL**

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

**OCTOBER 2005**

Approval of the Graduate School of Natural and Applied Sciences

---

Prof. Dr. Canan Özgen  
Director

I certify that thesis satisfies all the requirements as a thesis for the degree of Master of Science

---

Prof. Dr. Erdal Çokça  
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science

---

Prof. Dr. Ali Kalkanlı  
Co-Supervisor

---

Assoc. Prof. Dr. Lutfullah Turanlı  
Supervisor

Examining Committee Members

Prof. Dr. Mustafa Tokyay (METU, CE) \_\_\_\_\_

Assoc. Prof. Dr. Lutfullah Turanlı (METU, CE) \_\_\_\_\_

Prof. Dr. Ali Kalkanlı (METU, METE) \_\_\_\_\_

Prof. Dr. Abdullah Öztürk (METU, METE) \_\_\_\_\_

Prof. Asım Yeğınobalı (TÇMB) \_\_\_\_\_

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

Name, Last name:

Signature :

## **ABSTRACT**

### **INVESTIGATION OF THE EFFECTS OF TEMPERATURE ON PHYSICAL AND MECHANICAL PROPERTIES OF MONOLITHIC REFRACTORY MADE WITH POZZOLANIC MATERIALS**

MÖREL, B. Murat

M.S., Department of Civil Engineering

Supervisor: Assoc. Prof. Dr. Lutfullah Turanlı

Co-supervisor: Prof. Dr. Ali Kalkanlı

October 2005, 108 pages

In recent years, scientific studies are carried out to find new refractory material. Having good mechanical properties under very high temperatures, refractories are widely used in industries like iron, steel, glass, cement and pottery. Researches are focused on monolithic refractory making because of their superior properties comparing to conventional firebrick refractories. Providing a mono-block body, having no joints makes the monolithic refractories more durable at elevated temperatures. Easier production and installation are two main points that people are choosing monolithic refractories, thus an economy is made.

In this study, for monolithic refractory production, high alumina cement was used as binding material. It is known that the increase in alumina ( $\text{Al}_2\text{O}_3$ ) content increases the high temperature resistance, so that crushed firebrick, having 85%  $\text{Al}_2\text{O}_3$  was used as aggregate. Pozzolan materials, which are silica fume, fly ash, ground granulated firebrick and ground granulated blast furnace slag, were added to improve physical and mechanical properties of mortar. With the addition of steel fibres, change in compressive strength and flexural strength was observed.

Superplasticizer was used to understand its behaviour under high temperatures. Portland cement containing mortars were also prepared to make comparison with high alumina cement containing specimens.

Specimens were prepared in 5x5x5 cm and 4x4x16 cm prisms. They were cured for one day at curing room, then heated to 105°C and then heated to 1100°C. Weight, size and ultrasound velocity change, compressive strength and flexural strength tests were done to determine physical and mechanical properties of the monolithic refractories, before and after heating. Heated and non-heated specimens were pulverized for microstructural investigation with X-Ray diffraction (XRD) method.

Using high alumina cement with 50 – 60 % granulated blast furnace slag or granulated firebrick, by the weight of cement, and crushed firebrick as aggregate, a satisfactory monolithic refractory material was made. It was observed that, mechanical properties were decreased at the Portland cement used mortars after several times of heating and cooling cycles. Also, it was determined that the microstructure of the high alumina cement containing mortars did not deteriorate much at 1100°C, as long as there was no change observed from the results.

Key word: High Alumina Cement (HAC), Ground Granulated Firebrick, Silica Fume, Fly Ash, Ground Granulated Blast Furnace Slag, Steel Fibre, Monolithic Refractory

## ÖZ

### **PUZOLANİK MALZEMELERLE YAPILMIŞ MONOLİTİK REFRAKTERLERİN SICAKLIK ETKİSİNDE FİZİKSEL VE MEKANİK ÖZELLİKLERİNİN İNCELENMESİ**

MÖREL, B. Murat

Yüksek Lisans Tezi, İnşaat Müh. Bölümü

Tez Yöneticisi: Doç. Dr. Lutfullah Turanlı

Yardımcı Tez Yöneticisi: Prof. Dr. Ali Kalkanlı

Ekim 2005, 108 Sayfa

Son yıllarda yeni refrakter malzemeler bulmak için bilimsel araştırmalar yapılmaktadır. Yüksek sıcaklık altında iyi mekanik özelliklere sahip refrakterler, demir çelik, cam, çimento ve seramik endüstrilerinde geniş kullanım alanı bulmaktadır. Monolitik refrakterlerin geleneksel ısı tuğlalarına karşı üstün özelliklerinden dolayı, araştırmalar monolitik refrakterler üzerine odaklanmıştır. Bağlantı noktaları olmayan tek vucut bir sistem sunduğu için, monolitik refrakterler yüksek sıcaklıklara daha dayanıklıdır. Kolay üretimi ve uygulanması, ekonomik yönden de monolitik refrakterleri tercih sebebi yapmıştır.

Bu çalışmada yüksek alüminalı çimento, monolitik refrakter yapımında bağlayıcı madde olarak kullanılmıştır. Alümina ( $Al_2O_3$ ) miktarındaki artışın, yüksek sıcaklığa dayanıklılığı arttırdığı bilinmektedir. Bu yüzden %85 alüminaya sahip ateş tuğlası kırığı agrega olarak kullanılmıştır. Pozolanik malzemeler (silis dumanı, uçucu kül, öğütölmüş ısı tuğlası, öğütölmüş yüksek fırın cürufu) harcın fiziksel ve mekanik özelliklerini iyileştirmek için eklenmiştir. Çelik fiberler, yüksek sıcaklık

altında basınç ve çekme dayanımları değişimini gözlemlemek için eklenmiştir. Süper akışkanlaştırıcı, yüksek sıcaklık altındaki davranışını anlamak için kullanılmıştır. Yüksek alüminalı çimento içeren harçlar ile karşılaştırmak için Portland Çimentosu ihtiva eden harçlar da hazırlanmıştır.

Numuneler 5x5x5 cm ve 4x4x16cm prizmalar halinde hazırlanmıştır. Bir gün boyunca kür odasında kür edildikten sonra 105°C'ye ısıtılmışlar, sonrasında da 1100°C'ye ısıtılarak deneylere hazır hale getirilmişlerdir. Sırasıyla ağırlık, boyut ve ultrason değişimi testleri ile basınç ve çekme dayanımı testleri fiziksel ve mekanik özellikleri belirlemek için ısıtılmadan önce ve sonra yapılmıştır. Isıtılmış ve ısıtılmamış numuneler öğütülerek iç yapı değişimlerini incelemek üzere X-Ray testine (XRD) tabi tutulmuştur.

Yüksek alüminalı çimento ile %50 – 60 öğütülmüş yüksek fırın cürufu veya öğütülmüş ateş tuğlasının ısı tuğlası kırığı ile birlikte kullanımı yeterli düzeyde bir refrakter malzeme yapılmasına olanak vermiştir. Portland Çimentosu ihtiva eden numunelerde, devam eden ısıtma soğutma döngüleri sonrasında mekanik özelliklerde düşüş görülmüştür. Ayrıca X-Ray verileri neticesinde, yüksek alüminalı çimento içeren numunelerin 1100°C'ye ısıtıldıktan sonra iç yapılarında belirgin değişimler tespit edilmemiştir.

Anahtar kelimeler: Yüksek Alüminalı Çimento, Öğütülmüş Ateş Tuğlası, Silis Dumanı, Uçucu Kül, Öğütülmüş Yüksek Fırın Cürufu, Çelik Fiber, Monolitik Refrakter



## **ACKNOWLEDGEMENTS**

I would like to express my sincere appreciation to Assoc. Prof. Dr. Lutfullah Turanlı and Prof. Dr. Ali Kalkanlı for their suggestions, perfect assistance guidance and support for the success of this study.

I am thankful to Burak Uzal for his help and comments especially for microstructural investigations.

Thanks are extended to the staff of the Civil Engineering and Metallurgy Engineering Laboratory; Harun Koralay, Ali Yıldırım, Salih Yüce for their help during the experiments. Also I am thankful to my friends Bora Kurt, Burak Dursun, Gökalp Memiş for motivating me during this thesis.

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

## TABLE OF CONTENTS

PLAGIARISM .....	iii
ABSTRACT .....	iv
ÖZ .....	vi
ACKNOWLEDGEMENTS .....	viii
TABLE OF CONTENTS .....	ix
LIST OF TABLES .....	xii
LIST OF FIGURES .....	xiv

## CHAPTERS

1. INTRODUCTION .....	1
1.1. General .....	1
1.2. Objective and Scope .....	3
2. THEORETICAL CONSIDERATIONS .....	5
2.1. High Alumina Cement .....	5
2.1.1. History of Alumina Cement .....	5
2.1.2. Chemical Composition of High Alumina Cement .....	5
2.1.3. Compound Constitution of Commercial High Alumina Cements .....	7
2.1.3.1. The Aluminates and Silicates .....	7
2.1.3.1.a. $C_{12}A_7$ .....	7
2.1.3.1.b. CA .....	7
2.1.3.1.c. $CA_2$ .....	8
2.1.3.1.d. $\beta C_2S_2$ .....	8
2.1.3.1.e. $C_2AS$ (Gehlenite) .....	8
2.1.3.2. The Compounds Containing Iron .....	8
2.1.3.3. The Minor Constituents .....	9

2.1.4. Hydration of High Alumina Cement .....	10
2.1.4.1. Effect of Temperature on Hydration of HAC .....	12
2.1.4.2. Effect of Temperature on Hydrated HAC .....	13
2.2. Portland Cement .....	12
2.2.1. Chemical Composition of Portland Cement .....	13
2.2.2. Compound Constitution of Portland Cement .....	14
2.2.3. Hydration of Portland Cement .....	15
 3. REVIEW OF RESEARCH ON REFRACTORY MORTARS AND CONCRETE .....	 17
3.1. General .....	17
3.2. Use of Alumina in Refractory Mortars and Concretes .....	18
3.3. Use of High Alumina Cement as a Binder in Refractory Mortars and Concretes .....	18
3.3.1. Firing of HAC bonded Refractory Mortar and Concrete .....	20
3.4. Use of Portland Cement as a Binder in Refractory Mortars and Concretes ...	20
3.5. Use of Firebrick as Aggregate in Refractory Mortar and Concretes .....	21
3.5.1. The Grading of the Aggregate .....	25
3.5.2. Cement Content When Determining Aggregate Amount .....	26
3.6. Use of Pozzolans in Refractory Mortar and Concrete .....	29
 4. EXPERIMENTAL STUDY .....	 32
4.1. Experimental Program .....	32
4.2. Materials .....	37
4.2.1. High Alumina Cement and Portland Cement .....	37
4.2.2. Aggregate .....	38
4.2.3. Water .....	40
4.2.4. Pozzolans .....	40
4.2.5. Steel Fibre .....	41
4.2.6. Water Reducer Admixture – Superplasticizer .....	41
4.3. Investigation Methods .....	42

4.3.1. Firing Rate of the Specimens .....	42
4.3.2. Determination of Weight and Size Change of Specimens .....	43
4.3.3. Determination of Compressive Strength .....	44
4.3.4. Determination of Flexural Strength .....	44
4.3.5. Investigation of Change in Ultrasound Velocity .....	44
4.3.6. Microstructural Investigation of Specimens by X-Ray Diffraction (XRD) Method .....	45
4.4. Summary of Standards Used in Experiments .....	45
 5. TEST RESULTS AND DISCUSSIONS .....	 46
5.1. Setting Properties and Colour Change of Specimens .....	46
5.2. Weight Change in Specimens .....	53
5.3. Size Change in Specimens .....	60
5.4. Compressive Strength Test Results .....	63
5.5. Flexural Strength Test Results .....	70
5.6. Ultrasound Velocity Test Results .....	77
5.7. Investigation of Internal Structure by X-Ray Diffraction (XRD) Method ....	83
 6. CONCLUSIONS .....	 100
 7. RECOMMENDATIONS .....	 103
 REFERENCES .....	 104

## LIST OF TABLES

### TABLE

2.1 Chemical Composition of High Alumina Cement .....	6
2.2 Abbreviations for the Oxide Compositions of High Alumina Cement .....	6
2.3 Typical Mineralogical Phase Assemblages in HAC .....	11
2.4 Effect of Temperature on Hydration Reaction Products of HAC and Their Properties .....	12
2.5 Chemical Composition of Ordinary Portland Cement .....	14
2.6 Major Constituents of Portland Cement .....	14
2.7 Characteristics Hydration of the Portland Cement Compounds .....	15
3.1 Summary of HAC Used in Refractory Mortars and Concretes .....	19
3.2 Maximum Service Temperature of Generally Used Aggregates .....	22
3.3 Service Temperature Limits of Various HAC Mortars .....	24
4.1 Mortars Prepared in the Study with Their Designations .....	33
4.2 Abbreviations Used for Specimen Groups .....	35
4.3 Summary of Specimen Groups Including which Specimen Type .....	35
4.4 Mix Proportions for 1m <sup>3</sup> Mortar .....	36
4.5 Physical and Chemical Characteristics of HAC and Portland Cement .....	38
4.6 The Chemical Composition and Some Physical Properties of BS. 85P Firebrick .....	39
4.7 Gradation of the Crushed Firebrick Aggregate .....	39
4.8 Water Absorption Rate of the Crushed Firebrick Aggregate .....	39
4.9 Physical and Chemical Properties of Pozzolans Used in the Study .....	41
4.10 Technical Data of Viscocrete-3075 .....	42
4.11 Summary of Standards Used in Experiments .....	45
5.1 Weight Change of the Specimen Group FO .....	54
5.2 Weight Change of the Specimen Group C .....	55

5.3 Size Change of the Specimen Group FO .....	61
5.4 Size Change of the Specimen Group C .....	62
5.5 Compressive Strength Values of the Specimens .....	65
5.6 Flexural Strength Values of the Specimens .....	72
5.7 Ultrasound Velocity of the Specimen Group FO .....	78
5.8 Ultrasound Velocity of the Specimen Group C .....	79
5.9 Amounts of Compounds Forming the Materials .....	84
5.10 d-spacing Values of Firebrick .....	87
5.11 d-spacing Values of HAC .....	88
5.12 d-spacing Values of I – 7D.....	90
5.13 d-spacing Values of II – 7D .....	91
5.14 d-spacing Values of III – 7D.....	92
5.15 d-spacing Values of IV – 7D.....	93
5.16 d-spacing Values of V – 7D.....	94
5.17 d-spacing Values of I – FO .....	95
5.18 d-spacing Values of II – FO.....	96
5.19 d-spacing Values of III – FO.....	97
5.20 d-spacing Values of IV – FO .....	98
5.21 d-spacing Values of V – FO.....	99

## LIST OF FIGURES

### FIGURE

3.1 Effect of Cement Content and of Type of Aggregate on the Refractoriness of Castable Mixes .....	26
3.2 Effect of Cement Content on the Refractoriness and Strength of a Castable Mix .....	27
3.3 Strengths of HAC – Crushed Firebrick Concretes after 24hr. at 22°C and 110°C, 4 months at 300°C and 600°C, 5 hours at all Higher Temperatures .....	28
3.4 Linear changes occurring on heating Neat Hydrated HAC or Refractory Concrete for the first time .....	29
4.1 Ball-In-Hand Test .....	40
4.2 Firing Rate of the Specimen .....	43
5.1 Specimen IA before (left) and after (right) Heating to 1100°C .....	48
5.2 Specimen IB before (left) and after (right) Heating to 1100°C .....	48
5.3 Specimen IIA before (left) and after (right) Heating to 1100°C .....	49
5.4 Specimen IIB before (left) and after (right) Heating to 1100°C .....	49
5.5 Specimen IIIA before (left) and after (right) Heating to 1100°C .....	49
5.6 Specimen IIIB before (left) and after (right) Heating to 1100°C .....	50
5.7 Specimen IVA before (left) and after (right) Heating to 1100°C .....	50
5.8 Specimen IVB before (left) and after (right) Heating to 1100°C .....	50
5.9 Specimen VA before (left) and after (right) Heating to 1100°C .....	51
5.10 Specimen VB before (left) and after (right) Heating to 1100°C .....	51
5.11 Specimen VIA before (left) and after (right) Heating to 1100°C .....	51
5.12 Specimen VIB before (left) and after (right) Heating to 1100°C .....	52
5.13 Specimen VIIA before (left) and after (right) heating to 1100°C .....	53
5.14 Specimen VIIB before (left) and after (right) heating to 1100°C .....	53
5.15 Weight Change – Temperature Graph of Specimen Group I .....	56

5.16 Weight Change – Temperature Graph of Specimen Group II .....	56
5.17 Weight Change – Temperature Graph of Specimen Group III .....	57
5.18 Weight Change – Temperature Graph of Specimen Group IV .....	57
5.19 Weight Change – Temperature Graph of Specimen Group V .....	58
5.20 Weight Change – Temperature Graph of Specimen Group VI .....	58
5.21 Weight Change – Temperature Graph of Specimen Group VII .....	59
5.22 Weight Change – Temperature Graph of Specimen Group VIII .....	59
5.23 Compressive Strength Values of Specimen Group I .....	66
5.24 Compressive Strength Values of Specimen Group II .....	66
5.25 Compressive Strength Values of Specimen Group III .....	67
5.26 Compressive Strength Values of Specimen Group IV .....	67
5.27 Compressive Strength Values of Specimen Group V .....	68
5.28 Compressive Strength Values of Specimen Group VI .....	68
5.29 Compressive Strength Values of Specimen Group VII .....	69
5.30 Compressive Strength Values of Specimen Group VIII .....	69
5.31 Flexural Strength Values of Specimen Group I .....	73
5.32 Flexural Strength Values of Specimen Group II .....	73
5.33 Flexural Strength Values of Specimen Group III .....	74
5.34 Flexural Strength Values of Specimen Group IV .....	74
5.35 Flexural Strength Values of Specimen Group V .....	75
5.36 Flexural Strength Values of Specimen Group VI .....	75
5.37 Flexural Strength Values of Specimen Group VII .....	76
5.38 Flexural Strength Values of Specimen Group VIII .....	76
5.39 Ultrasound Velocity – Temperature Graph of Specimen Group I .....	80
5.40 Ultrasound Velocity – Temperature Graph of Specimen Group II .....	80
5.41 Ultrasound Velocity – Temperature Graph of Specimen Group III .....	81
5.42 Ultrasound Velocity – Temperature Graph of Specimen Group IV .....	81
5.43 Ultrasound Velocity – Temperature Graph of Specimen Group V .....	82
5.44 Ultrasound Velocity – Temperature Graph of Specimen Group VI .....	82
5.45 Ultrasound Velocity – Temperature Graph of Specimen Group VII .....	83
5.46 XRD Pattern of IA-FO .....	86



## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 General**

Refractories are kind of materials which can withstand elevated temperatures. Refractories are structural elements which also show acceptable mechanical properties under high temperatures. They are considered a unique industrial product used primarily in basic industries such as iron, steel, glass, cement and pottery.

During last two decades, a significant amount of attention has been paid to refractory ceramics. Especially researches on monolithic refractories still been continued. The word “monolithic” means a continuous body having no joints. The unique advantage of monolithic refractory is their continuous body. Without any joints, they provide a better structural integrity and can be installed with relative ease, requiring labours in less numbers and skill. [1]

Monolithic refractories differ from refractory bricks in that they are not shaped and fired before use, although the chemical and physical properties exhibit similar characteristics. Monolithic refractories do not need high energy for shaping and pre-firing. As a result it can be said that; manufacturing and delivery times are shorter, a significant amount of energy is saved, and complicated shapes can be easily made. Their linings are usually thinner than the corresponding brick structures, more durable because of the lack of joints, and finally monolithic refractories can be gunned, poured, troweled, rammed, patched or injected for the desired shape. [2, 3]

Alumina ( $\text{Al}_2\text{O}_3$ ) shows good performance on high temperatures. According to their alumina content, materials tend to resist high temperatures. In refractory production, if the binding material contains alumina, it will increase the heat resistance of the refractory material, and also monolithic refractories are expected to develop their strength in 24 hour time. For these reasons, high alumina cement (HAC) was chosen as a binding material in this study. High alumina cement is not generally used as a main structural material, and its primary purpose is a protective lining for brick, concrete and steel structures. [3]

Firebricks also contain high amounts of alumina because they are produced to withstand high temperatures. During the production process, crushed firebricks are obtained as a waste material. Having high amounts of alumina content and being a pre-fired material, Heikal stated that crushed firebricks can be used as aggregate for monolithic refractory making. [4]

Pozzolanic admixtures are used as admixtures in order to increase the mechanical properties and reduce the cement amount, so that it is possible to decrease production costs [5]. Fly ash, silica fume and blast furnace slag were used as pozzolans. As these pozzolans are pre-fired, they resist to high temperatures. Their fineness which decreases the permeability of the refractory material, increases the durability and strength [6].

Water reducer admixture (superplasticizer) and steel fibres were added to refractory mortar for examining their behaviour under extreme conditions like very high temperature.

There are various kinds of monolithic refractories which are mainly imported to Türkiye by different companies. High alumina cement, pozzolans and crushed firebrick are all domestic materials which are commercially available at the market. By using the different amounts of those materials, a satisfactory product can be made. Türkiye has vast underground sources that can be used as raw materials in

monolithic refractory making [7]. If it is succeeded, the cost of the product will be the 1/10 times of the similar imported products.

Monolithic refractories are environmental friendly products, because they can be recycled. Kabanov et al. [8] and Darmograi et al. [9] stated that refractory wastes can be granulated to 0 – 1 mm and can be used as aggregate. Their pre-fired property makes those waste materials durable to high temperatures.

## **1.2 Objective and Scope**

In this study main objective is to produce a monolithic refractory with domestic materials. By using high alumina cement, fly ash, silica fume, blast furnace slag and crushed firebrick, which are products of Turkiye, it is aimed to reduce production costs. However, in order to investigate the improvement in the mechanical properties of the refractory material, some export materials such as superplasticizer and steel fibres were added in small amounts.

In the experimental study high alumina cement was partially replaced by fly ash, silica fume, granulated blast furnace slag and granulated firebrick at various percentages by mass. Crushed firebrick was used for all of the specimens as aggregate. Steel fibres and superplasticizer were used only in the specimens that are heated to 1100°C.

The prepared mortar was moulded to 5x5x5 cm moulds for compressive strength, ultrasound velocity and weight change tests. 4x4x16 cm prism moulds were used for preparing specimens to flexural strength test and determining the size changes. Specimens were grouped into three. First part of the specimens was cured for 24 hours at 21°C in curing room. After one day curing, specimens were de-moulded and were put to furnace at 105°C for 24 hours in order to evaporate the free water for avoiding the formation of cracks while heating to 1100°C.

In next step, first part of the specimens was heated to 1100°C, and was left for one hour to stay at 1100°C. Then they were cooled to room temperature inside the furnace. After cooling, the tests were conducted

Second part of the specimens was cured as the way the first part of the specimens was. However, they were heated to 1100°C and cooled to room temperature for 10 times in order to understand heating cooling behaviour of the material in long run. Same non-destructive and destructive test were done to the second part of the specimens.

Third part of the specimens was cured for 7 days at 21°C in curing room, after de-moulding, and they were heated neither to 105°C nor to 1100°C. Again the same non-destructive and destructive tests were conducted to this part.

The microstructural investigation of the prepared mortars was done. Heated and non-heated specimens were pulverized for scanning them by using X-Ray Diffraction (XRD) method.

## **CHAPTER 2**

### **THEORETICAL CONSIDERATIONS**

#### **2.1 High Alumina Cement**

High alumina cement is obtained by fusing or sintering a mixture, in suitable proportions of aluminous and calcareous materials and grinding the resultant product to a fine powder [10].

##### **2.1.1 History of Alumina Cement**

In 1913, alumina cement was first produced according to a patent granted in France to Bied. This cement was giving in 24 hours, the strength reached by Portland cement after four weeks. It was completely resistant to many kinds of chemical attack to which Portland cement was known to fail sooner or later. In addition, it developed its optimum strength at a comparatively high water-cement ratio, thus giving a very workable concrete mix. These advantages were important enough to compensate for the higher price of this cement comparing to Portland cement. [11]

##### **2.1.2 Chemical Composition of High Alumina Cement**

High alumina cement is composed essentially of roughly equal proportions of alumina and lime, each usually within the range 36 – 42%, iron oxides up to 20% and a small percentage of silica of between 4 and 7 %. The iron oxides are present in both the ferrous and ferric states, the relative proportions depending on the extent to

which an oxidising atmosphere is maintained in the furnace during burning. Of the minor constituents, titania occurs to the extent of about 2 %, magnesia usually less than 2%, and sulphate less than 1%. The content of alkalies is less than in Portland cement. Insoluble matter may range around 2%. The cements usually show a gain on ignition owing to the oxidation of the ferrous oxide. [10] Table 2.1 shows the chemical composition of high alumina cement [1]

Table 2.1 Chemical Composition of High Alumina Cement [1]

<b>Chemical Components</b>	<b>Low Purity</b>	<b>Medium Purity</b>	<b>High Purity</b>
$\text{Al}_2\text{O}_3$	39 – 50 %	55 – 66 %	70 – 90 %
$\text{Fe}_2\text{O}_3$	7 – 16 %	1 – 3 %	0 – 0.4 %
$\text{CaO}$	35 – 42 %	26 – 36 %	9 – 28 %
$\text{SiO}_2$	4.5 – 9 %	3.5 – 6 %	0 – 0.3 %

In order to simplify the discussion of chemical compounds present in cements, the customary abbreviations will be used for the various oxides. Abbreviations are showed at the table 2.2 [12]

Table 2.2 Abbreviations for the Oxide Compositions of High Alumina Cement [12]

<b>Oxide</b>	<b>Abbreviation</b>	<b>Name</b>
$\text{CaO}$	C	Lime
$\text{Al}_2\text{O}_3$	A	Alumina
$\text{SiO}_2$	S	Silica
$\text{Fe}_2\text{O}_3$	F	Ferric Oxide
$\text{FeO}$	F	Ferrous Oxide
$\text{TiO}_2$	T	Titania
$\text{MgO}$	M	Magnesia
$\text{H}_2\text{O}$	H	Water

### **2.1.3 Compound Constitution of Commercial High Alumina Cements**

#### **2.1.3.1 The Aluminates and Silicates**

In those high alumina cements which have a relatively high  $\text{Al}_2\text{O}_3$  /  $\text{CaO}$  ratio, the calcium dialuminate ( $\text{CA}_2$ ) has been seen. A considerable portion of  $\text{CA}_2$  is present in certain of the special white high alumina cements used for high-duty refractory mortars or concretes. [12]

Accordingly, the aluminates and silicates which may be found in commercial HAC are  $\text{C}_{12}\text{A}_7$ ,  $\text{CA}$ ,  $\text{CA}_2$ ,  $\beta\text{C}_2\text{S}$ , and  $\text{C}_2\text{AS}$  [12].

