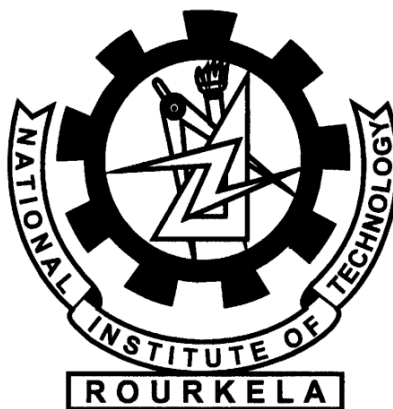# Effect of Filler Material Replacement on the Properties of the High Alumina Conventional Castables

A thesis submitted in the partial fulfillment of the requirements for the degree of Bachelor of Technology

By

Subhojeet Ghose

Roll No: 109CR0496

Effect of Filler Material Replacement on the Properties of the High Alumina Conventional Castables

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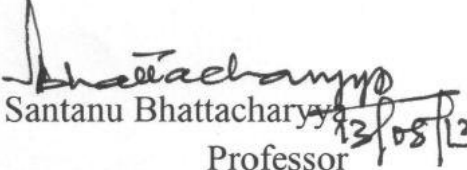
Roll No: 109CR0496

Supervisor: Santanu Bhattacharyya

CERTIFICATE

This is to certify that the thesis entitled, "Effect of Filler Material Replacement on the Properties of the High Alumina Conventional Castables" submitted by Subhojeet Ghose (109CR0496) for partial fulfillments of the requirements for the award of Bachelor of Technology degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ACKNOWLEDGEMENT

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CONTENTS

ABSTRACT

The demand for the monolithic refractories as compared to their shaped counterparts have been increasing over the years due to their distinct advantages like comparable durability, low cost and relatively easy installation procedure. Several attempts are being made in the optimization of the properties of these products. Among monolithics, refractory castables are the major ones which have replaced significant fraction of shaped refractories in the furnace lining. Among the castables, high alumina based castables are the most important type. This work focuses on the study of the properties of the conventional high alumina based refractory castables, firstly due to the reduction in the percentage of cement by reactive alumina and secondly due to the replacement of cement by micro-silica in the composition. The reduction in the percentage of cement improved the thermo-mechanical property which was indicated by the HMOR values and the incorporation of the micro-silica in the composition resulted in the development of good mechanical strength to the castables and also improved their thermo-mechanical properties. The improvement in mechanical properties and HMOR values for microsilica castables was definitely due to mullite formation. However as the microsilica content was only 4%, the fraction of mullite that formed on firing was also less. Therefore, though the enhancement was distinct but it was only by about 25%.

LIST OF TABLE USED

LIST OF FIGURES USED

LISTS OF ABBREVIATIONS USED

Sl.No.	Abbreviations used	Full Form
1	CAC	Calcium Aluminate Cement
2	XRD	X-Ray Diffraction
3	WTA	White Tabular Alumina
4	BD	Bulk Density
5	CCS	Cold Crushing Strength
6	CA	$CaO.Al_2O_3$
7	CA_2	$CaO.2Al_2O_3$
8	CAH_{10}	$CaO.Al_2O_3.10\ H_2O$
9	C_2AH_8	$2\ CaO.Al_2O_3.8H_2O$
10	C_3AH_6	$3\ CaO.Al_2O_3.6\ H_2O$
11	$C_{12}A_7$	$12\ CaO.7Al_2O_3$
12	C_3A	$3CaO.Al_2O_3$
13	CA_6	$CaO.Al_2O_3$
14	SEM	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

With the increase in the demand for refractories, several methods are being adapted so as to optimize the properties of the refractory materials. One such step is the advancement being made in the field of monolithics. Refractory castables are used as a replacement of the conventional refractory bricks for the furnace linings [1-2]. They are continuous mass and are free from corners and joints. The corners and the joints are usually the sites for maximum amount of corrosion, erosion and slag penetration. So, the life and durability of the refractory bricks are usually very poor. So, castables are mostly used in the furnace lining. Refractory castables are a homogenous mixture of the refractory aggregates and the binders.

Mostly cement is being used as a binder phase for the castables. The addition of cement also provides flow properties and leads to easy installation of the cement bonded castables usually reducing skilled labour. So, cement bonded castables are getting very popular these days. The present day practice is the reduction in the percentage of cement for increasing life and durability of the castables. The enhancement in properties is due to the reduction in the amount of the low melting phases in the castable which are mostly Anorthite and Gehlenite with reduction in the percentage of cement. This also improves the creep resistance and other thermo-mechanical properties of the castables. Since the replacement of cement is done through addition of purer and refractory grade raw material, the composition of the aggregate affects the properties of the castable especially their chemical resistance. Also the particle size distribution also affects the packing and the ultimate strength of the castables [3].

Present day trend is to use High Alumina based castables as it has extremely good chemical resistance against any corrosive medium. The incorporation of fumed silica in the composition improves the flowability and also leads to the formation of the mullite phase after sintering. The presence of these phases leads to improved mechanical strength, higher thermal shock resistance and better corrosion resistance as well.

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CHAPTER 2

LITERATURE REVIEW

2.1 REFRACTORIES:

Refractories are used to withstand very high temperatures. Refractories are inorganic, nonmetallic, and heterogeneous materials composed of thermally stable mineral aggregates, a binder phase and additives. **ASTM C71** defines refractories as "non-metallic materials having those chemical and physical properties that make them applicable for structures, or as components of systems, that are exposed to environments above 1,000°F (811 K; 538°C) [4].The main requirements of a refractory materials are

- High temperature stability
- High load bearing capacity
- Abrasion and wear resistance
- Erosion and corrosion resistance
- High thermal shock resistance
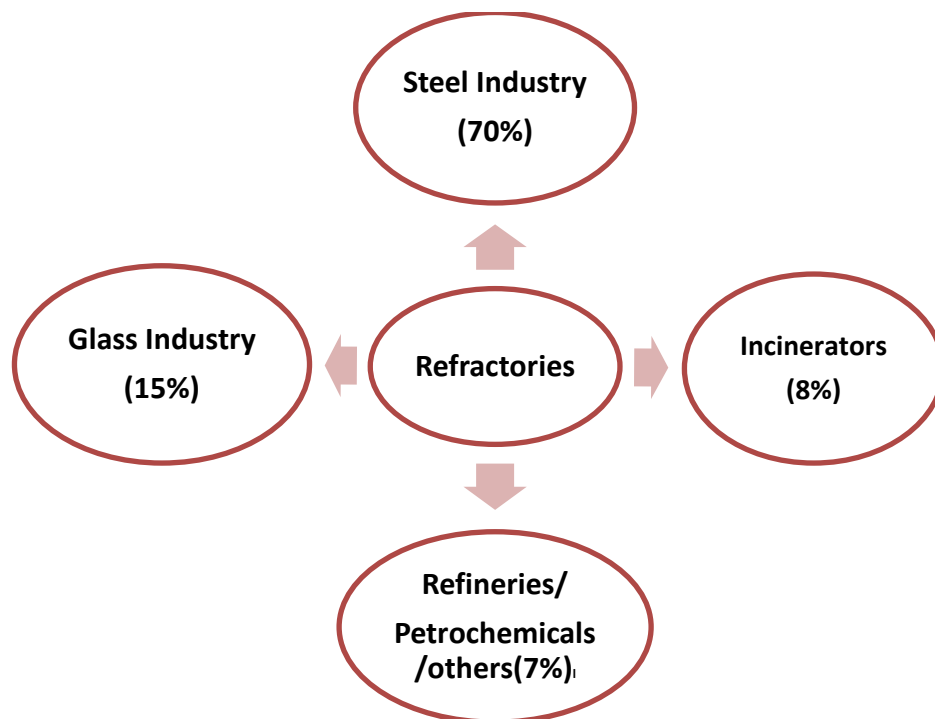
Fig 2.1: Application of Refractories [5].

2.2 CLASSIFICATION OF REFRACTORIES

1. **On basis of chemical nature**
   - Acidic Refractories: These are those refractories which are used in the presence of any acidic slags. The CaO/SiO_2 ratio (C/S ratio) for acidic refractories is < 1. Some examples of acidic refractories are Silica refractories, Fire Clay refractories etc. They are used in coke oven, glass tank furnace etc [6].
   - Basic Refractories: These are those refractories which are used in presence of basic slags. The CaO/SiO_2 ratio (C/S ratio) for basic refractories is >1. Ex: Magnesia refractories, Magnesia carbon refractories, Magnesia-chromite, dolomite refractories etc. They are used in the Blast Furnace, BOF, EAF, VOD etc. [6].
   - Neutral Refractories: These are those refractories which can withstand both acidic and basic slags. Ex: high alumina refractories. [6].

2. **On basis of Shape**:
   - Shaped refractories: They have fixed size and shapes. They are further classified into standard shapes and special shapes. Standard shapes are those which have a specific dimension that are conformed by most refractory manufacturers and are generally applicable to kilns or furnaces of the same types. Special shapes are those that are specifically made for applications in particular kilns or furnaces. Shaping processes include pressing, casting etc. [6].
   - Unshaped Refractories: These are without definite form and are only given shape upon application. These types are better known as monolithic refractories. The common examples are plastic masses, Ramming masses, castables, gunning masses, fettling mix, mortars etc. [6].

3. **On basis of porosity**:
   - Porous refractories: Contain air pores which act as insulators. They are used in the backup lining. [6].
   - Dense Refractories: They are used in the working lining of the furnaces. [6].

4. **On basis of carbon content:**
    - Carbon containing refractories: They have some carbon content in their composition for imparting corrosion and thermal shock resistance. They are again classified on the basis of their oxidation resistance. Ex: Magnesia carbon refractories. [6].

The Alumino Silicate refractories are further classified on the basis of their alumina content as: [6].

- Low Heat Duty (25%-30% Al_2O_3)
- Medium Heat duty (30%-35% Al_2O_3)
- High heat duty (35%-40% Al_2O_3)
- Super heat duty (40%-45% Al_2O_3)

The heat withstanding capacity is directly proportional to the alumina content in the composition.

