

LOW CEMENT HIGH ALUMINA CASTABLES: EFFECT OF DISTRIBUTION COEFFICIENTS

**A THESIS IN THE PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF BACHELOR OF TECHNOLOGY**

BY

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ROLL NO: 109CR0204



**DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA**

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NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA
CERTIFICATE

This is to certify that the thesis entitled, "***LOW CEMENT HIGH ALUMINA CASTABLES: Effect of distribution coefficients***" submitted by *Ms. Anvesha Parija (109CR0204)* in partial fulfilments for 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 her 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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13th May, 2013

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ANWESHA PARIJA
Anwesha Parija

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ABSTRACT

Refractory materials used in various areas of the iron and steel industry need to face severe challenges to meet critical operational parameters at high temperatures. Hence, the attention of refractory manufacturers has shifted towards unshaped refractories to substitute for conventional and shaped ones. Castables lead in all the areas among the different unshaped refractories. Refractory castables (which are used by casting method) are premixed combinations of refractory grain, matrix components, bonding agents, and additives. The proportions are varied accordingly to achieve the desired properties. Again flowability of the castables is very important for application (casting) purposes and their final performances. Better flow of any castable allows making a good lining and makes it possible too line an intricate shape. This flowability is dependent on the particle size distribution and packing of the castable system. But better flowing mass may indicate higher sphericity of particles, resulting lower strength, which is not acceptable for refractory application. Hence design of refractory castable system is challenging as it required opposing character of flowability with higher strengths. The present work targets to study the development of refractory castable system with particle size distribution (PSD) as per well-known Dinger Funk model for continuous distribution and study the developed properties of the castables for their flowability and various characteristics developed at different temperatures.

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LIST OF ABBREVIATIONS

Sl. No.	Abbreviation	Full form
1.	HAC	High Alumina Cement
2.	PSD	Particle Size Distribution
3.	XRD	X-Ray Diffraction
4.	WTA	White Tabular Alumina
5.	WFA	White Fused Alumina
6.	CPFT	Cumulative percent finer than
7.	BD	Bulk Density
8.	CCS	Cold Crushing Strength
9.	CA	$\text{CaO} \cdot \text{Al}_2\text{O}_3$
10.	CA2	$\text{CaO} \cdot 2\text{Al}_2\text{O}_3$
11.	CAH10	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$
12.	C2AH8	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$
13.	C3AH6	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$
14.	C12H7	$12\text{CaO} \cdot 7\text{H}_2\text{O}$

CHAPTER 1

INTRODUCTION

INTRODUCTION

Ceramic materials have been closely related to the development of human society from its very beginning. Ceramic technology is the most ancient technology; more than 24000 years old and at the same time is the most modern, dynamically developing and diversifying field. The ever-increasing uses of ceramics in different areas of space age technology have made it a field of strategic importance. Amongst the different classes of ceramics, **refractories** are the materials having those chemical and physical properties that make them applicable for structures or as components of system that are exposed to environments above 1000°F [as per ASTM nomenclature, 1984]. Hence refractories are the essential component for all high temperature processing. Refractories need to have heat with-standability, strength at elevated temperatures, resistance to corrosive atmosphere as per application [1, 2].

Refractories are that group of ceramic materials which are used to line vessel in which other materials like metals; glass and cements are manufactured at higher temperatures. They comprise of discontinuous large sized aggregate (filler) phases along with continuous finer binder phases in the matrix. They are mainly differentiated as **Shaped** and **Unshaped (Monolithics) refractories** [3].

Refractories have their application in various industries like:

- Iron & Steel Industry
- Cement Industry
- Aluminium Industry
- Tile Industry
- Petro Chemical Industries
- Oil Industries
- Glass Industries

In the last two decades the use of monolithics or unshaped refractories has been dominant over the preshaped refractories. It has been observed that the ratio of monolithics to preshaped refractories (bricks) has been increasing steadily because of the dramatic decrease in the consumption of the shaped ones [3].

“Monolithics” has come from words “mono” meaning single and “lithus” meaning stone/structure. It includes various material types and compositions, along with a wide range of bonding systems. Monolithics are single piece casts which takes the shape of equipment. Monolithics have emerged into a versatile class of refractory materials offering performance and cost-effectiveness superior to those of shaped ones. The success of monolithics is because of the significant advancements in the type and quality of their binders, aggregates, and admixtures in addition to their design creation and innovative installation techniques [3].

Monolithics have rapidly grown at the expense of bricks because of their faster, easier and cheaper installation; ready availability and minor corrosion susceptible lining joints, greater volume stability and better spalling resistance [4].

The iron and steel industry has undergone revolutionary changes because of the adaptation of various sophisticated processes to improve the quality and production of steel. The changes have been phenomenal. As a consequence, refractory materials used in various areas of the iron and steel industry need to face severe challenges to meet critical operational parameters at high temperature. Refractories should perform better with less down time, as has been imposed by steel manufacturers. Hence, the attention of refractory researchers, manufacturers and users has shifted towards unshaped refractories to substitute for the conventional and shaped ones. Among the different unshaped refractories, castables lead in all areas including Research & Development, as well as in manufacturing and application areas. Physical, mechanical, chemical and thermo-mechanical properties of various castables as well as their processing and bonding mechanisms are usually investigated [5].

The most significant advancement in monolithics technology was the development of *castables* based on Calcium Aluminate Cements. Refractory castables (which are used by casting method) are premixed combinations of refractory grain, matrix components, bonding agents, and additives. The proportions of each component used vary in each castable composition to achieve the desired properties essentially required for the intended application. The most commonly used hydraulic binder is Calcium Aluminate Cement in refractory castables compositions, but presence of CaO results in low melting phases in Alumina and Alumina-Silica refractory system [6]. The curing and dewatering steps must be carefully controlled to prevent explosive spalling. The material is mostly supplied dry but sometimes installed by ramming or vibro-casting along with the addition of proper amount of water or other liquid, which serves as the binder.

The classification of castables in accordance to **IS: 10570** are as follows:

1. **Conventional** – A castable containing greater than 2.5% calcium oxide on calcined basis.
 - a. **Dense castable**
 - b. **Insulating castable** – B.D having a maximum of 1.85 g/cc
2. **Low cement castable** – a castable containing calcium oxide greater than 1% and maximum of 2.5% on a calcined basis.
3. **Ultra low cement** – a castable containing calcium oxide greater than 0.2% and maximum of 1% on a calcined basis.
4. **No cement castable** – a castable containing calcium maximum of 0.2% on a calcined basis.
5. **Gunning material** – This material can be in the category of either conventional or low cement depending on its calcium oxide content. The gradation, based on calcium oxide content, is similar to that of castable. The installation of this product, however, is done by gunning machine.

While *conventional castables* containing the largest amount of cement make up the greatest percentage of those produced, use of reduced cement varieties like *low cement castables (LCC's)*

and *ultralow cement castables (ULCC's)*, have grown significantly over the last decade. This is due to the CaO present in the cement which leads to decline in the high-temperature properties.

Conventional castables consist 15-30% CAC, the amount being necessary to achieve satisfactory strength at low and intermediate temperatures. A comparatively large amount of water (0-5%) is taken up by the porosity of the aggregates which does not contribute to the hydraulic bond. The disadvantage of the conventional castables is closely related to the amount of cement present. The conversion of the bond phase between 250-350°C decreases the mechanical strength. The hot strength reaches a maximum value at 800-1000°C because of the formation of a ceramic bond. At elevated temperatures, the strength of silica containing castables decreases due to liquid formation. The hot strength can be improved by minimising the cement content of the castable [3].

The performance of alumina based castables has improved because of the reduction in the cement-content, thus diminishing the liquid phase formation at application temperatures and improving the corrosion and creep resistance. Thus low cement castables (LCC), ultra-low cement castables (ULCC), no cement castables (NCC) and self-flow castables (SFC) have popularised in the refractory industries [3-5]. Self-flow castables contain a greater amount of fines content while castables with lesser fines content require vibration to take shape. The amount of fines content in a castable is decided by the distribution coefficients. If it is less, then the castable has greater amount of finer particles. Usually the castable is self-flowing in nature if the distribution coefficient is less than 0.25 and vibratable if the distribution coefficient is more than 0.25 [7]. Self-flow castables flow under their own weight while vibratable castables require an external load. The binding phase used here is the high alumina cement (HAC). The major phases present are $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA), $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA_2) and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7). CA_2 phase is the slowest setting phase and C_{12}A_7 phase is the quickest setting phase. The setting time depends on the amount of CaO present in the phase. The higher the amount present, the more quick setting it is. The cements, mostly used as binders, mainly consist of CA_2 and CA phases [5-7]. The binding

phase and the fired temperature differentiate the castables. After preparation, drying and firing takes place. The physical properties are then tested to see which binder composition and firing temperature gives the best properties. Again flowability of the castables is very important for application (casting) purposes and their final performances. Better flow of any castable allows making a good lining and makes it possible too line an intricate shape. This flowability is dependent on the particle size distribution and packing of the castable system. But better flowing mass may indicate higher sphericity of particles, resulting lower strength, which is not acceptable for refractory application. Hence design of refractory castable system is challenging as it required opposing character of flowability with higher strengths.