##### **2.1.3.1.a $\text{C}_{12}\text{A}_7$**

This is usually found in small proportions in HAC. Other things remaining equal, the amount of  $\text{C}_{12}\text{A}_7$  in the cement rises when the  $\text{CaO}$  /  $\text{Al}_2\text{O}_3$  ratio is increased. This compound hydrates very rapidly, and if it is present in any substantial quantity, the cement tends to be quick-setting. There is also evidence that this effect is increased if the cement contains rather more alkali than usual. Consequently  $\text{C}_{12}\text{A}_7$  is not regarded as a very desirable constituent of HAC except in minor amounts. [12]

##### **2.1.3.1.b $\text{CA}$**

It is primarily responsible for the particular cementitious behaviour found in HAC. It is slow setting, particularly if rapidly cooled from the molten condition, but it subsequently hardens with great rapidity. It is believed that the maximum hydraulic activity at early ages is obtained by slowly cooling the molten cement composition in order to allow the fullest growth of  $\text{CA}$  crystals. If molten HAC compositions is entirely a glass, the resultant cement will hydrate and harden very slowly, but if kept under water, the ultimate strength appears to be normal. [12]

#### **2.1.3.1.c $CA_2$**

The pure compound reacts very slowly with water at room temperature, but hydration and strength development are accelerated by lime-water or solutions of high pH value. Once hydration of pure  $CA_2$  has started, the rate accordingly increases. [12]

#### **2.1.3.1.d $\beta C_2S_2$**

The dicalcium silicate is hydraulic but it hydrates relatively slowly, so that any contribution to concrete strength is not likely to be evident at very early ages. It has detected in HAC clinkers which contain not more than 5%  $SiO_2$ . [12]

#### **2.1.3.1.e $C_2AS$ (Gehlenite)**

In HAC of higher silica content, gehlenite appears as a regular constituent, often in considerable quantities. It has been shown that pure gehlenite reacts extremely slowly with water. However, it seems to have a greater hydraulic activity when present as a glass, and it will hydrate in lime-water. The presence of high proportions of gehlenite in HAC causes a reduction in the rapid hardening properties. It is for this reason that the silica content of HAC composition is kept low. [12]

### **2.1.3.2 The Compounds Containing Iron**

Most high alumina cements contain a relatively high proportion of iron oxides (up to 18%). 10%  $Fe_2O_3$  in HAC increases the hydraulic strength.  $Fe_2O_3$  (Ferric Oxide) forms calcium ferrite (CF) and dicalcium ferrite ( $C_2F$ ) and each may be present in HAC. [12]



### 2.1.3.3 The Minor Constituents

TiO<sub>2</sub> is always found in the cement in the amount of 1 – 3 %. It normally appears as calcium titanate, but it has also been suggested that, when the cement is rich in iron compounds, some of the titania may be combined as a calcium ferro-titanate. It has found that up to 4.5% TiO<sub>2</sub> has a beneficial effect on cement properties. [12]

Magnesia (MgO) is a constant component of HAC but the proportion is usually below 1%. It may replace ferrous iron in the composition of the pleochroic fibrous constituent, but unless the quantity of magnesia is abnormally high there is little evidence of spinel formation. [12]

The alkali content of ordinary HAC is much lower than that of Portland cement. It consists of both sodium (Na<sub>2</sub>O) and potassium (K<sub>2</sub>O) oxides, but in total they do not often exceed 0.3% (the corresponding figure for Portland cement is 0.5 – 1.3%). [12]

Total sulphur expressed as sulphuric anhydride (SO<sub>3</sub>) is usually not greatly in excess of 0.15% in the case of those high-alumina cements to which no addition of gypsum is made during grinding. HAC made by the blast-furnace method is relatively high in sulphur and may contain 0.5 – 1.0% sulphur as sulphide, together with an appreciable proportion of SO<sub>3</sub>.

The only other minor constituents of HAC consist of traces of compounds of manganese, phosphorus, derived from the raw materials, additives and the fuel used in the manufacture. [12]

#### 2.1.4 Hydration of High Alumina Cement

Constituents of the high alumina cement go into simultaneous and consecutive reactions with the presence of water. The setting and hardening of the cement is the result of these reactions. Hydration term is used for covering the all of these reactions. [10, 11, 12]

The terms “Hydration Products and Hydrates” are referred to the new solids formed after the hydration of the cement. The hydrates which may be produced by hydration of HAC include the metastable hexagonal compounds  $\text{CAH}_{10}$ ,  $\text{C}_2\text{AH}_8$ ,  $\text{C}_4\text{AH}_{13}$  and the stable cubic hydrate  $\text{C}_3\text{AH}_6$ . In presence of water, the rate of change of the metastable hydrates to the stable cubic hydrate is still very slow below  $25^\circ\text{C}$ , but it is accelerated by higher pH values. When HAC is hydrated in air, in the ordinary way, the presence of carbonato-aluminate ( $\text{C}_3\text{A}.\text{CaCO}_3.11\text{H}_2\text{O}$ ) must be expected and this compound can have an important influence on the characteristics of concrete and the mortar surfaces. [11]

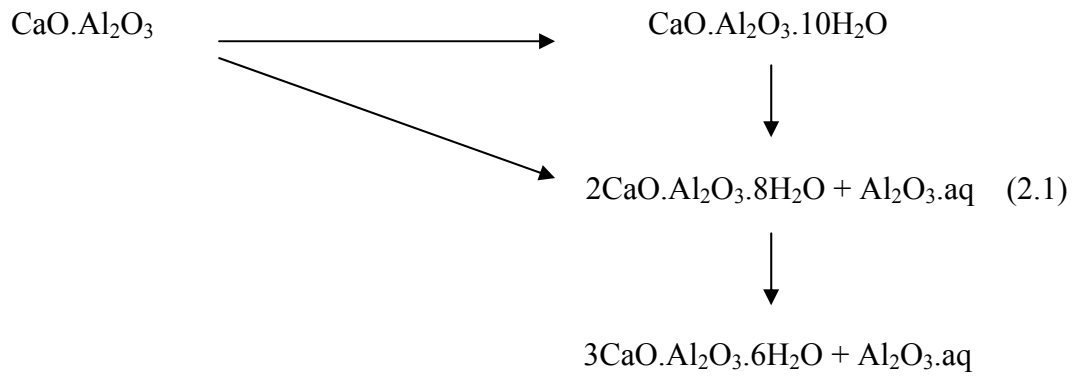
$\text{C}_2\text{S}$  will hydrate in the same way as it does in Portland cement, but any calcium hydroxide simultaneously liberated will, in this case, react with alumina gel, and residual “free lime” is not found in hardened HAC.  $\text{C}_2\text{AS}$  hydrates slowly especially when the compound occurs as a glass. Iron hydroxide gel, a rising by hydration of the iron compounds, may coat the calcium aluminate crystals and thus modify the rate of their hydration. [4]

Table 2.3 shows the mineralogical phase assemblages. [1]

Table 2.3 Typical Mineralogical Phase Assemblages in HAC [1]

Relative hydration rate	Low purity	Medium purity	High Purity
Fast	CA C <sub>12</sub> A <sub>7</sub> CA <sub>2</sub> C	CA C <sub>12</sub> A <sub>7</sub> CA <sub>2</sub> C	CA C <sub>12</sub> A <sub>7</sub> CA <sub>2</sub>
Slow	C <sub>2</sub> S C <sub>4</sub> AF C <sub>2</sub> AS	C <sub>2</sub> S C <sub>4</sub> AF C <sub>2</sub> AS	
Non-hydrating	CT A	CT A	A

The main hydration reaction in high alumina cement pastes is formulated at equation 2.1. [10]



#### 2.1.4.1 Effect of Temperature on Hydration of HAC

Temperature effect is the most important aspect on the hydration of HAC. HAC-bonded cement mortars can run into severe problems if the installation and curing temperature is below 21°C. Both  $\text{CAH}_{10}$  and  $\text{AH}_3$  (gel) are formed around this temperature. During heating, the gel prohibits the removal of steam due to the low permeability. Also, during heating, the  $\text{CAH}_{10}$  changes into  $\text{C}_2\text{AH}_8$  with significant volume change. A combination of these two factors causes problems during drying, which may result in explosive spalling and cracking of installed lining. [1]

The effect of casting and curing temperature of high alumina cement bonded mortars are shown at Table 2.4. [1]

Table 2.4 Effect of Temperature on Hydration Reaction Products of HAC and Their Properties [1]

Curing Temp. °C	Hydration Products of CA Phase	Physical Properties
		Density g/cm <sup>3</sup>
<21	$\text{CAH}_{10} + \text{AH}_3$ (gel)	1.72
21 – 35	$\text{C}_2\text{AH}_8 + \text{AH}_3$ (gel)	1.95 - 2.42
>45	$\text{C}_3\text{AH}_6 + \text{AH}_3$ (crystalline)	2.52 - 2.42

#### **2.1.4.2 Effect of Temperature on Hydrated HAC**

High alumina cement cured at high temperatures has a much reduced strength. This is related with the change in the nature of the hydration products. The compounds  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$  and  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$  produced at ordinary temperatures are metastable, and on prolonged ageing tend to change into the cubic compound  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ . At ordinary temperatures this change is very slow and may never occur in mortars kept dry, but it must be expected to occur, even though very slowly, in wet concretes. At high temperatures it occurs rapidly. [10]

### **2.2 Portland Cement**

Portland cement is produced by pulverizing clinker which is produced by burning the mixture of limestone and clayey raw materials with small amounts of gypsum. When combined with water, Portland cement shows hydraulic binding properties. [13]

The term “Hydraulic Binder” refers to a powder material that can gain strength underwater without being soluble.

The name Portland comes from an island named Portland in Britain. The building materials obtained from that island have similar properties with cement produced by limestone and clayey materials. In 1824 an English mason named this cement “Portland Cement”. Since that year the name remains same, although its properties have changed by the passing years. [13]

#### **2.2.1 Chemical Composition of Portland Cement**

Portland cement has four main oxides. These are lime ( $\text{CaO}$ ), silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and iron oxide ( $\text{Fe}_2\text{O}_3$ ). At Table 2.5 major and minor constituents of ordinary Portland cement is given. [13, 14]

Table 2.5 Chemical Composition of Ordinary Portland Cement [14]

Oxide	Abbreviation	Name	Weight %
CaO	C	Lime	60 – 67
SiO <sub>2</sub>	S	Silica	17 – 25
Al <sub>2</sub> O <sub>3</sub>	A	Alumina	3 – 8
Fe <sub>2</sub> O <sub>3</sub>	F	Ferric Oxide	0.5 – 6
MgO	M	Magnesia	0.1 – 4
K <sub>2</sub> O + Na <sub>2</sub> O	K + N	Alkalies	0.2 – 1.3
SO <sub>3</sub>	S*	Sulfurtrioxide	1 – 3
CO <sub>2</sub>	C*	Carbon dioxide	-
H <sub>2</sub> O	H	Water	-

### 2.2.2 Compound Constitution of Portland Cement

There are four major constituents in Portland cement clinker. These are given at Table 2.6 [10].

Table 2.6 Major Constituents of Portland Cement [14]

Name	Composition	Symbol	Mineral Name
Tricalcium silicate	3CaO.SiO <sub>2</sub>	C <sub>3</sub> S	Alite
Dicalcium silicate	2CaO.SiO <sub>2</sub>	C <sub>2</sub> S	Belite
Tricalcium aluminate	3CaO.Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A	
Tetracalcium aluminate	4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	C <sub>4</sub> AF	Celite

The compound C<sub>3</sub>S and C<sub>2</sub>S are responsible of the main strength gain in cement paste, as they have calcium silicate in their inner structures. However C<sub>3</sub>A and C<sub>4</sub>AF have small role in strength gain of Portland cement comparing to C<sub>3</sub>S and C<sub>2</sub>S.

### 2.2.3 Hydration of Portland Cement

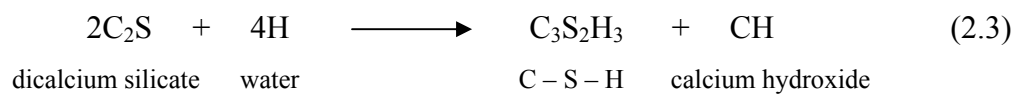
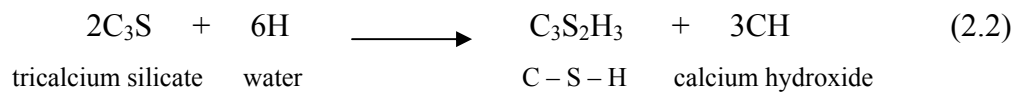
Portland cement is composed of a number of compounds, the reaction of which with water leads to the setting and hardening of the cement. These reactions all together are called hydration of Portland cement. [1]

The constituent Portland cement compounds undergo a series of chemical reactions when they are mixed with water. These reactions lead to form new solids which are responsible of the hardening of mortar or concrete. Hydration characteristics of the cement compounds are summarized at Table 2.7. [10, 14]

Table 2.7 Characteristics Hydration of the Portland Cement Compounds [14]

Compounds	Reaction Rate	Amount of Heat Liberated	Contribution to Cement	
			Strength	Heat Liberated
$C_3S$	Moderate	Moderate	High	High
$C_2S$	Slow	Low	Low initially	Low
$C_3A + CS^*H_2$	Fast	Very High	Low	Very High
$C_4AF + CS^*H_2$	Moderate	Moderate	Low	Moderate

The hydration reactions of the tricalcium silicate ( $C_3S$ ) with water (H) and dicalcium silicate ( $C_2S$ ) with water are shown in the Equation 2.2 and Equation 2.3 respectively. [13]



CH refers to calcium hydroxide ( $\text{CaO} \cdot \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$ ) according to cement chemistry.

Both  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  have same hydration products.  $\text{C}_3\text{S}_2\text{H}_3$  ( $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ) is called tobermorite which is also named as C – S – H (calcium – silica – hydrate) gel. The word “Gel” refers to group of colloidal solid materials. [13]

The amount of C – S – H gel in the hydrated Portland cement paste determines the strength, as it is the main hydration product of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ . [10]



## **CHAPTER 3**

### **REVIEW OF RESEARCH ON REFRACTORY MORTARS AND CONCRETE**

#### **3.1 General**

Refractory materials have been used since the old times where heat processing is involved. As technology improved, the need for better refractory materials has been increased. In the industries like glass, cement, steel and iron, temperatures above 1000°C are achieved. In order to resist those temperatures refractory materials are widely used.

Today, the usage of firebrick refractories have been started to replace by monolithic refractories. Because of their economy and ease of use, the applications of the monolithic refractories to the industry have been increased. In monolithic refractory, no shaping or firing is involved, so the manufacturing and delivery times are shorter, and fewer inventories are required by the user. It is easier to achieve desired complicated shapes. Monolithic refractories are more durable since building with bricks involves the use of mortars to join the bricks together, thus creating weak points in the structure. Monolithic refractories can be built around supports and may not need to be self-supporting in applications such as thick-brick arch linings. Monolithic linings are supported by fixed structures that operate as restraints against movement due to thermal changes. Thus, monolithic refractories provide longer durable linings. [3, 15, 16]

Norton and Banerjee stated that the alumina ( $\text{Al}_2\text{O}_3$ ) usage at the rate of 40% is suitable for exceeding 1000°C. However, not only the alumina content, but also

the other compounds forming the refractory material play an important role in high temperature usage, especially in the durability of the material above 1000°C. [12]

### **3.2 Use of Alumina in Refractory Mortars and Concretes**

According to Banerjee and Shubin, the majority of monolithic refractories are dominated by high alumina or alumina-silicate materials. As the alumina ( $\text{Al}_2\text{O}_3$ ) containing materials can withstand high temperatures, they are widely used as binders or aggregates. High alumina cement (HAC) is commercially available hydraulic binders. [1, 16]

### **3.3 Use of High Alumina Cement as a Binder in Refractory Mortars and Concretes**

A mortar or concrete which is high designed for to serve at high temperatures, must have adequate refractoriness, it must maintain sufficient mechanical strength after continuous heating or after frequent heating and cooling cycles. After all, the fired concrete must not deteriorate or lose strength when subsequently exposed to normal conditions like room temperature. [12]

High alumina cement (HAC) forms a strong bond between aggregates, and reaches high strength in the cold within 24 hours. Also, it has resistance to high temperatures, dilute acids and sulphates, which is characteristics of mortars or concretes made with this kind of cement. The drying shrinkage in air is comparable to that of ordinary concrete and the total shrinkage, after firing to the service temperature, is still very small and occurs without distortion of the concrete. [12]

According to Simonin et al. concretes made with high alumina cements can be brought up to temperature, and submitted to the working conditions in a furnace or kiln, as soon as they have hardened sufficiently. They do not require being pre-fired. Free water and water combined with the cement are driven off during the first

firing, and this process should be carried out at a reasonably slow rate. After the first firing, concrete is ready for thermal shocks. [12, 17]

As Taylor stated that, an increase in the alumina ( $\text{Al}_2\text{O}_3$ ) content in the high alumina cement (HAC), leads to more durable concretes to higher temperatures [18] In the studies of Robson, it is mentioned that how the refractoriness is changed by changing the percentage of calcium aluminate composition. A content of pure CA compound having 64.5% melts at  $1608^\circ\text{C}$ , calcium dialuminate ( $\text{CA}_2$ ) containing 78.5% has a fusion point of  $1770^\circ\text{C}$  [12]. However, obtaining those compounds is far from economic side, different compositions of alumina are used in the high alumina cements. A summary of types of HAC is given at Table 3.1 [18].

Table 3.1 Summary of HAC Used in Refractory Mortars and Concretes [18]

Type of HAC	Derivation	Colour of Cement	$\text{Al}_2\text{O}_3$ %	CaO %	$\text{SiO}_2$ %	$\text{Fe}_2\text{O}_3$ %	FeO %	MgO %	$\text{TiO}_2$ %
Ordinary grades of HAC	From red bauxite	Very dark	36.0	36.0	3.5	0.1	1.0	0.5	0.5
	a)by fusion b)by reductive fusion	grey to light grey	to 54.0	to 42.0	to 9.0	to 14.0	to 7.0	to 1.0	to 2.5
(Not Common)	From low-iron (white) bauxite	Very light grey	50.0	37.0	4.0	0.1	0.5	0.5	0.5
			to 55.0	to 39.0	to 6.0	to 6.0	to 4.0	to 1.0	to 1.0
Alumina-fortified HAC	Addition of $\text{Al}_2\text{O}_3$ to HAC made by reductive fusion	Grey - white	68.5	23.5	4.0	0.1	0.3	0.4	0.5
White HAC (72-80% $\text{Al}_2\text{O}_3$ )	From $\text{Al}_2\text{O}_3$ by sintering or fusion	(1) White	72-75	24-27	0.1	0.2	Tr.	0.25	Tr.
		(2)	79.0	18.0	0.1	0.3	Tr.	0.4	Tr.

### **3.3.1 Firing of HAC bonded Refractory Mortar and Concrete**

After the hydration of HAC, there may be quite large proportions of free water, and during the first firing of the concrete, the rate of temperature rise should be moderate.

“Some dehydration of the cement hydrates can occur at the same time as, or very shortly after, the elimination of free water, since the hexagonal hydrates lose part of their combined water below 100°C. The initial amount of water combined with aluminous cement is much greater and a larger amount of this water is much greater and a larger amount of this water is retained at elevated temperatures, particularly up to 300°C and again at 400 – 700°C comparing to ordinary Portland Cement.” says Taylor in his studies. [18]

The loss of combined water in refractory concrete is reflected in an increase of porosity. It is thought that good thermal shock resistance of refractory concretes made with HAC is partly due to the formation of internal pores. [12, 18]

According to Taylor, above 1100°C, thermal reactions occur between the cement dehydration products and the aggregate, leading to the growth of crystals and the formation of new refractory compounds. This “Ceramic Bond” formation gives an increase in strength. The strength of a fired refractory concrete to its limits may be higher than that due to its original hydraulic bond. [18]

However, in this study firing temperature did not exceed 1100°C, so the formation of ceramic bonds was not expected to be seen.

### **3.4 Use of Portland Cement as a Binder in Refractory Mortars and Concretes**

Portland cement production takes the major part of the whole cement production worldwide. Because of its economy and good mechanical properties after

hardening, it is widely used as a construction material. Despite their beneficial properties, Portland cements lose strength when they are heated to high temperatures like 700 – 800°C. Above these temperatures the hydration products of the Portland cement start to dehydrate, so it causes the loss of strength. [10, 11, 12]

The hydration of the calcium silicates which form the major part of Portland cements, release calcium hydroxide ( $\text{Ca(OH)}_2$ ). According to Antonovich et al. during heating the crystals of  $\text{Ca(OH)}_2$  of the size  $10^{(-6)}$  m turn into  $\text{CaO}$  crystals, usually of  $10^{(-9)}$  m in size [19]. Heikal says that this turn takes place between 500°C and 600°C [4]. As Antonovich et al. stated that the surface area of  $\text{CaO}$  is very large, so it often rehydrates in the humid environment [19]. Hung et al. showed that during rehydration, the volume of  $\text{Ca(OH)}_2$  expands by 44%, leading to the complete failure of hardened cement paste [20].

As reported by the ACI committee 547, ASTM – type Portland cements can be used in some refractory applications up to an approximate maximum of 1090°C (2000°F) with selected aggregates, if special precautions are taken to ensure a sound refractory concrete. Cyclic heating and cooling tends to disrupt Portland cement concretes. [3]

As Antonovich et al. stated that in his research, Portland cement concrete with refractory aggregates and disperse admixtures was used in the former USSR in 1950 – 1980. However, because of the great disadvantages observed (sharp decrease of compressive strength, when firing under 600 – 800°C, rather low application temperature, poor thermal shock resistance, etc.), concrete made with Portland cement had not found wide application in heating equipment. [20]

### **3.5 Use of Firebrick as Aggregate in Refractory Mortar and Concretes**

Temperature stability of the aggregate determine the maximum service conditions of a refractory mortar and concrete as they are used 60 – 80% by mass of

the whole mortar and concrete. Table 3.2 shows the maximum service temperature of generally used aggregates. These maximum temperatures are based on optimum conditions of binder and aggregate. Thermal properties of aggregates, such as volume change (expansion, shrinkage or crystalline inversion) and decomposition, can affect these maximum temperatures, along with the chemical composition of both aggregate and binder and the reactivity between these mix constituents. [3]

Table 3.2 Maximum Service Temperature of Generally Used Aggregates [3]

Aggregate	Remarks	Max. Temp (°C)
Alumina, tabular	Refractory, abrasion resistant	1870
Dolomitic limestone (gravel)	Abrasion and corrosion resistant	500
Fireclay, expanded	Insulating, abrasion and corrosion resistant	1640
Fireclay brick, crushed	Abrasion and corrosion resistant	1600
Flint fireclay, calcined		1650
Kaolin, calcined	Abrasion and corrosion resistant	1650
Mullite		1650
Perlite	Insulating	1340
Sand	Abrasion and corrosion resistant	300
Slag, blast furnace (air cooled)	Abrasion resistant	540
Slag, blast furnace (granulated)	Insulating, abrasion and corrosion resistant	1200
Trap rock, diabase	Abrasion and corrosion resistant	1000
Vermiculite	Insulating	1100

Crushed building brick may provide HAC mortars for use up to about 1000°C, and in brick works, the broken or rejected products of manufacture can often be employed economically in refractory concrete mixes for constructing or repairing all parts of the kiln where a high-duty refractory is not required. However over 1000°C spalling due to the expansion has to be considered. [2, 12]

According to Robson, for temperatures over 1000°C crushed alumina-silicate firebrick (containing 26 – 45%  $\text{Al}_2\text{O}_3$ ) may be used as aggregate and the refractory qualities of the concrete improve as the alumina content of the firebrick aggregate increases. [12]

The word “Firebrick” means “Any type of refractory brick specifically fireclay brick” according to ASTM [21]. As ASTM published that “Fire clay” means “An earthy or stony mineral aggregate that has as the essential constituent hydrous silicates of aluminium with or without free silica, plastic when sufficiently pulverized and wetted, rigid when subsequently dried, and suitable refractoriness for use in commercial refractory products.” [21]

In the studies of Heikal and Orhun, crushed firebrick aggregates were used in varying temperatures [4, 7]. Heikal used a special firebrick called Homra, which is constituted silica quartz, alumina-silicate, and anhydrate. Heikal fired the refractory material that is made with crushed Homra firebrick up to 600°C [4]. Orhun used crushed “Filyos” firebrick at the amount of 27% in his study. The maximum firing temperature of this refractory material was 1300°C [7]. Goberis et al. used fireclay based aggregate in their studies that they fired their refractory material up to 1300°C [22]. Table 3.3 shows the service temperature limits for various HAC mortars. [12]

Table 3.3 Service Temperature Limits of Various HAC Mortars [12]

Aggregate Type	Max. Temp (°C)		Notes
	Ordinary HAC	White HAC 72-80% Al <sub>2</sub> O <sub>3</sub>	
Silica gravel and sand	300	-	The temperature limit is set either by expansion of aggregate or by thermal decomposition of aggregate. Aggregate must be fine grained and basic (little or no free silica)
Limestone			
Basalt, dolerite	1000 – 1100	-	
Olivine, dunite, pyrophyllite	1000 – 1300	-	Dunite may require calcinations before use.
Pumice	1000	-	Useful insulating aggregate where available
Blast furnace slag (air cooled)	800 – 1000	-	Slag fines may affect setting and hardening of concrete
Building brick	800 – 1100	-	Useful heat resistant concretes for low-duty use.
Firebrick (26 – 45% Al <sub>2</sub> O <sub>3</sub> ), chamotte, fired kaolin	1200 – 1350	1300 – 1500	Refractoriness of mortars increases with Al <sub>2</sub> O <sub>3</sub> content of aggregate
Fired kyanite, silimanite, firebrick (>60% Al <sub>2</sub> O <sub>3</sub> ), mullite, calcined bauxite	1400 – 1500	1600 – 1650	Silimanite and andalusite can be used without heat treatment. Kyanite must be pre-fired to high temperature
Dead-burned magnesite, chromite-magnesia, chromite	1400 – 1600	1500 – 1650	Chromite may be used in the form of crushed chrome-brick
Silicon carbide	1600	1700	-
Corundum, fused Al <sub>2</sub> O <sub>3</sub> , tabular Al <sub>2</sub> O <sub>3</sub>	1500 – 1600	1800	Gives mortars of high strength, refractoriness and abrasion resistance
Zirconia	-	-	Expensive used for special purposes



Table 3.3 (continued)

Foamed slag	800 - 1000	-	Give lower strengths but better heat insulating properties than concretes made with the denser aggregates.
Expanded clay, shale, slate or fly ash	1000 - 1200	-	
Insulating brick (38 – 45% $\text{Al}_2\text{O}_3$ )	1200 - 1350	1300 – 1450	
Bubble alumina	-	1700	Relatively high strength mortar for insulation at the highest temperatures.
Calcined diatomite	800 - 1000	800 – 1000	Medium to low strength. Good insulation properties.
Vermiculite	900 - 1000	1000 – 1100	Low strength but highest insulation values.
Perlite	900 - 1000	1000 – 1100	

### 3.5.1 The Grading of the Aggregate

Aggregate grading is the most important point while designing a mortar or concrete mix. Aggregate grading determines the cement content as well as water content when achieving the desired properties of castable. However, there is a dilemma, whether to use a continuous grading containing all the sizes between maximum and minimum, or should the aggregate consists coarse aggregate and fine aggregate by omitting a range of intermediate sizes. The disadvantage of omitting intermediate sizes is segregation which is the tendency of the moving of coarse aggregates toward gravity while the fine aggregates push upwards with free water. Despite the segregation, omitting intermediate sizes provides an advantage of using

efficient cement amount, and also mortar or concrete is more suitable for vibratory compaction. The segregation problem is solved by continuous grading. [13]

### 3.5.2 Cement Content When Determining Aggregate Amount

Ordinary high alumina cements have less refractoriness than the aggregates employed, so the refractoriness of the concrete is determined by the amount of aggregate used in the mix. When the refractoriness of the aggregate is not greatly different from that of the cement, then the cement content has a minor influence on the refractoriness of the concrete [1, 2, 12]. Figure 3.1 shows the relation between the aggregate – cement ratio by the service temperature [12].