2.3 MONOLITHICS

The use of monolithic refractories has become very wide spread looking back at the last 20 years [1-2].These refractories do not have any specific shape and come in form of loose powders. They are called as monolithics which comes from the word "mono-lithus" meaning "Single stone". [6].These are the materials which are installed as some form of suspension/plastic mass that ultimately harden to form a solid mass. They contain some refractory grains as aggregates along with binder as the minor phase. The main properties of these materials are their respective high chemical inertness, better mechanical integrity, higher abrasion resistance and high thermal shock resistance at high temperatures.

ADVANTAGES OF MONOLITHIC REFRACTORIES [6].:

- Easy installation
- Less skill requirement during installation
- These unlike the shaped refractories are joint-less which leads to higher corrosion and abrasion resistance.
- Any desired shape can be made.

- Cheaper as no firing are required
- They help in repairing of the furnaces even in the working conditions.
- They are easy for transportation.

2.4 CASTABLES:

These are those types of monolithic products which can act as a substitution for the conventional refractory bricks used in the lining of the furnaces for high temperature applications. They consist of an aggregate phase and a binder phase which at the installation site is mixed with a liquid preferably water after which they set and hardens and develop a suitable amount of green strength in the system. Then they are subjected to firing after which they develop ceramic bond formation during sintering and the strength further increases. The majority of refractory castables use calcium aluminate cement as the bonding agent though in recent years other bonding systems have been employed. The ultimate properties of the refractory castables are affected by the particle size distribution, packing and the sintering temperature. Initial strength in the castable system is mostly developed due to the presence of binder which gets activated by the addition of liquid at the installation site. For instance the cement bonded castables show the following type of reaction mechanism at the installation site [7]:

$CA + H_2O = CAH_{10}$ (Temperature $<21°C$)

$CA + H_2O = C_2AH_8 + AH_3$ ($21°C <$ Temperature $< 40°C$)

$CA + H_2O = C_3AH_6 + AH_3$ (Temperature is $> 40°C$)
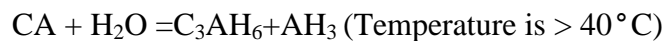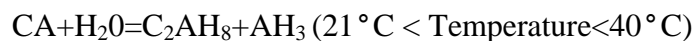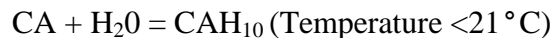
The crystal morphology of these calcium aluminate phases shown below:
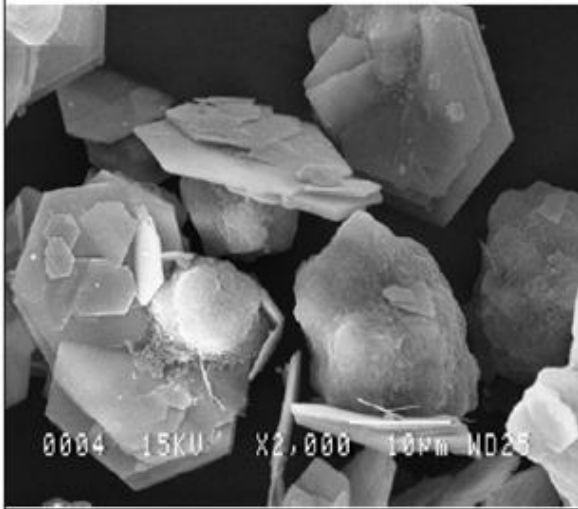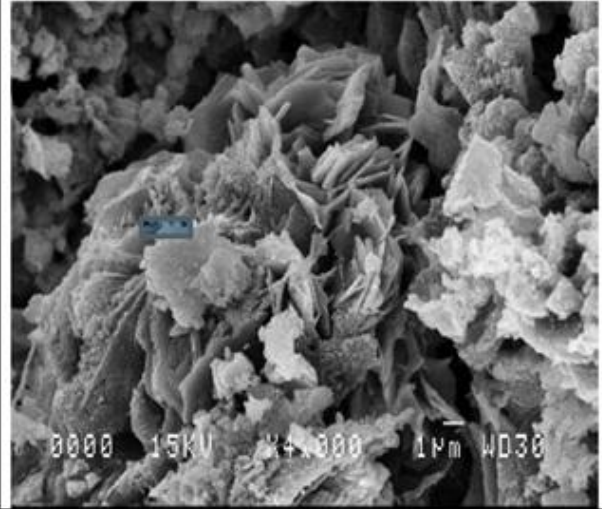
CAH$_{10}$ C$_2$AH$_8$
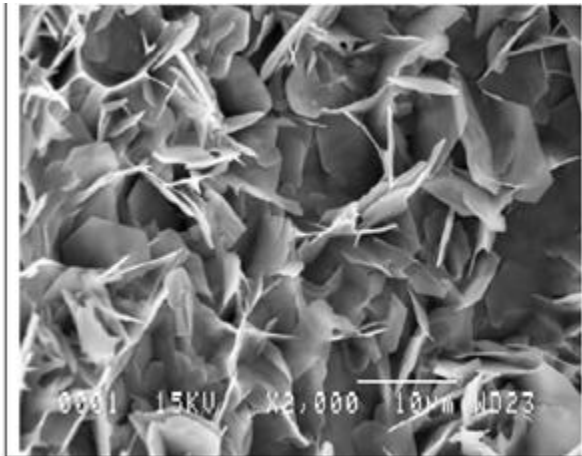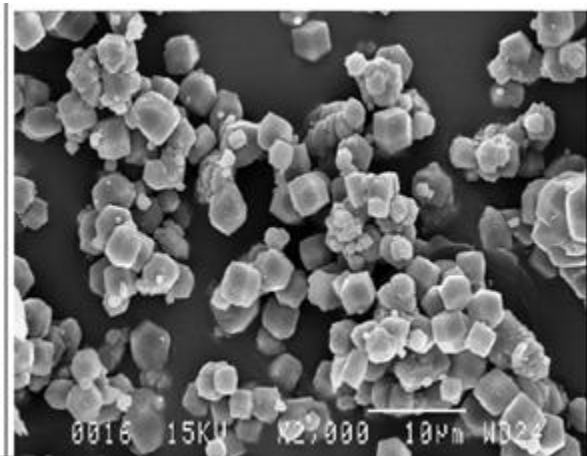
C$_4$AH$_{13}$ C$_3$AH$_6$

Fig: 2.2 : Crystallographic morphology of different hydraulic cement phases.[8]

C$_3$AH$_6$ phase is the thermodynamically most stable phase and is formed eventually. It has a cubic crystal structure. When the castable is heated the hydrated cement phase will undergo a dehydration process due to the loss of water in the form of water vapor over a temperature range. Dehydration occurs over a temperature range from 210°C to 370°C, with the peak dehydration being at 230°C and 315°C for AH$_3$ and C$_3$AH$_6$ respectively [9-10]. If the evolved vapors are not allowed to get released out then outward pressure will develop in the castable systems and this will result in spalling. CAC bonded castables also require careful drying for the escape of the

moisture as well as prevent the internal pressures of the water vapors [11]. Presence of unreacted water molecules in the castable system can also result in generation of porosity upon firing the castable due to the evaporation of the unbonded water molecules. This will result in spalling and reduction in strength of the castable. Therefore the usual practice is to cure the castables for longer duration for achieving maximum green density before firing is carried out. [12].

Cement bonded castables can be further classified on the basis of the percentage of cement used in the castable. They are: [6]

- Conventional Cement Castable (15% cement)
- Low Cement Castable (4-6% cement)
- Ultralow Cement Castable (1-3% cement)
- No Cement Castable

On basis of type of binders, Castables can be further classified as [6]

- Sol Bonded Castables
- Cement Bonded Castables
- Hydratable Alumina Bonded Castables
- Phosphate bonded Castables

Castables can also be classified on basis of flow as [6]:

- Self-flow castables
- Vibratable Castables

Most of the refractory castables also show the heterogeneous microstructure which consist of different type of phases .These can have different coefficient of thermal expansion and this can result in the development of stresses internally within the system and this can influence the thermo-mechanical properties [13-14].

On basis of chemical composition the castables can be further classified as :

- Alumina Castables
- Silica Based Castables

- Magnesia Castables

2.5 HIGH ALUMINA BASED CASTABLES:

High Alumina based castables are those type of castables in which the percentage of alumina in the composition varies from 45%-99%.These type of castables have a tendency to show very high refractoriness and good high temperature properties. Further the properties can be improved by incorporating new phases like mullite and spinel in these castable systems. The typical properties of the high Alumina refractory castables are [6]:

- High Mechanical Strength
- High Corrosion Resistance
- High Abrasion Resistance
- High Thermal Shock Resistance
- High Thermal Conductivity
- High Refractoriness

The presence of the alumina in the composition of the refractory aggregates in the range of 45-99% decides whether the refractory is a high alumina refractory or not. Some typical type of aggregates to be used in the composition of the refractory aggregate composition for the high alumina castables are [6]:

- White fused alumina
- Reactive alumina
- Tabular alumina
- Bauxite
- Brown fused alumina
- Calcined Alumina

On basis of the percentage of cement in the castables, the High Alumina based castables can be further classified as [6]:

- Conventional Cement Castable (10% Cement)
- Low Cement Castable (4-6% Cement)

- Ultra Low Cement Castable (1-3% Cement)
- No cement castable

2.6 LOW CEMENT CASTABLES:

These type of castables have an aggregate and a binder phase just like any other monolithic product. The only difference is in the percentage of the cement used as binder which is 4-6% in this case. This type of castable technology had developed in the 1970's.[6]

Some important characteristics of the low Cement Castables are [15-16]:

- Low Value of initial strength due to inadequate formation of hydraulic bonds due to lower percentage of cement in the composition
- Lesser faller in strength due to the loss of water in the form of water vapor from the castable
- Better amount of strength developed upon firing
- Better thermo-mechanical properties
- Lower percentage of low melting phases developed within the system after sintering

The properties of the low cement castables are further influenced by the addition of ultrafine components to the castable mixture. Also addition of deflocculants can also influence the flowability of the castables. The particle size distribution in the castable system also influences the packing of the castable and its ultimate strength [17].

The flowability of the low cement castables are usually expected to be lower because of the presence of lesser amount of cement and hence lesser amount of water which is very responsible for the flowability. So, usually we add a chemical compound called the deflocculant which will prevent the coagulation in the system and improve the flowabilty [6].

