DEVELOPMENT OF SHOTCRETING CASTABLE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF TECHNOLOGY

In

Ceramic Engineering

By

MANDVI SAXENA

DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA
MAY 2013

DEVELOPMENT OF SHOTCRETING CASTABLE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF TECHNOLOGY

In

Ceramic Engineering

By

MANDVI SAXENA

Under the Guidance

of

Prof. Swadesh Kumar Pratihar
&
Dr. Arup Kumar Samanta

DEPARTMENT OF CERAMIC ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA
MAY 2013

Department of Ceramic Engineering
NATIONAL INSTITUTE OF TECHNOLOGY,
ROURKELA
Orissa-769008

CERTIFICATE

This is to certify that the thesis entitled **"DEVELOPMENT OF SHOTCRETING CASTABLES"** submitted by Miss Mandvi Saxena to the National Institute of Technology, Rourkela in partial fulfilment of the requirements for the award of the degree of Master of Technology in Ceramic Engineering is a record of bonafide research work carried out by her under our supervision and guidance. Her thesis, in our opinion, is worthy of consideration for the award of degree of Master of Technology in accordance with the regulations of the institute.

The results embodied in this thesis have not been submitted to any other university or institute for the award of a Degree.

Supervisor	Supervisor
Prof. Swadesh Kumar Pratihar	Dr. Arup Kumar Samanta
Department of Ceramic Engineering	TRL Krosaki Refractories Limited
National Institute of Technology	Belpahar
Rourkela	

ACKNOWLEDGEMENT

This report is the result of one year of work whereby I have been supported by many people. It is a pleasant aspect that now I have the opportunity to express my deep gratitude for all of them.

I take this great opportunity to express my thanks and deepest regard towards my supervisor **Prof. Swadesh Kumar Pratihar**, Department of Ceramic Engineering, National Institute of Technology, Rourkela and **Dr. Arup Kumar Samanta**, TRL Krosaki Refractories Limited, Belpahar for their guidance and continuous support during research work and writing of this thesis.

I also express my thanks to **Dr. Sukumar. Adak, (**Vice President, Technology, TRL Krosaki Refractories Limited) for giving me to an opportunity to work at TRL Krosaki Refractories Limited, Belpahar and providing me the necessary facilities. I also express my sincere thanks to **Miss. Smita Satpathy** (Manager, TRL Krosaki Refractory Limited, Belpahar), for her important suggestions and support during this work and her availability when I needed her advises.

I am thankful to Prof. Sumit Pal (Faculty advisor) to for his valuable suggestions and help. I am also thankful to Prof.J.Bera, Prof. H.S. Maity, Prof. S. Bhattacharya, Prof. B.B. Nayak, Prof. D. Sarkar, Prof. R. Sarkar, Prof. R. Mazumder, Prof. S. Behera, Prof. Sudip Das Gupta, Prof. Sunipa Bhattacharya and Prof. A. Chowdhury for their suggestions and support.

My heart feels great pleasure by remembering the time spent with my friends Tynee Bhowmick, Gaurav K. Gugliani, Denny K. Philip, Aditya P. Shirimali, Uttam K. Chanda and Subham Mahoto. It was a pleasurable experience to work with them.

No suitable words traced in the presently available vocabulary to express my full respect to my **Mom, Dad,** and **my family.**

All other persons who helped me either in educational life or during the personal life I want to say a single word **“THANK YOU**” which expresses all**.**

MANDVI SAXENA

TABLE OF CONTENT:

LIST OF FIGURES:

LIST OF TABLES:

ABSTRACT

Particle packing is one of important parameters, which dictates physical and thermo-mechanical properties of refractories. Fillers play a substantial role in the packing behaviour of low cement castable. Fine filler particles fill the voids of the castable aggregate leading to a high packing density of the castable and thereby decrease the cement as well as water requirement of the castable. Micro-silica and calcined alumina are normally used as filler materials in the development of low cement castable. It has been established that these fine fillers particles are responsible to provide ceramic bond and the intermediate temperature and provides high strength at high temperature due to formation of secondary mullite. In the present work an attempt has been made to develop low cement castable with suitable filler addition. Effect of particle size and particle size distribution of calcined alumina filler has been studied in order to achieve high flow behaviour in low cement 70% alumina based vibratable castable formulation. This alumina filler particle has further been used to optimize and develop a suitable self-flow castable, wherein the amount of micro-silica and calcined alumina amount has been optimized. Physical and thermo-mechanical properties of the castables thus developed have also been studied in detail. Attempt has also been made to study the effect of setting accelerator amount on the properties of self-flow castable thus developed with an aim for shotcreating application.