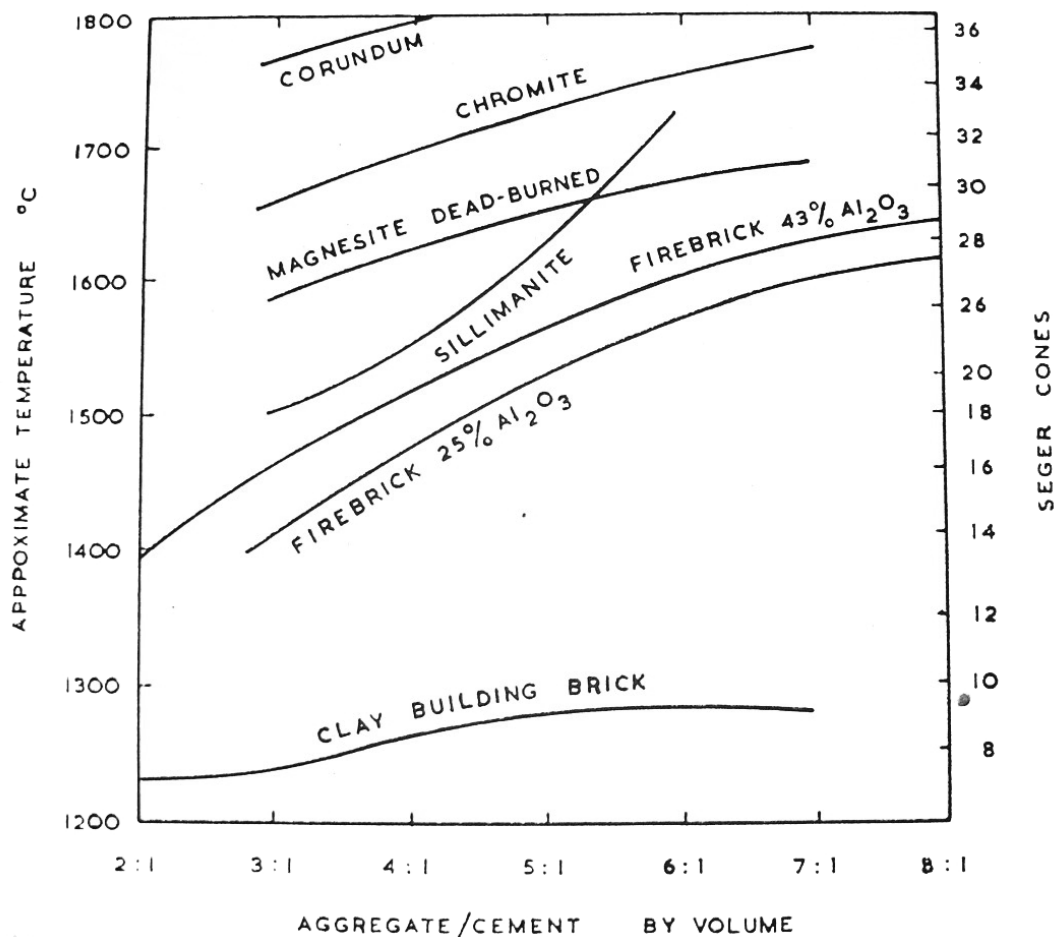


Figure 3.1 Effect of Cement Content and of Type of Aggregate on the Refractoriness of Castable Mixes [12]

In the studies of Robson, it is stated that the change of cement content in refractory material leads to the changes to the strength of the concrete after firing. This relation is showed at the Figure 3.2 and Figure 3.3 [12].

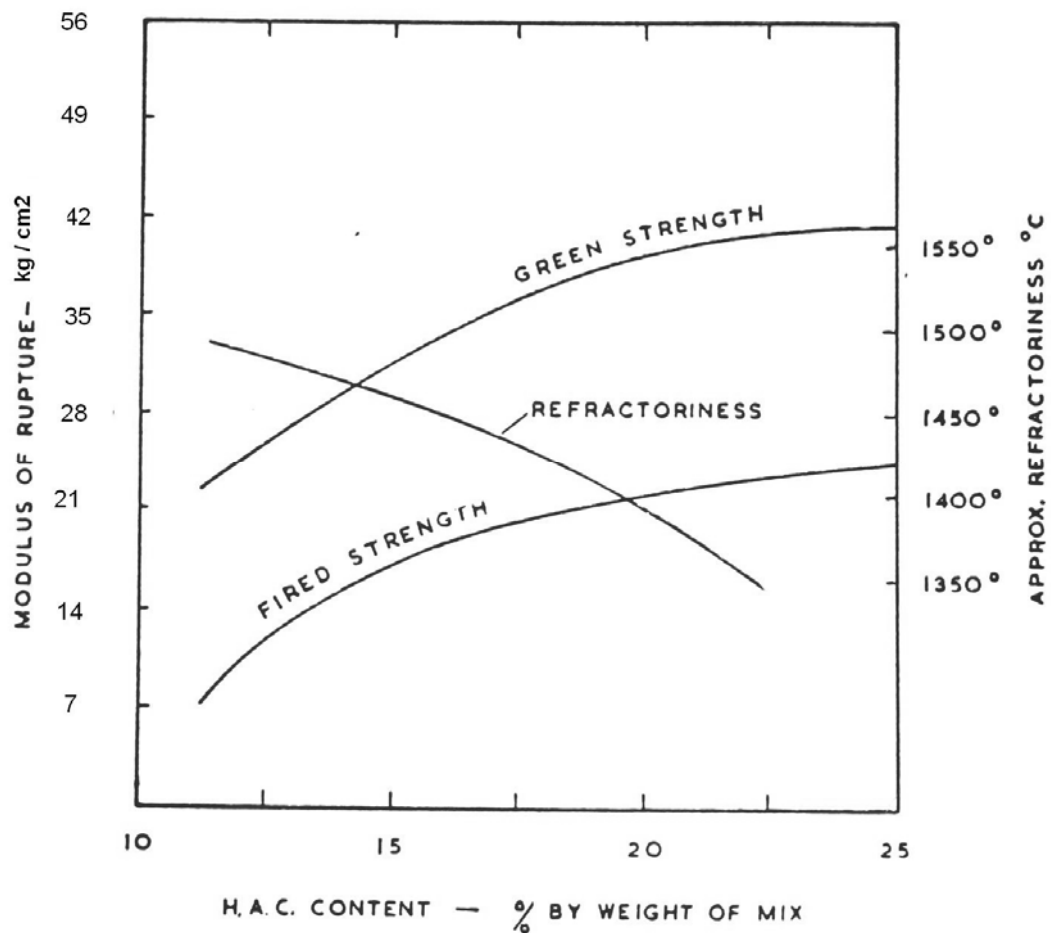


Figure 3.2 Effect of Cement Content on the Refractoriness and Strength of a Castable Mix [12]

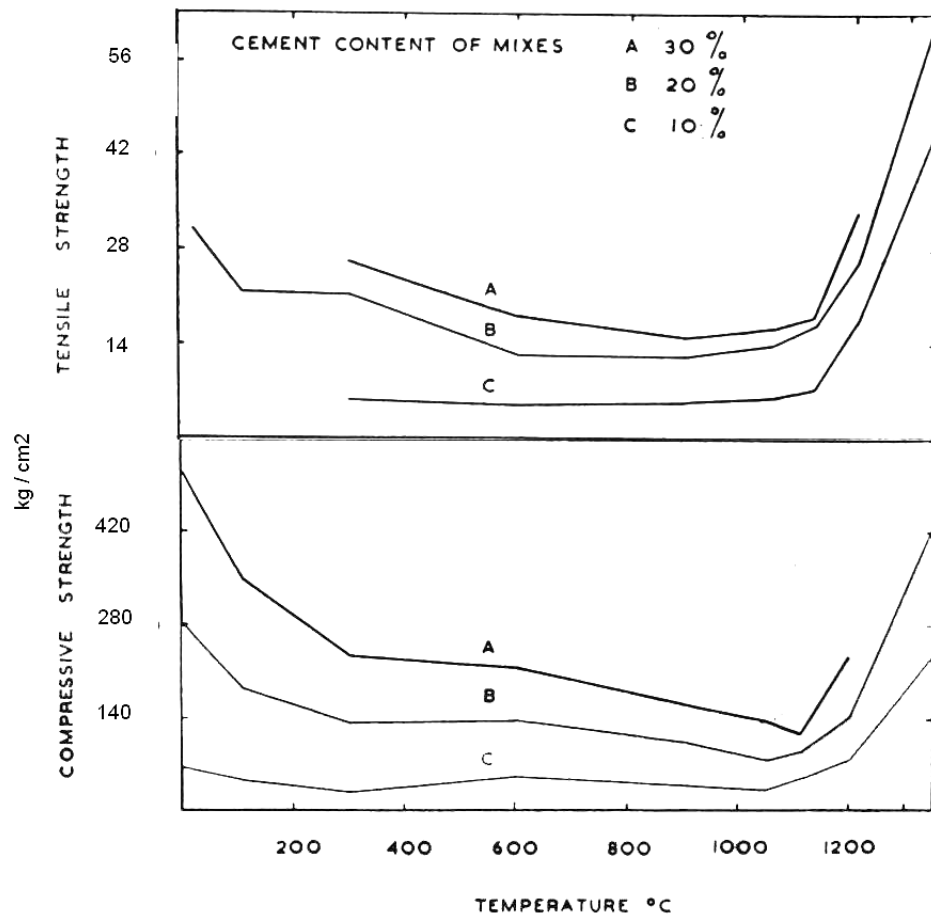


Figure 3.3 Strengths of HAC – Crushed Firebrick Concretes after 24hr. at 22°C and 110°C, 4 months at 300°C and 600°C, 5 hours at all Higher Temperatures [12]

Expansion and shrinkage are two main problems that must be taken into consideration in refractory materials. As the firebrick and high alumina cement have different thermal expansion behaviours, when they are used together, the refractory material obtained shows a different behaviour than them. This interrelation is showed at Figure 3.4 [12]

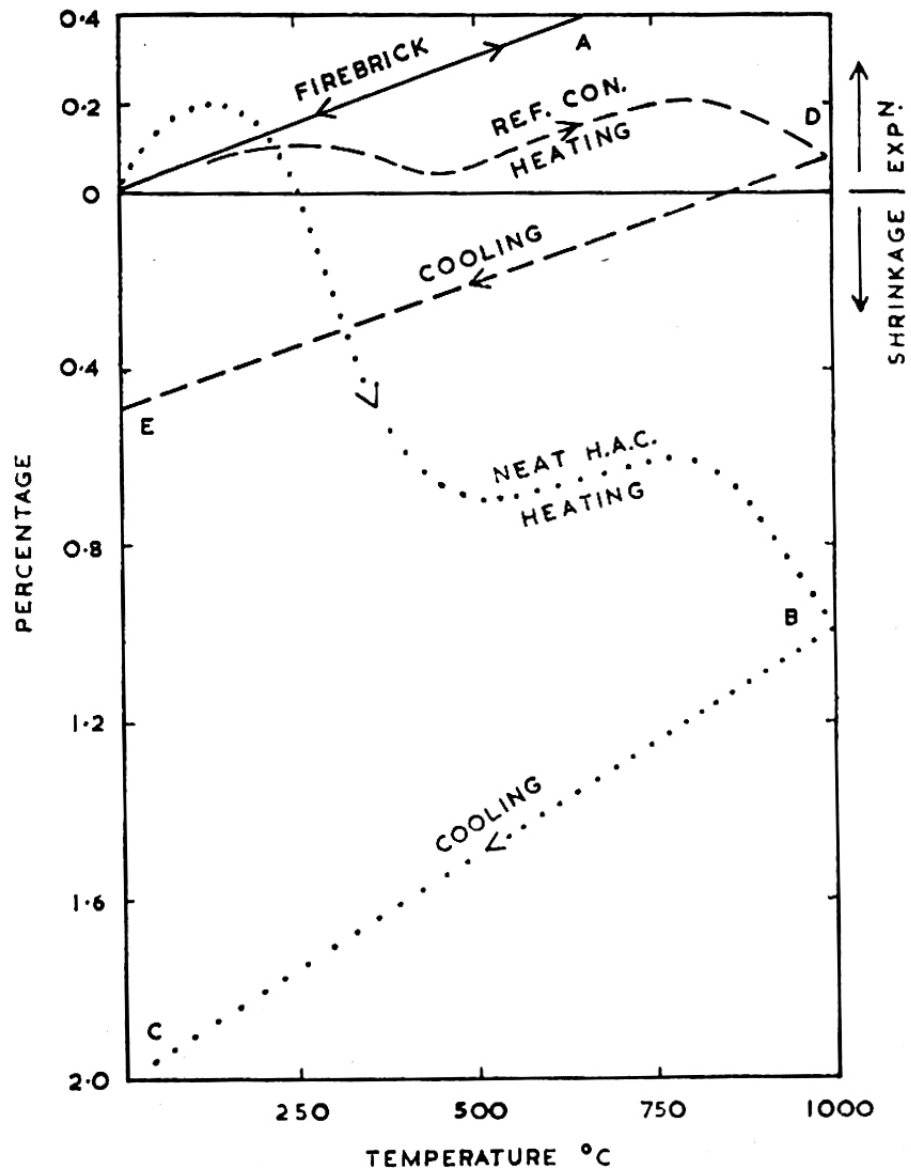


Figure 3.4 Linear changes occurring on heating Neat Hydrated HAC or Refractory Concrete for the first time [12]

### 3.6 Use of Pozzolans in Refractory Mortar and Concrete

According to ASTM C 125, pozzolans are “Siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but

will in finely divided form and in presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form possessing cementitious properties.” [23]

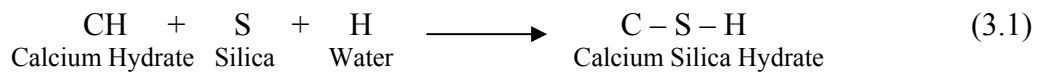
According to Erdoğan, “Fly ash is the finely divided residue or the very fine ash resulting as a by-product from the combustion of powdered coal in the power plants for providing the energy for electricity generation and transported from the firebox through the boiler by flue gases into precipitators.” [5]

It is defined in the ASTM C 1240 that “Silica fume is a very fine pozzolanic material, composed mostly of amorphous silica produced by electric arc furnaces as a by-product of the production of elemental silicon or ferro-silicon alloys.” [24]

As defined in ASTM C 989 “Blast furnace slag is the non metallic product, consisting essentially of silicates and aluminosilicates of calcium and other bases that is developed in a molten condition simultaneously with iron in a blast furnace.” [25]

In Portland cement hydration, calcium silica hydrate gel is the main product which provides the main strength to the mortar or concrete. At the end of the hydration of Portland cement, calcium hydroxide also exists as secondary product. However, calcium hydroxide does not provide a strength as well as calcium silica hydrate. Excessive silica supplied from pozzolans leads to a chemical reaction with calcium hydroxide in the presence of moisture. [5]

This reaction is showed at the Equation 3.1



Despite the formation of C – S – H gel in Portland cement hydration, there is no such a product in high alumina cements. In high alumina cements main strength providing product is calcium alumina hydrate (C – A – H). As the alumina amount is

high in HAC, neither  $\text{CaO}$  (C) nor  $\text{CaO} \cdot \text{H}_2\text{O}$  (CH) is formed, because both of them react with alumina to form C – A – H, so that the reaction, showed at Equation 3.1 does not take place. [10, 11]

Pozzolanic materials can be used in refractory material as a fine material to reduce pores, improve workability and resist high temperatures as they are pre-fired materials. Comparing to equivalent Portland cement mixes HAC are more difficult to float or trowel, which bleed more easily. Therefore, an increase in the proportion of fine to coarse aggregate improves workability. [12]

Silica fume is used in the studies of Nonnet et al. with high alumina cement. Mixes are fired to  $1600^\circ\text{C}$  to investigate C – A – S formation. It is observed that the presence of silica does not significantly affect the high temperature sequence of formation of the silicon-free calcium aluminates. [26]

In the studies of Poon et al. concretes containing pozzolanic materials were heated up to  $800^\circ\text{C}$ . The fly ash containing high strength concretes showed the best performance at elevated temperatures followed by the granulated blast furnace slag and silica fume concretes. However, in normal strength concretes granulated blast furnace slag gave the best performance followed by fly ash. [6]

## **CHAPTER 4**

### **EXPERIMENTAL STUDY**

#### **4.1 Experimental Program**

By using high alumina cement as a binder, crushed firebrick as an aggregate with various proportions of silica fume (SF), fly ash (FA), granulated blast furnace slag (GBFS), and granulated firebrick (GFB), ten mortars with or without steel fibres were produced. Also four mortars were prepared with Portland cement as a binder, crushed firebrick as an aggregate with granulated blast furnace slag and granulated firebrick with or without steel fibres. A commercially available monolithic refractory was used as reference material with or without steel fibres.

All mortars prepared are summarized with their abbreviated names and description at Table 4.1



Table 4.1 Mortars Prepared in the Study with Their Designations

Designation	Cement Used	Pozzolan Used	Steel Fibre Used
IA	HAC	-	-
IB	HAC	-	ME446
IIA	HAC	SF	-
IIB	HAC	SF	ME446
IIIA	HAC	FA	-
IIIB	HAC	FA	ME446
IVA	HAC	GBFS	-
IVB	HAC	GBFS	ME446
VA	HAC	GFB	-
VB	HAC	GFB	ME446
VIA	Portland Cement	GBFS	-
VIB	Portland Cement	GBFS	ME446
VIIA	Portland Cement	GFB	-
VIIB	Portland Cement	GFB	ME446
VIIIA	* Commercially available monolithic refractory		-
VIIIB	* Commercially available monolithic refractory		ME446

\* Commercially available Monolithic Refractory: Kil & Taş Refrakter

SF : Silica Fume

FA : Fly Ash

GBFS: Granulated Blast Furnace Slag

GFB : Granulated Firebrick

A : No Steel Fibre containing

B : Steel Fibre ME446 containing

Three observation groups were made, with each sixteen types of specimen. First group was cured at curing room at 21°C for seven days, satisfying the ASTM C 511 [27]. Second group was cured at 21°C for one day, and then heated to 105°C for preventing the cracking of specimens due to fast evaporation of free water when heated to higher temperatures, finally heated to 1100°C. Specimens were kept one hour at 1100°C, and then the furnace was closed to let it cool to the room temperature. Third group was cured as the same way as the second group, but the specimens were cooled down and heated ten times in order to simulate the real service conditions. Goberis et al. studied mortars made with high alumina cement that were heated and cooled down seven times to investigate the behaviours of the refractory material that had been made [28].

In order to understand the bonding behaviour of steel fibres, another group of high alumina cement and steel fibre containing specimens were heated to 1100°C after curing seven days in curing room. Also to investigate the strength change of the superplasticizer added mortars, a group of high alumina cement containing specimens with superplasticizer were heated to 1100°C after they were cured as the same way as second specimen group.

Table 4.2 gives the abbreviations used for naming the specimen groups and Table 4.3 gives the summary of which specimen group include which specimen type.

Table 4.2 Abbreviations Used for Specimen Groups

Abbreviation	Description
7D	7 Days : Specimens were cured for seven days. (ASTM C 511 [28])
FO	Fired Once : Specimens were heated to 1100°C and kept 1 hour at 1100°C, then cooled to room temperature inside the furnace
C	Cycle : FO had been done for ten times
7D – FO	FO after seven days of curing at curing room
Ad – FO	Superplasticizer admixture containing specimen then treated as FO

Table 4.3 Summary of Specimen Groups Including which Specimen Type

Name of Group	Name of Specimen Type							
	I	II	III	IV	V	VI	VII	VIII
7D	+	+	+	+	+	+	+	+
FO	+	+	+	+	+	+	+	+
C	+	+	+	+	+	+	+	+
7D – FO	+	+	+	+	+			
Ad - FO	+	+	+	+	+			

In Table 4.4 mix proportions for 1m<sup>3</sup> refractory mortar is given.

Table 4.4 Mix Proportions for 1m<sup>3</sup> Mortar

Specimen Type	Cement (kg)	Water* (l)	Aggregate (kg)	Pozzolan (kg)
I	500 – HAC	242,5	1500	-
II	425 – HAC	270	1500	75 – SF
III	250 – HAC	225	1500	250 – FA
IV	200 – HAC	270	1500	300 – GBFS
V	250 – HAC	250	1500	250 – GFB
VI	150 – Portland C	285	1500	350 – GBFS
VII	150 – Portland C	285	1500	350 – GFB
VIII	2000 - Commercial Monolithic Refractory	250	-	-

\* Water amount was determined by ball-in-hand test according to ASTM C 860 [29]

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

- a) Determination of some physical properties of high alumina cement, pozzolans, granulated firebrick and crushed firebrick;
  - Fineness and particle size distribution of high alumina cement pozzolans, granulated firebrick
  - Granulation and water absorption tests for crushed firebrick

b) Determination of various physical and mechanical properties of 7D, FO, C specimens;

- Weight change
- Size change
- Compressive strength test
- Flexural strength test
- Ultrasound test

c) Determination of internal changes of specimens after firing;

- X-Ray Diffraction (XRD) test method

## **4.2 Materials**

### **4.2.1 High Alumina Cement and Portland Cement**

In the study, “ISIDAÇ 40” high alumina cement, product of Çimsa, Mersin and an ordinary Portland cement, PÇ 42.5 obtained from Yibitaş – Lafarge cement factory, satisfying the ASTM C 150 [30], was used as binding materials. Physical properties and chemical compositions of the cements are given in Table 4.5

After the sieve test, it was found that the HAC particles passing 45µm sieve was 75%, and for Portland cement it was 73.6%. The median particle size was 15µm and 13.8µm respectively.

Table 4.5 Physical and Chemical Characteristics of HAC and Portland Cement

Property	HAC	Portland Cement
Specific Gravity ( $\text{g/cm}^3$ )	3.1	3.11
Fineness ( $\text{cm}^2/\text{g}$ )	3100	3250
Oxides (%)		
$\text{Al}_2\text{O}_3$	40.7	5.4
$\text{CaO}$	38.2	63.7
$\text{SiO}_2$	2.2	20.1
$\text{Fe}_2\text{O}_3$	17.0	2.8
$\text{MgO}$	0.8	1.5
$\text{SO}_3$	0.02	0.47
$\text{Na}_2\text{O}$	0.02	0.21
$\text{K}_2\text{O}$	0.05	0.65
$\text{TiO}_2$	2.1	-
Loss on ignition	0.3	0.84

#### 4.2.2 Aggregate

Crushed firebrick BS. 85P, product of “Filyos Ateş Tuğlası Sanayi”, was used as aggregate in the study. The chemical composition of the firebrick, the gradation and the water absorption of the aggregate is given in Table 4.6, Table 4.7 and Table 4.8 respectively. All the aggregate tests were performed according to ASTM C 702 [31], ASTM C 136 [32], ASTM C 70 [33], and ASTM C 128 [34].

Table 4.6 The Chemical Composition and Some Physical Properties of BS. 85P  
Firebrick

Chemical Composition		
Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> % (max)	TiO <sub>2</sub> % (max)
85	2.0	3.2
Physical Properties		
Density (gr/cm <sup>3</sup> )	Fire Resistance (°C)	
2.7	1560	

Table 4.7 Gradation of the Crushed Firebrick Aggregate

Sieve No.	Retained on each Sieve %	Cumulative Retained %	Cumulative Passing %
4	0	0	100
8	13.4	13.4	86.6
16	35.6	49.0	51.0
30	21.4	70.4	29.6
50	12.7	82.7	17.3
100	7	90.0	10.0
Passing 100	10	100	0

Table 4.8 Water Absorption Rate of the Crushed Firebrick Aggregate

Surface Dry Water		
Saturated Weight (g)	Dry Weight (g)	Absorption Rate (%)
500	470	6.4

### 4.2.3 Water

Tap water that was colourless, odourless and was assumed to be free from organic matter and alkalis was used in the study as mixing water. ASTM C 860 was used to determine the consistency of refractory mortar [29]. Figure 4.1 shows the ball-in-hand test [29].

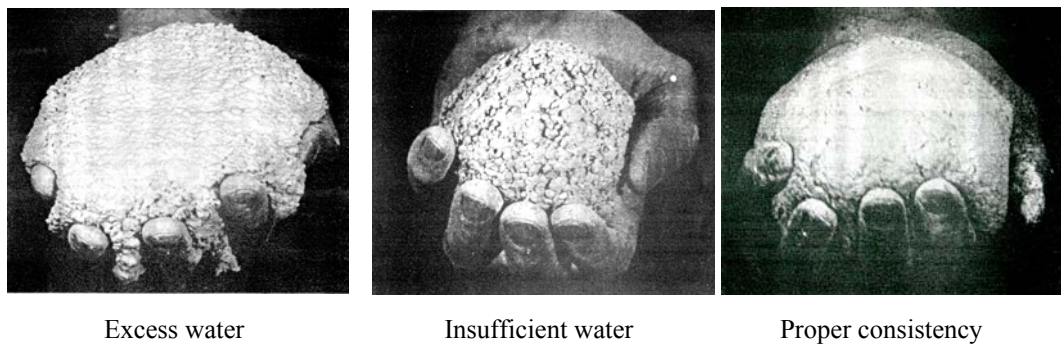


Figure 4.1 Ball-In-Hand Test [29]

### 4.2.4 Pozzolans

All commercially available pozzolans; silica fume, fly ash (class F), and ground granulated blast furnace slag were used in the study. BS. 85P firebrick, product of Filyos Ateş Tuğlası Sanayi, was ground granulated to the fineness of Blaine  $3915 \text{ cm}^2/\text{g}$  to be used as pozzolan. Physical and chemical properties of the pozzolans are given at Table 4.9.



Table 4.9 Physical and Chemical Properties of Pozzolans Used in the Study

Property	Silica Fume	Fly Ash (Class F)	Granulated Blast Furnace Slag	Granulated Firebrick
Specific Gravity ( $\text{g/cm}^3$ )	2.11	2.04	2.78	2.7
Fineness ( $\text{cm}^2/\text{g}$ )	-	3400	1800	3915
Oxides (%)				
$\text{SiO}_2$	93.6	59.18	36.88	-
$\text{Al}_2\text{O}_3$	-	22.68	15.2	85
$\text{Fe}_2\text{O}_3$	-	6.44	0.7	2.0
$\text{CaO}$	2.26	4.28	35.48	-
$\text{MgO}$	-	3.07	9.95	-
$\text{TiO}_2$	-	-	-	3.2

#### 4.2.5 Steel Fibre

A special heat resistant steel fibre, ME446, product of FibreTech, was used in the study. Fibres were 12mm in length, 0.16mm in diameter. They were added in the amount of 1% by the volume of the total mortar.

#### 4.2.6 Water Reducer Admixture – Superplasticizer

In order to reduce water amount in castables, superplasticizers are used. As pozzolan addition increases water requirement of mortars for a given flow, superplasticizer which is a chemical admixture, is required for mortars containing high amounts of pozzolans. By decreasing water cement ratio, an increase in compressive strength and flexural strength was expected. [5, 10, 13]

A superplasticizer, Viscocrete – 3075 by Sika, commercially available from market, was used in fixed dosage of 1.5% by weight of total cementitious material, only in group Ad-FO. Aim of using the superplasticizer only in one group was to

investigate the mechanical properties of fired refractories containing superplasticizer. Technical data of the Viscocrete-3075 is shown in Table 4.10.

Table 4.10 Technical Data of Viscocrete-3075

Type	Modified polycarboxylate – based liquid
Colour	Light brown
Density	1.07 ± 0.02 kg/m <sup>3</sup>

### 4.3 Investigation Methods

#### 4.3.1 Firing Rate of the Specimens

A controlled firing rate of the furnace is important in refractory material production. Before achieving the service temperatures of the material, pre-heating up to 105°C, for one day, is needed in order to evaporate the excess water from the refractory material, so that the cracks, due to the rapid evaporation of free water at elevated temperatures, are prevented. After the one day curing at 105°C, refractory material is ready to be heated to higher temperatures.

In the study, controlled firing rate was achieved with an electric furnace, which could be programmed to the desired temperature of 1100°C. After staying one hour at 1100°C, furnace was turned off and the specimens were left inside to cool down to room temperature.

In Figure 4.2 firing rate of the specimens is shown after one day curing at 105°C.

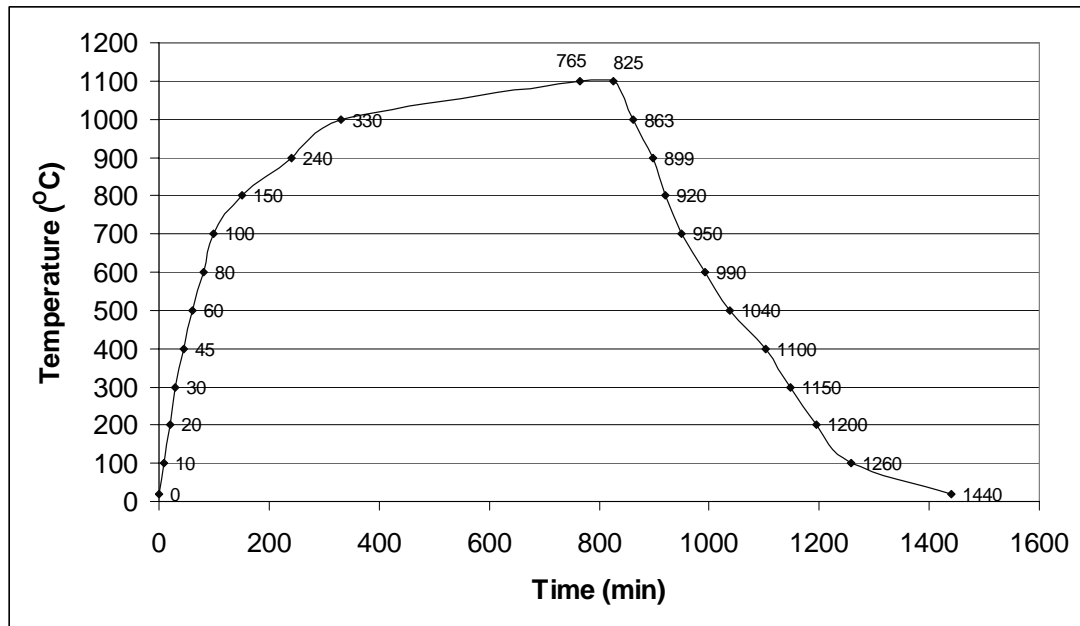


Figure 4.2 Firing Rate of the Specimen

#### 4.3.2 Determination of Weight and Size Change of Specimens

In order to determine the physical changes in the specimens, weight and size changes were investigated after one day of curing in curing room, after one day curing at 105°C, and after firing to 1100°C.