2.7 MULLITE:

Mullite is a solid solution of Alumina and silica. Theoretically, mullite has 72% Alumina and 28% silica in the composition. Mullite has several advantages of being a refractory material. It has extremely good thermal shock resistance and high refractoriness and good mechanical

strength. This is always a desired phase in the alumino-silicate systems for refractory applications. Sintering behaviour of mullite-containing powders has been studied over a range of chemical compositions (Al_2O_3/SiO_2 ratio). It has been found that the observed lattice parameters of mullite samples are highly influenced by minor compositional changes and different thermal conditions such as temperature of synthesis and both heating and cooling rate. The properties of mullite are highly influenced by the nature of the starting raw materials. Mostly alumino silicate based materials are used as the starting raw materials. It has been reported that among the naturally occurring raw materials, silimanite group of minerals mostly leads to the formation of equi axed mullite grains and kaolinite leads to needle-like grains.[18]

Some of the typical properties of mullite are [19]:

- Good thermal shock resistance
- Low thermal conductivity
- Good strength
- Wear resistant
- Usable to high temperatures

Mullite phase is highly desirable for the following types of applications

- Protection tubes
- Furnace liners
- Electrical insulators

Fig 2.3 SEM Pictures of needle shaped mullite synthesized hydrothermally in small druses of volcanic rocks of the Eifel mountains, Germany [20]

2.8 BAUXITE:

Bauxite ($Al_2O_3.2H_2O$) is a naturally occurring source of aluminum and alumina and is a mixture of Gibbsite [$Al(OH)_3$], Bohemite [$AlO(OH)$] and diaspore [α-$AlO(OH$] along with impurities like TiO_2, Gohetite (($FeO(OH)$) and Haematite (Fe_2O_3). Bauxite owing to its low cost is used as an aggregate in the refractory castable and can act as an important source of Alumina. Commercially two different grades of bauxite are available. They are Chinese Bauxite and Indian Bauxite. Chinese Bauxite is of a purer grade having ˜ 94% Alumina whereas Indian Bauxite has ˜ 88% Alumina in the composition. [21]

2.9 TABULAR ALUMINA:

It is obtained by pressing the calcined alumina obtained from Baeyer's process in the shape of balls and then firing them to a temperature of 1800-1900 °C. It undergoes densification and

sintering upon firing and we get a nearly pore free structure which shows the following types of properties [6]:

- high refractoriness
- high bulk density,
- High thermal shock resistance,
- High wear-resistance
- high purity
- High chemical resistance,
- complete crystal tabularization
- low porosity.

It is called as tabular Alumina because the crystals are arranged in a tabular manner. Due to the manufacturing process the Tabular Alumina is a very costly material. Tabular Alumina is further subdivided into [6].

- White Tabular Alumina(WTA)
- Brown Tabular Alumina(BTA)

Tabular Alumina is a highly dense material. It is mostly sintered through the solid state sintering route to achieve maximum possible density. Almatis is a leading producer of Tabular Alumina in the world [22]. The Tabular Alumina is also available in the form of WTA and BTA fines. It is an important component of the aggregate phase of the castable and impart very high mechanical strength and high abrasion resistance and very high thermal shock resistance owing to its high thermal conductivity due to its narrow porosity and low coefficient of thermal expansion.

Table 2.1 Physical Properties of Almatis Tabular Alumina [22]

Bulk Density	3.5
Apparent Porosity(%)	5
Water Absorption(%)	1.5

Fig 2.4 : SEM Pictures of Almatis Tabular Alumina [22]

2.10 WHITE FUSED ALUMINA:

White fused Alumina is obtained by arc melting the Baeyer's Alumina and then cooling it. It is of very pure grade and free from iron impurities. Due to its massive and large grain size white fused alumina has very high chemical resistance. Some of the other characteristics properties of the White fused Alumina are [6]:

- higher hardness
- light lower toughness comparing with brown fused alumina
- high purity
- ability of self-sharpening
- better cutting,
- higher efficiency
- good thermal stability

Fig 2.5 White Fused Alumina [5]

2.11 CALCIUM ALUMINATE CEMENT (BINDER):

Calcium Aluminate Cement or High Alumina Cement or simply Aluminous Cement is a hydraulic binder used as a binder for the refractory castables and other monolithic products. They set and harden at the installation site upon mixing with water and provides strength to the system. It is based on the Calcium Aluminate phases unlike the Calcium Silicate Cement in the Ordinary Portland Cement. There are several phases in the $CaO-Al_2O_3$ phase diagram. They are C_3A, CA, CA_2, CA_6. In the Calcium Aluminate Cement the phases that are mostly maintained are CA and CA_2. The rate of hydration of each of the phases is determined by the percentage of CaO content in it. Higher the percentage of CaO in the phase composition, higher will be the rate of hydration which gives C_3A a flash setting property due to its rapid hydration. It rapidly sets and hardens upon water addition. While the most hydraulic phase is CA, CA_6 is the non-hydraulic phase and has the highest amount of refractoriness due to very high percentage of alumina in the composition. The different phases in the $CaO-Al_2O_3$ system is as shown

Fig 2.6 CaO-Al$_2$O$_3$ phase diagram [23]
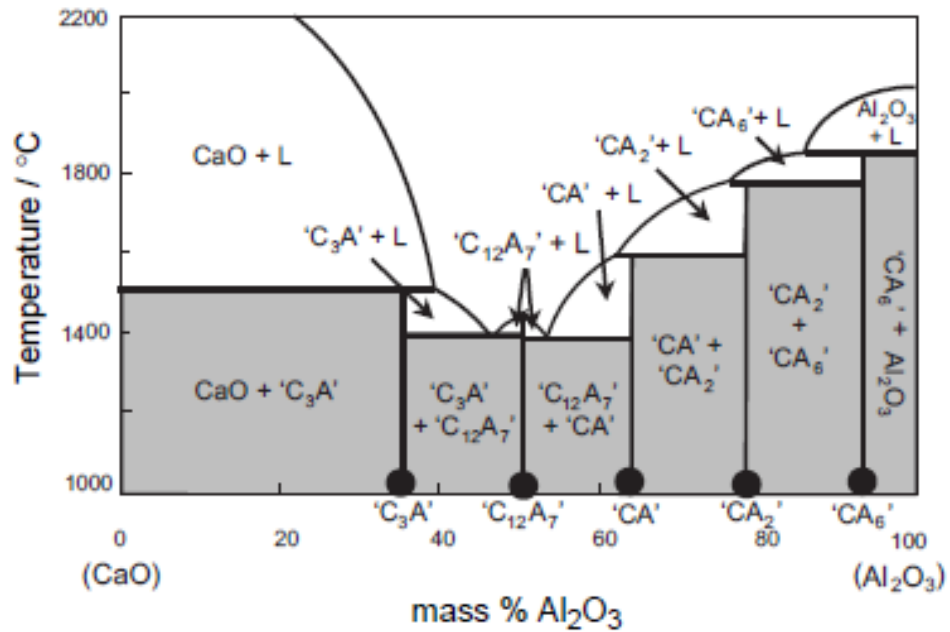
Some of the major properties of the Calcium aluminate Cement are:

- Higher refractoriness
- Provides high strength to the matrix
- High Corrosion Resistance
- Lower Initial Setting Time but shorter final setting time compared to Portland cement
- Improved Thermal shock resistance

Upon addition of water the Calcium Aluminate phases gets hydrated as per the following reaction scheme [23]
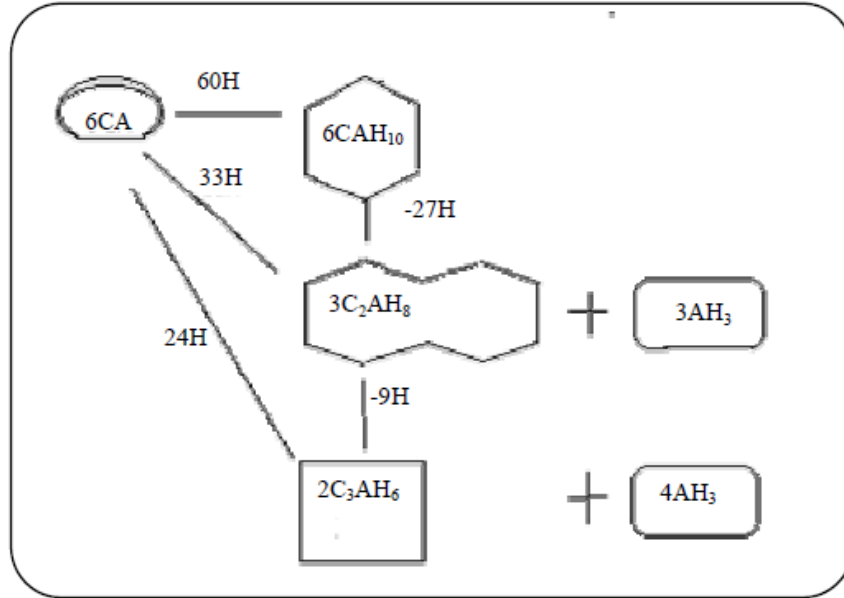
Fig:2.7: Reaction Mechanism of hydration of the Calcium Aluminate Phases [23]

FILLER MATERIALS

2.12 REACTIVE ALUMINA:

Reactive Alumina is obtained through extensive grinding of the calcined alumina obtained from Baeyer's process in a ceramic lined ball mill for more than 24 hours [24]. The final crystal size is nearly less than 1μm.Due to its finer particle size they have high sintering, densification and reactivity rates. They also readily react with other components like microsilica to form mullite a material of strategic importance in refractory. They also undergo spinel formation upon sintering with MgO.