CHAPTER-I

INTRODUCTION

1. INTRODUCTION

Monolithic or unshaped refractories namely, castables, gunning mixes, ramming mass, morters etc. has advantages form the point of view of application and performances over shaped refractories. Major advantage of monolithic refractory is that it makes joint less structure so that it shows high corrosion and erosion resistance. Monolithic refectories not required shaping and firing, so that significant amount of energy is saved also complicated shapes are prepared. Early development of monolithic refractories lies with the development of conventional castables. Conventional castable made with the combination of aggregate and high alumina cement binders. Earlier work shows that particle size distribution of aggregate for conventional castable had distribution coefficient 0.33 to 0.26. Cement content in conventional castable is around 15-20%. Water requirement to provide suitable rheology for casting is of the order of 10% as it contains high amount cement. The required water is utilized for i) fill up the porosity within the aggregates, ii) hydration of cement binders and iii) provides improved flowability through wetting the aggregates surface . Room temperature strength of conventional castables is due to the hydraulic bond formed by hydration of cement. However, these hydraulic bonds dissociates at intermediate temperature zone due to de-hydroxylation of cement hydrates. These leads to a substantial increase in porosity and consequent decrease in strength of the castable in the intermediate temperature range. Among the several other disadvantage of conventional castable, the high CaO content in the composition is of importance as it may form some calcium-alumino-silicate glass, which substantially reduces themo-mechanical properties of the castable. These problems associated with conventional castable could be reduced by lowering the cement content.

In early 80'S, development of low cement castable (LCC) has made remarkable improvement on the development and application of monolithic refractories. Development of LCC lies with the partial substitution of high alumina cement binder of conventional castable with some filler material like micro-silica and calcined alumina. Filler materials fill the voids between the aggregate, there by reduces the water requirement. Micro-fine filler materials reduce the cement content and increase the initial packing density of the castable. Theoretically, composition with high packing density requires low amount of water as comparison to castable had improper packing as a result mechanical and physical properties of the castable improves. Micro-silica and calcined alumina has small particle size in range of microns. Hence form ceramic bond at intermediate temperature and increases the strength of the castable at intermediate temperature. Further, reduced the cement content has been taken care off in the development of ultra-low cement castable; no cement castable, chemical bonded castable wherein different types of binders like hydraulic alumina, clay, silica sol, and alumina sol etc has been used as a replacement of cement bond.

Low cement castable, ultra low cement castable etc. have some disadvantages like it shows poor flow behaviour. The vibration and a suitable mould are required for placement of low cement castable on refractory lining. Application of these castables requires high men powder. To overcome the mould requirement gunning technology has been adopted. The composition of gunning mass is similar to that of the vibratable castable except the addition of a quick setting. In this technique dry mix of castable pump in to the pipe to the nozzle. Water and setting additive is mixed at nozzle and spray by air pressure which sticks at lining surface.

In order to overcome the problem associated with the vibration during application of LCC researchers and scientists have been working around the globe to develop self-flow castable. Self-flow castable, flow of castable takes place under the action of gravity. For self-flow castable, mix has to be dispersed properly. Flow behaviour depends on the particle size distribution of the aggregate. It has been well established that for self-flow castable distribution coefficient of the aggregate has to be in the range of 0.21 to 0.25. As distribution coefficient decreases, the amount of fines in the castable composition also increases. For good flow dispersion of the particle is an important criteria. Fine powder shows tendency of agglomeration and coarse particle shows friction that hindered the flow. Fine powder increases the separation between the coarse aggregates that reduce the friction effect and thus flow increases.