In all sixteen types of specimens, each change was searched for three specimens of same type. For determining weight change 5x5x5 cm specimens were used. Weight changes were measured with an electronic weighing machine with an accuracy of 0.01g.

In the study, it was impossible to determine the size change by using 1in.x1in.x12in. specimens, having steel nodes at the ends of the specimen. As the steel nodes and refractory mortars have different thermal expansion coefficients, it is hard to understand which material, either steel or mortar, expand more at 1100°C. Also the bonding between the steel and mortar would be affected at 1100°C.

According to these estimations and some previously made experiments, 4x4x16 cm specimens were used for determining the size change of the specimens. Size change was measured from the longest part of the specimen, because it is easy to see the changes. Measurement device was a calliper compass having an accuracy of 0.1mm.

#### **4.3.3 Determination of Compressive Strength**

For determining the compressive strength of refractories made, 5x5x5 cm specimens were prepared, satisfying the conditions of 7D, FO, C, 7D-FO and Ad-FO. Tests were conducted as stated in ASTM C 109[35]. However the flow limit of ASTM C 109 was not taken into account, because it is determined by ball-in-hand test as stated in ASTM C 860 [29], and water amounts of mortars were noted.

#### **4.3.4 Determination of Flexural Strength**

Flexural strength experiments were conducted according to ASTM C 293 [36], despite the water amount was determined by ASTM C 860 [29] in this study. 4x4x16 cm specimens were prepared as the specimen groups of 7D, FO, C, 7D-FO, Ad-FO.

#### **4.3.5 Investigation of Change in Ultrasound Velocity**

In the study the change of ultrasound velocity was investigated at the specimens after one day of curing at curing room, after one day curing at 105°C and finally after firing to 1100°C. As the loss of excess water after heating to 105°C and the loss of hydrated water after heating to 1100°C, changes were detected at the ultrasound velocity measurements of the specimens. For this test 5x5x5 cm specimens were used.

#### **4.3.6 Microstructural Investigation of Specimens by X-Ray Diffraction (XRD) Method**

For determining the internal changes of specimens after firing, X-Ray Diffraction Method was used. Pulverized firebrick, high alumina cement, fly ash, silica fume, and granulated blast furnace slag were scanned initially before analyzing the refractories. After that 7D and FO specimens were pulverized for X-Ray Diffraction investigation. From the results obtained from the mechanical tests, Portland cement containing mortars were not needed to scan.

#### **4.4 Summary of Standards Used in Experiments**

In Table 4.11 the summary of standards that were used in the experiments are given.

Table 4.11 Summary of Standards Used in Experiments

Test Performed	Relevant Standard
Reducing Field Samples of Aggregate	ASTM C 702 [31]
Sieve Analysis of Fine and Coarse Aggregate	ASTM C 136 [32]
Surface Moisture in Fine Aggregate	ASTM C 70 [33]
Specific Gravity and Absorption of Fine Aggregate	ASTM C 128 [34]
Consistency of Refractory Mortar	ASTM C 860 [29]
Compressive Strength	ASTM C 109 [35]
Flexural Strength	ASTM C 293 [36]

## **CHAPTER 5**

### **TEST RESULTS AND DISCUSSIONS**

#### **5.1 Setting Properties and Colour Change of Specimens**

Water amount of the specimens prepared in this study were determined according to ASTM C 860 [29] as mentioned on Chapter 4. As the specimens have varying water amounts and different types of pozzolans, their setting properties were different than each other. In Table 4.4 in previous chapter, water amounts are shown for each type of specimen.

While mixing, moulding and de-moulding, specimens were observed. According to these observations;

- Specimens IA and IB had an acceptable workability, but not the best. Initial setting was observed within an hour of time. After de-moulding, pores were visible to naked eye. Those specimens were the most porous ones. This can be explained by having less fine material among the other specimens. After curing at 21°C, their colour was the darkest grey, comparing to the other specimens, and it turned to a very dark brown after heating to 1100°C.
- Specimens IIA and IIB had a better workability than the IA and IB. After three hour initial setting was observed. However after 24 hour curing at 21°C, they were not hardened like other specimens, but they were still well enough to be heated. Their porous structure was clearly seen after de-moulding. After Group I specimens, they were second porous ones. Porosity was a result of having less pozzolan amount comparing to other pozzolan containing specimens. Their colour was slightly lighter than IA and

IB after curing at 21°C. However after heating to 1100°C, it turned to a very light brown, close to yellow, colour.

- Specimens IIIA, IIIB, IVA, IVB, VA and VB exhibited similar setting properties. Group IV and V had the best workability among other specimen groups. Group III had slightly worse workability than group IV and V. Initial setting was observed within an hour time at both of them. After de-moulding, fewer pores were seen comparing to I and II. This is because of having more pozzolanic material in their inner structure. III and IV had similar colours of light grey after curing at 21°C, and light yellowy brown after heating to 1100°C, despite Group V had light yellowy grey colour after 21°C curing, and very light yellowy brown colour after heating to 1100°C. The reason that Group V had a yellowy grey colour after 21°C curing is, having 50% cement replaced by granulated firebrick which is yellow in colour.
- Specimens VIA, VIB, VIIA and VIIB had the same workability and setting properties, as they consisted of Portland cement. Their workability showed similar properties with group V. The initial settings of the mortars were very slow comparing to those having high alumina cement. After 24 hour curing at 21°C, they could be able to be de-moulded, but they still needed more curing at 21°C. However in order to obtain same conditions, they were treated as the way refractory specifications had declared [1, 2, 3]. The porous structure of them was similar to IV and V. After curing at 21°C, they had light grey colour. Heating to 1100°C, changed the colour of VI to light yellowy grey, and VII to beige.
- Specimens containing steel fibres (denoted with letter B), had a more porous structure than the specimens did not contain (denoted with letter A). As the steel fibres were coarser than the fine aggregates used, they increased the coarse material amount in the mortars. With this increase, specimens having fibres exhibited a more porous structure as they had the same water amount.

Workabilities of the specimens were all close to each other that the difference was minor between them. In Figures 5.1 to 5.14, porous structure and the colour change after heating to 1100°C is shown respectively.

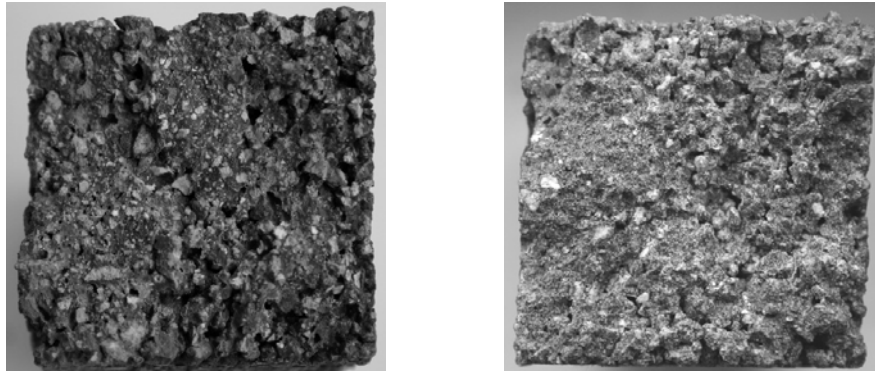


Figure 5.1 Specimen IA before (left) and after (right) heating to 1100°C.

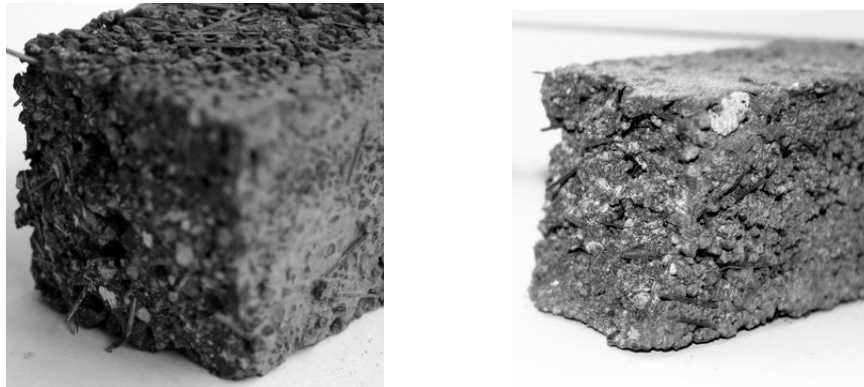


Figure 5.2 Specimen IB before (left) and after (right) heating to 1100°C.



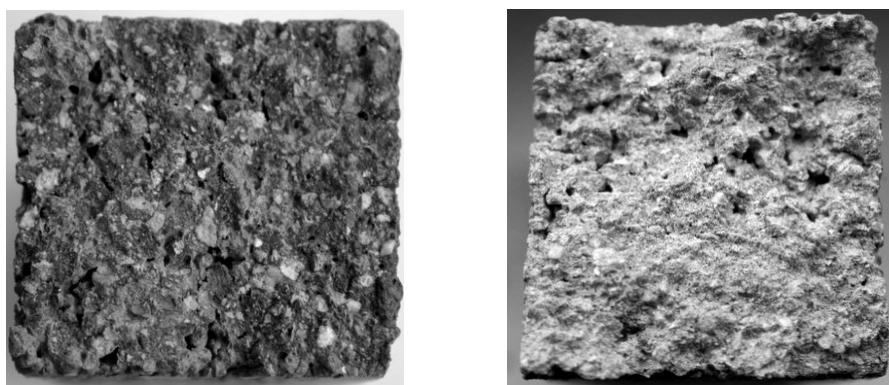


Figure 5.3 Specimen IIA before (left) and after (right) heating to 1100°C.

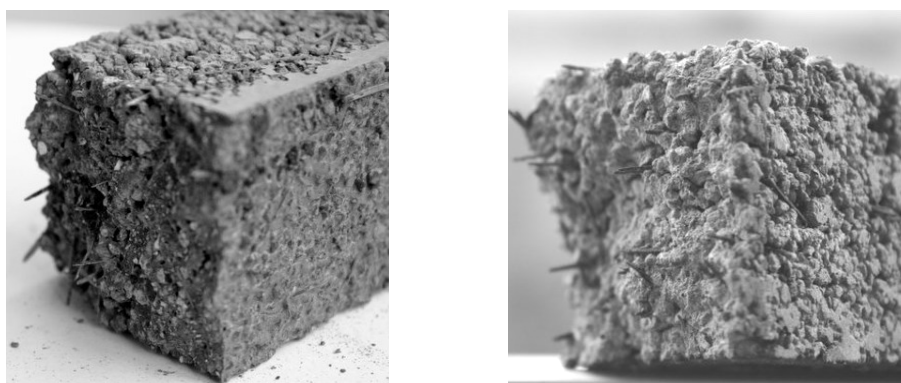


Figure 5.4 Specimen IIB before (left) and after (right) heating to 1100°C.

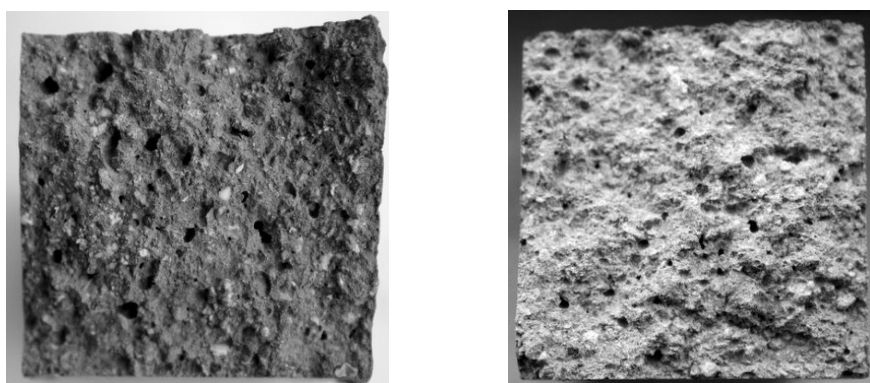


Figure 5.5 Specimen IIIA before (left) and after (right) heating to 1100°C.

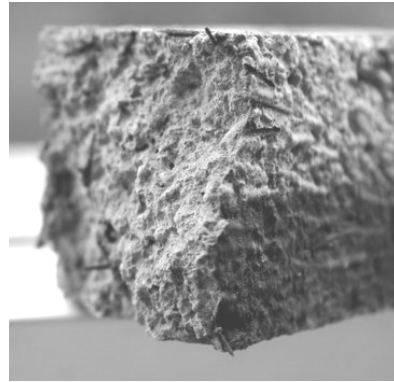


Figure 5.6 Specimen IIIB before (left) and after (right) heating to 1100°C.



Figure 5.7 Specimen IVA before (left) and after (right) heating to 1100°C.

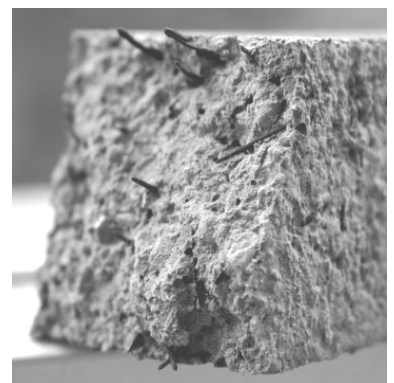


Figure 5.8 Specimen IVB before (left) and after (right) heating to 1100°C.

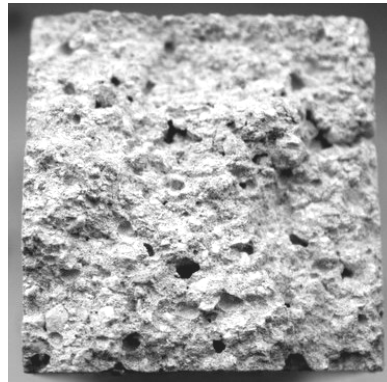
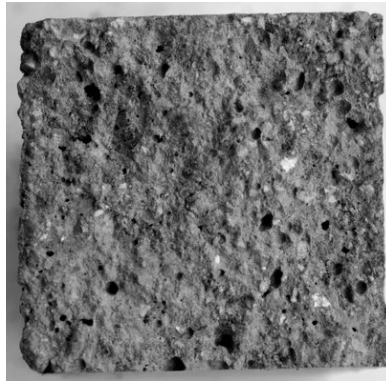


Figure 5.9 Specimen VA before (left) and after (right) heating to 1100°C.

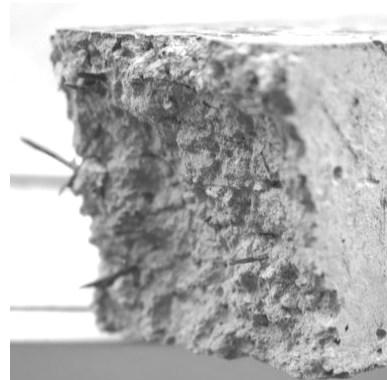


Figure 5.10 Specimen VB before (left) and after (right) heating to 1100°C.

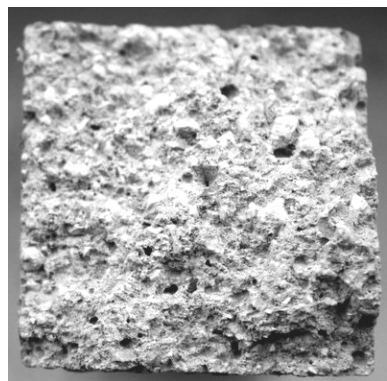
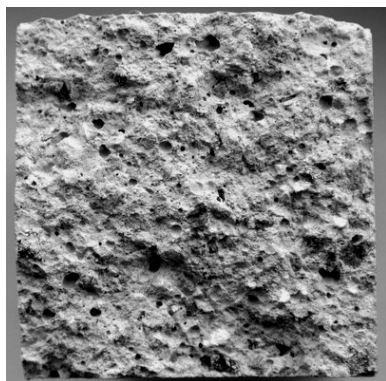


Figure 5.11 Specimen VIA before (left) and after (right) heating to 1100°C.

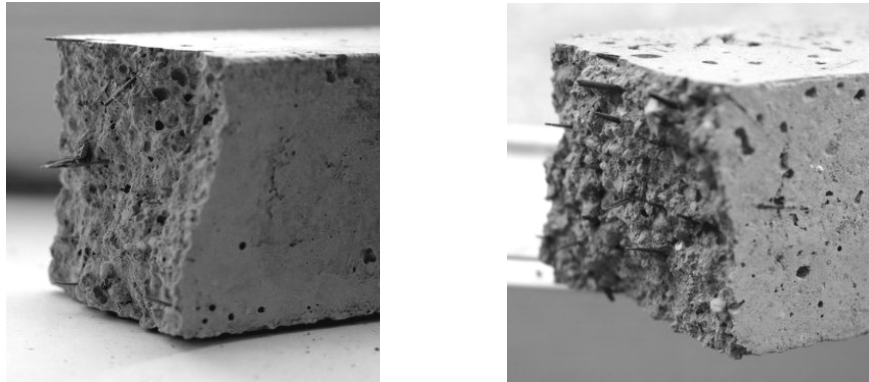


Figure 5.12 Specimen VIB before (left) and after (right) heating to 1100°C.

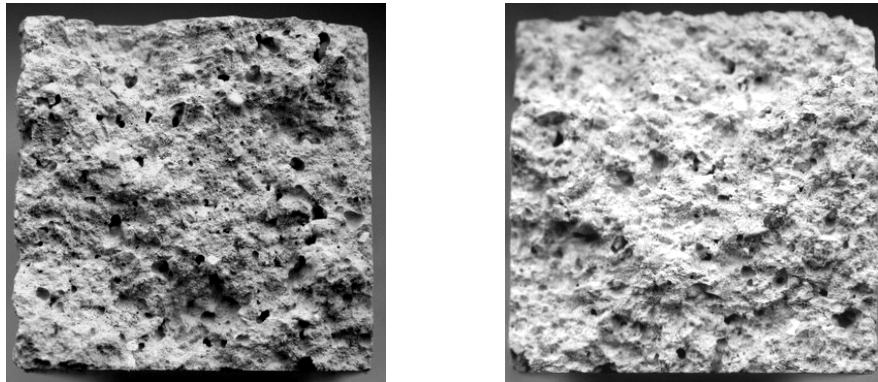


Figure 5.13 Specimen VIIA before (left) and after (right) heating to 1100°C.

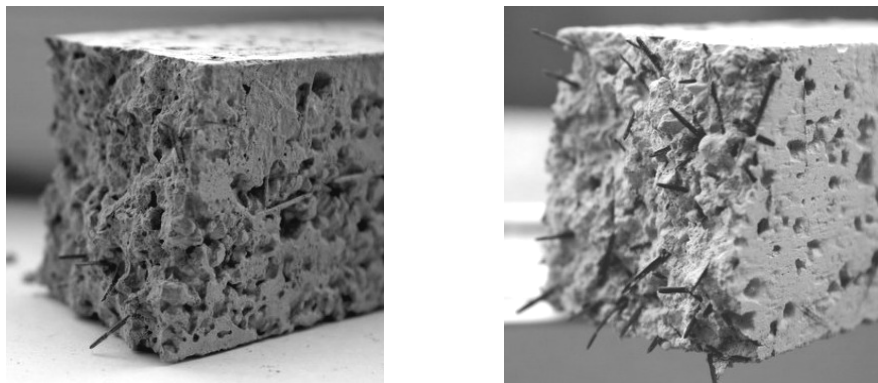


Figure 5.14 Specimen VIIB before (left) and after (right) heating to 1100°C.

## 5.2 Weight Change in Specimens

Free water inside the mortar is related with the water/cement ratio, which defines the amount of cement to be hydrated. If there is excess water that does not take place in hydration reactions, it will evaporate by the time, causing pores inside the hardened mortar. In the study the evaporation of excess water was obtained by keeping specimens at 105°C for 24 hour. First weight loss of the specimens was related to this evaporation process. When specimens were subjected to 1100°C temperature, they lost 9% - 10.5% weight altogether comparing to 21°C curing. The second weight loss is related to the loss of hydrated water inside the specimens. As stated in the “Review of the Study” part, Lea [10] and Robson [12] showed in their studies that after 600°C hydrated water loss in high alumina cements is visible.

In Table 5.1 and Table 5.2, weight change of the Group FO and Group C specimens are given. Weight loss after one turn of heating to 1100°C and ten turns of heating to 1100°C are similar. Both specimen groups had water content of the whole mortar weight of 11% to 12.5%. From Table 5.1, it is seen that weight loss varies from 8.5% to 10.5%. It is known that aggregate and the pozzolanic materials are all pre-fired. Thus the weight losses of the specimens were due to the loss of excess and some of the hydrated water. Heating and cooling cycles did not affect the overall weight loss.

It is shown in Tables 5.1 and 5.2 that the most of the weight loss is observed at the silica fume containing group, which is II. As the Group II is the one of the highest water containing group, higher weight loss was predicted. Also in the groups containing Portland cement, initial weight loss was high according to the slower hydration reactions comparing to high alumina cements. A result cannot be achieved in the Group VIII due to the unavailability of the constituents of the commercial product. Minus sign shows the weight loss at the tables.

In Figures 5.15 to 5.22, graphs of Tables 5.1 and 5.2 are given.

Table 5.1 Weight Change of the Specimen Group FO

Specimen Name	Weight Change (%)		
	After 21°C	After 105°C	After 1100°C
IA-FO	0	-3,3	-8,6
IB-FO	0	-3,2	-8,9
IIA-FO	0	-4,5	-10,6
IIB-FO	0	-4,1	-9,8
IIIA-FO	0	-5,1	-10,3
IIIB-FO	0	-5,0	-9,4
IVA-FO	0	-4,3	-8,9
IVB-FO	0	-3,8	-9,3
VA-FO	0	-4,5	-9,1
VB-FO	0	-4,6	-8,7
VIA-FO	0	-6,6	-9,9
VIB-FO	0	-6,0	-9,9
VIIA-FO	0	-8,4	-10,1
VIIB-FO	0	-7,7	-9,3
VIIIA-FO	0	-2,0	-10,2
VIIIB-FO	0	-3,5	-10,7

Table 5.2 Weight Change of the Specimen Group C

Specimen Name	Weight Change (%)		
	After 21°C	After 105°C	After 1100°C
IA-C	0	-3,6	-8,8
IB-C	0	-3,1	-8,2
IIA-C	0	-4,7	-10,6
IIB-C	0	-4,3	-9,5
IIIA-C	0	-5,3	-10,2
IIIB-C	0	-4,9	-8,9
IVA-C	0	-5,5	-9,1
IVB-C	0	-5,9	-9,7
VA-C	0	-5,6	-9,5
VB-C	0	-5,3	-9,0
VIA-C	0	-6,9	-10,5
VIB-C	0	-6,6	-10,0
VIIA-C	0	-8,2	-10,0
VIIB-C	0	-7,5	-9,1
VIIIA-C	0	-2,1	-10,4
VIIIB-C	0	-3,4	-10,6