CHAPTER 2

LITERATURE REVIEW

LITERATURE REVIEW

2.1 REFRACTORIES:

Refractory is a ceramic material capable of withstanding high temperatures and high load even under the utmost conditions of highly corrosive and abrasive environments. According to ASTM C-71 refractories are materials having those physical and chemical properties that make them suitable for structures exposed to temperatures above 1000°F.

Refractories are classified on the basis of chemical nature, shape, porosity, percentage of carbon content, heat withstanding capacity, and purity. On the basis of shape, refractories are further divided into shaped and unshaped refractories.

Shaped refractories are manufactured by pressing while unshaped ones (monolithics) are either self-flowing or vibratable in their types [1-4].

2.2 MONOLITHICS:

The term ‘monolithics’ comes from two words namely ‘mono’ meaning single and ‘lithus’ meaning stone. They are premixed combinations comprising of refractory grains as the aggregate phase, binder which is the matrix phase, and other additives. These materials finally harden on mixing with a liquid, mostly water, to form a solid mass. The reasons for the success of monolithics, over shaped bricks, are their quick availability, easier and cheaper installation, and lesser corrosion susceptible lining joints, greater spalling resistance, and better volume stability [6,7].

2.3 CASTABLES:

A significant advance in monolithics technology was the development of castables based on Calcium Aluminate Cements. Refractory castables comprise of graded refractory aggregates

and hydraulically setting cement of calcium aluminate variety, with other additives for specific purposes. The material is usually supplied dry and may be installed with the appropriate addition of water or other liquid, which serves as binder.

On the basis of flow, castables are sub-divided into self-flow and vibratable castables. Self-flow refractories mechanically flow under their own weight to take the shape of the mould whereas vibratable refractories require vibration to take the shape of the mould [11-15].

2.4 PARTICLE SIZE DISTRIBUTION:

There are two types of particle packing in refractories namely discrete packing and continuous packing. The type of packing plays a very crucial role in monolithics.

The discrete packing model was proposed by Furnas. He stated that the maximum packing density can be obtained when the smaller sized particles fill the voids between the larger sized particles.

Andreasen model assumed that particles could not be of a particular size rather they fall within a narrow size range.

The CPFT (cumulative percent finer than) equation according to Andreasen is given by:

$$\text{CPFT} = (d/D)^q \times 100$$

where d denotes the particle size for calculating CPFT,

D denotes the maximum particle size, and

q denotes the distribution coefficient also known as q -value.

Andreasen's model did not assume any minimum particle size for calculating CPFT. Instead he assumed that the particles are infinitesimally small which was practically not possible. So the Andreasen's model was modified by Dinger Funk who assumed a certain minimum particle size for calculating CPFT thus making it more practical.

Thus the CPFT according to the Dinger Funk model is given by:

$$\text{CPFT} = \frac{(D^q - D_{\min}^q)}{(D_{\max}^q - D_{\min}^q)} \times 100$$

Where D denotes the particle size for calculating CPFT,

D_{min} denotes the minimum particle size,

D_{max} denotes the maximum particle size, and

q denotes the distribution coefficient.

It was found that castables require a unique but contradictory character of flowability and strength. Higher packing pertains to densification which in turn increases strength but results in less flow due to friction. Hence highest packing is not the only criterion. Thus the new packing model that is considered is the continuous particle size distribution.

Packing should be optimum such that the castable requires minimal water for setting implying less porosity which will give a higher packing density. Thus the castable will have improved physical properties in terms of CCS (cold crushing strength) and HMOR (hot modulus of rupture).

The flow characteristics of the castable (whether self-flowing or vibratable) is determined by the distribution coefficients. The castable is self-flowing in nature if 'q' is less than 0.25 else it is vibratable in nature. Lower the q-value the greater amount of fines in the batch implying greater flowability.

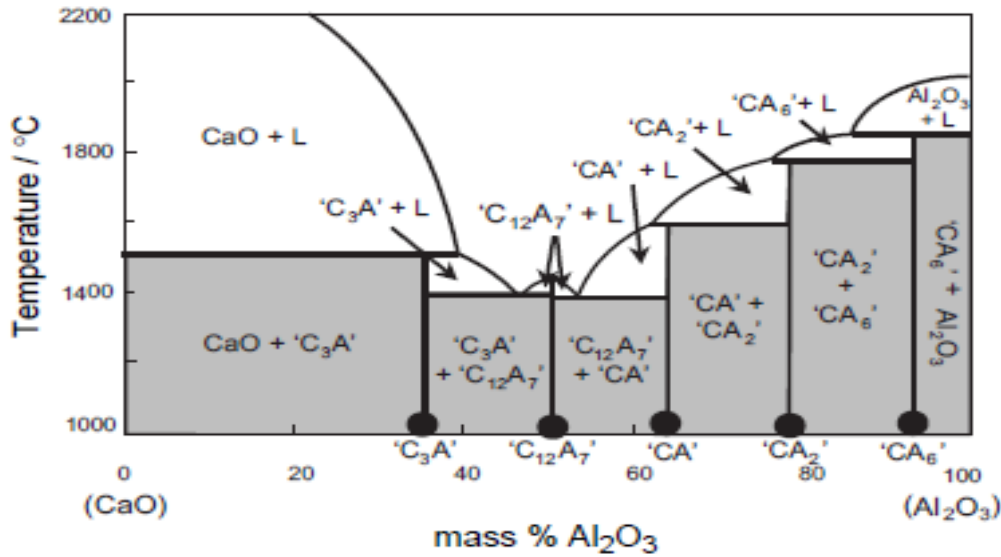
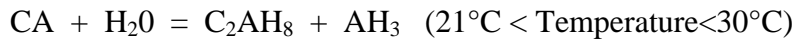
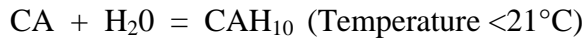


Figure 1: CaO-Al₂O₃ phase diagram [17]

Self-flowing castables thus have to possess greater amount of fine particles in order to be self-flowing in nature. Cement bonded castables have HAC (high alumina cement) as their bonding phase. HAC has the following phases namely CA, CA₂ and C₁₂A₇. C₁₂A₇ is the quickest setting phase and CA₂ is the most time taking phase in terms of setting. The amount of CaO determines the setting time. The greater it is the more quick that phase sets which is because of the absorption of water by CaO. The HAC absorbs water causing the setting of castable. On addition of water to the batch physical and chemical reactions take place in high alumina cement. The hydration phenomenon helps in converting the amorphous powder to different hydrated phases. These hydrated phases break down on firing to form very reactive products, which again recrystallize to form anhydrous calcium aluminates, the major phase being CA. Water addition creates a suspension in which the solid dissolves. Calcium Aluminate hydrates is formed during the process. Nucleation and growth takes place allowing more anhydrous CA hydrates into the solution. This mechanism results in the formation of interlocking bonds between the particles leading to the strengthening of the structure. As the temperature is increased to intermediate level the hydration bonds break resulting in the

weakening to the castables and at elevated temperatures the strength of castable is higher due to sintering.



At temperatures below 20°C, CAH₁₀ forms which is hexagonal in form and at temperatures above 30°C, C₃AH₆ rapidly forms which is the cubic hydrate phase. At the in between temperatures the metastable hexagonal hydrate phase C₂AH₈ forms which converts to C₃AH₆ phase with temperature rise [11, 12, 24].