Self-flow castable had a disadvantage, which is the requirement of a mould for placing the castable in to the furnace lining. In the 1990s, another application technique has been adopted for placing the castable on the furnace lining known as shotcreting technique. In shotcreting, self-flow castable with 100% flow value pumped in to the pipe line to the nozzle. At nozzle castable mixed with setting accelerator and spray in to the application area. The advantages of shotcreting over gunning technique that, in shotcreting, castable was premixed with water to gets homogeneous mixture that gave homogeneous properties but in case of gunning water was added at nozzle, there is lack of homogenization of mixture that decreased the property of the gunning mix. Due to lack of homogenization and mixing dust releases at nozzle point also shows high rebound loss. Shotcreting shows good lining, without any lamination and voids structure with good mechanical and physical properties.

The present study aimed to develop a 70% Al_2O_3 shortcreting castable. The study has been carried out in three phases. The effect of particle size and particle size distribution of filler calcined alumina has been studied in order to achieve a good flow behaviour in vibro-flow LCC castable in Phase I. Self-flow castable has been developed with the optimized calcined alumina and the effect of amount of micro-silica and calcined alumina has been studied in order to get 100% flow with minimum amount of water requirement in Stage II. In the third phase an attempt has been made to develop a self-flow castable with a suitable setting accelerator with a aim for shortcreting application. Physical and mechanical properties of the castable developed in each step has been characterized in detail.

The present thesis has been divided into six chapters. Chapter I give a brief introduction of the thesis, chapter II detailed a comprehensive literature review of the subject. Objective of the present work has been written in chapter III and chapter IV detailed the experimental technique adopted in the present study. Results and discussion on the present study has been included in chapter V. Finally Chapter VI summarizes the conclusions of the present study.

CHAPTER-II

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Castable Refractory

The past two decade had witnesses the remarkable improvement in unshaped refractory over shaped refractory, both in preparation and application technology. The unshaped refractory had superior properties in terms of labour productivity, installation efficiency, adaptability, energy saving, joint less, service life, etc over shaped refractory. Monolithic refractory have increasingly been used, especially in metallurgical furnace in place of shaped refractory [1,2].

Unshaped refractory are generally classified on the basis of their method of use in variety of application. Classifications of monolithic refractory are given below [3].

i) Conventional castable refractory
ii) Pumpable refractory,
iii) Injectable refractory,
iv) Plastic mass refractory
v) Ramming mass refractory
vi) Gunning mass refractory
vii) Dry vibratables

2.2 Castable Refractory Composition

Castable Refractories are premixed combination of aggregate, matrix component, binder and admixture. The batch formulation of refractories castable and their required percentages are shown in Table II.I [4].

Table II.I Batch formulation of refractory castable

Aggregate	40-80 %
Binders	2-30 %
Modifiers	5-30%
Admixture	$\leq$ 1%

Previously, raw materials used in refractory castable are burned natural raw material and rejected materials from shaped refractory. As a result service temperature and properties are limited for unshaped refractory. With the advances of synthesized and purified raw materials available now a days there exists a remarkably improvement in properties of refractory castable [1]. Refractory aggregate, whose size range are in between 300 µm to 20mm are the main component of castable and are used as a skeleton of castable. Castable can be formed based on desired chemistry, mineralogy and physical properties. Table II.II shows some important aggregate that mostly used in castable.

Table II.II Composition and service temperature of different aggregate [4]

Aggregate	**Al_2O_3 (%)**	**SiO_2 (%)**	**Max. service temperature (^{0}C)**
Tabular or white fused alumina	99	0	1870
Brown fused alumina	94-98	1-2	1760
S.A. and Chinese Bauxite	84–90	5-7	170
Sintered or fused mullite	74–76	19-24	1760
Andalusite	57-61	38-40	1760
Calcined kaolin and flint clay	40–47	49-55	1650
Pyrophyllite	13–30	65-80	1425
Fused silica	0	99.7	1370

2.3 Binders

In alumina–silicate castable system, with the development of high alumina cement, calcium aluminate cement is used as a principal binding agent. Past 20 years, special castables have been developed using non cement binder such as hydraulic alumina, clay, silica, and alumina gel. On the other hand some other chemical binders have also been considered over past few years. Chemical binder for monolithic refractories can be classified into two groups; inorganic and organic. Inorganic binders contain some impurity which is harmful for monolithic refractory at high temperature [1, 4].