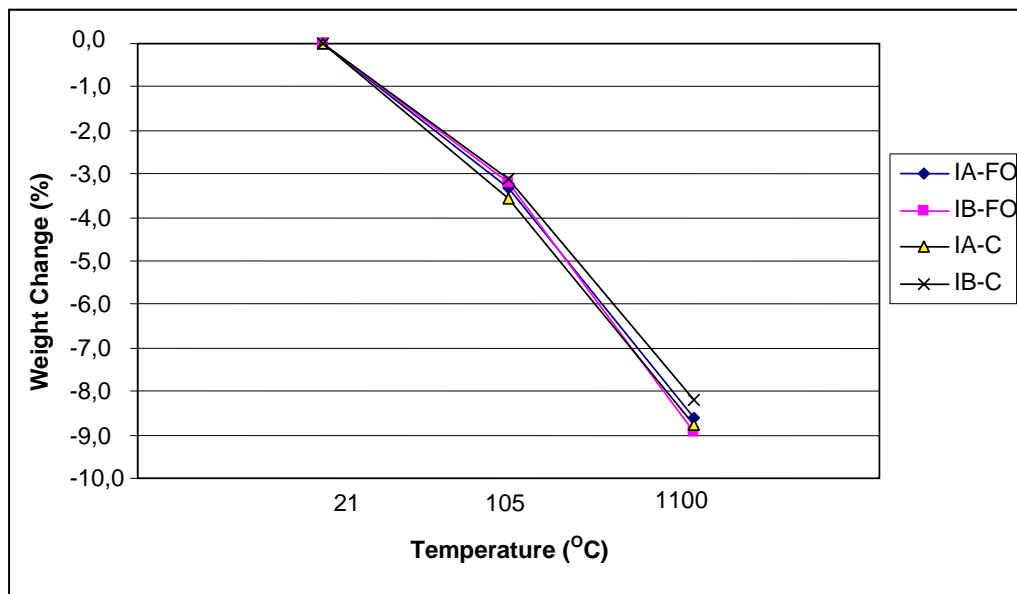


Figure 5.15 Weight Change – Temperature Graph of Specimen Group I

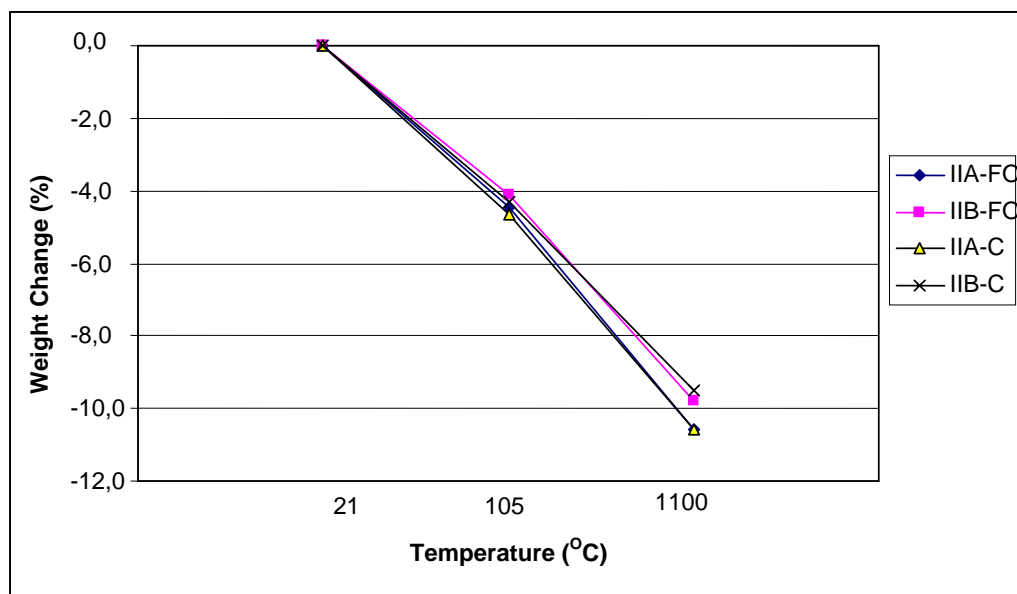


Figure 5.16 Weight Change – Temperature Graph of Specimen Group II



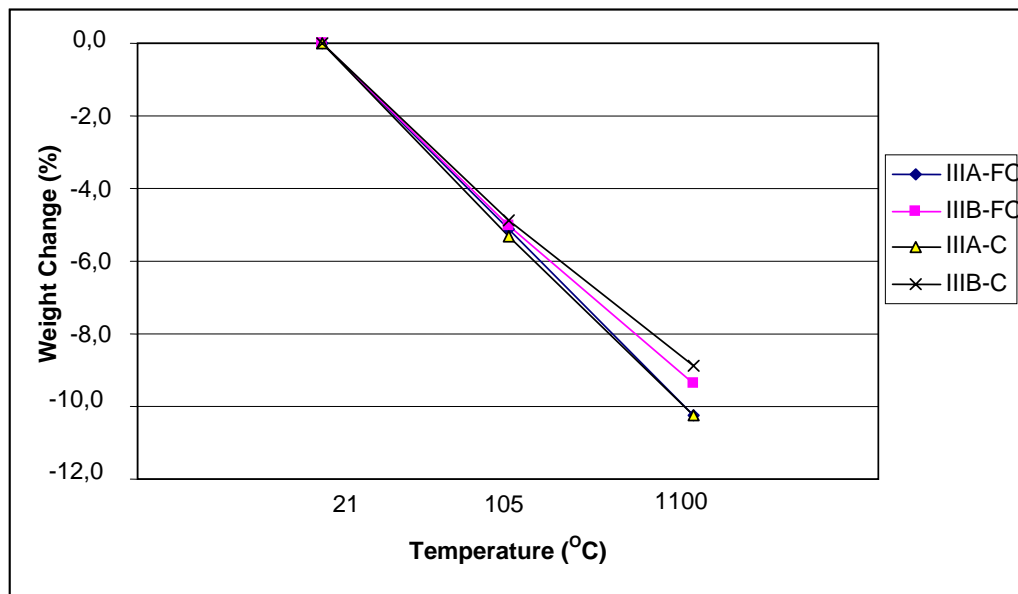


Figure 5.17 Weight Change – Temperature Graph of Specimen Group III

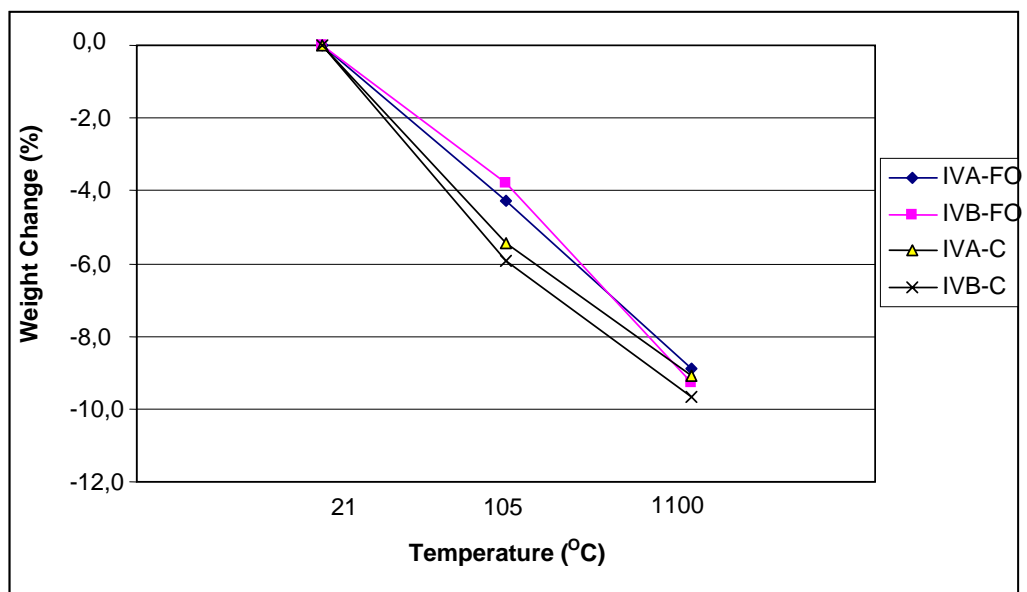


Figure 5.18 Weight Change – Temperature Graph of Specimen Group IV

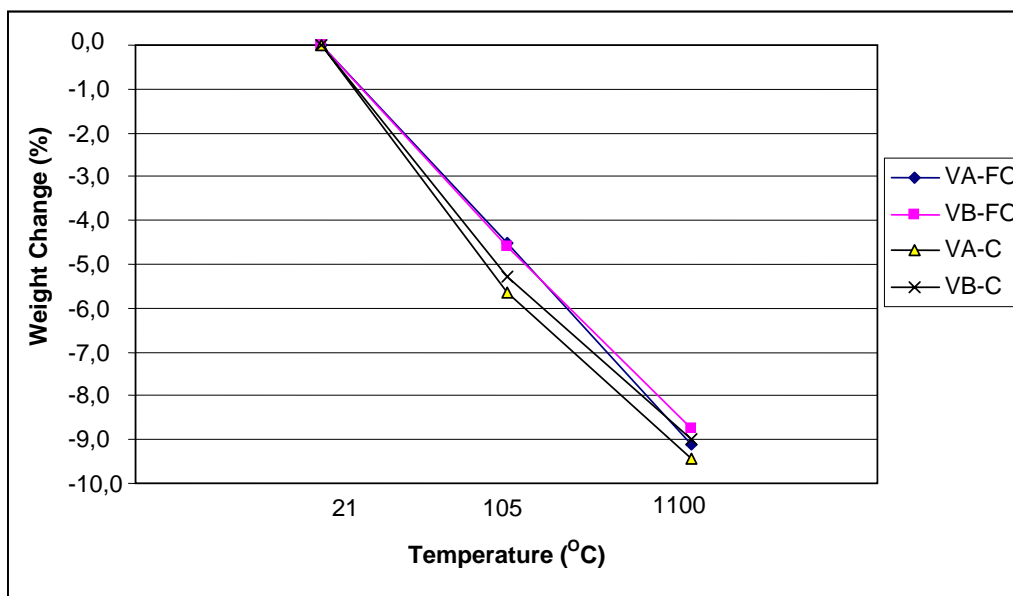


Figure 5.19 Weight Change – Temperature Graph of Specimen Group V

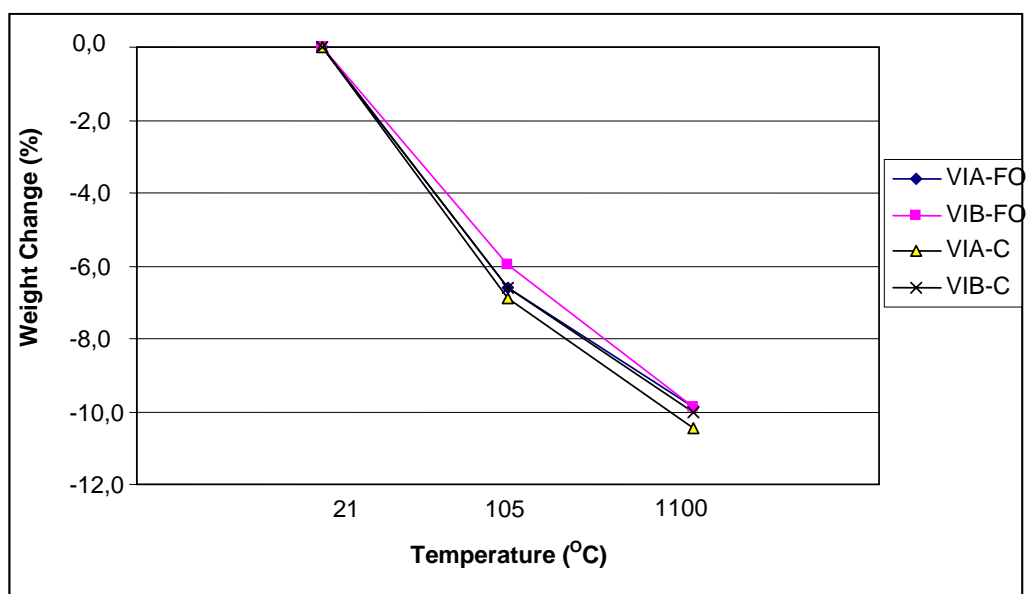


Figure 5.20 Weight Change – Temperature Graph of Specimen Group VI

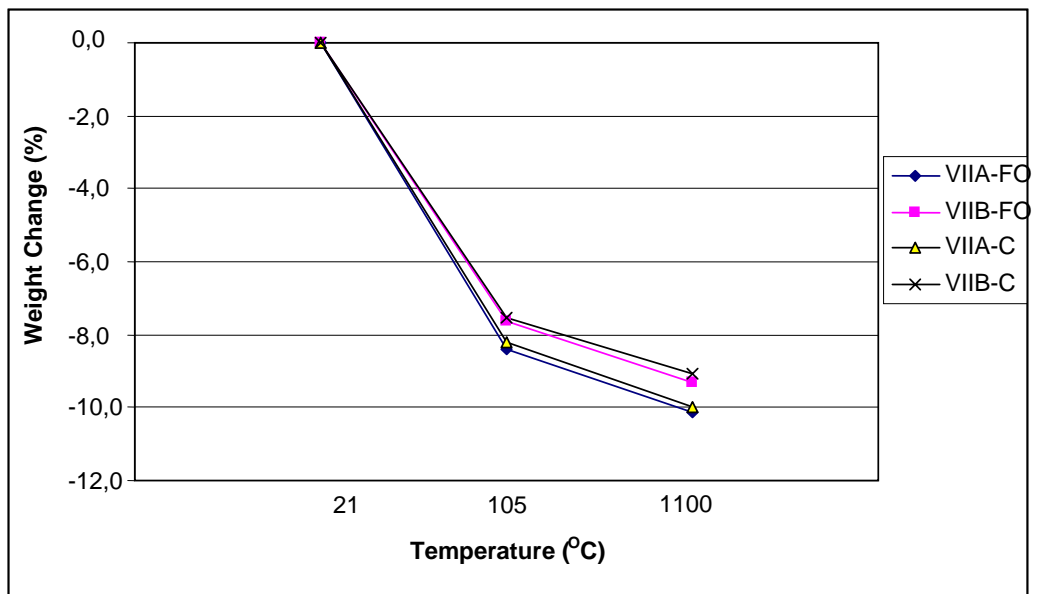


Figure 5.21 Weight Change – Temperature Graph of Specimen Group VII

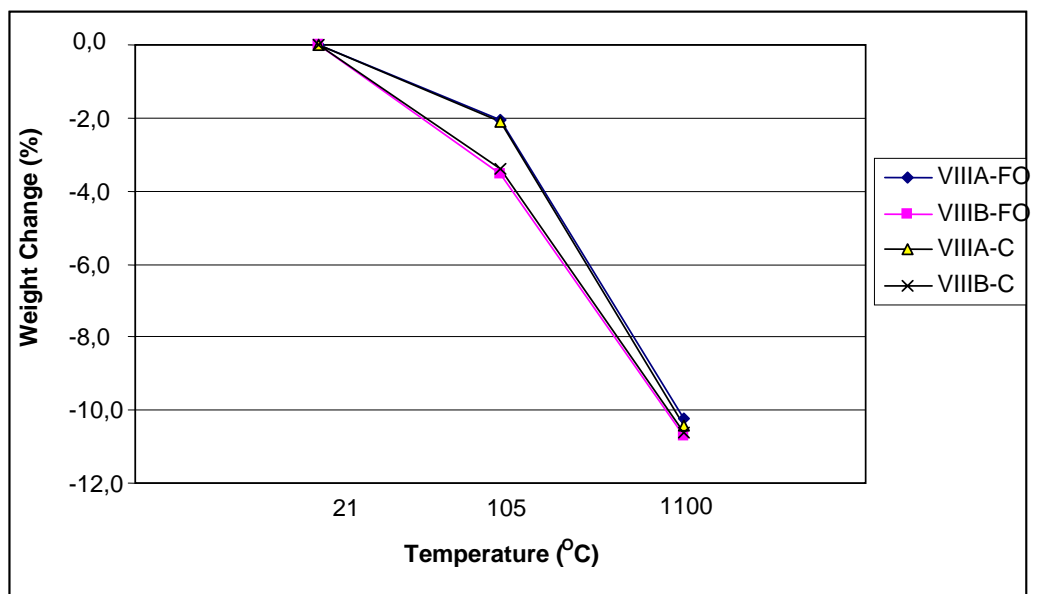


Figure 5.22 Weight Change – Temperature Graph of Specimen Group VIII

### 5.3 Size Change in Specimens

Size change of the refractory materials should be very small in order to achieve a long service life. Size change of the specimens were investigated after 21°C curing at curing room, after heating to 105°C, and after heating to 1100°C. Size change of the specimens was measured from the longest part of the 4x4x16 cm specimens. Long term size changes were determined from the C (Cycle) specimen group. In Table 5.3 and 5.4, the size changes of the specimen groups FO and C are given. Minus sign shows the contraction in specimens.

It is seen from the results that the size change of the specimens were very small. The largest size change was observed at specimens containing Portland cement. However, after multiple turns of heating and cooling, it is seen that the size change of most of the specimens were reduced. It was balanced after the multiple cycles. The usage of steel fibres also reduced the size change. Specimen Group II (containing silica fume) had the best results among other specimens, both in one turn of heating and cooling, and ten turns of heating and cooling. However, the Group V (containing granulated firebrick) seemed to be the best after first heating and cooling, the results of the Group II was better after the continuous cycles of heating and cooling.

Contraction of the specimens could be explained by the loss of hydrated water. However, the expansion of the specimens could be the result of the aggregate used. As it is known that heated materials expand, it was hard to make estimation for possible results of expansion, because so many variables included.

Table 5.3 Size Change of the Specimen Group FO

Specimen Name	Size Change (%)		
	After 21°C	After 105°C	After 1100°C
IA-FO	0	0	-0,23
IB-FO	0	0	0,02
IIA-FO	0	0	-0,19
IIB-FO	0	0	-0,04
IIIA-FO	0	0	-0,35
IIIB-FO	0	0	-0,10
IVA-FO	0	0	-0,44
IVB-FO	0	0	-0,12
VA-FO	0	0	0,04
VB-FO	0	0	0,04
VIA-FO	0	0	-0,62
VIB-FO	0	0	-0,35
VIIA-FO	0	0	0,32
VIIB-FO	0	0	0,36
VIIIA-FO	0	0	0,56
VIIIB-FO	0	0	0,35

Table 5.4 Size Change of the Specimen Group C

Specimen Name	Size Change (%)		
	After 21°C	After 105°C	After 1100°C
IA-C	0	0	0,08
IB-C	0	0	0,33
IIA-C	0	0	0,08
IIB-C	0	0	0,02
IIIA-C	0	0	-0,10
IIIB-C	0	0	0,30
IVA-C	0	0	-0,13
IVB-C	0	0	-0,13
VA-C	0	0	0,23
VB-C	0	0	0,58
VIA-C	0	0	-0,33
VIB-C	0	0	0,25
VIIA-C	0	0	0,23
VIIB-C	0	0	0,52
VIIIA-C	0	0	-0,15
VIIIB-C	0	0	0,08

## 5.4 Compressive Strength Test Results

Compression tests were conducted on the 5x5x5 cm specimens. Table 5.5 shows the compression values of the specimens. As mentioned at Chapter 4, superplastizer was only used at the specimens containing high alumina cement in order to investigate the effect of water reducing agent to compressive strength at 1100°C. Specimen group 7D-FO, which was cured for seven days at 21°C then heated to 1100°C, were prepared to understand if seven days of curing at curing room increases the compressive strength after heating.

From the compressive test results listed in Table 5.5, it is seen that there is a strength loss after heating to 1100°C. However the usage of superlasticizer reduced the strength loss, even it increased the compressive strength value comparing to seven days cured no superplasticizer used specimens. Steel fibre addition did not affect the compression value in a considerable way, despite of their high cost. When specimens were investigated after complete failure, it was observed that the bonding between the mortar and steel fibres after heating to 1100°C, were so weak that it could easily be pulled out from the hardened mortar by hand. The possible cause of the slipping of the fibres will be discussed at Section 5.5. The varying compressive strength values are given in Figures 5.23 to 5.28 for each type of specimen group, consecutively.

When the table of compression values (Table 5.5) is examined, it is seen that the best compressive strength results were obtained from the seven days cured group II (containing silica fume) specimens. After heating one day cured specimens, the best results were achieved with the granulated blast furnace slag containing specimen group (Group IV). Also after the long term heating cooling cycles, the best results were obtained from the Group IV. The most convenient results, which imply a less reduction in the compression values before and after heating, were obtained from the Group IV. When water reducer admixture was used to investigate the compressive strength change after heating to 1100°C, it was observed that again the

Group IV had the best results. Group IV had again the best compression values, when the specimens were cured for seven days at 21°C then heated to 1100°C. However, refractory materials had to be ready for heating after one day delay, so seven days of curing is not economically suitable. In this study 7D-FO specimens were prepared to understand if the bonding between the mortar and the steel fibre increases by the time before heating.

In the Portland cement containing specimen groups (VI and VII), a distinct reduction was observed in the compressive strength of the material after ten turns of heating and cooling. As previous researchers [1, 2, 10, 11, 12] did not advise the usage of Portland cement for a binder at refractory mortars, it is also seen in this study that Portland cements did not have a good performance like high alumina cements.

The compression values of commercially available refractory material are given at Table 5.5 to give an idea on the strength of this high cost material.



Table 5.5 Compressive Strength Values of the Specimens

Specimen Name	Compressive Strength (MPa)				
	7D	FO	C	7D - FO	Ad - FO
IA	47,4	10,5	15,4	15,2	36,2
IB	52,5	12,5	14,0	11,2	35,1
IIA	70,9	15,8	15,2	15,1	43,3
IIB	65,9	16,2	14,9	10,2	34,7
IIIA	32,0	15,9	13,8	13,8	27,7
IIIB	30,3	10,4	12,9	14,5	29,9
IVA	29,7	18,0	16,1	23,1	41,3
IVB	32,2	15,9	13,3	22,6	34,0
VA	47,4	14,0	12,9	11,6	33,1
VB	31,0	14,4	13,1	9,8	31,8
VIA	26,5	15,8	8,5		
VIB	32,4	14,7	8,8		
VIIA	11,2	11,4	7,6		
VIIB	12,4	10,3	10,1		
VIIIA	60,8	51,2	50,6		
VIIIB	58,4	48,4	47,8		