(C denotes CaO, A denotes Al₂O₃ and H denotes H₂O)

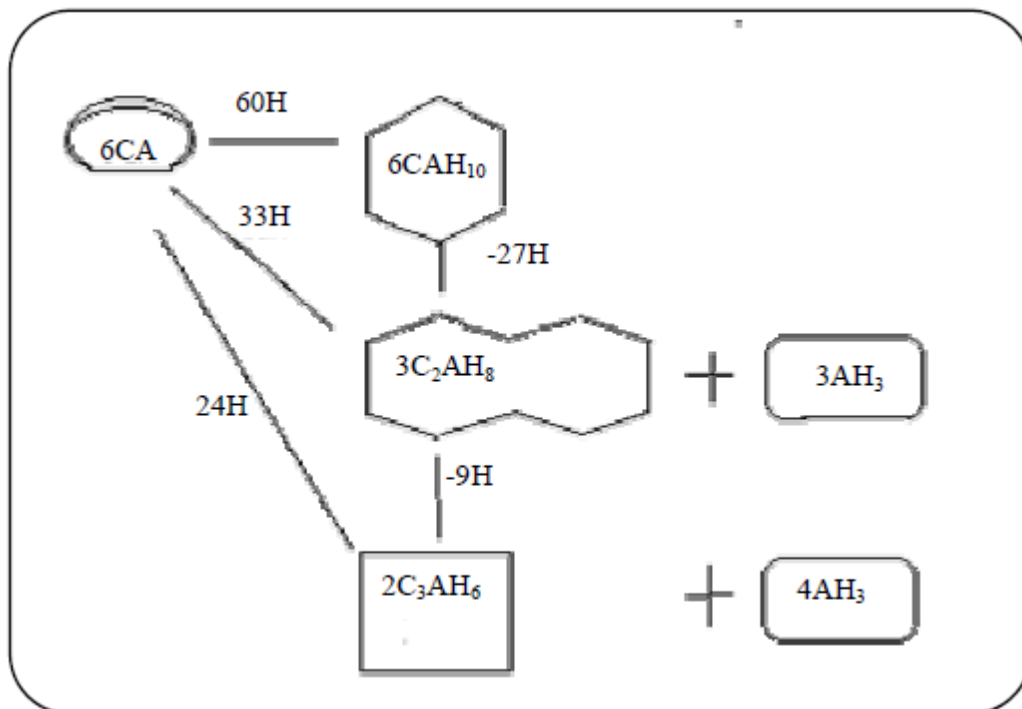


Figure 2: Reaction Mechanism of hydration of the Calcium Aluminate Phases [17]

OBJECTIVE

The aim of this project is to study the effect of various distribution coefficients on the properties of low cement high alumina castables according to the Dinger-Funk's continuous particle size distribution model. The work deals with a comparative assessment of self-flow with vibratables which has not been carried out in a single work earlier and is important for various refractory applications, mainly in iron & steel industries.

CHAPTER 3

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PROCEDURE

Batch formulation

Sampling of raw materials:

Coarse aggregates - White tabular alumina (WTA), White fused alumina (WFA)

Fine aggregates - WTA fines/Reactive Alumina

Binder – High alumina cement (HAC)

Additives –

Deflocculant - Ammonium Polymethacrylate: *for dispersion and flow*

Anti-setting agent - Citric acid: *optimises setting character of cement*

Fume Silica: *flow modifier, fillers*

Organic fibre: *to avoid explosive spalling during drying*

By keeping $q = 0.21, 0.23, 0.27 \text{ \& } 0.29$ we calculate the percentage of particles required in the various size ranges for a batch of 2.6 kg each. **Citric acid** (0.1 wt. %) and **Ammonium polymethacrylate** (0.3 wt. %) were added to the above batch along with the optimum amount of water during the mixing process.

The amount of fume silica is 5 wt. % & cement is 4 wt. %.

The raw materials were then sieved in order to keep the aggregate sizes in a particular size range.

Size fraction(in mm)	Raw Material
-3 mm to +2 mm	White Tabular Alumina
-2 mm to +1 mm	White Tabular Alumina
-1 mm to +0.5 mm	White Tabular Alumina
-0.5 mm to +0.3mm	White Fused Alumina
-0.3 mm to +0.15 mm	White Fused Alumina
-0.15 mm to +0.001 mm	Reactive Alumina (CL 370)/ WTA Fines

3.1 Table showing the size fractions and the corresponding raw material

Characterisation of raw materials:

The XRD analysis of high alumina cement is carried out for identifying the various phases present in it. It is done by the X-ray powder diffraction technique.

Chemical analysis was done for characterizing the raw material provided by the supplier. The presence of various oxides is as follows:

CONSTITUENT	WTA GRAIN	WFA GRAIN	ALUMINA FINES	FUME SILICA	HAC
SiO₂	0.03	0.1	0.2	96.2	0.21
Al₂O₃	99.34	98.93	98.1	0.4	71.64
Fe₂O₃	0.035	0.06	0.06	0.1	0.11
TiO₂	-	Trace	0.11	-	-
CaO	-	0.1	-	0.2	26.91
MgO	-	-	-	0.1	0.32
Na₂O+K₂O	0.15	0.4	0.35	0.4	0.27

3.2 Table showing the chemical constituents of the respective raw materials

Other properties found out are:

PROPERTY	WTA GRAIN	WFA GRAIN	ALUMINA FINES	FUME SILICA	HAC
LOI	-	-	0.2	0.9	-
AVERAGE SIZE	-	-	6-8μ	45μ	-
BULK DENSITY	3.61 g/cc	3.77 g/cc	-	-	-
APPARENT POROSITY	3.93%	1.8%	-	-	-
SPECIFIC SURFACE AREA	-	-	-	20 m ² /gm	4400 cm ² /gm
PHASE ANALYSIS	Corundum	Corundum	Corundum	Amorphous	CA ₂ , CA

3.3 Table showing the physical properties of the raw material

By keeping the distribution coefficients at 0.21, 0.23, 0.27, 0.29 we calculate the percentage of particles required in the various size ranges for batch formation and correspondingly the weights of the material required in the various size ranges are calculated for a batch of 2.6 kg.

We calculate the required CPFT for each size using the Dinger and Funk's equation:

$$\text{CPFT} = \frac{(D^q - D_{\min}^q)}{(D_{\max}^q - D_{\min}^q)} \times 100$$

For q=0.21

Particle size (in mm)	CPFT (in %)
3	100
2	89.97
1	74.69
0.5	61.47
0.3	52.89
0.15	42.63
0.001	0

3.4 Table showing particle size and the corresponding CPFT for 0.21

Particle size (in mm)	Percentage of particles present in that size range
-3 mm to +2 mm	10.03
-2 mm to +1 mm	15.28
-1 mm to +0.5 mm	13.22
-0.5 mm to +0.3mm	8.58
-0.3 mm to +0.15 mm	10.26
-0.15 mm to +0.001 mm	42.63

3.5 Table showing the various size ranges and the percentage of particles present in the size range for 0.21

Batch composition of high alumina cement castable is as follows:

Particle size (in mm)	Percentage of particles in size range	Amount required in 1.3 kgs batch(in gms)
-3 mm to +2 mm(White Tabular Alumina)	10.03	130.39
-2 mm to +1 mm(White Tabular Alumina)	15.28	198.64
-1 mm to +0.5 mm(White Tabular Alumina)	13.22	171.86
-0.5 mm to +0.3mm(White Fused Alumina)	8.58	111.54
-0.3 mm to +0.15 mm(White Fused Alumina)	10.26	133.38
-0.15 mm to +0.001 mm(Reactive Alumina(CL 370)/WTA fines,Cement,Microsilica)	42.63	437.19

3.6 Table showing the various size ranges and the amount of particles in the size range present in the batch for 0.21

For q=0.23

Particle size (in mm)	CPFT (in %)
3	100
2	89.42
1	73.46
0.5	59.86
0.3	51.13
0.15	40.82
0.001	0

3.7 Table showing particle size and the corresponding CPFT for 0.23

Particle size (in mm)	Percentage of particles present in that size range
-3 mm to +2 mm	10.58
-2 mm to +1 mm	15.96
-1 mm to +0.5 mm	13.6
-0.5 mm to +0.3mm	8.73
-0.3 mm to +0.15 mm	10.31
-0.15 mm to +0.001 mm	40.82

3.8 Table showing the various size ranges and the percentage of particles present in the size range for 0.23

Batch composition of high alumina cement castable is as follows:

Particle size (in mm)	Percentage of particles in size range	Amount required in kgs batch(in gms)
-3 mm to +2 mm(White Tabular Alumina)	10.58	137.54
-2 mm to +1 mm(White Tabular Alumina)	15.96	207.48
-1 mm to +0.5 mm(White Tabular Alumina)	13.6	176.8
-0.5 mm to +0.3mm(White Fused Alumina)	8.73	113.49
-0.3 mm to +0.15 mm(White Fused Alumina)	10.31	134.03
-0.15 mm to +0.001 mm(Reactive Alumina(CL 370)/WTA fines,Cement,Microsilica)	40.82	413.66

3.9 Table showing the various size ranges and the amount of particles in the size range present in the batch for 0.23

For q=0.27

Particle size (in mm)	CPFT (in %)
3	100
2	88.28
1	70.99
0.5	56.65
0.3	47.68
0.15	37.32
0.001	0

3.10 Table showing particle size and the corresponding CPFT for 0.27

Particle size (in mm)	Percentage of particles present in that size range
-3 mm to +2 mm	11.72
-2 mm to +1 mm	7.29
-1 mm to +0.5 mm	14.34
-0.5 mm to +0.3mm	8.97
-0.3 mm to +0.15 mm	10.36
-0.15 mm to +0.001 mm	37.32

3.11 Table showing the various size ranges and the percentage of particles present in the size range for 0.27

Batch composition of high alumina cement castable is as follows:

Particle size (in mm)	Percentage of particles in size range	Amount required in kgs batch(in gms)
-3 mm to +2 mm(White Tabular Alumina)	11.72	152.36
-2 mm to +1 mm(White Tabular Alumina)	7.29	224.77
-1 mm to +0.5 mm(White Tabular Alumina)	14.34	186.42
-0.5 mm to +0.3mm(White Fused Alumina)	8.97	116.61
-0.3 mm to +0.15 mm(White Fused Alumina)	10.36	134.68
-0.15 mm to +0.001 mm(Reactive Alumina(CL 370)/WTA fines,Cement,Microsilica)	37.32	368.16

3.12 Table showing the various size ranges and the amount of particles in the size range present in the batch for 0.27

For q=0.29

Particle size (in mm)	CPFT (in %)
3	100
2	87.7
1	69.75
0.5	55.07
0.3	45.99
0.15	35.64
0.001	0

3.13 Table showing particle size and the corresponding CPFT for 0.29

Particle size (in mm)	Percentage of particles present in that size range
-3 mm to +2 mm	12.3
-2 mm to +1 mm	17.95
-1 mm to +0.5 mm	14.68
-0.5 mm to +0.3mm	9.08
-0.3 mm to +0.15 mm	10.35
-0.15 mm to +0.001 mm	35.64

3.14 Table showing the various size ranges and the percentage of particles present in the size range for 0.29

Batch composition of high alumina cement castable is as follows:

Particle size (in mm)	Percentage of particles in size range	Amount required in kgs batch(in gms)	1.3
-3 mm to +2 mm(White Tabular Alumina)	12.3	159.9	
-2 mm to +1 mm(White Tabular Alumina)	17.95	233.35	
-1 mm to +0.5 mm(White Tabular Alumina)	14.68	190.84	
-0.5 mm to +0.3mm(White Fused Alumina)	9.08	118.04	
-0.3 mm to +0.15 mm(White Fused Alumina)	10.35	134.55	
-0.15 mm to +0.001 mm(Reactive Alumina(CL 370)/WTA fines,Cement,Microsilica)	35.64	346.32	

3.15 Table showing the various size ranges and the amount of particles in the size range present in the batch for 0.29

Citric acid (0.1 wt. %) and polyammonium methacrylate (0.3 wt. %) were added to the batch along with optimum amount of water during the mixing process.

PREPARATION OF CASTABLE SAMPLE

Mixing

The coarser and the finer fractions of the batch were first dry mixed separately in the Hobart mixer. After proper mixing among themselves they are mixed together in the mixer. Citric acid and ammonium polymethacrylate were added at the end along with the gradual addition of water.



During Mixing



Figure 3: Hobart Mixer

Casting

Water is added until self flowability is reached. After proper homogenising in the Hobart mixer, it is taken out and then poured in the iron moulds of size 50mm x 50mm x 50mm which have already been lubricated by grease. The excess mix is taken out and the resultant mix is smoothed by a trowel. The moulds are kept in the normal atmosphere for 24 hours for setting.

In case of vibratables, vibrating table is used for vibration.



Figure 4: showing 50 mm mould and Hobart mixer

Drying

The moulds are unscrewed and the set castables are demould. Then the moulds are cleaned with sandpaper for further casting processes. Then the taken out castables are put in the dryer for 24 hours at 110°C. Then the weight and dimension of the castables are measured with the help of weighing balance and vernier callipers respectively.



Firing

After drying, the samples were fired at 950°C for 2 hours and 1550°C for 2 hours. After firing the dimensions of the samples were again measured with the help of vernier callipers.

Characterization of the products

The following properties of the samples were measured for dried and different temperatures fired samples. Each data point represents an average value of three samples.

Bulk Density

The weight of the dried sample is taken and its dimension is measured with the help of vernier callipers and its volume (length x breadth x height) is calculated. Bulk density is then calculated by dividing weight by volume.

Bulk Density=weight/ (length x breadth x height) (units gm. /cc)

The same is done for the fired samples.

Cold Crushing Strength

The cold crushing strength of the samples is measured by a compressive Tester. Cold crushing strength is defined as the maximum amount of load the sample can withstand before complete breakage .Cold crushing strength is given by the formula load/area. (Units kg/cm²)

Load at which fracture occurs in kN, Area of the Samples in cm²

Flowability Test

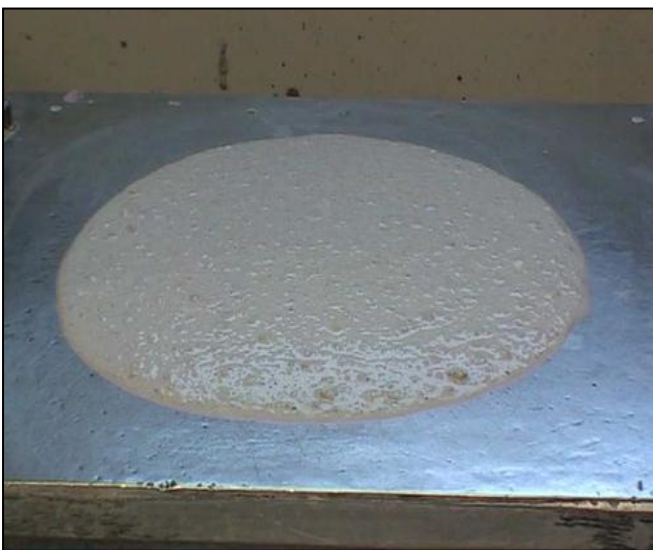
The flow value of the castables is found out using an ASTM C 230 flow cup of height 5 cm and base 10 cm. After 30 seconds the flow value is measured by measuring the change in the diameter of the base with the help of a ruler and the values are reported in mm.



Figure 5: ASTM C-230 flow cup



The cone is removed and the castable is allowed to spread out by gravity alone. Free-flow value attains some 150%.



30 seconds vibration brings the patty to flow almost out of its edges. Vibra-flow attains around 200%.

PHASE ANALYSIS by XRD:

The X-ray diffraction method was used for determining the phases in the castable fired at 1550 °C. The castable was crushed and grounded to very fine powders using a mortar pestle and then subjected to XRD for identification of the phases after sintering. XRD measurements are performed at a 3 °C/min scan rate using an X-ray diffractometer operated at 40 keV and 30 mA. The X- Ray data was plotted using the Expert Pro software and the peaks were matched with JCPDS software to get the phases present.

CHAPTER 4

RESULTS & DISCUSSIONS

RESULTS & DISCUSSIONS

Particle size distribution (PSD)

The graph for cumulative percent finer than (CPFT) for each particle size is plotted as follows:

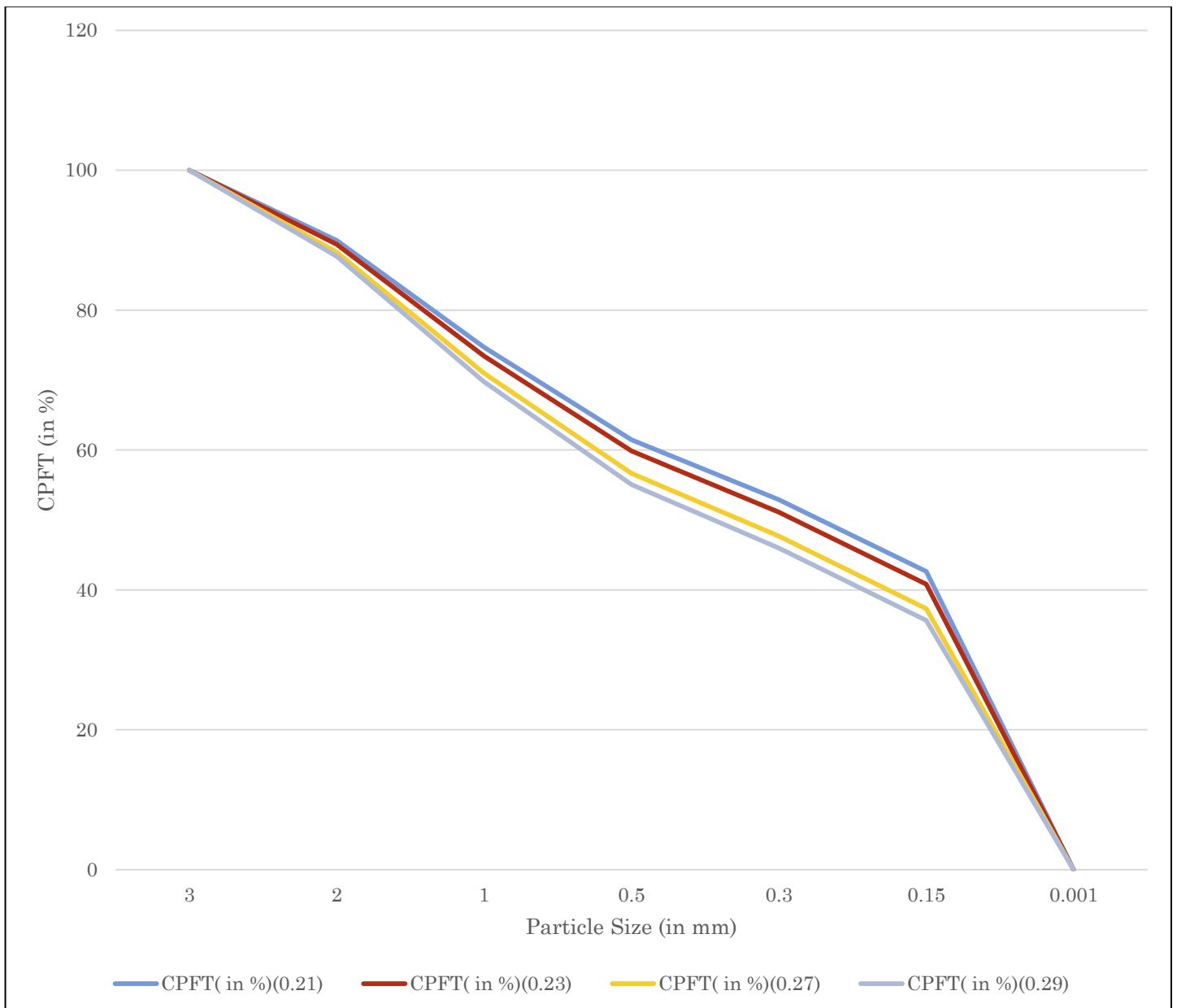


Figure 6: Plot of CPFT v/s PSD

Raw Material characterization

XRD analysis of CA-14 cement samples is done.

XRD analysis of CA-14 cement

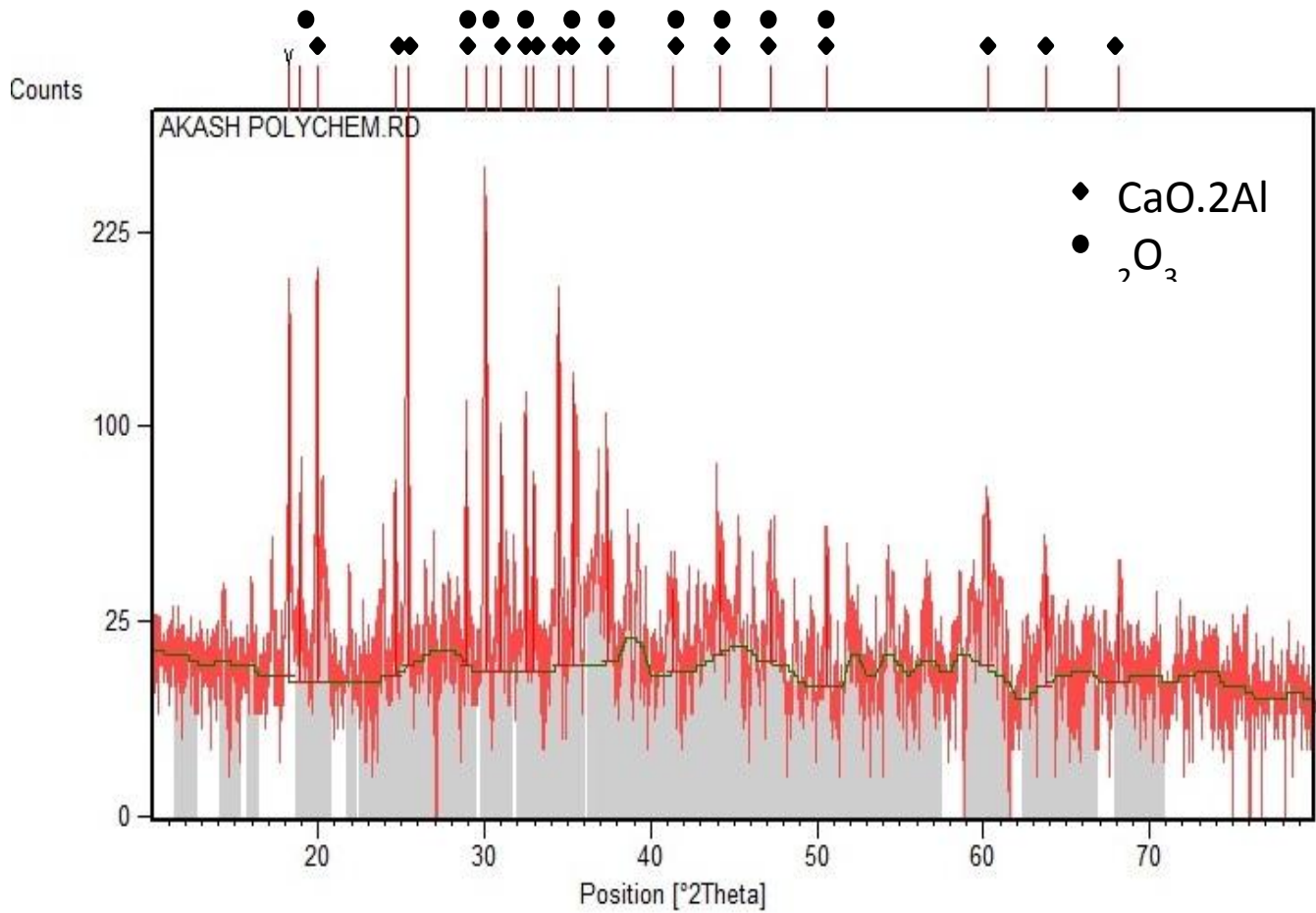


Figure 7: XRD analysis of CA-14 cement

Characterization of sample

Water required for casting

For samples with WTA fines

q=0.21

Water required = 91 ml (7 wt. %)

q=0.23

Water required = 85 ml (6.5 wt. %)

q=0.27

Water required = 71 ml (5.46 wt. %)

q=0.29

Water required = 68 ml (5.23 wt. %)

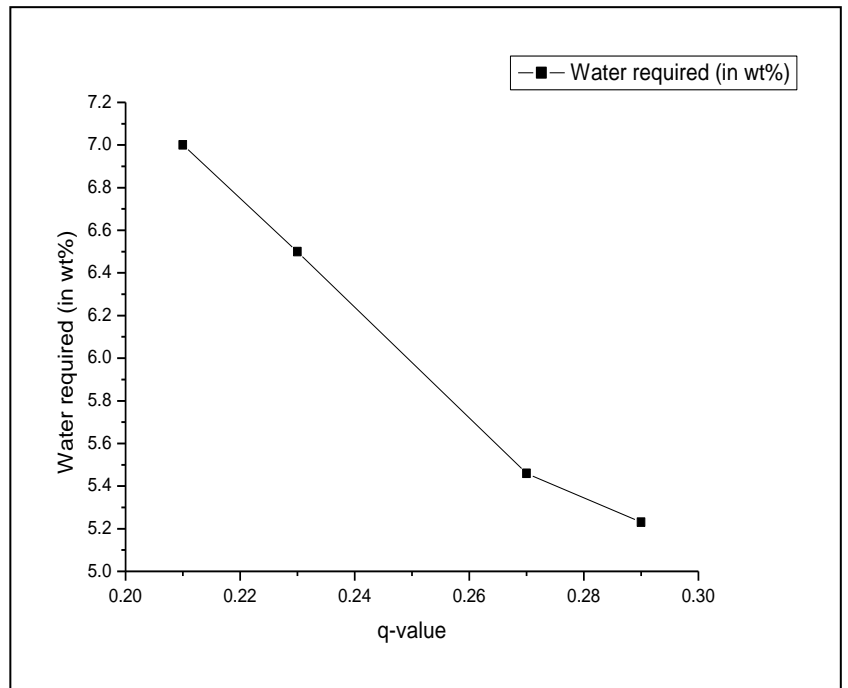


Figure 8: showing water requirement for the different q values

For samples with reactive alumina

q=0.21

Water required = 75 ml (5 wt.%)

q=0.23

Water required = 71 ml (5.46 wt.%)

q=0.27

Water required = 85 ml (5.3 wt. %)

q=0.29

Water required = 80 ml (5.3 wt. %)