2.13 FUMED SILICA

Fumed Silica or microsilica is also used as a filler material for the castable. It is also known as pyrogenic silica because it produced in a flame. It consists of microscopic droplets of amorphous silica which are fused into branched, chainlike and three-dimensional secondary particles which then agglomerate into the tertiary particles [25]. It has extremely low bulk density and high surface area. It has the tendency to undergo sintering with reactive alumina and form mullite and this phase is highly advantageous for refractory applications.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 MATERIALS AND METHODS

The raw materials that were used were:

*Aggregate***:** White Fused Alumina, Reactive Alumina, Tabular Alumina, Bauxite,

Binder: Calcium Aluminate Cement (Polychem, CA 14)

Filler: Microsilica, Reactive Alumina

The Reactive alumina (A-16 SG) of grain size (<1 µm) and Tabular Alumina of size (1-3mm) were used. The chemical composition is given in the Table 3.2 below. The white fused Alumina which had an average particle size of 0.5-1 mm was collected from Hindalco India, and the Bauxite of 75 mesh grain size was obtained from M/S Tata Krosaki Refractories, Belpahar Orissa. Calcium aluminate cement (CAC) was used as a binder. Two commercial varieties of CAC were used i.e CA 14 (Almatis) and Polychem (Polychem Rourkela). The weight percentage of CAC, white fused alumina, tabular alumina, reactive alumina and bauxite used in the castables are shown below:

Table 3.1 Composition of the castable

WEIGHT PERCENTAGE IN THE BATCH			
	Castable 1	**Castable2**	**Castable 3**
WFA(0.5mm-1mm)	15	15	15
Reactive Alumina	30	34	30
Tabular Alumina (1-3 mm)	30	30	30
Bauxite (75 mesh)	15	15	15
Fumed Silica	-	-	4
HAC	10	6	6
Water	12.5	7	7

The chemical composition of the several aggregates is as shown in the Table below:

Table 3.2 Chemical Composition of the Batch

CHEMICAL COMPOSITION OF THE BATCH							
	Tabular Alumina	Bauxite	Calcined Alumina	Reactive Alumina	WFA (0.5mm-1mm)	CAC (%) Polychem	CAC (%) CA 14
Al_2O_3	99.5	90	97.56	99.8	99	71.48	71.42
Fe_2O_3	-	1.40	0.11	0.02	0.2	-	0.11
TiO_2	-	2.50	Traces	-	-	-	-
B_2O_3	-	-	-	<0.01	-	-	-
CaO	-	-	0.51	0.03	-	24.6	26.91
SiO_2	<0.09	-	Traces	0.02	-	0.4	0.20
Na_2O	<0.4	0.25	0.49	0.07	0.2	0.05	0.14
K_2O	-	0.25	0.08	-	0.2	0.05	0.14
MgO	-	-	0.61	0.04	-	0.2	0.31
LOI	-	-	0.37	-	-	-	-

3.2 CASTING AND SPECIMEN PREPARATION

Three different types of castables were prepared according to batch composition given in table 2.1.The castables were shaped as per the following flowcharts.

FLOW CHART FOR CONVENTIONAL CEMENT CASTABLE

Tabular Alumina + **White fused Alumina** + **Bauxite**

(Mixed for 15 minutes)

↓

Reactive Alumina (30%)

(Mixed for 10 minutes)

↓

Aggregate Mixer

+ **CAC (10%) + Water (12%)**

(Mixed for 5 minutes)

↓
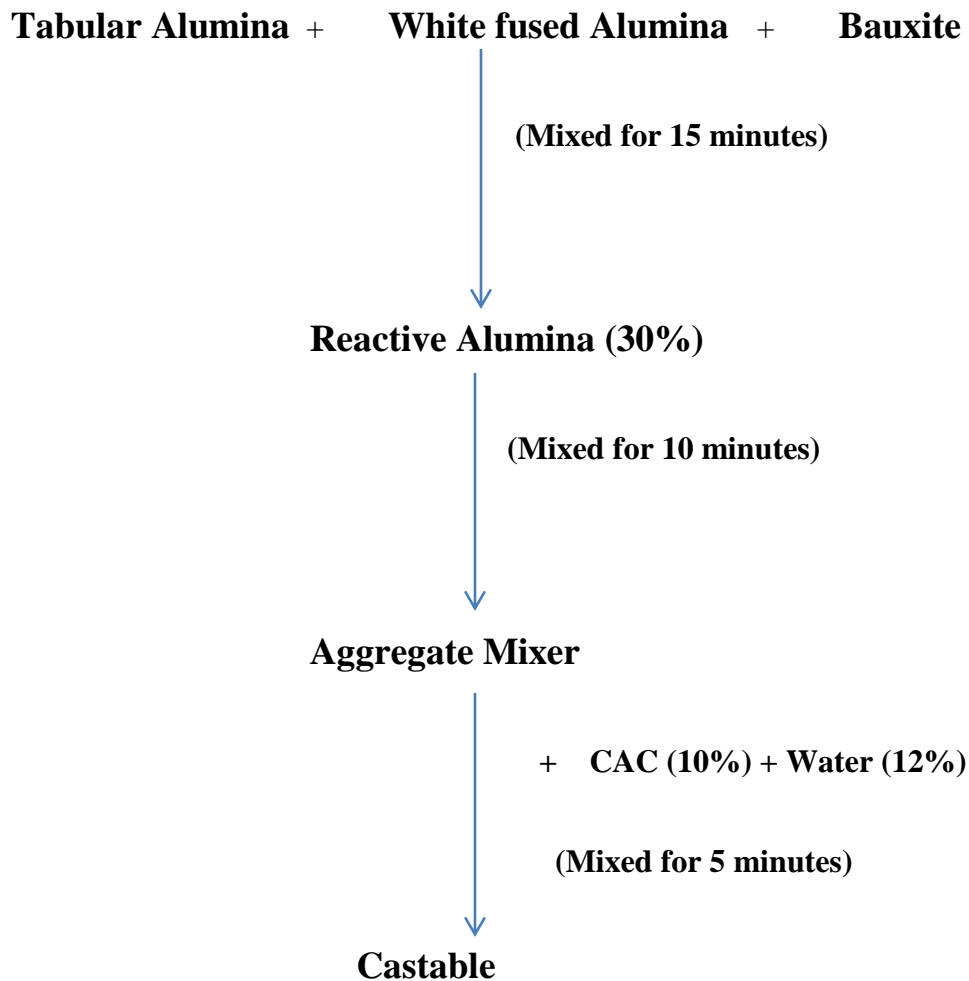
Castable

N.B All mixing were done in Hobart Mixer (5 kg capacity)

Fig 3.1: Flow chart for Conventional Cement Castable

FLOW CHART FOR LOW CEMENT CASTABLE

Tabular Alumina + **White fused Alumina** + **Bauxite**

(Mixed for 15 minutes)

↓

Reactive Alumina (34%)

(Mixed for 10 minutes)

↓

Aggregate Mixer

+ **CAC (6%)+ Water (7%)**

(Mixed for 5 minutes)

↓
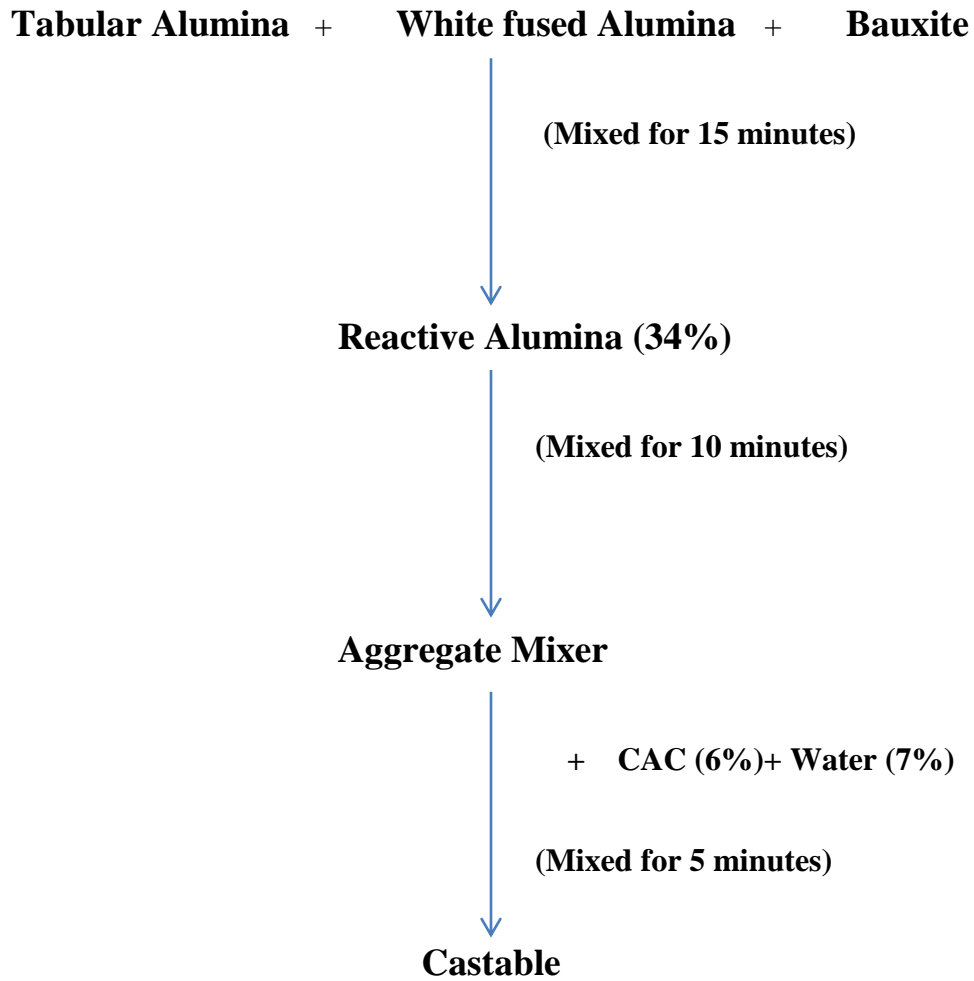
Castable

N.B All mixing were done in Hobart Mixer (5 kg capacity)

Fig 3.2: Flow chart for Low Cement Castable

FLOW CHART FOR LOW CEMENT CASTABLE

Tabular Alumina + **White fused Alumina** + **Bauxite**

(Mixed in for 15 minutes)

↓

Reactive Alumina (30%)

(Mixed for 10 minutes)

↓

Fumed Silica

↓

Aggregate Mixer

+ **CAC (6%)+ Water (7%)**

(Mixed for 5 minutes)