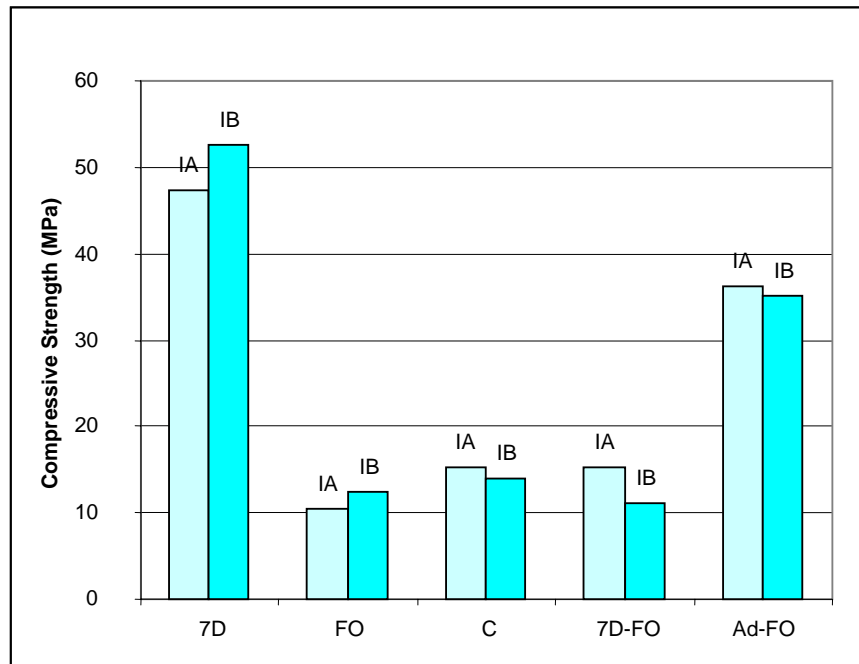


Figure 5.23 Compressive Strength Values of Specimen Group I

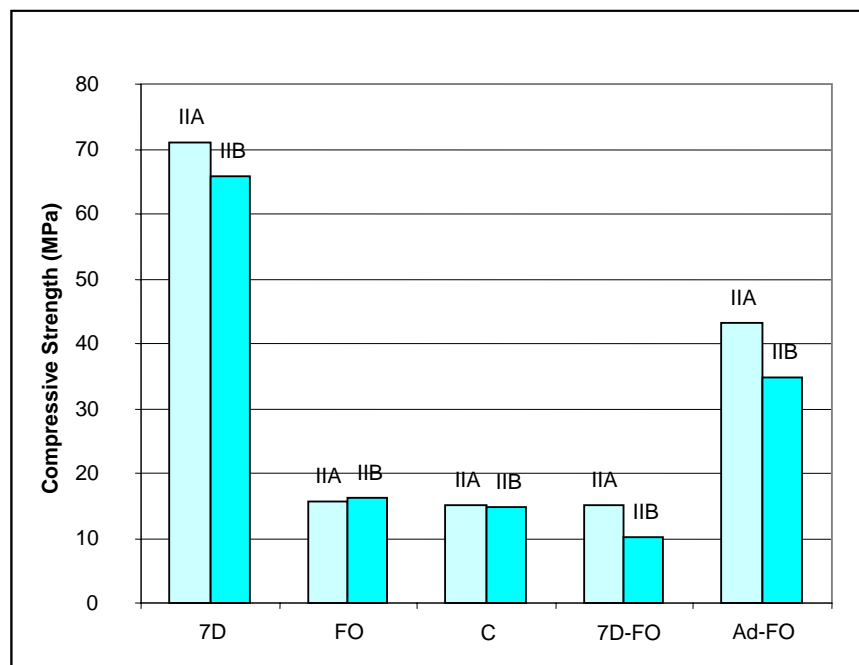


Figure 5.24 Compressive Strength Values of Specimen Group II

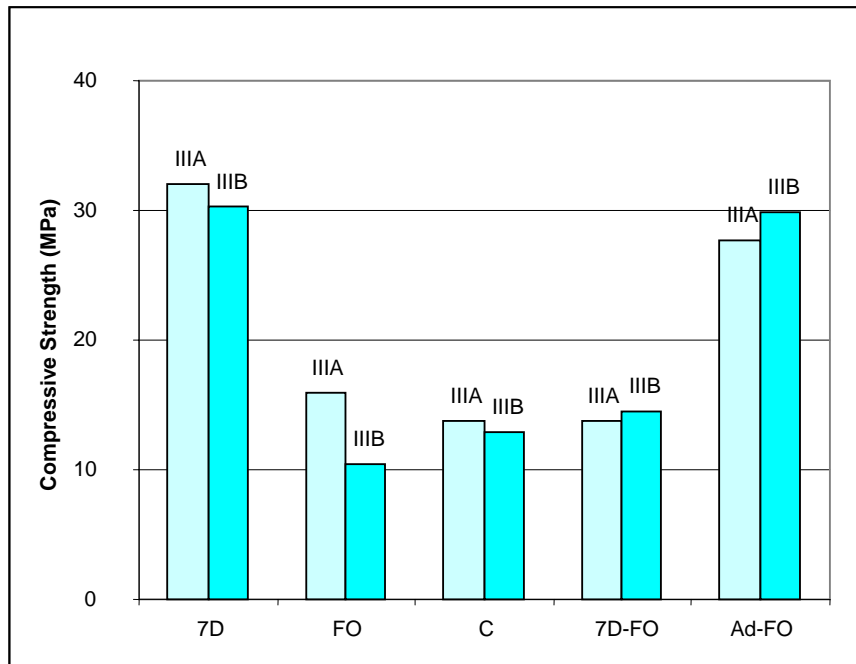


Figure 5.25 Compressive Strength Values of Specimen Group III

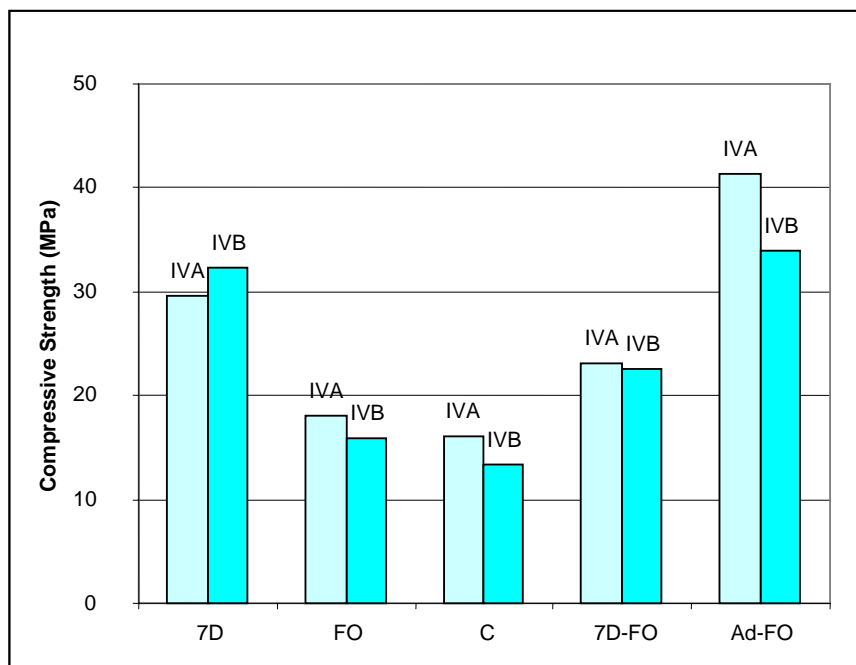


Figure 5.26 Compressive Strength Values of Specimen Group IV

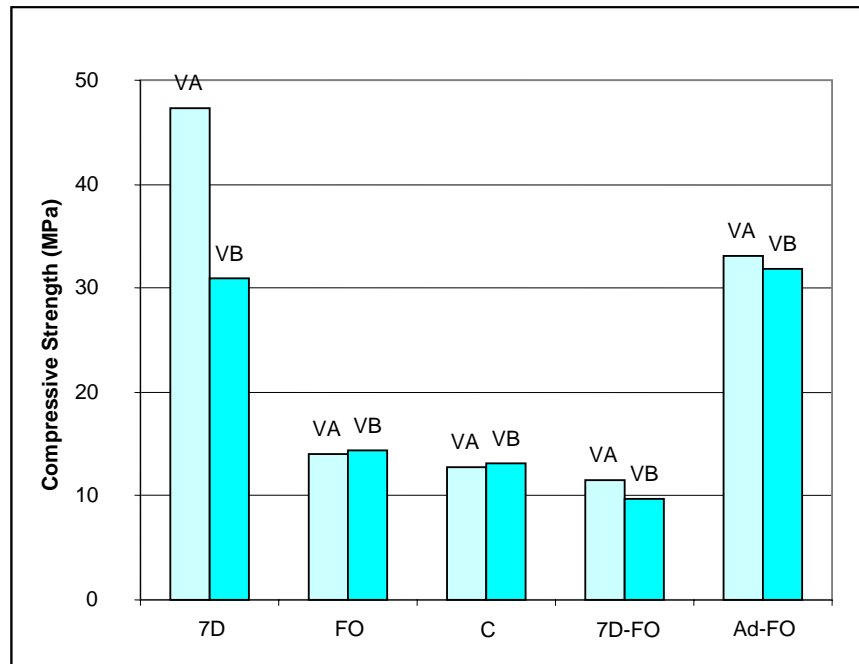


Figure 5.27 Compressive Strength Values of Specimen Group V

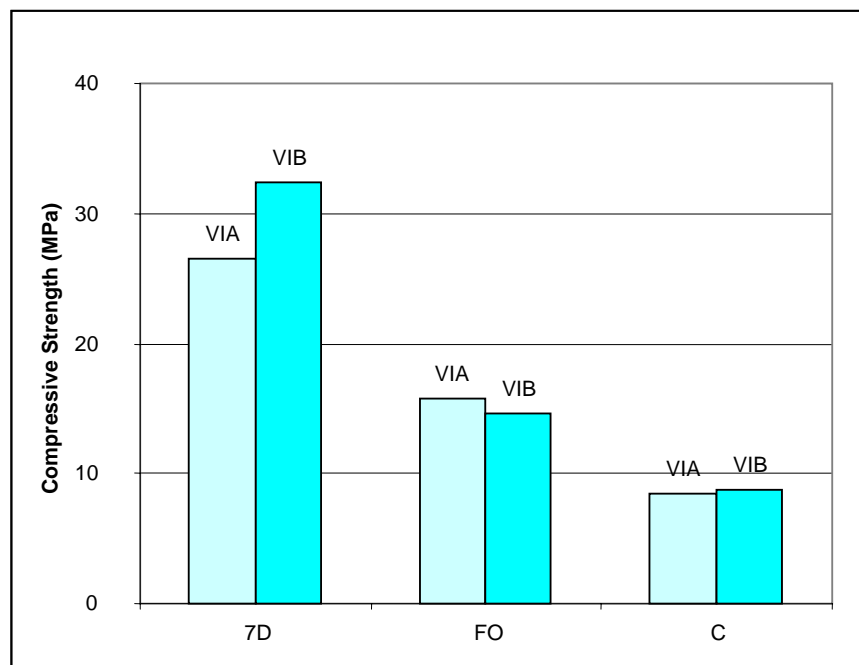


Figure 5.28 Compressive Strength Values of Specimen Group VI

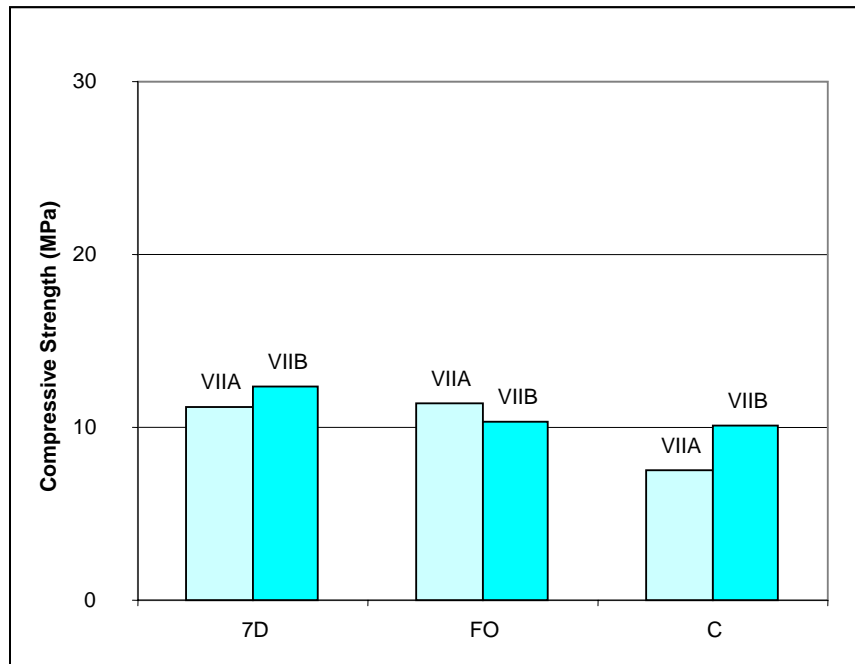


Figure 5.29 Compressive Strength Values of Specimen Group VII

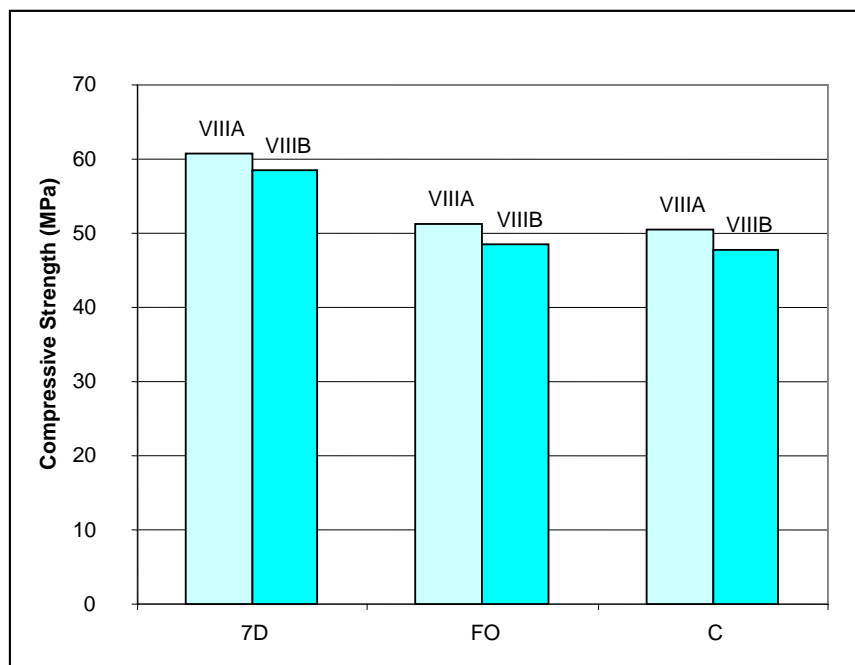


Figure 5.30 Compressive Strength Values of Specimen Group VIII

## 5.5 Flexural Strength Test Results

Flexural strength of the refractory materials was determined from the 4x4x16cm specimens. Specimen groups 7D, FO, C, 7D-FO and Ad-FO were used for flexural strength test. At Table 5.6, test results are given for each group of specimen. As mentioned in Section 5.4, water reducer admixture was used to determine the change in the mechanical properties of the refractory materials, and the specimens, seven days cured at 21°C then heated to 1100°C, were used to determine the change in the bonding strength of the steel fibres. With the increase in the bonding value of the fibres, an increase in the flexural strength was expected.

When the results are examined from Table 5.6, it is seen that the fibre containing specimens had a lower flexural strength values than the ones did not have. From the figures 5.2, 5.4, 5.6, 5.8, 5.10, 5.12, 5.14 it is clearly seen that the fibres were undamaged. This means, fibres were slipped out from the hardened mortar when a force was applied. 7D results shows that the fibres were increased the flexural strength, so there was a bonding between mortar and fibres. However, when the specimens were heated to 1100°C, the flexural strength of the specimens was reduced. After the failure of the specimens under tensional forces, it was observed that, there was a slag like covering, reducing the bonding between mortar and the fibre, on the surface of the fibres. After heating to 1100°C, fibres caused spaces as the volume of themselves. This leads to reduction in the cross-section of the specimen prepared. With the application of tensile force, it collapsed at lower values than the no-fibre used ones. Seven days of curing were thought to lead an increase in the flexural strength of the specimens after heating to 1100°C, but it was also observed that curing time did not increase the flexural strength of fibre containing, heated specimens, and it reduced the strength of the material by the reason explained above. Cailleux et al. concluded in their research that heating leads to a decohesion of the fibre – refractory castable interface caused by the thermal expansion mismatch between the two components [37].

From the Table 5.6, the specimen Group I had the best flexural strength at seven days cured group. When the specimens were heated to 1100°C, Group IV (containing granulated blast furnace slag) had better results than the other specimens. However, the addition of water reducer admixture increased the flexural strength of the Group V (containing granulated firebrick) more than the Group IV.

The Portland cement containing specimens had lower values of flexural strength than the high alumina cement containing specimens. Portland cement did not perform well enough at flexural test as they did not at compressive strength test.

Figures 5.31 to 5.38 give the comparison between the flexural strength values of the groups 7D, FO, C, 7D-FO, Ad-FO for each type of specimen.

Table 5.6 Flexural Strength Values of the Specimens

Specimen Name	Flexural Strength (MPa)				
	7D	FO	C	7D - FO	Ad - FO
IA	7,2	2,4	2,0	2,3	5,4
IB	7,6	2,1	1,8	1,5	6,6
IIA	6,9	2,2	2,4	2,2	7,5
IIB	6,0	2,1	1,9	1,5	5,6
IIIA	5,7	2,4	2,3	2,8	6,8
IIIB	5,2	2,1	1,7	2,3	5,8
IVA	5,6	3,9	3,0	3,9	6,9
IVB	5,1	2,9	2,5	3,6	8,2
VA	6,0	2,1	2,6	1,9	8,4
VB	7,4	2,2	2,2	1,5	7,1
VIA	6,3	1,7	1,4		
VIB	7,4	1,8	1,5		
VIIA	3,1	1,6	1,7		
VIIB	3,1	1,5	2,2		
VIIIA		12,0	13,3		
VIIIB		9,5	12,5		



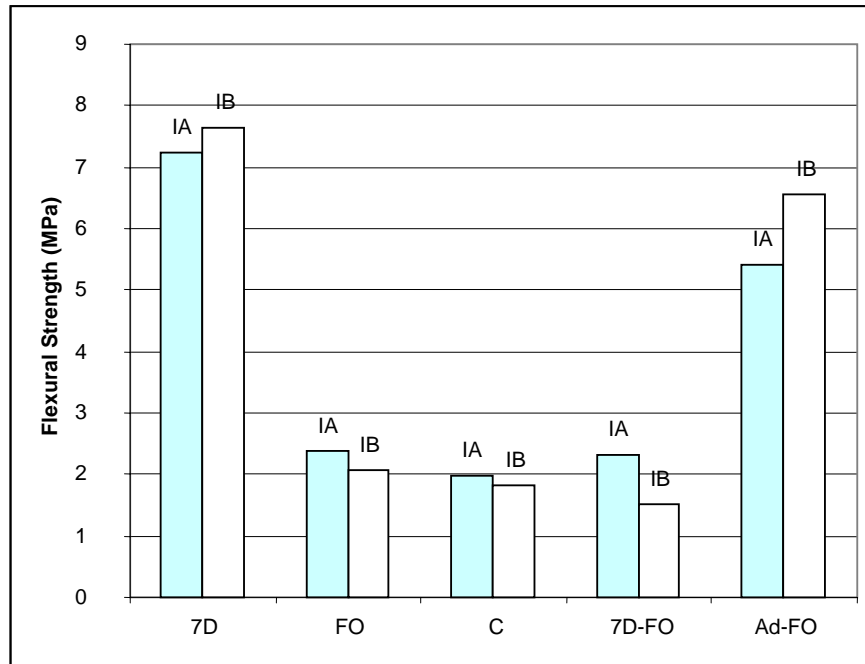


Figure 5.31 Flexural Strength Values of Specimen Group I

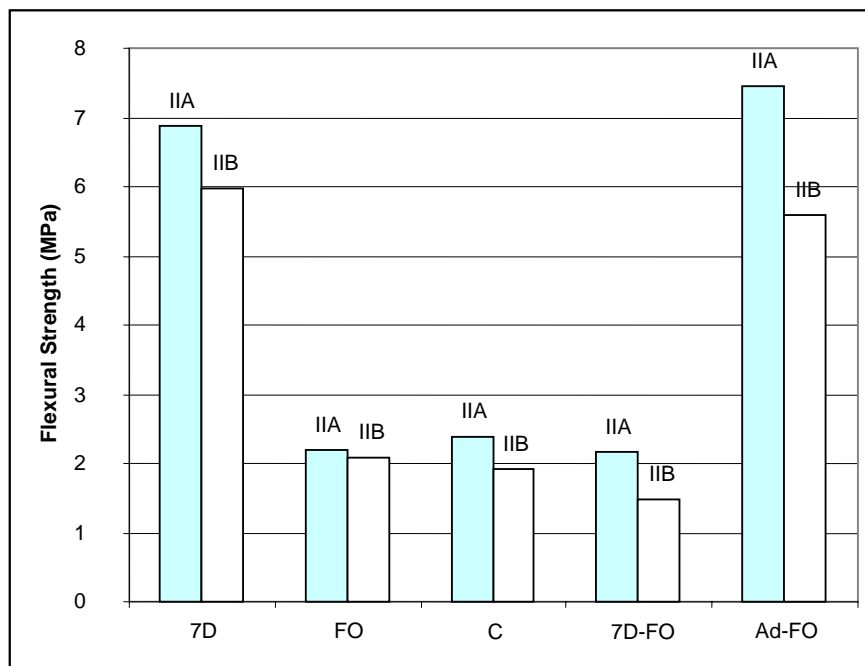


Figure 5.32 Flexural Strength Values of Specimen Group II

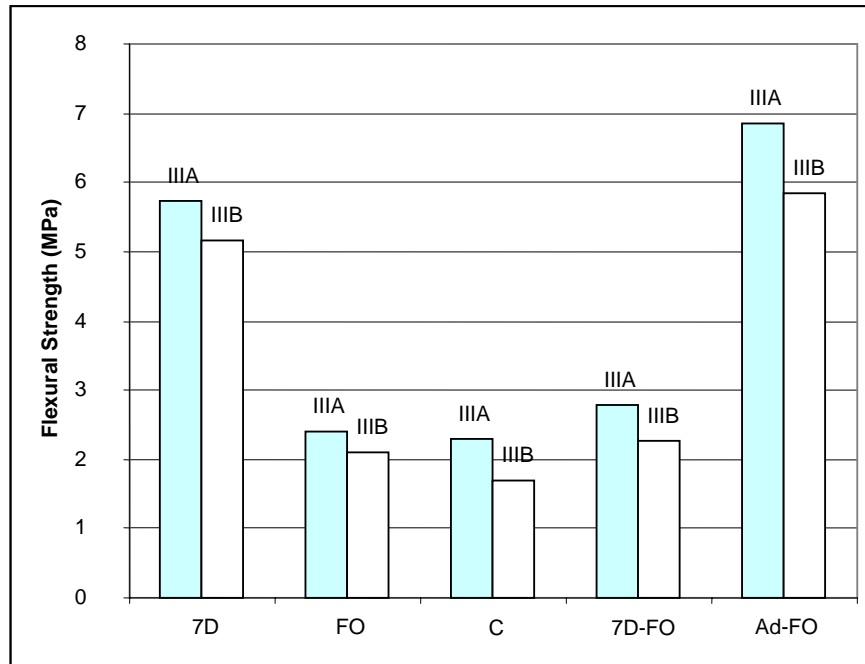


Figure 5.33 Flexural Strength Values of Specimen Group III

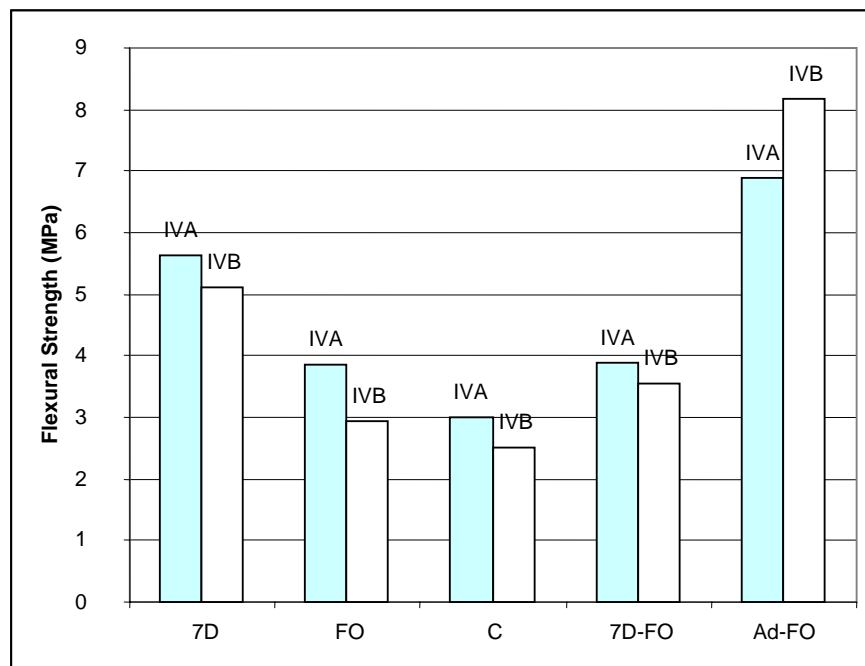


Figure 5.34 Flexural Strength Values of Specimen Group IV

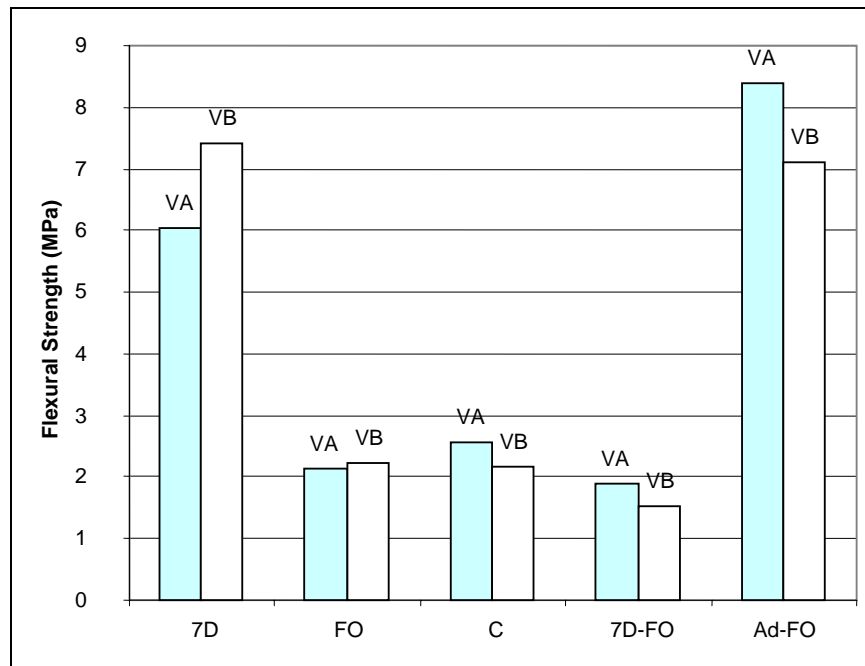


Figure 5.35 Flexural Strength Values of Specimen Group V

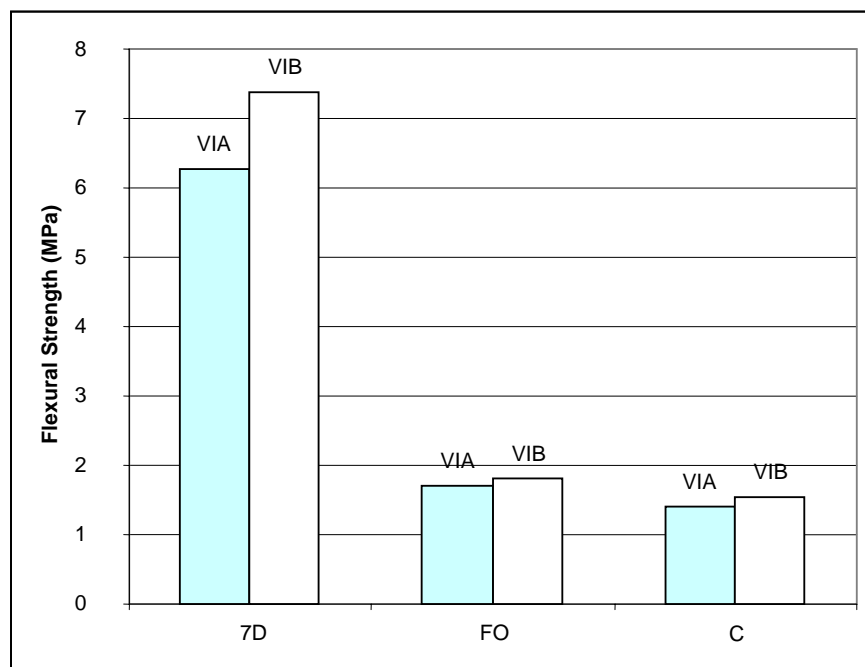


Figure 5.36 Flexural Strength Values of Specimen Group VI

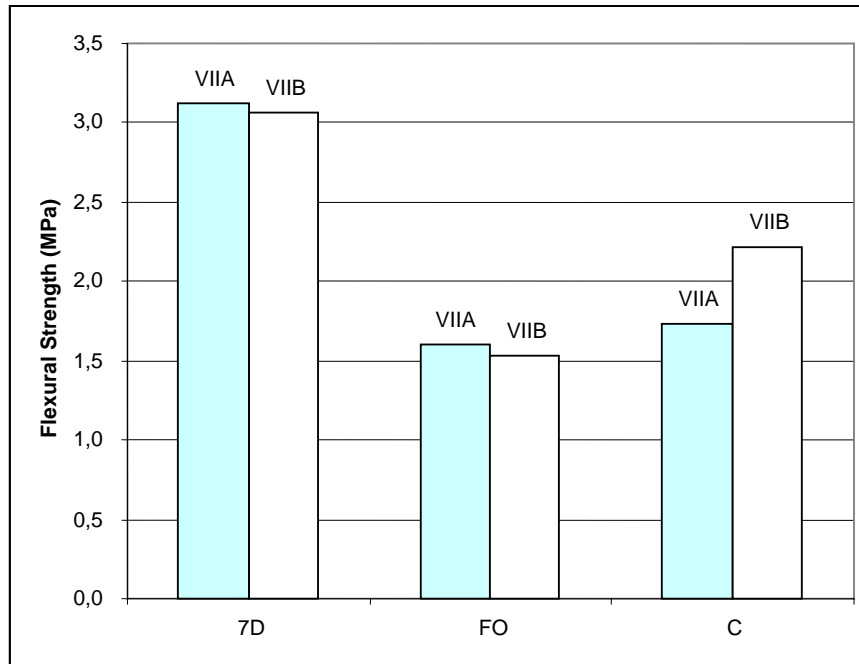


Figure 5.37 Flexural Strength Values of Specimen Group VII

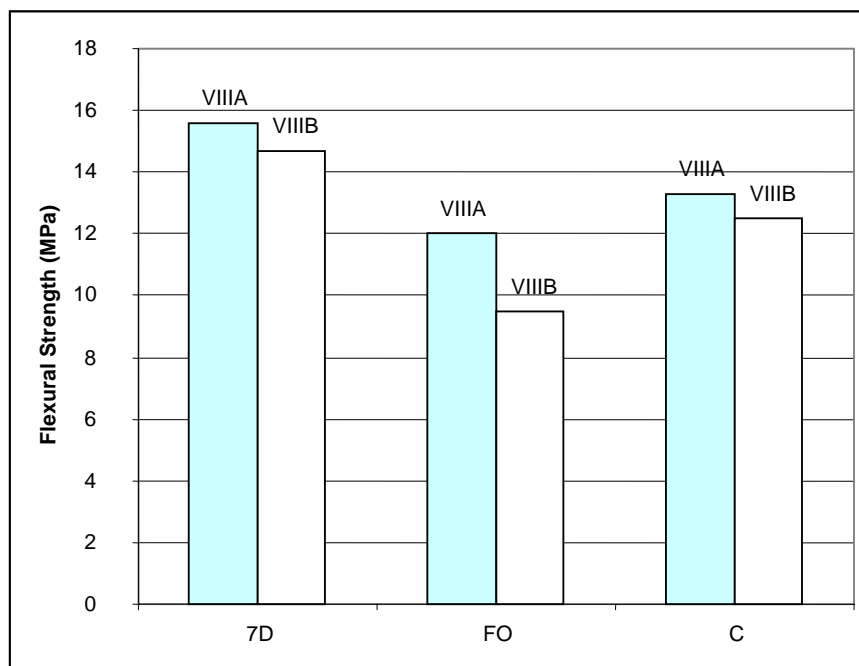


Figure 5.38 Flexural Strength Values of Specimen Group VIII

## 5.6 Ultrasound Velocity Test Results

Ultrasound test was conducted on the 5x5x5 cm specimens. Readings were taken after curing the specimens at 21°C for one day, after heating the specimens to 105°C, and after heating to 1100°C. All the consecutive readings were taken from the same sides of the specimens in order to prevent erroneous results, as the readings differ for each side of the specimen due to the force applied during the placement of the mortar to the moulds.

When the data obtained from the ultrasound test was examined at Table 5.7 and Table 5.8, it is seen that, except Portland cement containing specimens, a decrease occurred at the ultrasound velocity after heating to 105°C. However, after heating to 1100°C, there was a higher decrease in ultrasound velocity than the decrease observed after 105°C.

The examination of ultrasound velocity after ten turns of heating and cooling showed that high alumina cement containing specimens had a similar ultrasound velocity with the ones only heated to 1100°C once. However, Portland cement containing specimens showed a greater decrease in the ultrasound velocity after ten turns. This means that in long term usage of the Portland cement containing mortars will lead to internal changes, whereas the internal structure of the high alumina cement containing mortars will differentiate lesser than them after intervals of heating and cooling.

The figures 5.39 to 5.45 show the change of ultrasound velocity for each type of specimen group with and without steel fibres. Possible cause for the decrease of the ultrasound velocity could be the loss of hydrated water leading pores inside the refractory.