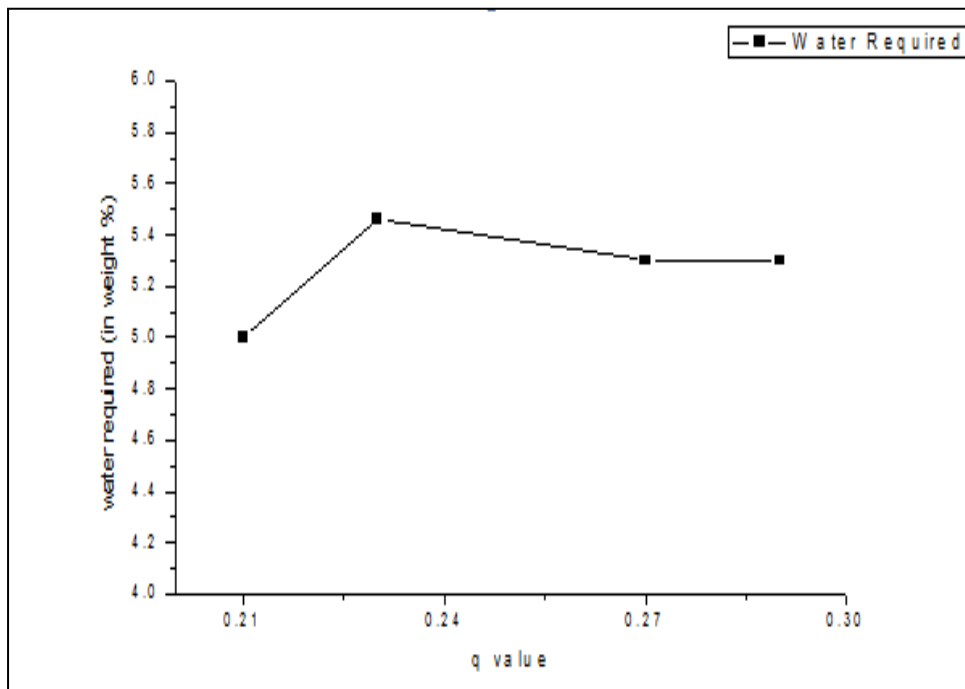


Figure 9: showing water requirement for different q values

Water is added to get the desired flowability in the castables. Water requirement increases with increase in percentage of cement binder due to the property of CaO to absorb water.

Bulk Density

The weight of the samples is first measured using a weighing balance then the dimensions of the sample are measured using vernier callipers. The sample volume is then calculated (length x breadth x height). The bulk density is obtained by the formula weight/volume.

Plot of Bulk Density vs. Firing Temperature

For WTA fines

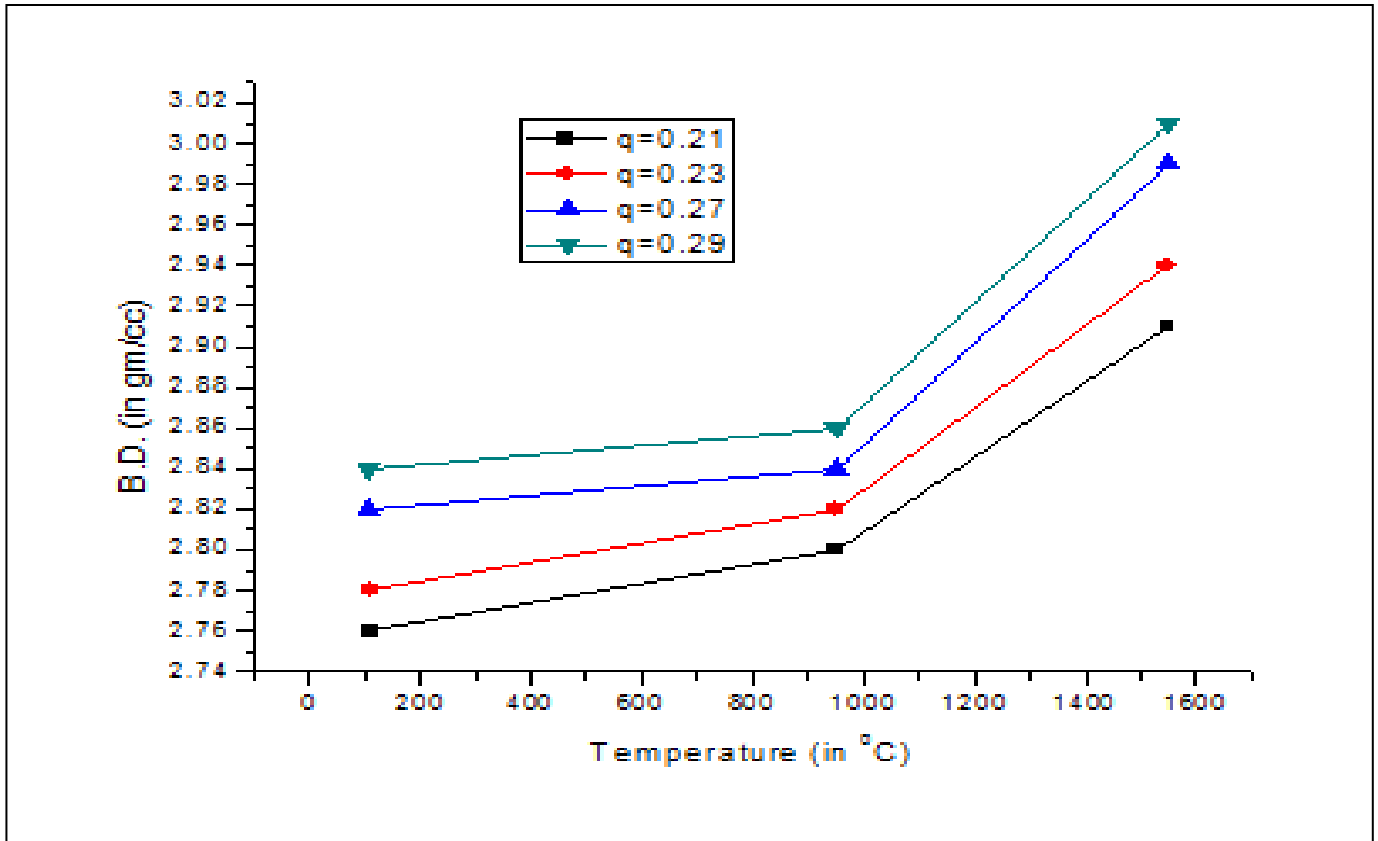


Figure 10: Plot of B.D vs. Temp. for WTA fines

For Reactive Alumina

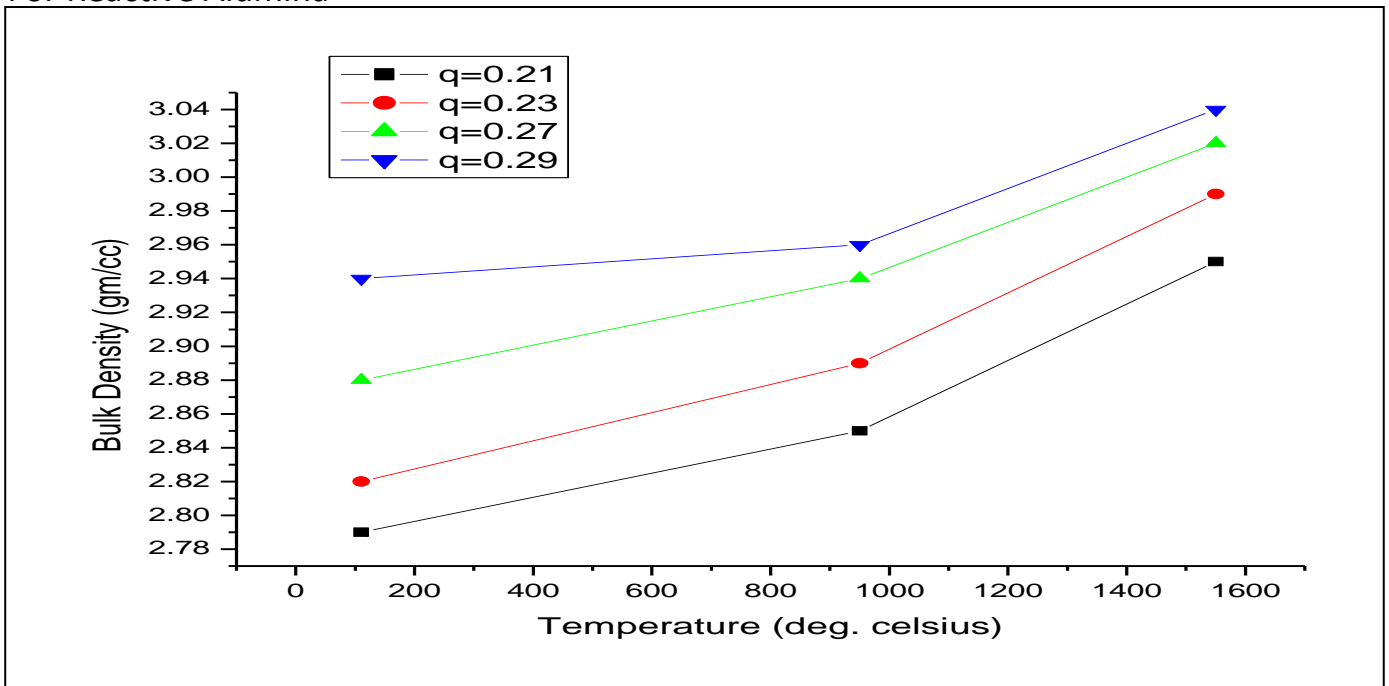


Figure 11: Plot of B.D vs. Temp. for Reactive Alumina

From the graphs the bulk density of the sample increases with increase in firing temperature due to densification which occurs with reduction of porosity. The bulk density of samples with Reactive Alumina is higher than the samples with WTA fines. This is because reactive alumina samples require less water resulting in lower porosity thus higher bulk density.