↓
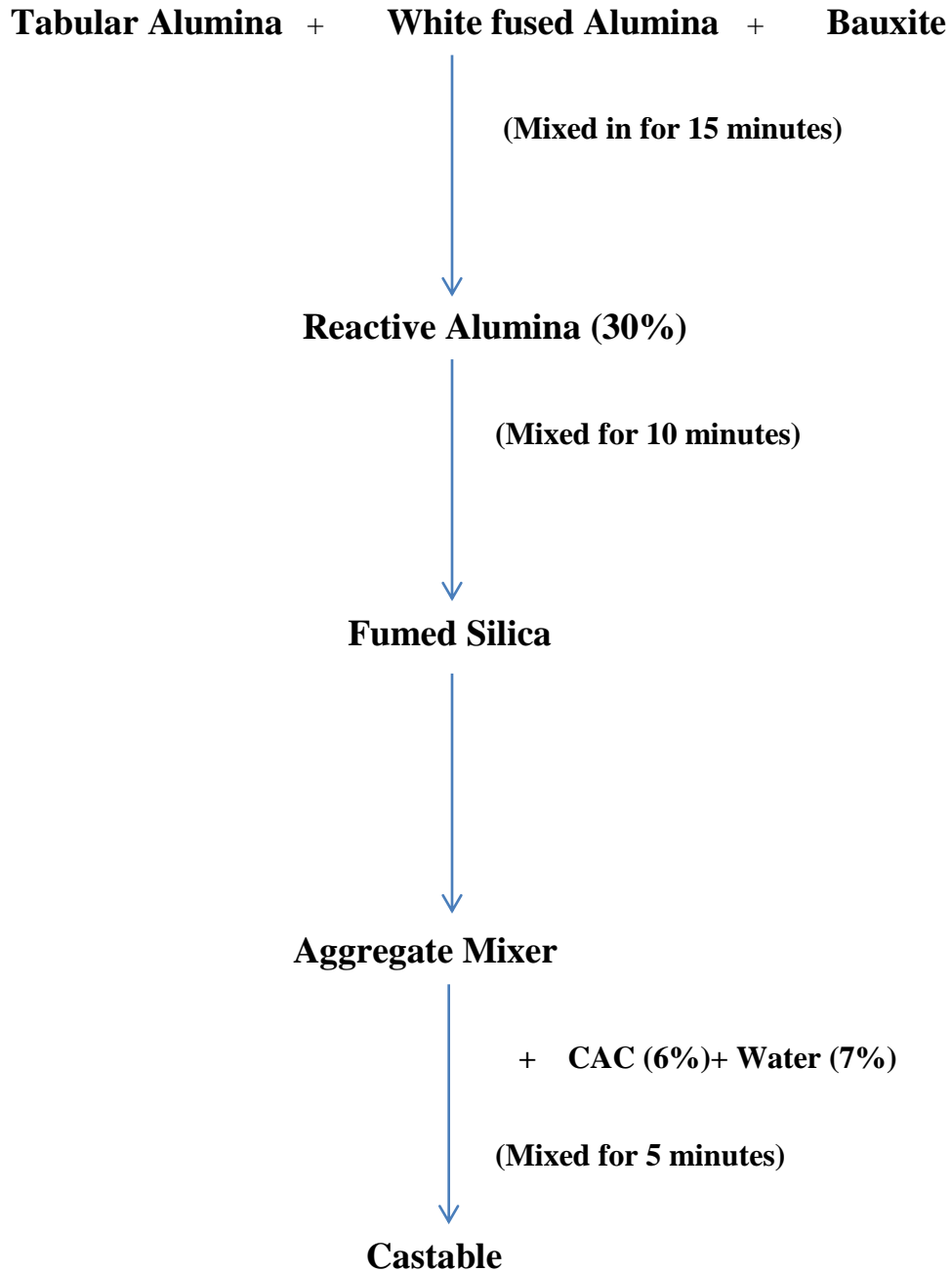
Castable

N.B All mixing were done in Hobart Mixer (5 kg capacity)

Fig 3.3 Flow chart for Low Cement Castable

The required amount of CAC was weighed separately and kept away in an evacuated desiccator because of its hygroscopic nature. The mixing sequence is as shown in the fig 3.1, 3.2, 3.3. The coarser components were taken first and mixed thoroughly in a Hobart mixer for 15 minutes followed by the addition of the finer particles and thoroughly mixed for about 10 minutes. During the final stage of casting, the CAC was added to the batch followed by thorough mixing. Required amount of water (12% for Castable 1 and 7% for Castable 2 and Castable 3) was added during the final mixing stage. The resultant mixture was then rapidly poured into the steel mould (dimension 50mm x 50 mm x 50mm) for setting and hardening. The mould was covered with a wet cloth and kept in air atmosphere for about 24 hours for humidity drying. After 24 hours the cubes were demolded and the blocks were subsequently kept in cool water for curing at a room temperature for different time periods viz 1 day, 3days, 7 days, 14 days, 28 days .The batch composition of the castables is shown in Table 3.3. This is calculated using the data mentioned in the Table 3.2.

Table 3.3 Chemical Composition of the Castable

Weight Percentage in Castable			
	Castable 1	**Castable 2**	**Castable 3**
Al_2O_3	87.41	88.58	84.59
Fe_2O_3	0.51	0.50	0.51
TiO_2	0.26	0.26	0.26
B_2O_3	0.001	0.002	0.002
CaO	3.15	1.93	1.93
SiO_2	8.17	8.15	12.12
Na_2O	0.21	0.21	0.21
K_2O	0.02	0.02	0.03
MgO	0.26	0.26	0.26
LOI	0.09	0.09	0.09

CHAPTER 4

TESTING AND CHARACTERIZATION

4.1 DETERMINATION OF COLD CRUSHING STRENGTH (CCS):

The cured samples were removed from water and oven dried for about 24 hours at 110 °C and then analyzed for its strength. The CCS of the castables was determined by the following equation:

$$\textbf{CCS = L/A} \qquad \text{…………..………..eqn (4. 1)}$$

where, CCS= Cold Crushing Strength (kg/cm^2), L=Load at which fracture occurs (kg) and A= Area of the sample (cm^2). The CCS was determined for 3 specimens and the mean of the 3 values were reported.

The fired CCS of the castables was determined after firing the green samples at 1650 °C for 2 hours. The initial heating rate was 5 ^{O}C/min up to 1000 ^{O}C followed by heating at 3 ^{O}C/min up to desired temperature. The castable blocks were furnace cooled and then CCS was determined as described above.

4.2 DETERMINATION OF BULK DENSITY OF AS CURED AND AS FIRED CASTABLES:

After the desired curing time was over, the samples were removed from water and oven dried for about 24 hour at 110 °C and then analyzed for its bulk density. The bulk density of the samples was calculated by taking the weight of each of the castable sample and then dividing the weight by the volume. It is calculated by the formula:

$$\textbf{BD= Mass/Volume} \qquad \text{………………… eqn. (4.2)}$$

To determine the fired BD of the castables the samples were subjected to sintering at 1650 °C after initial curing of 7 days. Firing was done in a programed controllable furnace.During sintering the initial heating rate is 5 ^{O}C/min up to 1000 ^{O}C and then reduced to 3 ^{O}C/min up to desired temperature. The castable blocks were then cooled and then subjected to BD determination as described above.

4.3 DETERMINATION OF FLOWABILITY:

The flowability of the castables was determined by the help of flow cone. The base diameter of the flow cone was 100 mm and the top diameter was 70 mm. The castables of desired composition was prepared by thoroughly mixing the aggregates, fillers and binder as shown in Fig 3.1 and was poured into the flow cone. The system was placed on the vibratable table and vibrated for 2 minutes. The material flowed as a result of vibration and the change in the base diameter was noted down. The difference was indicative of the flowaility of the castables. Larger the diameter greater is the flowability of the castable.

If X is the measured diameter of the base after vibration then the flowabilty is given by:

$$\textbf{Flowability = (X-100) mm} \ldots\ldots\ldots\ldots\ldots \text{eqn (4.3)}$$

4.4 DETERMINATION OF HOT MODULUS OF RUPTURE (HMOR):

Hot Modulus of Rupture (HMOR) is the maximum load at which the refractory material will break under a 3 point bending system under hot conditions. For calculating the HMOR of the samples, the aggregates and the binder were thoroughly mixed as per the sequence shown in the Fig 3.1.The castable was prepared and poured into the bar shaped moulds of dimensions 150mm x 25mm x 25mm.The cast was demoulded after 24 hours and then subjected to curing for 7 days in water. After 7 days the samples were removed from water and then subjected to drying in a oven for 24 hours at a temperature of $110°C$. The dried samples were subjected to sintering at 1650 $°C$ with soaking time of 2 hours at 1650 $°C$. During sintering the initial heating rate was 5 ^OC/min up to 1000 ^OC followed by heating rate of 3 ^OC/min up to desired temperature. After firing the samples were furnace cooled and then taken out of the furnace.The sintered samples were subjected to HMOR analysis. The loading rate was 1.3 kg/sec and the heating rate of 8^OC/min up to 1000 ^OC and then reduced to 5^OC/min up to desired temperature of $1400°C$. The mean value of 3 readings for each type of castable was considered.

The HMOR was calculated as per the formula:

$$\textbf{HMOR=(3*P*L)/2B*D}^2 \ldots\ldots\ldots\ldots\ldots..\text{eqn(4.4)}$$

Here, P=Load (kg) at which the sample failed.

L= Span length

B= Breadth of the sample

D= Height of the sample

4.5 PHASE ANALYSIS:

The phases in the fired castable was observed by XRD. The fired castable was crushed and ground to very fine powders using a mortar pestle and then subjected to XRD analysis to identify the phases formed after sintering. The scan was performed at a 2 ^{O}C/min scan rate at 40 kV and 30 mA. The X- ray data was plotted using the X'Pert Pro software and the peaks were matched with JCPDS files to get the phases.
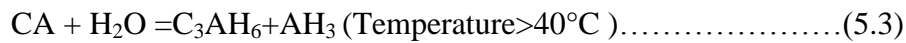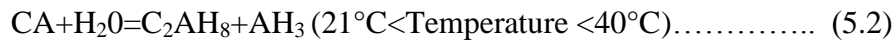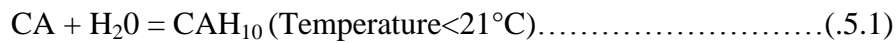
4.6 MICROSTRUCTURAL ANALYSIS:

SEM analysis was carried out on a crushed powder of the sintered castable. The powder was sprayed on an aluminium stub and gold coated. The sample were observed at 30 kV accelerating voltage at a working distance of 10 mm.