2.3.1 Calcium aluminate cement

Calcium aluminate cement (CAC) containing castables had a rich history of over 80 years. Involvement of CAC in castables refractories had been coming from conventional castables to ultra-low cement castables. CAC contain different phases such as $C_{12}A_7$, CA, CA_2, CA_6 based on CaO and Al_2O_3 ratio, among these calcium monoaluminate (CA) and calcium dialuminate (CA_2) are most important phases for castables manufacturing. Calcium monoaluminate ($CaO.Al_2O_3$) has high melting point ($1600^{O}C$) and developed high strength during short time. Whereas, CA_2 is a secondary phase in CAC's and has higher melting point (1700-$1765^{O}C$) than CA phase but requires more time to set due to its low hydraulic activity. Hydraulic activity of CAC decreased with increasing Al_2O_3/CaO ratio. CAC contain impurities such as rich iron and high silica because of these impurities, CAC contain C_4AF, C_2S and C_2AS phases. C_2AS (gehlenite) is an undesirable phase as it might decrease the refractoriness of castable [5, 6].

2.3.1.1 Hydration of calcium aluminate cement

Hydration of cement is strongly depends upon time and temperature. Below 10^0C CAH_{10} phase started forming and continue up to 27^0C and between 10-27^OC CAH_{10} and C_2AH_8 formed together. Above 27^0C, formation of C_3AH_6 occurs with gibbsite (AH_3). CAH_{10} is meta-stable phase and with respect to time and temperature it changed first to C_2AH_8 rather than C_3AH_6. AH_3 also changed with temperature, at low temperature it exists as a gel and with increase in temperature it converts into crystalline form. Table II.III shows hydration reaction of high alumina cement with respect to temperature and time. Mechanism of hydration involved three steps, dissolution, nucleation and precipitation. Nucleation and precipitation time is also called period of flow decay or working time and precipitation time is called hardening and strength development time [5, 7].

Table II.III Hydration reaction for monocalcium aluminate with respect to temperature and time [5]

Temperature	Hydration reaction
< 10^OC	$CA + 10H \rightarrow CAH_{10}$
10 – 27^OC	$2CA + 11H \rightarrow C2AH8$
	$CA + 10H \rightarrow CA3$
>27^OC	$3CA + 12H \rightarrow C3AH6 + 2AH3$
Temperature + time	$2CAH10 \rightarrow C2AH8 + AH3 + 9H$
	$3C2AH8 \rightarrow 2C3AH6 + AH3 + 9H$

2.3.1.2 De-hydration of calcium aluminate cement hydrate:

In the process of dehydration, the bond phases undergo various transformations with respect to temperature and these transformations influenced the properties of castable. Around 110^0C for 24 hrs, Residual CA and CA_2 phase showed hydration behaviour. At this point strength has maximum value. Between 100-400^{O}C, AH_3 and C_3AH_6 decompose into amorphous anhydrous and water vapour remove and strength decreased due to porosity increased around 13 to 17%. C_3AH_6 continue to dehydrate to $C_{12}A_7H$ at 400 - 900^{O}C and porosity increased around 23%. Cement phase re-crystallize in to $C_{12}A_7$ than CA at 800 – 1100^{O}C, at this time porosity reaches maximum value around 25%. At temperature around 1100 to 1300^{O}C, 30% CA_2 phase formed and above 1300^{O}C CA_6 phase formed from CA_2 [5].

2.4 Fillers

Conventional castable contain high amount of cement that's why it required maximum amount of water. To decrease cement content, modifiers were added. These modifiers filled the voids between the aggregate, so that porosity decreased as well as amount of cement required. With decreasing cement contain, water requirement also decreased. Clay, kaolin dust, micro-silica, micro-chromite, reactive alumina etc. are used as a modifiers. Among these fines particles, micro-silica and reactive alumina are most common modifiers. The size of micro-silica and reactive alumina is around 0.2-0.5µm and 1-10µm respectively. At high temperature they react each other or with the matrix and form mullite phase which imparts high strength [26,8].

2.5 Additives

Additives or admixture are widely used in unshaped refractory. These additives modifies several physical properties of the castables namely workability, setting time etc. and thereby the performance of castable. They are divided into many groups based on their work in castable such as; additives give effect on workability (dispersant, plasticizer etc), also changed their setting time (accelerator and retarder) and improve their performance at application area (sintering aid, anti-explosion agent and anti-oxidant etc) [1, 9].