Flow values

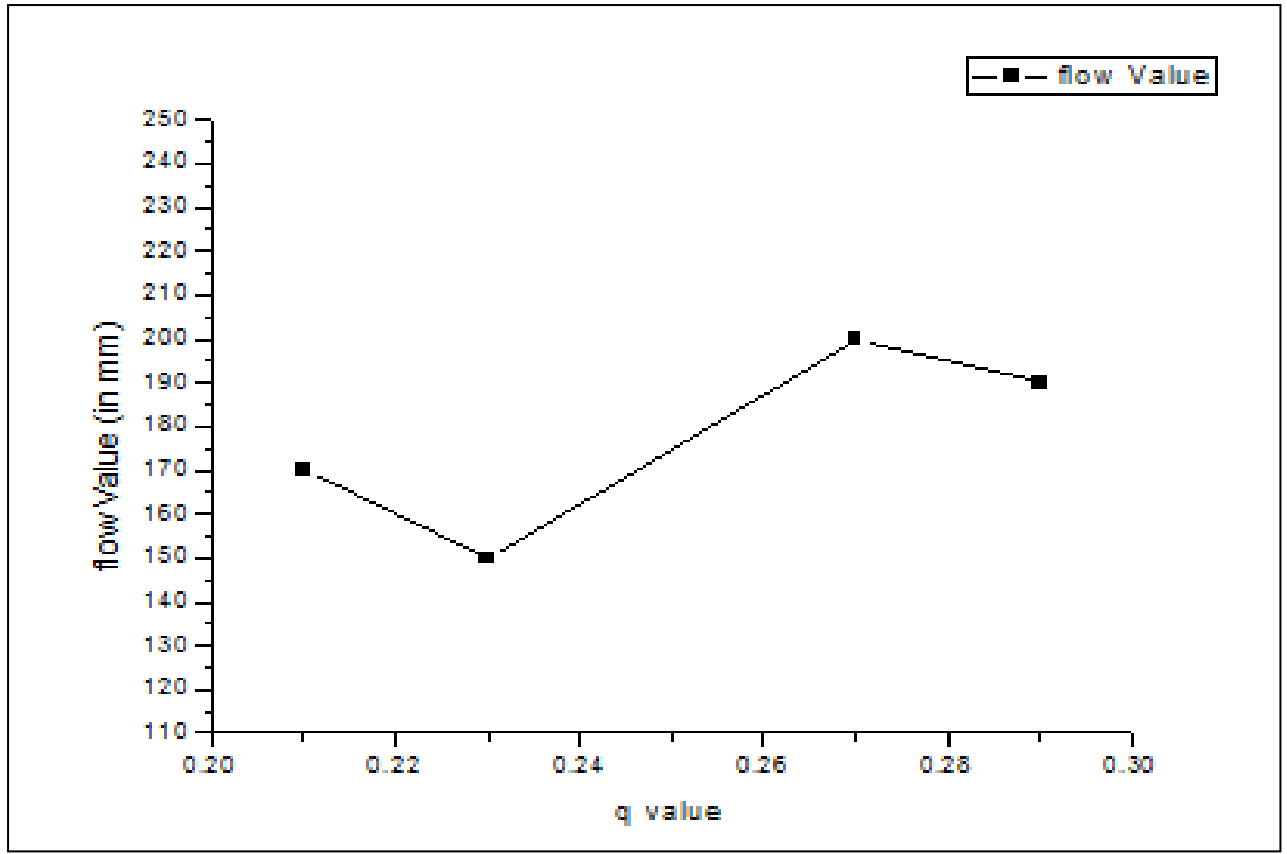


Figure 12: The graph shows the different flow values obtained for various q-values.

Cold Crushing Strength

The cold crushing strength is calculated as the maximum load per unit area that the sample can take before breakage, the formula being load/area in kg/cm².