CHAPTER 5

RESULTS AND   DISCUSSION

5.1 VARIATION OF BULK DENSITY AND COLD CRUSHING STRENGTH WITH RESPECT TO CURING PERIOD:

The variation of the Bulk Density of the castables prepared with different types of Calcium Aluminate cements as a function of curing time is shown in the Figures 5.1-5.3. The castables were cured in water for 1 day, 3 days, 7 days, 14 days and 28 days. It is observed that the bulk density of the castables increases with increase in curing time. This was due to the formation of the hydraulic bonds resulting from the hydration of the cement phases due to the reaction with water as per the following equations [7]:

$CA + H_2 0 = CAH_{10}$ (Temperature<21°C)………………………(.5.1)

$CA + H_2 0 = C_2 AH_8 + AH_3$ (21°C<Temperature <40°C)………….. (5.2)

$CA + H_2 O = C_3 AH_6 + AH_3$ (Temperature>40°C)…………………(5.3)

It has been further observed that the Bulk Density of the castables with CA 14 as the binder is higher than the castables with Polychem as the binder. This could be because of the difference in the quality of the two cements which gives different hydration products in both the cements and also the difference in their particle size which in turn affects their reactivity with water. It has also been observed that after 5-7 days of curing of the castables, the bulk density reached a constant value and there after no significant changes were observed in the value of the bulk density of the castables. The variation of the CCS of the castables with respect to the curing time is also shown in the Figures 5.4-5.7.It was observed that the CCS variation with respect to the curing time was very much similar to the variation of Bulk Density with respect to the curing time. This was due to the increase in the degree of formation of the hydraulic bonds as a result of hydration.
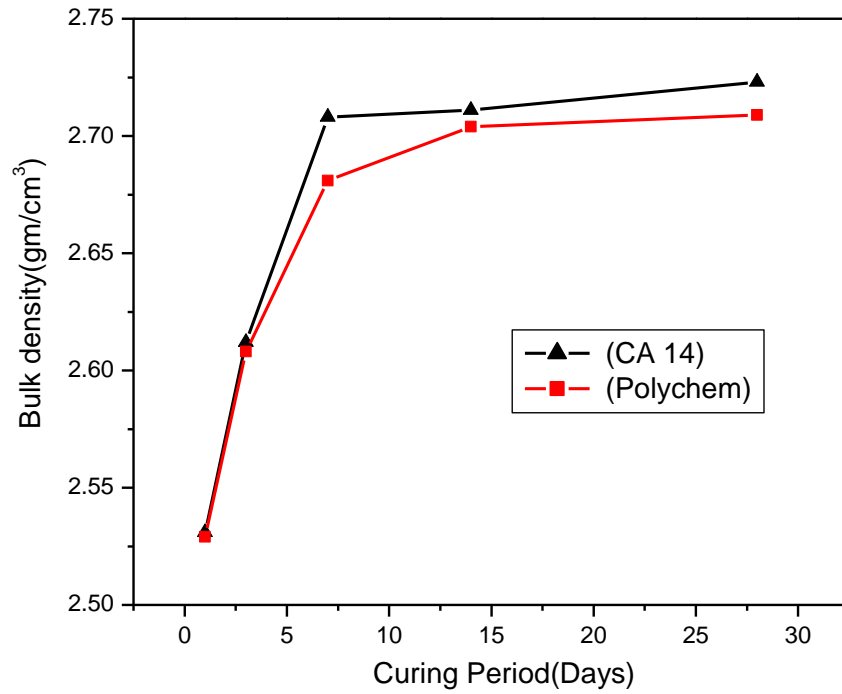
Fig 5.1: Variation of the Bulk Density with curing time of Castable 1
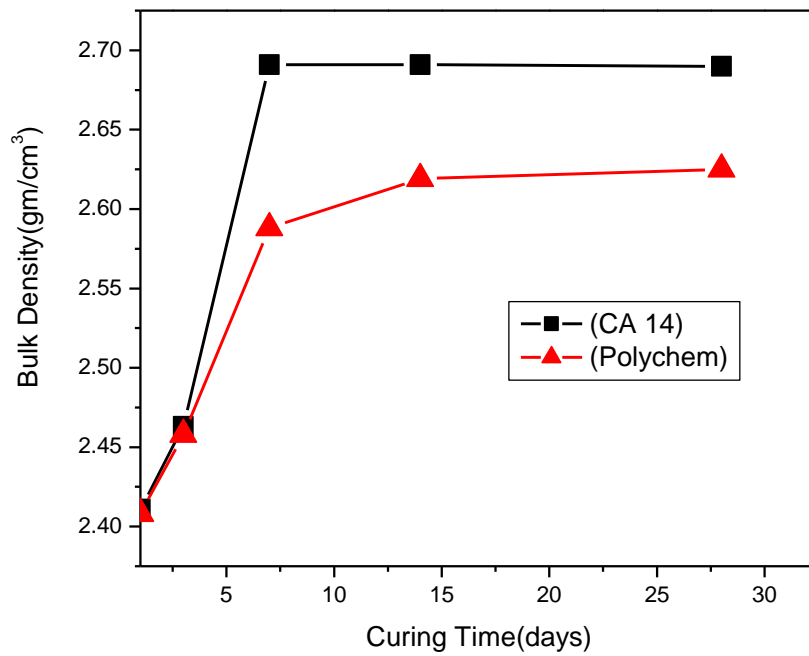

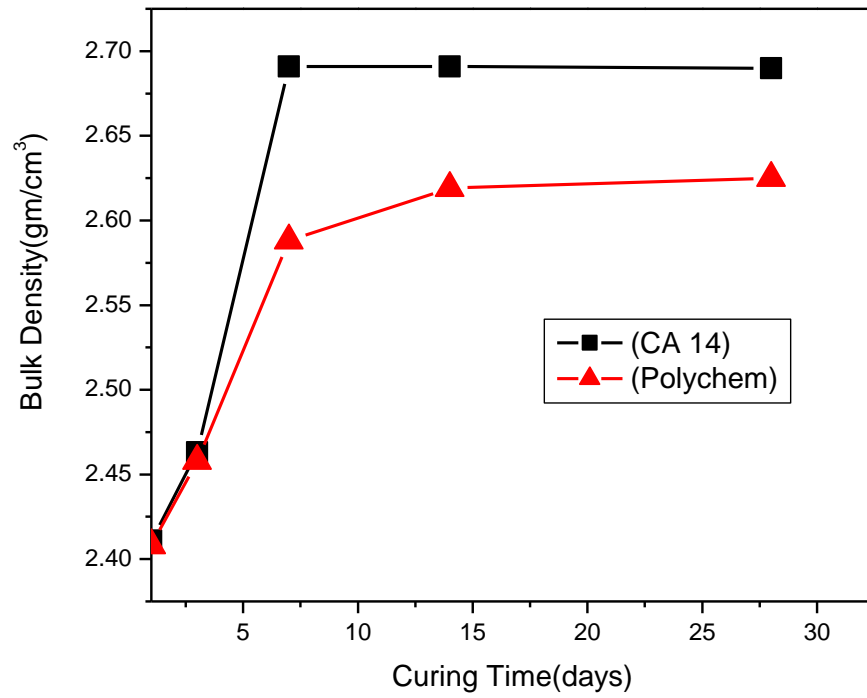**Fig 5.2: Variation of the Bulk Density with curing time of Castable 2**

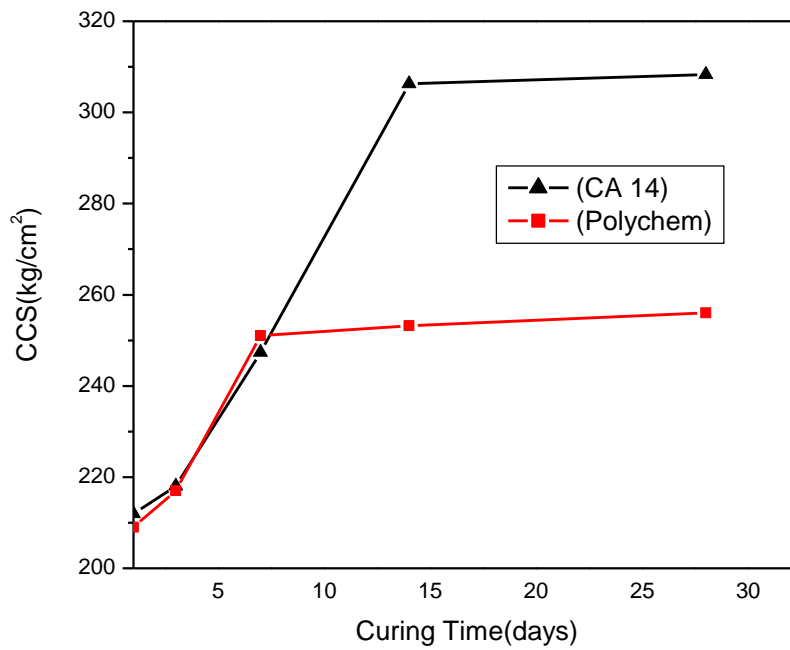**Fig 5.3: Variation of the Bulk Density with curing time of Castable 3**