Table 5.7 Ultrasound Velocity of the Specimen Group FO

Specimen Name	Ultrasound Velocity (m/sec)		
	After 21°C	After 105°C	After 1100°C
IA-FO	4098	3571	2259
IB-FO	3659	3158	1838
IIA-FO	4167	3226	2226
IIB-FO	3807	3138	2072
IIIA-FO	3968	3067	2435
IIIB-FO	3958	3112	1901
IVA-FO	3513	2930	2451
IVB-FO	2879	2752	2232
VA-FO	3759	2907	2340
VB-FO	4132	2959	2005
VIA-FO	2935	3580	2137
VIB-FO	3067	2773	2022
VIIA-FO	2530	2591	2078
VIIB-FO	2467	2655	1863

Table 5.8 Ultrasound Velocity of the Specimen Group C

Specimen Name	Ultrasound Velocity (m/sec)		
	After 21°C	After 105°C	After 1100°C
IA-C	3968	3937	2269
IB-C	3906	3589	1852
IIA-C	3836	3641	2140
IIB-C	4021	3686	1590
IIIA-C	3927	3254	2400
IIIB-C	3632	2970	1767
IVA-C	3472	2935	2273
IVB-C	3191	2618	1876
VA-C	3817	2560	2169
VB-C	4076	2778	1742
VIA-C	2930	3067	1252
VIB-C	3080	2650	1234
VIIA-C	2508	2773	1284
VIIB-C	2698	2976	1245

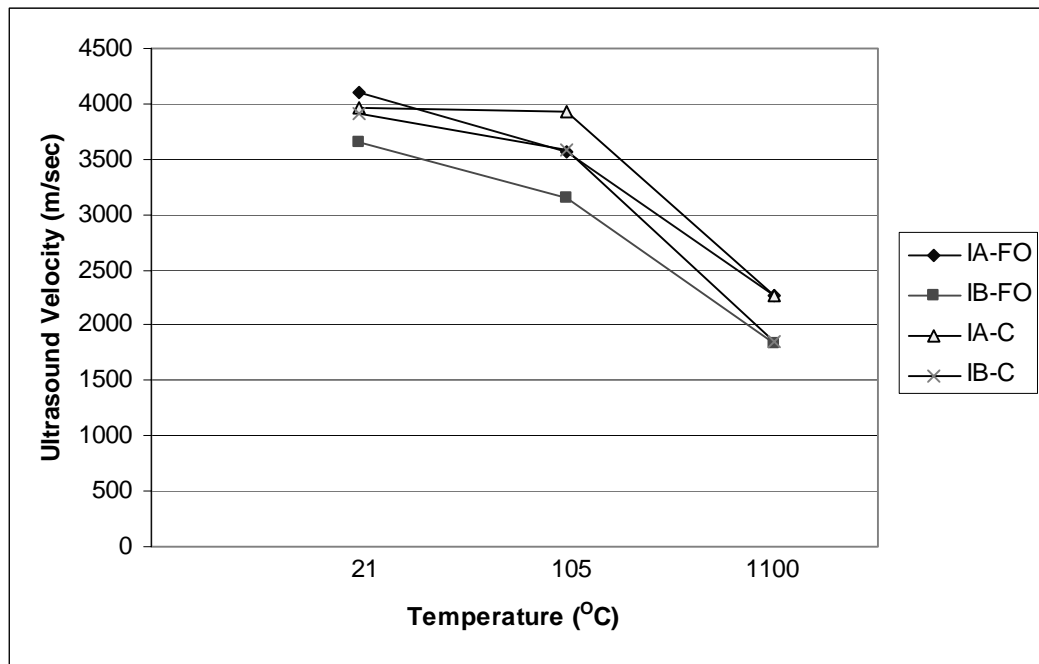


Figure 5.39 Ultrasound Velocity – Temperature Graph of Specimen Group I

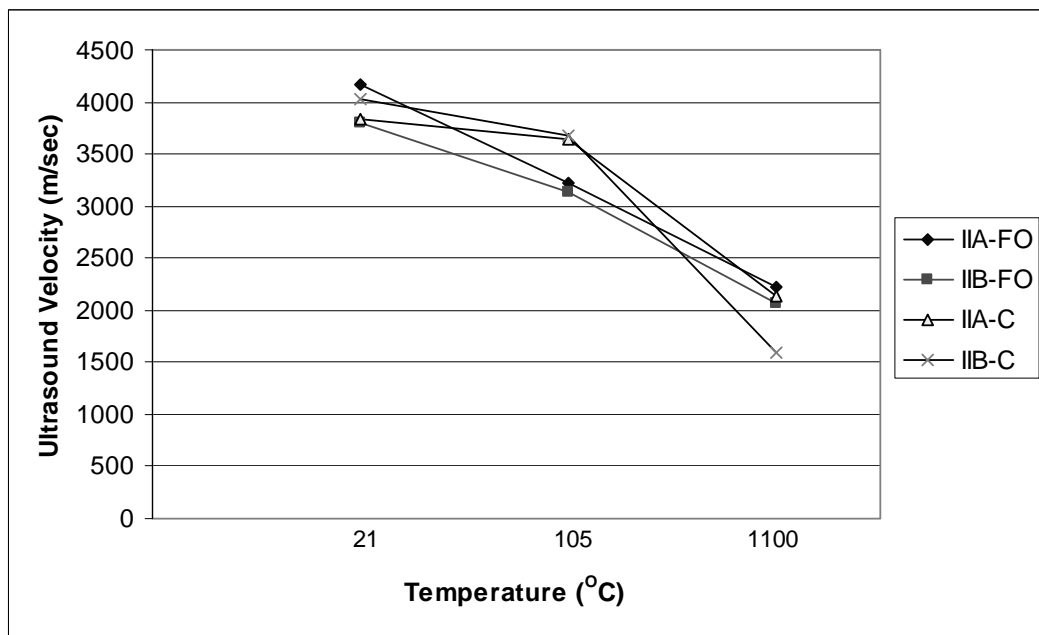


Figure 5.40 Ultrasound Velocity – Temperature Graph of Specimen Group II



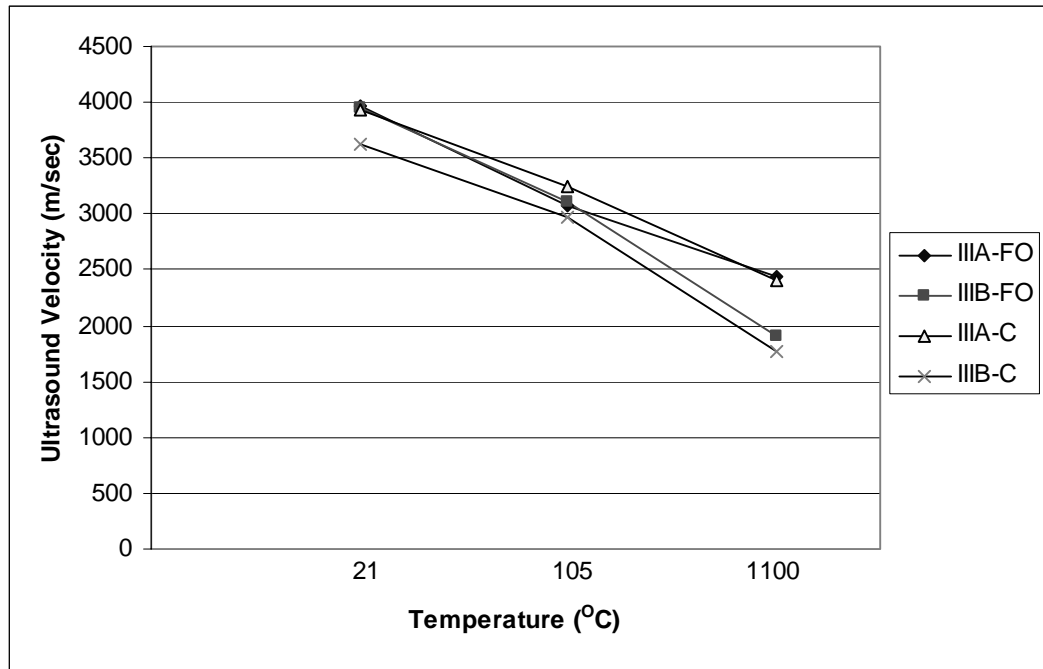


Figure 5.41 Ultrasound Velocity – Temperature Graph of Specimen Group III

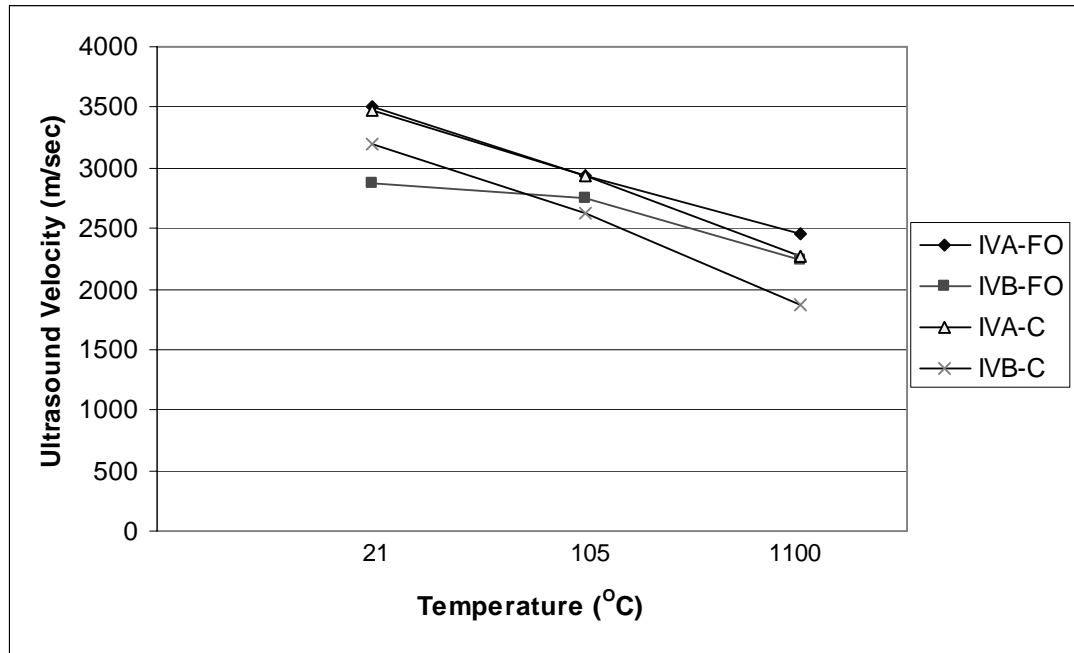


Figure 5.42 Ultrasound Velocity – Temperature Graph of Specimen Group IV

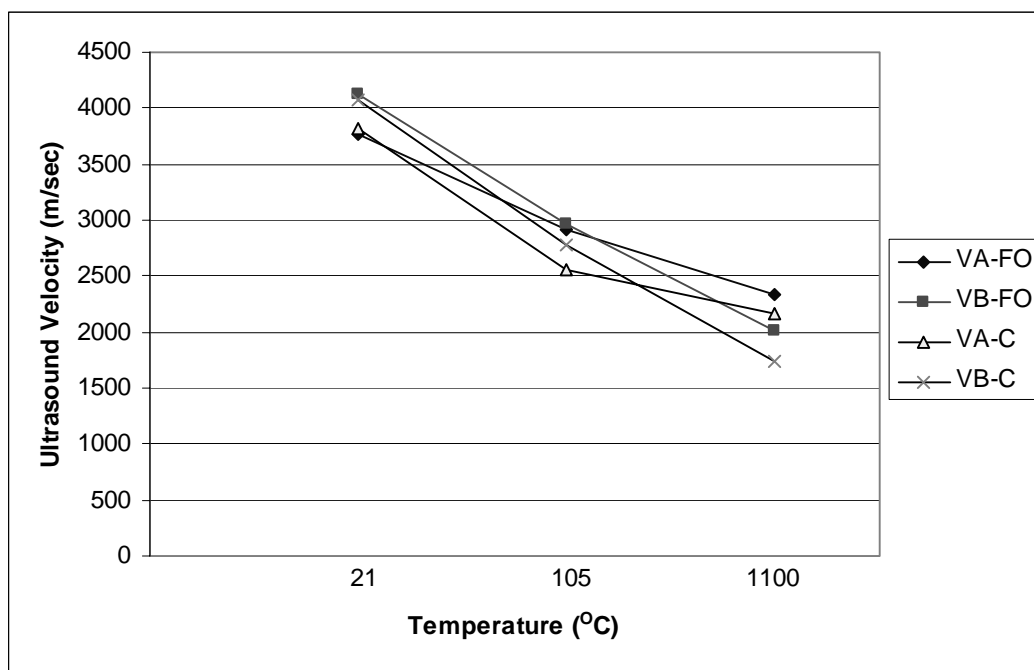


Figure 5.43 Ultrasound Velocity – Temperature Graph of Specimen Group V

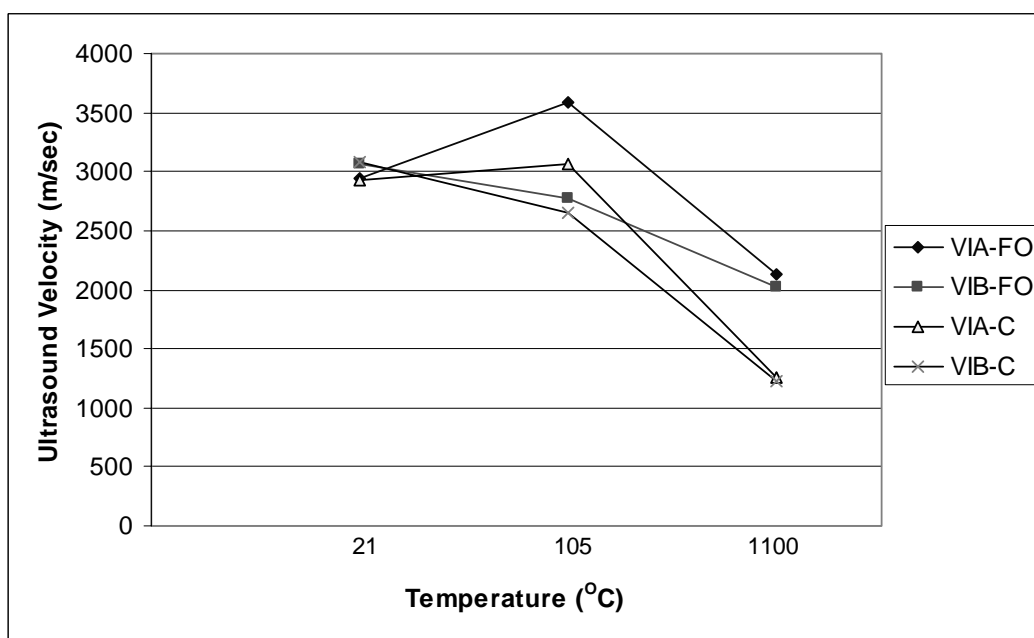


Figure 5.44 Ultrasound Velocity – Temperature Graph of Specimen Group VI

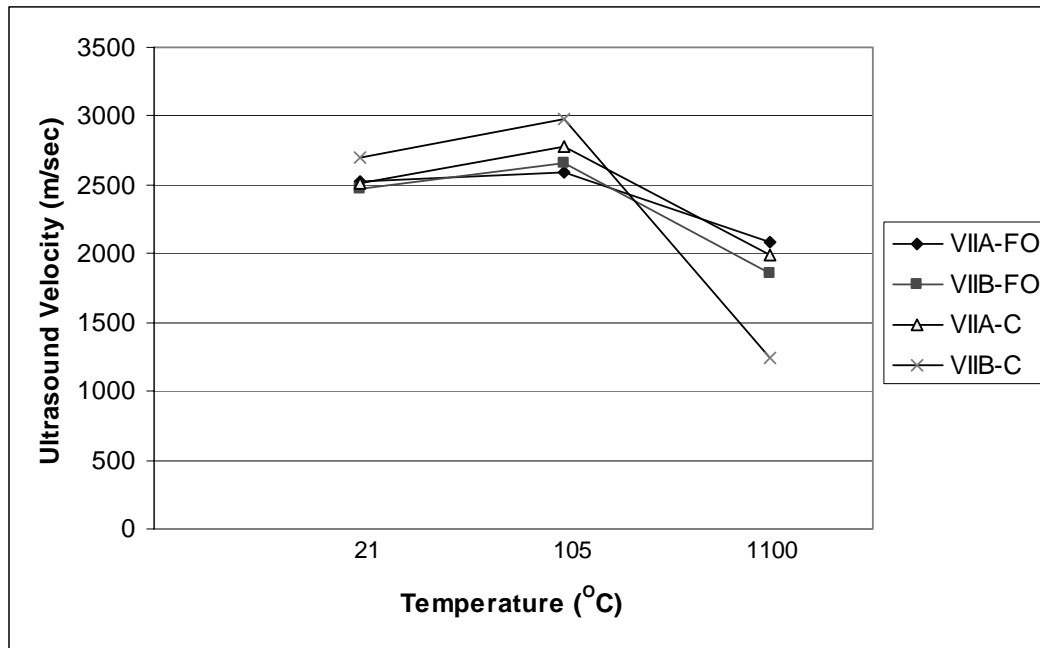


Figure 5.45 Ultrasound Velocity – Temperature Graph of Specimen Group VII

### 5.7 Investigation of Internal Structure by X-Ray Diffraction (XRD) Method

For the determination of the internal changes after heating of the specimens, XRD Method was used. In order to make a comparison between the raw materials and the product, high alumina cement, pulverized firebrick, silica fume, fly ash and granulated blast furnace slag were initially scanned. The characteristic d-spacing values of firebrick and HAC are given at the Table 5.10 and 5.11 respectively. As silica fume was found to be an amorphous material, its d-spacing values are not estimated.

Figure 5.46 shows the XRD pattern of the IA-FO. Tables 5.12 to 5.21 give the d-spacing values of the mortars prepared with high alumina cement. For

comparison of the d – spacing values and oxides found in the specimens, XRD results of the non-heated and heated specimens are given respectively at the tables.

As firebrick constituted the majority (70 – 80 % by weight) of the mortars, the intensity of firebrick was the highest in all of the specimens. It made difficult to understand the changes occurred in the hydrated cement paste. As far as it is seen from the results that, there was no great change determined in the internal structure of the specimens after heating to 1100°C. Phase changes that might be occurred between the interfacing materials were not observed as firebrick occupied a great volume. Being a pre-fired material (fired to 1300°C during its production process), no internal change occurred in the firebrick. These estimations are made according to the tables 5.10 to 5.21. The amounts of compounds forming the raw materials and mortars are given at Table 5.9.

Table 5.9 Amounts of Compounds Forming the Materials

Material	Compounds (wt%)					
	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	TiO <sub>2</sub>
Firebrick	85.0	0	1.5	0	0	3.2
HAC	40.7	38.2	17.0	2.2	0.8	2.1
I	73.93	9.55	5.38	0.55	0.2	2.93
II	72.4	8.2	4.74	3.96	0.17	2.85
III	71.67	5.31	4.05	7.67	0.48	2.66
IV	70.1	9.14	1.8	5.75	1.57	2.61
V	79.46	4.78	3.44	0.475	0.1	3.06

At each table left column is used for major d – spacing values of investigated materials. Consecutive column show the d – spacing values of investigated possible oxides found at the materials. Dark highlighted oxide names are the possible oxide forms that corresponds the peak values of the material investigated. Numbers show the major peak points corresponding to equivalent d – spacing values of the oxides. Darker highlighted colours indicate the higher intensities. Four or five numbers were highlighted as being highest intensities.

At Table 5.10 it seen that  $\alpha$  –  $\text{Al}_2\text{O}_3$  and  $\gamma$  -  $\text{Al}_2\text{O}_3$  are found as alumina in the firebrick. The amounts of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  in firebrick are very low comparing the  $\text{Al}_2\text{O}_3$  as it is seen at Table 5.9. However,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  were determined in the XRD test results. Simple form of  $\text{TiO}_2$  and  $\epsilon$  -  $\text{Fe}_2\text{O}_3$  were seen in the firebrick as well. The aim of the XRD test of the firebrick was to determine the forms of  $\text{Al}_2\text{O}_3$  so that the possible changes in the alumina would be followed in the heated mortars.

At Table 5.11, the non-hydrated HAC test results were given. The major oxides found in the HAC were highlighted. After the hydration of the HAC,  $3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O}$  was determined from the XRD test. At Tables 5.12 to 5.16, it is seen that the hydration product  $3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O}$  was found at the mortars. Also the  $\text{Al}_2\text{O}_3$  was found in  $\alpha$  –  $\text{Al}_2\text{O}_3$  and  $\gamma$  -  $\text{Al}_2\text{O}_3$  forms in the specimens before heating. The determination of  $3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  was important so as to compare the oxides found in the heated specimens.

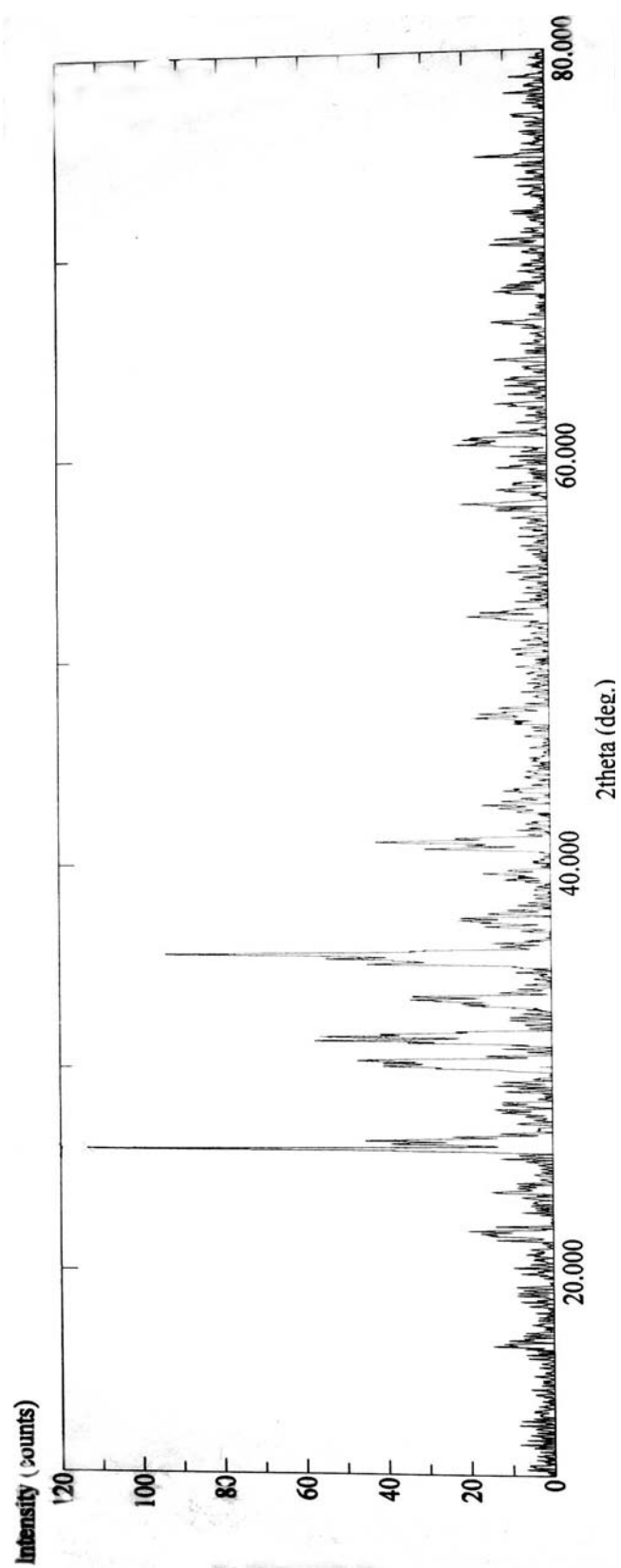


Figure 5.46 XRD Pattern of IA-FO

Table 5.10 d - spacing Values of Firebrick

	Determination of Al <sub>2</sub> O <sub>3</sub>										Determination of TiO <sub>2</sub>				Determination of Fe <sub>2</sub> O <sub>3</sub>					
	α-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	ι-Al <sub>2</sub> O <sub>3</sub>	θ-Al <sub>2</sub> O <sub>3</sub>	ε-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	χ-Al <sub>2</sub> O <sub>3</sub>	κ-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub> Brookite	β-TiO <sub>2</sub>	TiO <sub>2</sub> Rutile	TiO <sub>2</sub> Anatase	α-Fe <sub>2</sub> O <sub>3</sub> Hematite	γ-Fe <sub>2</sub> O <sub>3</sub> Maghemite	ε-Fe <sub>2</sub> O <sub>3</sub> Maghemite	η-Fe <sub>2</sub> O <sub>3</sub> Maghemite	ζ-Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> Hematite
FireBrick																				
d - value																				
5,452			5,45	5,45	4,57	4,8	6,2	5,02								5,95	6,43		6,01	
3,527		4,56		4,54	4,5	4,07	4,5	4,55	4,6		3,51	3,5	3,25	3,52			4,32		4,36	
3,493	3,479										3,47					3,86			4,15	3,85
3,436			3,47		4,11		3,04	4,07								3,75				
															3,66	3,5		3,6		3,686
2,981																3,216	3,23			
2,901		2,8	2,92	2,837	3,23	2,728	2,88	2,79	2,87	2,8	2,9	2,841	2,85				2,95	2,98	2,95	3
2,705			2,72	2,73	2,707	2,601		2,7	2,73		2,729	2,749	2,75			2,799	2,74	2,78	2,74	
2,559	2,552		2,59	2,566	2,573			2,57	2,58						2,69	2,642	2,55	2,52		2,703
2,442				2,444	2,451	2,46		2,41	2,43	2,4	2,476	2,45	2,47	2,49	2,378	2,51	2,521	2,46	2,4	2,35
2,387	2,379	2,39		2,315	2,34	2,402	2,41	2,32	2,28	2,27	2,409	2,396	2,41	2,19	2,332	2,201	2,37	2,201		2,208
		2,28	2,34	2,257	2,318	2,279	2,12	2,11	1,99		2,244	2,262	2,17			2,24			2,11	
2,128			2,24		2,282			2,06			2,133	2,15	2,12			2,089	1,98	2,08	2	2,01
2,095	2,085	1,977	2,15	2,019	2,185			1,99	1,95	1,97	1,969	2,118		1,892			1,94			1,92
			1,88	1,9094		1,986		1,95	1,91		1,893	1,996	2,01						1,87	
					1,979	1,953	1,96	1,87	1,8		1,851	1,83			1,838	1,822		1,81		1,8428
					1,947	1,914		1,82	1,54											
1,743	1,74		1,73					1,74	1,51			1,748					1,74			1,72
1,703											1,691	1,697	1,7	1,69	1,6999	1,69	1,702	1,7		
1,674								1,64			1,662	1,663	1,67						1,66	
1,604	1,601	1,52	1,55	1,5426							1,61	1,646	1,65	1,6665		1,608		1,61	1,58	1,61
1,528													1,62				1,54			1,53
1,522																	1,52			
1,514	1,404	1,395	1,288		1,4883	1,517			1,49		1,461	1,48		1,4808	1,484		1,47	1,48		1,4873
											1,452									
			1,4526	1,407				1,49	1,45	1,52		1,404	1,4		1,452					1,4543
1,374				1,3883	1,39	1,396	1,395	1,45	1,4	1,4		1,396		1,36	1,2649		1,39			1,42
1,239								1,43	1,39	1,21		1,323			1,31					1,39
		1,14						1,39	1,29	1,14			1,14							1,3133
		0,806						1,34	1,26	1,03					1,141			1,09		1,1416

Table 5.11 d - spacing Values of HAC

	Determination of Constituents						
HAC d - value	12CaO.7Al <sub>2</sub> O <sub>3</sub>	CaO.2Al <sub>2</sub> O <sub>3</sub>	CaO.2Al <sub>2</sub> O <sub>3</sub>	4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	2CaO.Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub>	CaO.Al <sub>2</sub> O <sub>3</sub>	CaO (Lime)
4,935	4,8944						
4,695						4,67	
4,414		4,4312	4,44				
		3,5962	3,6022		3,7		
3,459		3,4834	3,5054				
3,070	3,2041	3,0777	3,3236		3,07		
2,985	2,9972		3,0808				
2,977						2,971	
2,969						2,966	
2,828		2,8725	2,8781		2,84		
2,778							2,778
2,771		2,7532	2,7507	2,77			
2,688	2,6808	2,7159	2,7098				
2,636	2,4472	2,6037	2,7003	2,63			
2,586		2,5888	2,6052	2,19			
2,527		2,5278	2,5956	2,15		2,518	2,405
2,41		2,4235	2,5311		2,41		
		2,3277	2,4363		2,29		
2,192	2,1888		2,3257				
2,027		2,0518	2,0539	2,03			
1,929	1,9448			1,92	1,92		
		1,7939	1,8002	1,85	1,81		
		1,7561	1,7643	1,81			
1,748				1,73	1,75		1,701
1,703							
1,568	1,6625			1,57			
1,534	1,6021	1,5312	1,5342	1,53			
		1,5285		1,49			1,451
1,452				1,45			
				1,42	1,37		
	1,3936			1,39			
				1,36			
				1,32			
				1,21			
				1			



D – spacing values of the heated specimens were given at the Tables 5.17 to 5.21. It is clear from the results that the same oxides found in the specimens before heating, was found again in the specimens after heating. There were small shifts in some peak points when compared to non-heated state, but the new peak points also corresponds to oxides found in the non-heated specimens.

The amount of alumina occupies the most of the specimen volume as firebrick was used in high amounts (70 – 80 % by weight). The  $\alpha - \text{Al}_2\text{O}_3$  and  $\gamma - \text{Al}_2\text{O}_3$  were seen in all of the specimens. Thus the major oxide, alumina, was found to be unchanged. The refractoriness of the mortars was provided by the alumina so the unchanged state of alumina was thought to be an advantage for the new refractory made.