CCS vs. firing temperature

For WTA fines

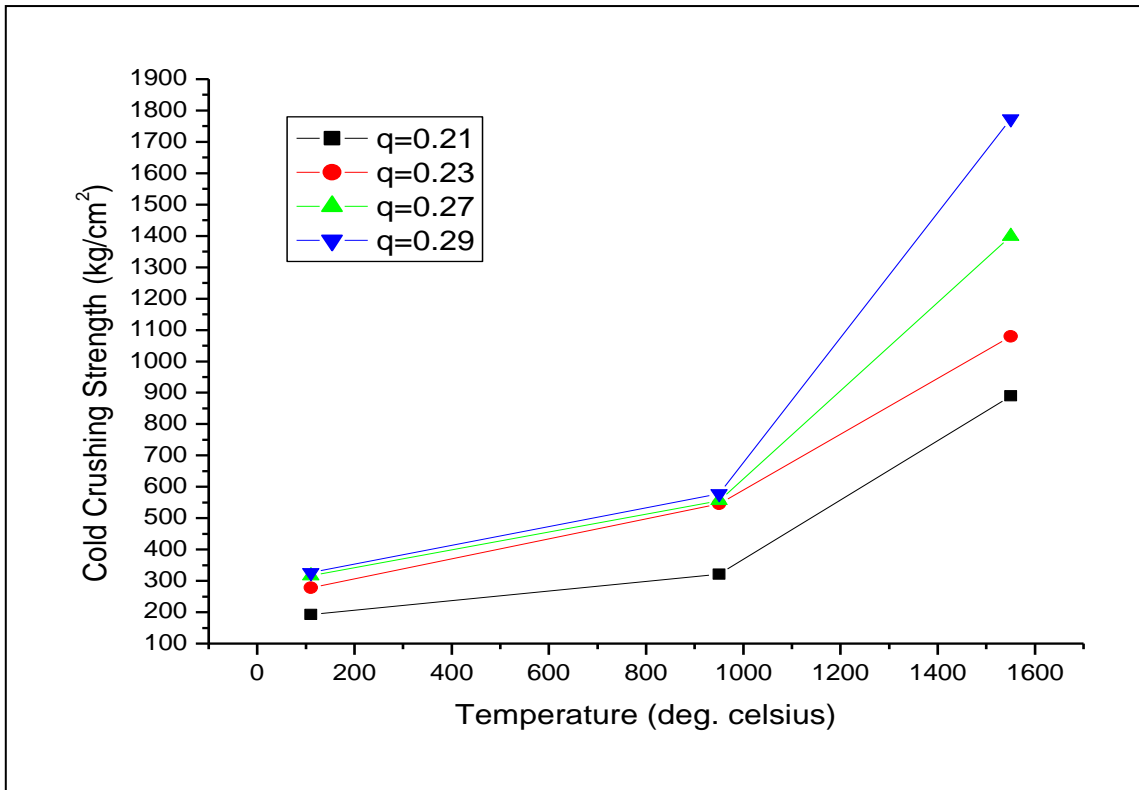


Figure 13: Plot of CCS vs. Temp. for WTA fines

For Reactive Alumina

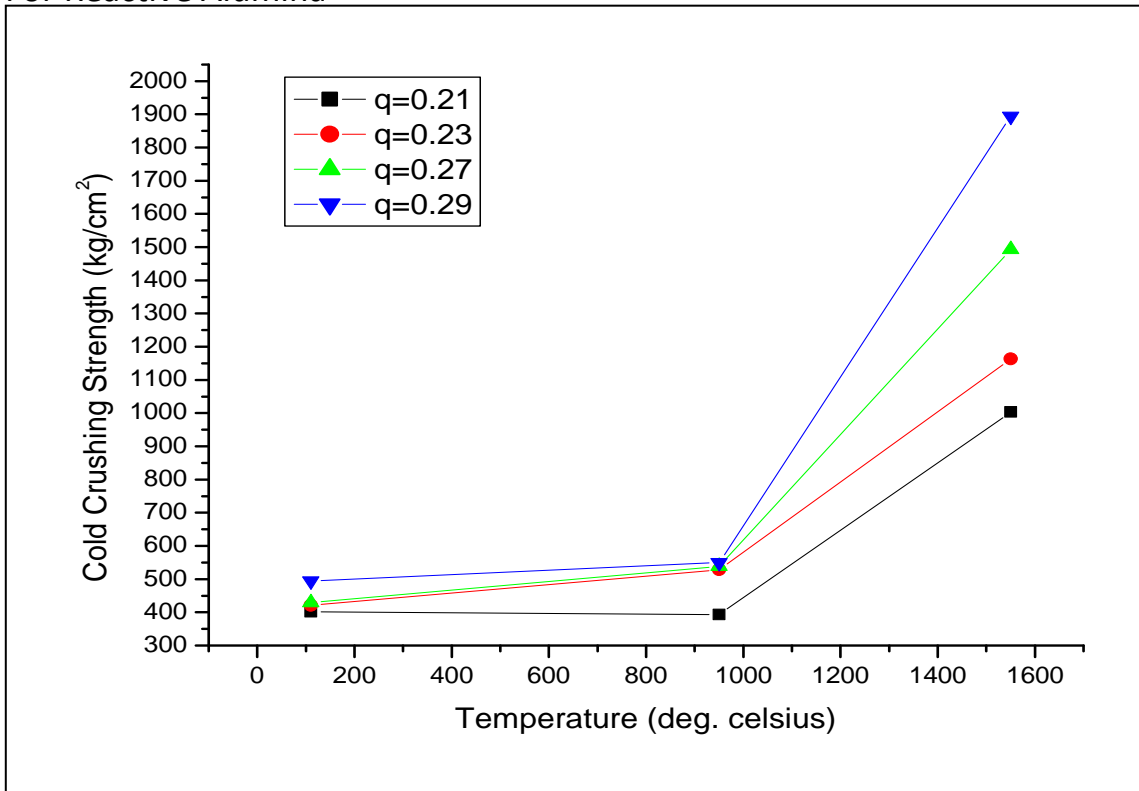


Figure 14: Plot of B.D vs. Temp. for WTA fines

X-Ray Diffraction (XRD)

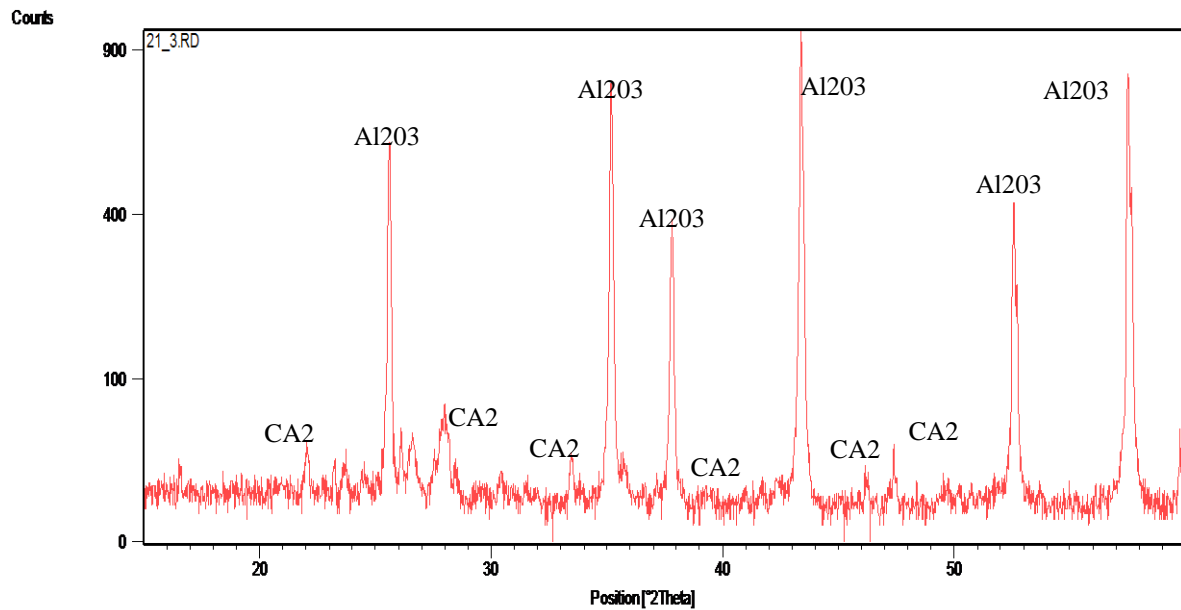


Figure 15: XRD Analysis of $q=0.21$ castable samples

- Self-flowing and vibratable castables were developed using theoretical distribution coefficients ranging from 0.21 to 0.29.
- Study has been done by using the fine fraction as WTA fine and reactive alumina. Use of reactive alumina requires lesser extent of moisture and results better flow values. Also better flow values provide better compaction, so better densification and strength development. All reactive alumina containing samples showed dried strength above 400 kg/cm^2 .
- Density values of 3.04 g/cc was achieved and a strength value of about 1900 kg/cm^2 was obtained for 1550°C samples.
- High fired strength was obtained due to reaction between fine alumina and CA phase forming CA_2 phases, resulting better bonding and strength.

CHAPTER 5

CONCLUSION

CONCLUSIONS

- Self-flowing nature was obtained for q values 0.21 and 0.23 and vibratable castables were developed for q values 0.27 and 0.29 for both WTA fines and reactive alumina containing compositions.
- Reactive alumina, being a fine alumina with controlled particle size distribution, required less amount of water and resulted better flow values.
- Very high density and strength values for both dried and fired samples were obtained in the compositions.
- Reaction between Ca and fine alumina forming only CA_2 is the reason for high strength development at higher temperatures.
- The study is based on the incorporation of theoretical concept in already practiced commercial product of high alumina low cement castable refractory. The main application areas are DRI Kiln lining, Inlet cone & Burner pipe of Cement Rotary Kiln, Cement Kiln cooler section, Incinerator lining.
- Incorporation of theoretical concepts in commercial products will improve its performance in Iron and Steel industries and other high temperature applications.
- Both self-flowing and vibratable castables are designed and developed using controlled particle size distribution through theoretical distribution coefficients. The study shows improved characteristics of the developed products for practical applications.
- All the raw materials and additives used for the study are being practiced commercially and enhance the applicability of the study for practical use.

CHAPTER 6

REFERENCES

REFERENCES

1. “Particle size distribution design in a self-flow Alumina refractory castable without cement”, Abilio P.Silva, Ana M.Segadaes, Devezas, *Advances in Science and Technology* Vol.45(2006).
2. “Lets make a castable”, Bjorn Myhre, *Refractories Applications & news* Vol.3, no. 3-4(2008).
3. W. E. Lee, W. Vieira, S. Zhang, K. G. Ahari, H. Sarpoolaky and C. Parr, —Castable Refractory Concrete, *Intern. Mat. Rev.*, **46** [3] 145-167 (2001).
4. J.S. Masaryk, Development and use of low cement self flow castables, in: *Proc. UNITECR*, Sao Paulo, Brazil, pp. 527–538 (1993).
5. “Particle size distribution design in a self-flow Alumina refractory castable without cement”, Abilio P.Silva, Ana M.Segadaes, Devezas, *Advances in Science and Technology* Vol.45(2006).
6. “Recent developments in Monolithic refractories”, Subrata Banerjee, ACSB(1998).
7. “The use of particle size distribution in development of refractory castables”, Bjorn Myhre & Aase M.Hundere, XXV ALAFAR Congress(1996).
8. “Whitewares Particle Packing III – Discrete vs Continuous Particle Sizes”, D.R.Dinger, J.E.Funk, USA, *Interceram* 41(1992)[3] 176-179.
9. “The Packing of Solid particles: A review”, Anil N.Patankar & G.Mandal, Vol 39(4)(1980).
10. S. K. Das, R. Sarkar, P. K. Mondal and S. Mukherjee, —No cement high alumina self flow castable, *American Ceramic Society Bulletin*, 82 [2] 55 – 59 (2003).
11. “Refractory Calcium Aluminate Cements”, Review Paper, Parker & Sharp, University of Sheffield.
12. “The Impact of Calcium Aluminate Cement hydration upon the properties of refractory castables”, presented at TARJ meeting, C.Parr, F.Simonin,(2004).

13. "Optimization of Aluminate Cements with 70% and 80% of alumina based castables", Paulo Cesar, C.Parr, Refractories Applications,(2000).
14. US Patent 392214, (1976)
15. US Patent 6287999B1,(2001)
16. EP 0686611 B1,(1998)
17. US Patent 4762811 (1988)
18. The Hydration Products of a Refractory Calcium Aluminate Cement at Intermediate Temperatures, Nilforoushan, Mohammad Reza*; Talebian, Nasrien
19. US Patent 6022593(2000)
20. US Patent 5681786(1997)
21. "Calcium aluminate cement based castables for demanding applications", presented at 1st Monolithics Conference, C.Parr, Thomas A. Bier, (1997).
22. www.google.com
23. B.N.Samaddar, —Principles of powder processing- packing of powders, IRMA journal Vol- XXXIV no.4,2001.
24. Myhre B. and Hundere A. S., "The use of particle size distribution in development of refractory castables", Presented at the XXV ALAFAR Congress, San Carlos De Bariloche, Argentina, Dec 1-4 (1996).
25. "High alumina self-flow castable with different binders", Ritwik Sarkar and Akash Satpathy, Refractories World Forum, 4 [2] 129-133 (2012).