Fig 5.4: Variation of the CCS with curing time of Castable 1
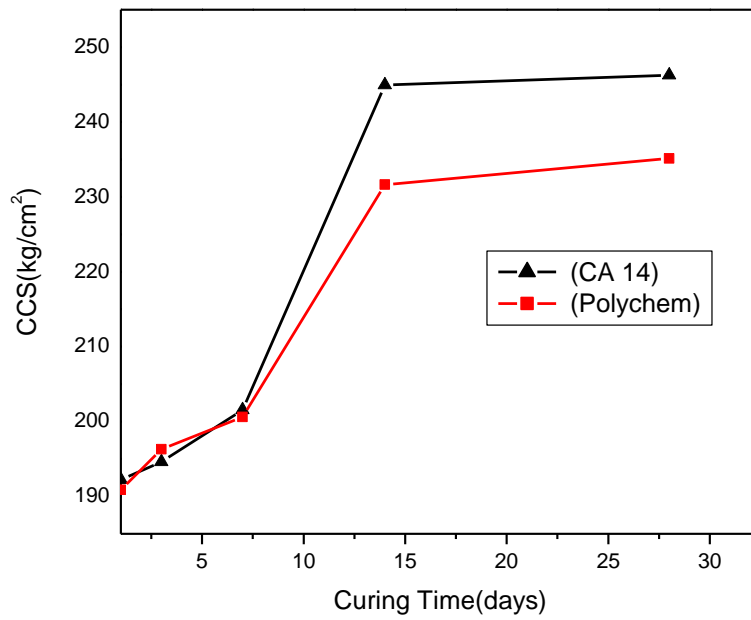
Fig 5.5: Variation of the CCS with curing time of Castable 2
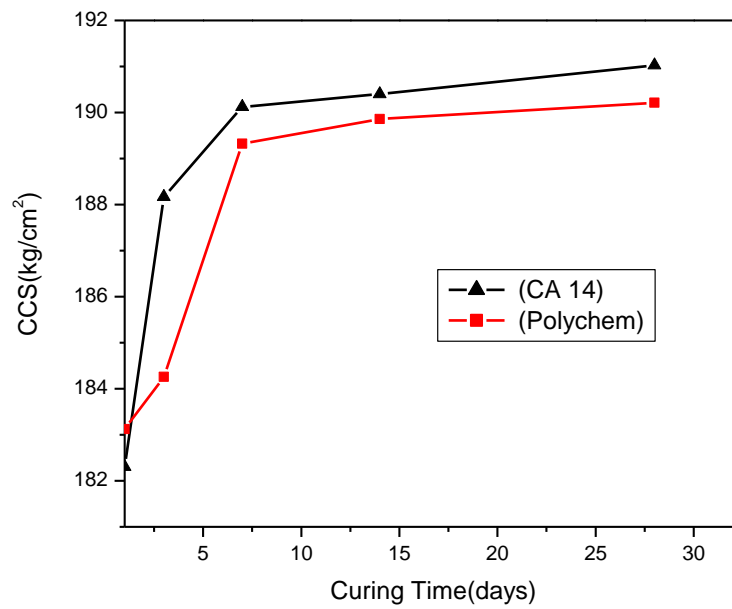

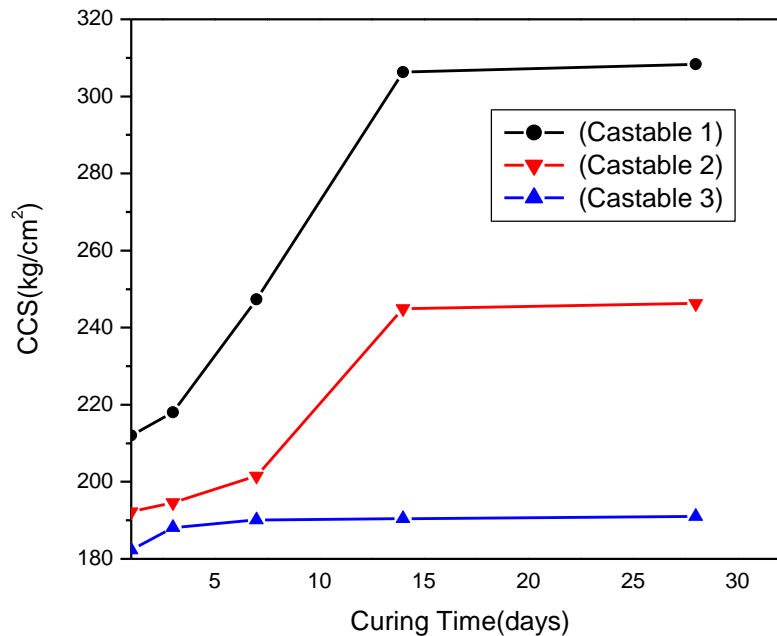**Fig 5.6: Variation of the CCS with curing time of Castable 3**

Fig 5.7: Variation of the CCS with curing time of the three different castables with CA 14 as binder

From Figure 5.7 it is seen that the Castable 1 (conventional cement type) shows a higher value of CCS as compared to the castable 2 and castable 3.This is because the Castable 1 is a conventional cement type of castable containing 10% cement. Higher percentage of cement in the composition allows castables to have higher percentage of hydraulic bonds upon water addition. This fills up the porosity and holds the aggregates strongly as compared to the castable 2 and castable 3 which are low cement type (6 % cement). This imparts more green strength to the castable 1 as compared to the castable 3.

5.2 STUDY OF THE FIRED STRENGTH OF THE CASTABLES:

All the 3 types of castables were fired at 1650°C. The graphical representation of the cold compressive strengths of the fired castables after firing at 1650°C is as shown in the Fig 5.8.
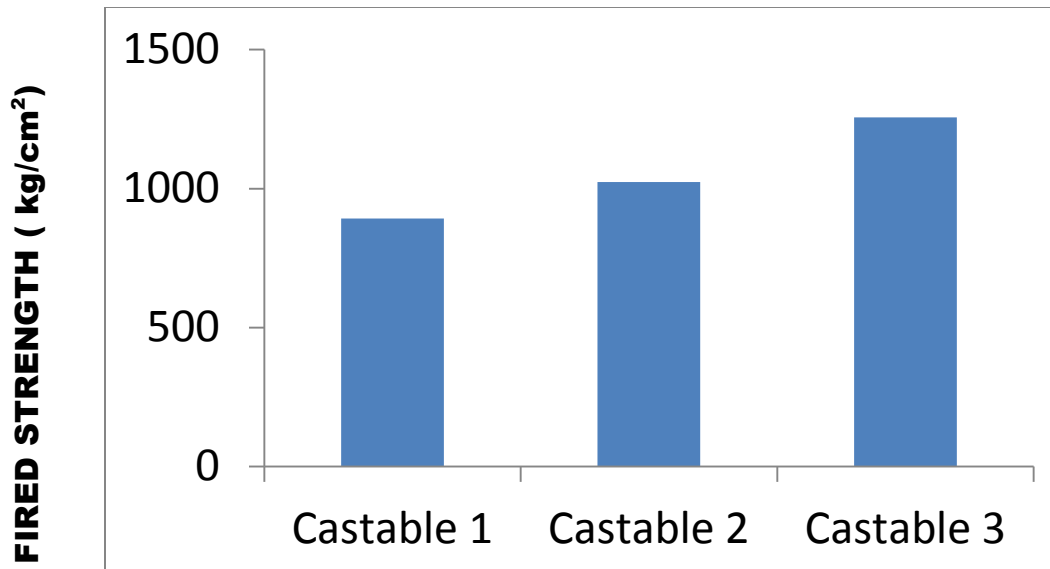
Fig 5.8: Fired strength of the Castables

Fig 5.8 shows that the fired strength of the Castable 1 is (892.70 kg/cm^2) is lower than the castable 2 (1024.2 kg/cm^2) and castable 3 (1256.6 kg/cm^2). The lower strength of the castables is due to the higher percentage of cement (10%) in this conventional cement castable. On firing gradual loss of water occurs due to the dehydration of the cement. So, castable 1 develops higher porosity resulting in the reduction of strength. However for the castable 2 and castable 3 both of which are of low cement type have lesser amount of cement (6%).Hence the quantity of water required for the hydration of the cement phases is also less. This leads to lower gradual loss of water in the form of water vapor due to the dehydration of the cement phases in both castable 2 and castable 3 and consequently this result in higher density. Hence fired strength of castable 2 and 3 is higher than the Castable1. Further the compressive strength developed in the castable 3 is much higher as compared to the others. This appears to be due to the presence of 4% microsilica which had replaced reactive alumina in castable 3 .During sintering mullite formation occurs due to the reaction between microsilica and reactive alumina. This mullite phase is likely to provide an interlocking grain structure which imparts higher compressive strength to the castable.

5.3 STUDY OF THE FLOWABILITY OF THE CASTABLES:

The flowability of the castables was determined following the procedure described in section 4.5.The comparative study is as shown in the following diagram (fig 5.9)
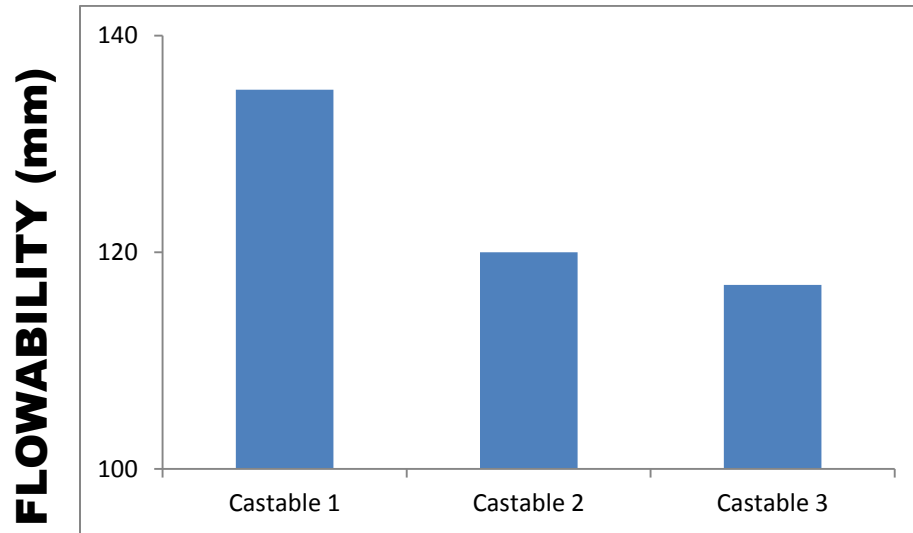

Fig 5.9: Flowability of the Castables

From the above Figure it is seen that the flowability of the conventional cement type of castable (castable 1) was maximum followed by the castable 2 and castable 3.This could be due to the fact that castable 1 is a conventional cement type of castable. It is having a greater percentage of cement in the composition as compared to the other castables. Due to greater quantity of cement greater amount of water addition is required for this castable which enhanced the flowability. Castable 2 has a greater quantity of reactive alumina (34%) in the composition. This material has a very fine particle size and hence has very high reactivity. Upon water addition in presence of cement as a binder it results in the formation of an amorphous gel like phase of AH_3 ($Al_2O_3.3H_2O$) [26]. This phase imparts a greater amount of gel like phase to the castable which accounts for the lesser flowability as compared to the castable 1.Similarly in castable 3, although the presence of micro silica is expected to enhance the flow property,but the simultaneous presence of cement, reactive alumina and microslica probably leads to the formation of a gel like structure which reduces its flowability.