2.5.1 Dispersant

Dispersion of particles plays a vital role in the development of castable refractory. Absence of particle dispersion causes agglomeration of the particles because of Vander Waals attractive force. Because of agglomeration viscosity of castable increased therefore, large amount of water is required to increase flowability of the castable [4]. To prevent the agglomeration, there are three mechanism to disperse the particle in the suspension, these are; electrostatic, steric and electrosteric stabilization. Refractory castables are usually dispersed through the electrostatic mechanism. In electrostatic mechanism, the repulsion generated between the particles due to electrostatic charge on the particle. These dispersant are multivalent anions. These ions absorbed on the particle surface and create electric charge on the particles. The presence of the counter ions creates an electric double layer which in turns increases the repulsion force and also increases the Zeta potential of the oxide grains in the castable. The repulsion between electric double layers overcome the Vander Waals attractive force and prevents agglomeration and flocculation of the particles in a castable system [10].

2.5.2 Accelerator and Retarder

There are many installation technologies that required quick setting, like gunning and shotcreting. Accelerator is used to give flash setting of castable. Setting additives or accelerators are classified in three groups; inorganic (sodium silicate, calcium chloride etc); organic polyelectrolyte (sodium polyacrilate) and viscosity enhancing polymer (hydroxyethyl cellulose). Inorganic admixture increased ionic strength of system and increased particle attraction and agglomeration. Organic polyelectrolyte has high molecular weight and creates bridge between the particles. Hydroxyethyl cellulose type polymers are water soluble, non-ionic and semi-synthetic that generates a thixotropic lubricant gel and increased liquid viscosity [11]. Retarder used to increase the setting time of castable. Citric acid is good retarder also shows water reduction and increasing the setting time.

2.6 Classification of Castable Refractory

Castables can be classified on the basis of cement content and their placement method such as some castables are applied on application area with the help of external energy (vibration) and some are without it. The classifications of castable are given below [4].

1) CaO content
   - Conventional castable → 15-35% cement
   - Cement Castable → 5-8% cement
   - Ultra low cement Castable → 2-3% cement
   - No cement castable → <1% cement
2) Flow/placement method
   - Vibratable
   - Self-flow
   - Shotcreting
   - Gunning

2.7 Role of Paticle Size Distribution in Refractory Castable

Particle size distribution (PSD) play important role in castable refectory because of two reasons. These reasons are given below [12].

1) To achieve an optimum packing and good flowability with low water percentage.
2) PSD also indicates that the castable is either vibratable or self-flow.

Particle size distribution also affects the rheological behaviour of castable during installation in application area. In order to achieve good particle size distribution there are two packing methods; gap sizing and continuous sizing. In gap sizing, there are more than two graded aggregates mixtures are used to achieve high packing density but it has a disadvantage that it has low flowability. However, most ceramic castables are fabricated by continuous particle size distribution [4]. In continuous distribution, particles are distributed from some maximum to minimum size. Furnas and Andreasen proposed a model of PSD to produce different flowability of powder. Furnas model is complicated, cumbersome and theoretical. Andreasen equation is widely used in castable body formulation and has been given by Eq. 2.1 [13, 14].

$$CPFT = \left(\frac{d}{D}\right)^{q} \times 100 \ldots\ldots\ldots (2.1)$$

Andreasen equation was further modified by Dinger and Funk [15] and modified equation (Eq. 2.2) is given below:

$$CPFT = \frac{d^{q} - d_{m}^{q}}{D^{q} - d_{m}^{q}} \times 100 \ldots\ldots\ldots\ldots (2.2)$$

Where: CPFT = Cumulative percent finer than (volume fraction)

d = Particle size

d_m = Minimum panicle size of the distribution

D = Maximum particle size

q = Distribution coefficient

Dinger and Funk [12] found that if q-value is less than or equal to 0.37, there is a possibility to achieve 100% packing density, on the other hand if q-value is more than 0.37, porosity never goes to zero. Andreasen found that to achieve good flow, q-value should not exceed 0.3. It has also been reported on the basis of fused alumina system that if q – value changed from 0.2 to 0.3, flow pattern of castable is changed. If q- value is close to 0.3, castable is vibratable and if it is less than 0.25, castable shows self-flow properties. The q-value indicates the amount of fine content in the castable aggregate formulation. If q-value decreased, there is increased in the amount of fine content in the castable and this fine content helps in filling the voids and also create separation among aggregate thereby, promoting good flow of the castable.