Table 5.12 d - spacing Values of I-7D

IA - 7Days d - value	Determination of 3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O		Determination of Al <sub>2</sub> O <sub>3</sub>									
	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	α-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	ι-Al <sub>2</sub> O <sub>3</sub>	θ-Al <sub>2</sub> O <sub>3</sub>	ε-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	χ-Al <sub>2</sub> O <sub>3</sub>	κ-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>
5,34					5,45	5,45				6,2		
5,155	5,1329	5,1276									5,02	
				4,56		4,54	4,5	4,57	4,8	4,5	4,55	4,6
3,47	4,4452	4,4406					4,11	4,07			4,07	
3,36	3,3602	3,3568	3,479		3,47		3,23			3,04	2,87	
	3,1432	3,14										
	2,8114	2,8085										
2,688				2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,541	2,5664	2,5638	2,552		2,72	2,73				2,7		
	2,4657	2,4632	2,379	2,39	2,34	2,444	2,451	2,46	2,41	2,57		
							2,34					
2,291	2,2955	2,2931				2,315	2,318	2,402		2,41	2,43	2,4
				2,28	2,24	2,257	2,282	2,279		2,32	2,28	2,27
2,083			2,085		2,15	2,019	2,185					
2,027	2,0396	2,0375										
									2,12	2,11		
				1,977		1,9094	1,979	1,986	1,96	1,99	1,99	1,97
					1,88		1,947	1,953		1,95	1,95	1,92
	1,7435	1,7417						1,914		1,87	1,91	1,4
	1,7109	1,7079	1,74		1,73					1,82	1,8	1,21
	1,6801	1,6784								1,74	1,54	1,14
1,599	1,5716	1,57	1,601							1,64	1,51	1,03
				1,52	1,55	1,5426		1,517		1,49	1,49	
						1,4883		1,407		1,45	1,45	
			1,404	1,395		1,4526	1,39	1,396	1,395	1,39	1,39	
			1,374			1,3883				1,34		
			1,239		1,288						1,29	

Table 5.13 d - spacing Values of II-7D

IIA - 7Days d - value	Determination of 3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O		Determination of Al <sub>2</sub> O <sub>3</sub>									
	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	α-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	ι-Al <sub>2</sub> O <sub>3</sub>	θ-Al <sub>2</sub> O <sub>3</sub>	ε-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	χ-Al <sub>2</sub> O <sub>3</sub>	κ-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>
5,423					5,45	5,45				6,2		
5,104		5,1329									5,02	
				4,56		4,54	4,5	4,57	4,8	4,5	4,55	4,6
	4,4452	4,4406					4,11	4,07			4,07	
3,47			3,479		3,47		3,23			3,04	2,87	
	3,3602	3,3568										
	3,1432	3,14										
2,785	2,8114	2,8085										
2,702				2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,574					2,72	2,73				2,7		
2,556	2,5664	2,5638	2,552		2,59	2,566	2,573	2,601			2,58	
	2,4657	2,4632	2,379	2,39	2,34	2,444	2,451	2,46	2,41	2,57		
							2,34					
						2,315	2,318	2,402		2,41	2,43	2,4
2,284	2,2955	2,2931			2,24	2,257	2,282	2,279		2,32	2,28	2,27
				2,28	2,15	2,019	2,185					
2,091			2,085									
2,087	2,0396	2,0375							2,12	2,11		
						1,9094	1,979	1,986	1,96	1,99	1,99	1,97
				1,977	1,88		1,947	1,953		1,95	1,95	1,52
								1,914		1,87	1,91	1,4
	1,7435	1,7417			1,73					1,82	1,8	1,21
	1,7109	1,7079	1,74							1,74	1,54	1,14
	1,6801	1,6784								1,64	1,51	1,03
1,601	1,5716	1,57	1,601		1,55	1,5426		1,517		1,49	1,49	
				1,52		1,4883		1,407		1,45	1,45	
						1,4526	1,39	1,396	1,395	1,39	1,39	
			1,404	1,395		1,3883				1,34		
			1,374		1,288							1,29
			1,239									1,26

Table 5.14 d - spacing Values of III-7D

III A - 7Days d - value	Determination of 3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O		Determination of Al <sub>2</sub> O <sub>3</sub>									
	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	α-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	ι-Al <sub>2</sub> O <sub>3</sub>	θ-Al <sub>2</sub> O <sub>3</sub>	ε-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	χ-Al <sub>2</sub> O <sub>3</sub>	κ-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>
5,452						5,45	5,45			6,2		
5,104	5,1329	5,1276									5,02	
				4,56			4,54	4,5	4,57	4,8	4,5	4,6
3,475	4,4452	4,4406						4,11	4,07		4,07	
			3,479			3,47		3,23		3,04	2,87	
	3,3602	3,3568										
	3,1432	3,14										
2,785	2,8114	2,8085		2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,732					2,72	2,73				2,7		
2,562	2,5664	2,5638	2,552		2,59	2,566	2,573	2,601			2,58	
	2,4657	2,4632	2,379	2,39	2,34	2,444	2,451	2,46	2,41	2,57		
							2,34					
2,3	2,2955	2,2931				2,315	2,318	2,402		2,41	2,43	2,4
				2,28	2,24	2,257	2,282	2,279		2,32	2,28	2,27
2,093			2,085		2,15	2,019	2,185					
2,02	2,0396	2,0375										
									2,12	2,11		
				1,977		1,9094	1,979	1,986	1,96	1,99	1,99	1,97
					1,88		1,947	1,953		1,95	1,95	1,52
	1,7435	1,7417						1,914		1,87	1,91	1,4
	1,7109	1,7079	1,74		1,73					1,82	1,8	1,21
	1,6801	1,6784								1,74	1,54	1,14
1,605	1,5716	1,57	1,601							1,64	1,51	1,03
				1,52	1,55	1,5426		1,517		1,49	1,49	
						1,4883		1,407		1,45	1,45	
			1,404	1,395		1,4526	1,39	1,396	1,395	1,39	1,39	
			1,374			1,3883				1,34		
			1,239		1,288						1,29	

Table 5.15 d - spacing Values of IV-7D

IVA - 7Days d - value	Determination of 3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O		Determination of Al <sub>2</sub> O <sub>3</sub>									
	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	α-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	ι-Al <sub>2</sub> O <sub>3</sub>	θ-Al <sub>2</sub> O <sub>3</sub>	ε-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	χ-Al <sub>2</sub> O <sub>3</sub>	κ-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>
5,45					5,45	5,45				6,2		
5,18	5,1329	5,1276									5,02	
				4,56		4,54	4,5	4,57	4,8	4,5	4,55	4,6
	4,4452	4,4406					4,11	4,07			4,07	
3,459			3,479		3,47		3,23			3,04	2,87	
	3,3602	3,3568										
	3,1432	3,14										
2,843	2,8114	2,8085		2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,708					2,72	2,73				2,7		
2,538	2,5664	2,5638	2,552		2,59	2,566	2,573	2,601			2,58	
	2,4657	2,4632	2,379	2,39	2,34	2,444	2,451	2,46	2,41	2,57		
							2,34					
2,282	2,2955	2,2931				2,315	2,318	2,402		2,41	2,43	2,4
				2,28	2,24	2,257	2,282	2,279		2,32	2,28	2,27
2,077			2,085		2,15	2,019	2,185					
2,027	2,0396	2,0375										
				1,977		1,9094	1,979	1,986	2,12	2,11		
					1,88		1,947	1,953	1,96	1,99	1,99	1,97
	1,7435	1,7417						1,914		1,95	1,95	1,52
	1,7109	1,7079	1,74		1,73					1,87	1,91	1,4
	1,6801	1,6784								1,82	1,8	1,21
1,601	1,5716	1,57	1,601							1,74	1,54	1,14
				1,52	1,55	1,5426				1,64	1,51	1,03
								1,517		1,49	1,49	
						1,4883		1,407		1,45	1,45	
			1,404	1,395		1,4526	1,39	1,396	1,395	1,39	1,39	
			1,374			1,3883				1,34		
			1,239		1,288						1,29	

Table 5.16 d - spacing Values of V-7D

VA - 7Days d - value	Determination of 3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O		Determination of Al <sub>2</sub> O <sub>3</sub>									
	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	α-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	ι-Al <sub>2</sub> O <sub>3</sub>	θ-Al <sub>2</sub> O <sub>3</sub>	ε-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	χ-Al <sub>2</sub> O <sub>3</sub>	κ-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>
5,45					5,45	5,45				6,2		
5,104	5,1329	5,1276									5,02	
				4,56		4,54	4,5	4,57	4,8	4,5	4,55	4,6
	4,4452	4,4406					4,11	4,07			4,07	
3,425			3,479		3,47		3,23			3,04	2,87	
	3,3602	3,3568										
	3,1432	3,14										
2,785	2,8114	2,8085		2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,72					2,72	2,73				2,7		
2,61					2,59	2,566	2,573	2,601			2,58	
2,515	2,5664	2,5638	2,552		2,34	2,444	2,451	2,46	2,41	2,57		
	2,4657	2,4632	2,379	2,39			2,34					
						2,315	2,318	2,402		2,41	2,43	2,4
2,272	2,2955	2,2931			2,24	2,257	2,282	2,279		2,32	2,28	2,27
				2,28	2,15	2,019	2,185					
2,066			2,085									
2,06	2,0396	2,0375							2,12	2,11		
						1,9094	1,979	1,986	1,96	1,99	1,99	1,97
				1,977	1,88		1,947	1,953		1,95	1,95	1,52
								1,914		1,87	1,91	1,4
	1,7435	1,7417			1,73					1,82	1,8	1,21
	1,7109	1,7079	1,74							1,74	1,54	1,14
	1,6801	1,6784								1,64	1,51	1,03
1,59	1,5716	1,57	1,601		1,55	1,5426		1,517		1,49	1,49	
				1,52		1,4883		1,407		1,45	1,45	
						1,4526	1,39	1,396	1,395	1,39	1,39	
			1,404	1,395		1,3883				1,34		
			1,374		1,288						1,29	
			1,239								1,26	

Table 5.17 d - spacing Values of I-FO

IA - FO d - value	Determination of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$		Determination of $\text{Al}_2\text{O}_3$									
	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$\alpha\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\iota\text{-Al}_2\text{O}_3$	$\theta\text{-Al}_2\text{O}_3$	$\epsilon\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\chi\text{-Al}_2\text{O}_3$	$\kappa\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\eta\text{-Al}_2\text{O}_3$
5,46						5,45	5,45			6,2		
											5,02	
	5,1329	5,1276										
				4,56			4,54	4,5	4,57	4,8	4,5	4,6
	4,4452	4,4406						4,11	4,07			4,07
3,4268			3,479			3,47		3,23		3,04	2,87	
3,3783												
	3,3602	3,3568										
	3,1432	3,14										
	2,8114	2,8085										
				2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,5573	2,5664	2,5638	2,552		2,72	2,73				2,7		
	2,4657	2,4632	2,379	2,39	2,34	2,444	2,451	2,46	2,41	2,57		
							2,34					
	2,2955	2,2931					2,315	2,318	2,402	2,41	2,43	2,4
				2,28	2,24	2,257	2,282	2,279		2,32	2,28	2,27
			2,085		2,15	2,019	2,185					
2,05	2,0396	2,0375										
									2,12	2,11		
				1,977		1,9094	1,979	1,986	1,96	1,99	1,99	1,97
					1,88		1,947	1,953		1,95	1,95	1,52
	1,7435	1,7417						1,914		1,87	1,91	1,4
	1,7109	1,7079	1,74		1,73					1,82	1,8	1,21
	1,6801	1,6784								1,74	1,54	1,14
	1,5716	1,57	1,601							1,64	1,51	1,03
				1,52	1,55	1,5426		1,517		1,49	1,49	
						1,4883		1,407		1,45	1,45	
			1,404	1,395		1,4526	1,39	1,396	1,395	1,39	1,39	
			1,374			1,3883				1,34		
			1,239		1,288						1,29	

Table 5.18 d - spacing Values of II-FO

IIA - FO d - value	Determination of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$		Determination of $\text{Al}_2\text{O}_3$									
	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$\alpha\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\iota\text{-Al}_2\text{O}_3$	$\theta\text{-Al}_2\text{O}_3$	$\epsilon\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\chi\text{-Al}_2\text{O}_3$	$\kappa\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\eta\text{-Al}_2\text{O}_3$
5,4668						5,45	5,45				6,2	
												5,02
	5,1329	5,1276										
				4,56			4,54	4,5	4,57	4,8	4,5	4,55
	4,4452	4,4406						4,11	4,07			4,07
3,4822			3,479			3,47		3,23		3,04	2,87	
3,3909	3,3602	3,3568										
	3,1432	3,14										
	2,8114	2,8085			2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73
2,6994						2,72	2,73				2,7	
2,5517	2,5664	2,5638	2,552			2,59	2,566	2,573	2,601			
	2,4657	2,4632	2,379	2,39	2,34	2,34	2,444	2,451	2,46	2,41	2,57	
								2,34				
2,3008	2,2955	2,2931					2,315	2,318	2,402		2,41	2,43
				2,28	2,24	2,257	2,257	2,282	2,279		2,32	2,28
2,0869			2,085			2,15	2,019	2,185				
2,0869	2,0396	2,0375										
										2,12	2,11	
				1,977			1,9094	1,979	1,986	1,96	1,99	1,97
					1,88			1,947	1,953		1,95	1,95
	1,7435	1,7417							1,914		1,87	1,91
	1,7109	1,7079	1,74		1,73						1,82	1,8
	1,6801	1,6784									1,74	1,54
1,6035	1,5716	1,57	1,601								1,64	1,51
				1,52	1,55		1,5426		1,517		1,49	1,49
							1,4883		1,407		1,45	1,45
			1,404	1,395			1,4526	1,39	1,396	1,395	1,39	1,39
			1,374				1,3883				1,34	
			1,239			1,288						1,29



Table 5.19 d - spacing Values of III-FO

IIIA - FO d - value	Determination of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$		Determination of $\text{Al}_2\text{O}_3$									
	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$\alpha\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\iota\text{-Al}_2\text{O}_3$	$\theta\text{-Al}_2\text{O}_3$	$\epsilon\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\chi\text{-Al}_2\text{O}_3$	$\kappa\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\eta\text{-Al}_2\text{O}_3$
5,4668					5,45	5,45				6,2		
		5,1329	5,1276								5,02	
		4,4452	4,4406	4,56		4,54	4,5	4,57	4,8	4,5	4,55	4,6
3,501							4,11	4,07			4,07	
3,3732		3,3602	3,3568		3,47		3,23			3,04	2,87	
		3,1432	3,14									
		2,8114	2,8085	2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,725					2,72	2,73				2,7		
2,5845					2,59	2,566	2,573	2,601			2,58	
2,5587		2,5664	2,5638		2,34	2,444	2,451	2,46	2,41	2,57		
		2,4657	2,4632	2,39			2,34					
							2,315	2,318		2,41	2,43	2,4
2,41		2,2955	2,2931		2,24	2,257	2,282	2,279		2,32	2,28	2,27
				2,28	2,15	2,019	2,185					
2,0934												
2,0352		2,0396	2,0375						2,12	2,11		
						1,9094	1,979	1,986	1,96	1,99	1,99	1,97
				1,977	1,88		1,947	1,953		1,95	1,95	1,52
								1,914		1,87	1,91	1,4
1,7584		1,7435	1,7417		1,73					1,82	1,8	1,21
		1,7109	1,7079	1,74						1,74	1,54	1,14
		1,6801	1,6784							1,64	1,51	1,03
1,6045		1,5716	1,57			1,55	1,5426	1,517		1,49	1,49	
						1,52	1,4883	1,407		1,45	1,45	
							1,4526	1,39	1,396	1,395	1,39	1,39
				1,404	1,395		1,3883			1,34		
				1,374		1,288					1,29	
				1,239							1,26	

Table 5.20 d - spacing Values of IV-FO

IVA - FO d - value	Determination of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$		Determination of $\text{Al}_2\text{O}_3$									
	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	$\alpha\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$	$\iota\text{-Al}_2\text{O}_3$	$\theta\text{-Al}_2\text{O}_3$	$\epsilon\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\chi\text{-Al}_2\text{O}_3$	$\kappa\text{-Al}_2\text{O}_3$	$\delta\text{-Al}_2\text{O}_3$	$\eta\text{-Al}_2\text{O}_3$
5,4468					5,45	5,45				6,2		
	5,1329	5,1276									5,02	
	4,4452	4,4406		4,56			4,54	4,5	4,57	4,8	4,55	4,6
3,4609			3,479		3,47			4,11	4,07		4,07	
3,3657	3,3602	3,3588						3,23		3,04	2,87	
3,1379	3,1432	3,14										
2,8554	2,8114	2,8085		2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,6962					2,72	2,73				2,7		
2,5715					2,59	2,566	2,573	2,601			2,58	
2,5531	2,5664	2,5638	2,552		2,34	2,444	2,451	2,46	2,41	2,57		
	2,4657	2,4632	2,379	2,39			2,34					
						2,315	2,318	2,402		2,41	2,43	2,4
2,2962	2,2955	2,2931			2,24	2,257	2,282	2,279		2,32	2,28	2,27
2,0888			2,085	2,28	2,15	2,019	2,185					
2,0404	2,0396	2,0375										
						1,9094	1,979	1,986	2,12	2,11		
				1,977	1,88		1,947	1,953	1,96	1,99	1,99	1,97
								1,914		1,95	1,95	1,52
1,7416	1,7435	1,7417			1,73					1,87	1,91	1,4
	1,7109	1,7079	1,74							1,82	1,8	1,21
	1,6801	1,6784								1,74	1,54	1,14
1,6035	1,5716	1,57	1,601							1,64	1,51	1,03
					1,55	1,5426		1,517		1,49	1,49	
				1,52		1,4883		1,407		1,45	1,45	
						1,4526	1,39	1,396	1,395	1,39	1,39	
			1,404	1,395		1,3883				1,34		
			1,374		1,288						1,29	
			1,239								1,26	

Table 5.21 d - spacing Values of V-FO

VA - FO d - value	Determination of 3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O		Determination of Al <sub>2</sub> O <sub>3</sub>									
	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	3CaO.Al <sub>2</sub> O <sub>3</sub> .6H <sub>2</sub> O	α-Al <sub>2</sub> O <sub>3</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	ι-Al <sub>2</sub> O <sub>3</sub>	θ-Al <sub>2</sub> O <sub>3</sub>	ε-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	χ-Al <sub>2</sub> O <sub>3</sub>	κ-Al <sub>2</sub> O <sub>3</sub>	δ-Al <sub>2</sub> O <sub>3</sub>	η-Al <sub>2</sub> O <sub>3</sub>
5,4203					5,45	5,45				6,2		
		5,1329	5,1276								5,02	
				4,56		4,54	4,5	4,57	4,8	4,5	4,55	4,6
3,4929		4,4452	4,4406				4,11	4,07			4,07	
3,3558		3,3602	3,3588				3,23			3,04	2,87	
		3,1432	3,14									
2,8082		2,8114	2,8085									
2,7201				2,8	2,92	2,837	2,707	2,728	2,88	2,79	2,73	2,8
2,5503		2,5664	2,5638		2,72	2,73				2,7		
		2,4657	2,4632	2,552	2,59	2,566	2,573	2,601			2,58	
				2,379	2,39	2,444	2,451	2,46	2,41	2,57		
							2,34					
2,2962		2,2955	2,2931			2,315	2,318	2,402		2,41	2,43	2,4
				2,28	2,24	2,257	2,282	2,279		2,32	2,28	2,27
2,0915				2,085	2,15	2,019	2,185					
		2,0396	2,0375									
				1,977		1,9094	1,979	1,986	2,12	2,11		
					1,88		1,947	1,953	1,96	1,99	1,99	1,97
1,744	1,7435	1,7417						1,914		1,87	1,91	1,4
	1,7109	1,7079	1,74		1,73					1,82	1,8	1,21
	1,6801	1,6784								1,74	1,54	1,14
1,6035			1,601							1,64	1,51	1,03
1,5829	1,5716	1,57			1,55	1,5426						
				1,52		1,4883		1,517		1,49	1,49	
			1,404	1,395		1,4526	1,39	1,407		1,45	1,45	
			1,374			1,3883		1,396	1,395	1,39	1,39	
			1,239		1,288					1,34		

## **CHAPTER 6**

### **CONCLUSIONS**

According to the results and observations derived from the study, following conclusions can be drawn;

1. Specimens containing HAC (high alumina cement) and granulated blast furnace slag (Group IV) and granulated firebrick (Group V), had the best workability among the other specimen groups. After failure of the specimens in flexural strength test, smaller pores were observed by naked eye at both of these groups comparing to other types. Thus, an increase in the fine material leads to a less porous structure.
2. HAC containing specimens were hardened faster than the Portland cement containing ones. HAC containing groups de-moulded easily after one day of curing at 21°C. Although silica fume slowed down the initial hardening of mortar, Portland cement containing specimens were still the slowest.
3. Steel fibre usage increased the amount of coarse particles found in the mortars, so a more porous structure was observed at the specimens containing steel fibres.
4. Weight loss of the specimens varied from 8.5% to 10.5%, as the water content of the specimens varied from 11% to 12.5%. All the materials used in the study were pre-fired materials that no weight loss was expected from them. Due to these reasons weight loss was related with the loss of excess water and hydrated water. The reason of high loss of water in Portland cement containing specimens after heating to 105°C was the slower rate of hydration reaction comparing to HAC containing specimens. Silica fume containing group (Group II) lost the highest weight as expected, because of

its high water content. Ten turns of heating and cooling did not make any considerable changes in weight comparing to one turn of heating and cooling.

5. HAC containing mortars had small changes in size after heating to 1100°C. After several turns of heating and cooling, less change in size was observed, which means specimens became more stable to size changes in long run. Group IV (containing granulated blast furnace slag) had the smallest change in size after first heating to 1100°C. However, Group II (containing silica fume) had the best results after ten turns of heating and cooling. Steel fibre addition reduced the size change of the mortars prepared.
6. Water reducer admixture (superplasticizer) addition increased the compressive strength of the specimens that were heated to 1100°C. Steel fibre addition did not affect the compressive strength, even strength loss was observed at the specimens. One day curing at 21°C is sufficient to achieve a good service compressive strength at 1100°C for HAC containing specimens. A decrease in compressive strength was seen in the Portland cement containing specimens in long run when heated to 1100°C for several times. Group IV (containing granulated blast furnace slag) ideal compressive strength change before and after the heating to 1100°C.
7. Steel fibre addition (1% by the volume of the mortar) did not improve the flexural strength of the specimens. Using 1.5% water reducer by the volume of water increased the flexural strength of the specimens. Group IV (containing granulated blast furnace slag) had the best flexural strength test results according to change before and after the heating to 1100°C.
8. Seven days of curing at 21°C did not improve the bonding between steel fibres (1% by the volume of the mortar) and the mortars. Also heating to 1100°C caused a decrease in the bonding of steel fibres to mortar.
9. Heating of the specimens decreased the ultrasound velocity. Change in ultrasound velocity was higher in Portland cement containing mortars after ten turns of heating and cooling. As a result Portland cement containing

specimens were affected more from the heat than the ones containing HAC in long run.

10. Specimens having higher ultrasound velocity had higher compressive strength values. Group IV had the smallest decrease in ultrasound velocity as it had the smallest decrease in the compressive strength values after heating.
11. No major changes in the micro structure of the specimens were observed from the X-Ray Diffraction (XRD) method, after heating to 1100°C. Same compounds were seen in the XRD data before and after the heating to 1100°C. Phase changes that would probably occurred at the surfaces of the compounds that were in contact with each other, could not be observed as the firebrick amount occupied about 75% by weight of the specimens , and no change in the firebrick was observed as it was a pre-fired material.

## **CHAPTER 7**

### **RECOMMENDATIONS**

In this study, an economical refractory mortar was tried to be prepared with high amounts of domestic materials. Physical and mechanical properties of the prepared specimens were investigated. According to experimental results following recommendations can be made;

1. High alumina cement as a binder crushed firebrick as an aggregate and granulated blast furnace slag or granulated firebrick as pozzolanic materials seemed to be a good constituents of a refractory material. Adding different amounts of pozzolanic materials and mixing two types of pozzolanic materials should be investigated.
2. Water reducer admixture (1.5% by the volume of water) improved the compressive and flexural strength of the mortars. Other types of water reducer admixtures should be used in varying amounts to determine the most suitable admixture for the high alumina cement containing mortars.
3. More than ten turns of heating and cooling cycles should be made to understand the real service life of the refractory prepared. Crack propagation should be observed after each cycle.
4. Abrasion and chemical resistance of the material should be investigated for understanding its service behaviour.
5. Different types of aggregate should be used other than crushed fire brick to determine the best and the cheap aggregate for the refractory material prepared.
6. Prepared refractory mortar should be heated higher than 1100°C in order to investigate the ceramic bonds that will happen to form between the constituent compounds of the material.

## REFERENCES

1. Banerjee, S., Monolithic Refractories, American Ceramic Society, 1998
2. Norton, F.H., Refractories, McGraw-Hill, New York, USA, 1970
3. ACI Committee 547, “Refractory Concrete: Abstract of State-of-the-Art Report”, Concrete International: Design & Construction, V.1, No:5, May 1979, Revised 1983, Reapproved 1997
4. Heikal, M., “Effect of Temperature on the Physico-mechanical and Mineralogical Properties of Homra Pozzolanic Cement Pastes” Cement and Concrete Research, Vol. 30, 2000, pages 1835 – 1839
5. Erdoğan, T.Y., Admixtures for Concrete, Middle East Technical University, Ankara, 1997
6. Poon, C., Azhar, S., Anson, M., Wong, Y., “Comparison of the Strength and Durability Performance of Normal and High Strength Pozzolanic Concretes at Elevated Temperatures”, Cement and Concrete Research, Vol. 31, 2001, pages 1291 – 1300
7. Orhun, O., “Production possibility of Imported Refractory Mortars with the Domestic Raw Materials”, MTA, Ankara, 1972 (in Turkish)
8. Kabanov, Y.A., Stolyarski, O.A., Sadovski, V.G., Simachkov, S.K., “Recycling Refractory Wastes”, Metallurgist, Vol. 48, Nos. 1-2, 2004



9. Darmograi, A.F., Stolyarskii, O.A., Sadovski, V.G., Altynbekov, B.Zh., “Production of Refractory Concretes and Refractory Concrete Products from Recycled Refractories”, *Metallurgist*, Vol. 46, Nos. 05-06, 2002
10. Lea, F.M., *The Chemistry of Cement and Concrete*, Edward Arnold LTD. London, UK, 1956
11. Czirmin, W., *Cement Chemistry and Physics for Civil Engineers*, Crosby Lockwood & Son Ltd., London, UK, 1962
12. Robson, T.D., *High Alumina Cements and Concretes*, John Willey & Sons Inc., New York, USA, 1962
13. Erdoğan, T.Y., *Beton*, Middle East Technical University, Ankara, 2003
14. Mindess, S., Young, J.F., *Concrete*, Prentice – Hall, New Jersey, USA, 1981
15. Santos, W.N., “Effect of Moisture and Porosity on the Thermal Properties of a Conventional Refractory Concrete”, *Journal of European Ceramic Society*, No. 23, 2003, pages 745 – 755
16. Shubin, V.I., “Refractories at the User”, *Refractories and Industrial Ceramics*, Vol. 42, Nos. 3-4, 2001
17. Simonin, F., Olagnon, C., Maximilian, S., Fantozzi, G., “Room Temperature Quasi-brittle Behaviour of an Aluminous Refractory Concrete After Firing”, *Journal of the European Ceramic Society*, Vol. 22, 2002, pages 165 – 172
18. Taylor, H.F.W., *The Chemistry of Cements*, Academic Press Inc., London, 1964

19. Antonovich, V., Goberis, S., “ The Effect of Different Admixture on the Properties of Refractory Concrete with Portland Cement”, Materials Science, Vol. 9, No. 4, 2003
20. Hung, Y., Wong, Y., Poon, C., Anson, M., “Impact of High Temperature on PFA Concrete”, Cement and Concrete Research. No.31, 2001, pages 1065 – 1073
21. ASTM C 71, “Standard Terminology Relating to Refractories”, American Society for Testing Materials, 1991
22. Goberis, S., Stonis, R., “An Air-setting Refractory Mortar Using A Composite Binder”, Refractories and Industrial Ceramics, Vol. 42, Nos. 7, 2001, pages 300 – 303
23. ASTM C 125, “Standard Terminology Relating to Concrete and Concrete Aggregates”, American Society for Testing Materials, 1993
24. ASTM C 1240, “Standard Specification for Silica Fume for Use in Hydraulic-cement Concrete and Mortar”, American Society for Testing Materials, 1993
25. ASTM C 989, “Standard Specification for Ground Granulated Blast-Furnace Slag for use in Concrete and Mortars”, American Society for Testing Materials, 1989
26. Nonnet, E., Lequeux, N. Boch, P., “Elastic Properties of High Alumina Cement Castables from Room Temperature to 1600<sup>0</sup>C”, Journal of European Ceramic Society, No. 19, 1999, pages 1575 – 1583

27. ASTM C 511, “Specification for Moist Cabinets, moist Rooms and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes”, American Society for Testing Materials, 1993
28. Goberis, S., Pundene, I., “A Study of the Heat Resistance of Low-cement High Temperature Concretes”, Refractories and Industrial Ceramics, Vol. 42, Nos. 1-2, 2001, pages 83 – 87
29. ASTM C 860, “Standard Practices for Determining and Measuring Consistency of Refractory Concretes”, American Society for Testing Materials, 1991
30. ASTM C 150, “ Standard Specification for Portland Cement”, American Society for Testing Materials, 1992
31. ASTM C 702, “Standard Practise for Reducing Field Samples of Aggregate to Testing Size”, American Society for Testing Materials, 1987
32. ASTM C 136, “Standard Test Method for Sieve Analysis of Fine and Coarse Aggregate” American Society for Testing Materials, 1992
33. ASTM C 70, “Standard Test Method for Surface Moisture in Fine Aggregate”, American Society for Testing Materials, 1979
34. ASTM C 128, “Standard Test Method for Specific Gravity and Absorption of Fine Aggregate”, American Society for Testing Materials, 1993
35. ASTM C 109, “Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (using 2-in. or 50mm cube specimens)”, American Society for Testing Materials, 1992

36. ASTM C 293, “Standard Test Method for Flexural Strength of Concrete (using simple beam with centre-point loading)”, American Society for Testing Materials, 1979
37. Cailleux, E., Cutaral, T., Bernhart, G., “Pullout of Steel Fibres From a Refractory Castable: Experiment and Modelling”, Mechanics of Materials, Vol. 37, 2005, pages 427 – 445