5.4 STUDY OF THE HMOR OF THE CASTABLES:

HMOR of the castables was measured at 1400 °C. The HMOR was determined for three samples of each castable composition. The comparative study of the HMOR of the different castable compositions is as shown in the Figure 5.10 below:
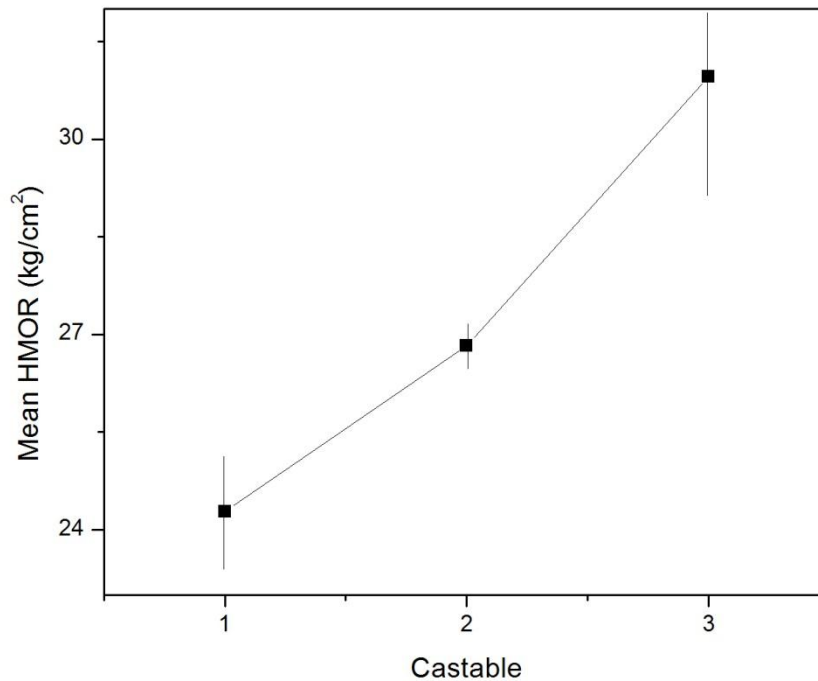

Fig 5.10: Mean HMOR of all the three castables fired at 1650 °C

It is observed that at any loading rate the HMOR of Castable 1 is much lower as compared to the HMOR values of the castable 2 and castable 3.This is because the castable 1 is a conventional cement type of castable with very high percentage of cement (10% cement). Table 3.3 indicates that the percentage of CaO in the castable 1 is very high i.e. 3.152% as compared to the castable 2 and castable 3 where it is 1.9328% and 1.932% respectively. This results in the formation of higher amount of low melting phases like anorthite ($CaO.Al_2O_3.2H_2O$) and Gehlenite ($2CaO.Al_2O_3.SiO_2$) upon firing. These are low melting compounds and form a liquid phase around 1250 °C. This liquid phase coats the surface of the grains and reduces the degree of

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atomic bonding between the grains. The presence of this liquid phase results in increased grain boundary sliding and hence easy plastic deformation in the sample and ultimately the HMOR of the sample is reduced. It is also further observed that the HMOR of the castable 2 is lower than the castable 3.This is because in castable 3 a small fraction of reactive alumina was replaced with fumed silica as the filler. This resulted in the formation of mullite phase upon sintering at 1650°C.This mullite phase has better refractoriness, better mechanical strength, higher RUL and better creep resistance. Due to this, the castable 3 shows a higher value of HMOR as compared to the castable 2.

5.5 PHASE ANALYSIS BY XRD:

The Castable 3 was sintered at 1650°C for 3 hours and then crushed and grounded in a mortar pestle and then subjected to X Ray Analysis by the process as described in sec 2.7. The XRD analysis shows the presence of mullite and corundum. Mullite is formed by the sintering reactions taking place between reactive alumina and fumed silica upon sintering at 1650°C. However due to the close d spacing corundum and mullite, separate mullite peaks could be identified as most of the prominent peaks overlapped with those of corundum.
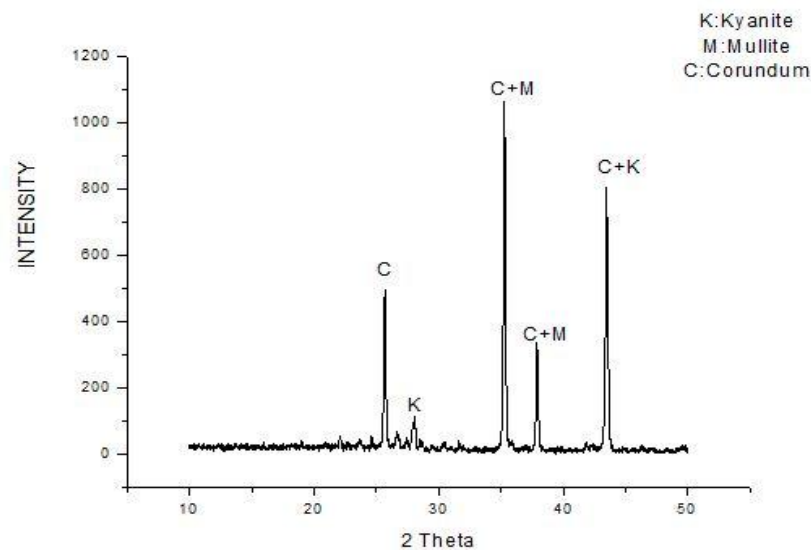

Fig 5.11:XRD Analysis of the castable 3

The mullite phase was matched with the JCPDS file no. 02-1160 and the corundum phase was matched with the JCPDS file no. 71-1124.Similarly the kyanite phase was matched with the JCPDS file no:03-0513

5.6 MICROSTRUCTURAL ANALYSIS BY SEM:

The castable 3 samples were fired at a temperature of 1650 °C for 3 hours. It was then crushed and ground to very fine particle size. These powdered samples were subjected to microstructural analysis using SEM (Fig 5.12) The SEM image show the development of needle shaped crystals. Mullite phase has a needle shaped microstructure. So, the SEM analysis also supports the development of small amount of mullite phase in the microstructure. The SEM micrograph is as shown.
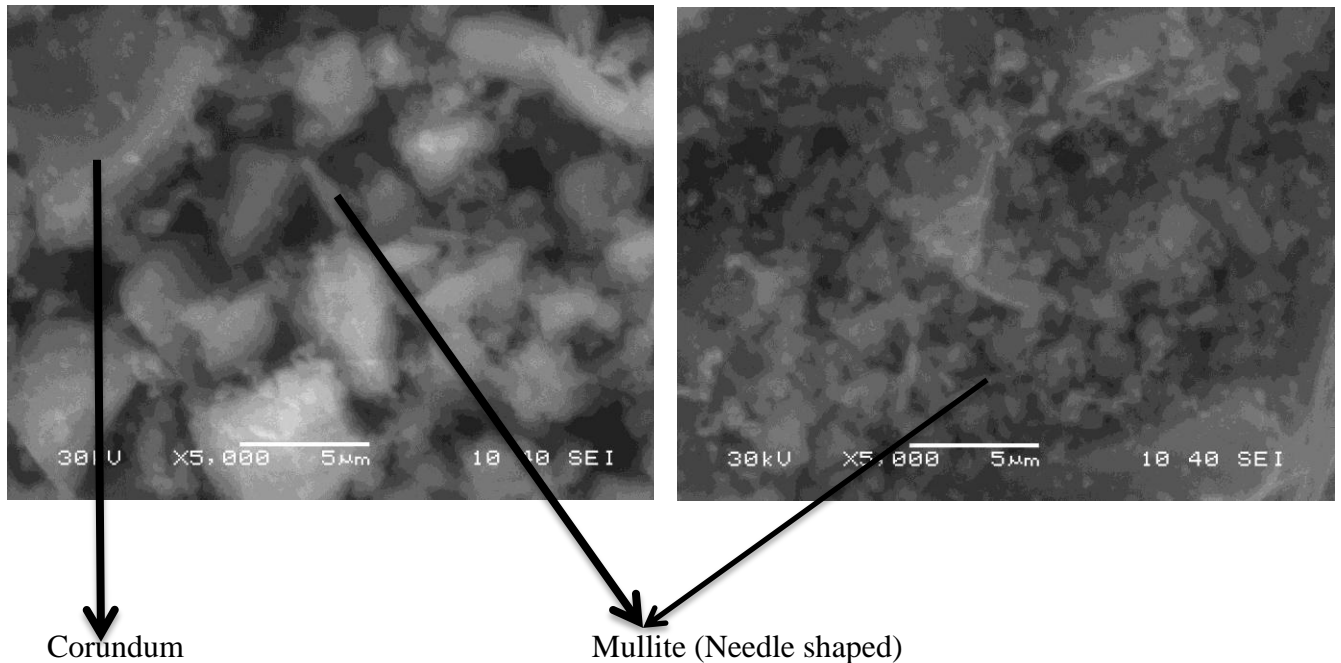

Corundum   Mullite (Needle shaped)

Fig 5.12: SEM Analysis of the castable 3

CHAPTER 6

SUMMARY

This study was aimed to observe the effect of reactive alumina and micro-silica on the properties of a high alumina cement bonded conventional refractory castable. In the first step 10% cement was reduced to 6% with replacement with 4% reactive alumina. This replacement improved the thermo-mechanical properties of the castables as indicated by the HMOR values. In the second step, 4% of reactive alumina was replaced with 4% micro-silica. This second step replacement also improved the mechanical and the thermo-mechanical properties of the refractory castable. Upon phase analysis of the castable (with reactive alumina/micro-silica combination) revealed the development of mullite in the composition. The presence of additional mullite phase was responsible for the improvement in the properties of the refractory castables. These low cement high Alumina based castables with a proper combination of reactive alumina and fumed silica/micro-silica as the filler can be used for any variety refractory application like in the Iron and Steel industry, glass industry, refineries, oil industries, tile industries etc.

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