Low cement castable is divided into two groups on the basis of q-value and that division is given below:

- Vibratable castable
- Self-flow castable

S. Ganguli et. al. [16] prepared 80% Al_2O_3 based low cement castable with varying q-value from 0.25 to 0.33. It has been observed that q- value 0.31 required low amount of water as compared to other. It could be correlated with loose filled density (LFD) of the castable. Castable prepared with q-value 0.31 had high LFD. So that castable had q-value 0.31 had better packing as compared to other. Castable prepared with q-value had high flow value, high apparent porosity, Bulk density, CCS, CMOR and HMOR. It could be also correlated with LFD of the castable.

Bjorn Myhre [17] prepared castables with white fuse alumina, calcined alumina and micro-silica with q- value 0.37 and 0.26. It has been observed that q-value 0.37 required high amount of water and micro-silica as comparison to q-value 0.26 to achieve high flow value. Castable with q-value 0.26 had high amount of fines, that fines create separation between particles and increase the flow value of the castable. It has also been reported that as the percentage of micro-silica increases the flow value at a low water percentage.

Y. Kutmen Kalpakli [18] studied the effect of particle size distribution on the physical, chemical properties and corrosion mechanism of ultra-low cement castable. Superfine (<0.04µm) fraction of reactive alumina, calcined alumina, silica fume and calcium aluminate cement has been used as additives. Particle size distribution coefficient q-value has been varied in the range 0.21-0.26 with a step of 0.01 for the formulation of the castable batches. The water requirement of the castables was reported to increase in q-value of the castable. This phenomenon has been attributed with the fact that with decreasing q-value specific surface area of the particle increased therefore, less water is required. Bulk density and cold crushing strength increased with increasing in q-value.

E. Karadeniz et. al. [19] prepared low cement self-flow castable with varying q-value from 0.2 to 0.25. It could be observed that castable prepared with q- value 0.23 shows high self-flow value as compared to other. It could be due to castable with q-value 0.23 had high initial packing density so that it required low amount of water that give better flow. It could also observe that fines powder created the gap between the particles and reduced the friction low between the grains and increase the flow.

Toshisiko Kando et. al. [20] stuided the relationship between grain size distribution and fluidity of castable. The castables has been prepared with coarse grain (6-2.5mm), medium grain (2.5 -1mm) and fine <1mm. It has been reported that castables castables prepared with coarse and fine aggregates equal to 40%, showed a tendency of segregation of fine powder. However, the castables prepared with 30% coarse and 10% medium the fine powder segregation was found to be miniumum. The segregation of fine powder leads to the formation of large voides in the castable matrix. It has also been reported that flow value of the castables decreased with increasing coarse particles.

Aya Kusunoki et. al. [21] also investigated the effect of particle size on the fluidity of castable. It has been reported that fluidity of the castables depends on both particle size as well as batch formulation. It has also been reported that the castables formulations with high amount of fine fraction aggregates showed high fluidity. It has been concluded that fine aggregate fractions in the castable formulations has a strong influences on the flowability of the castables.

Particle size distribution also influenced the physical and mechanical properties of castable refractory such as CCS, CMOR, thermo-mechanical properties like HMOR [22]. PSD also play important role on rheology, drying behaviour and permeability of castable [23].

S. Ganguli et. al. [22] had also investigated the effect of particle size distribution on the physical, mechanical and thermo-mechanical properties of Al_2O_3-$MgAl_2O_4$ self-flow castable. WTA, $MgAl_2O_4$ spinel, reactive alumina, cement and special additives has been used as starting raw material. Loose Fill Density (LFD) was reported to be good for castable with q-value 0.22 as compared to that formulated with q- value like 0.20 and 0.24. Casting water demand was found to increase with increasing q- value from 0.22 to 0.24. CCS, CMOR, B.D. and HMOR were also found to be high for castable formulated with q-value 0.22. It was found that CCS, CMOR decreased with increasing firing temperature up to $800^{O}C$, due to de-hydroxylation after that it increases with increase in temperature up to $1500^{O}C$ due to densification. XRD studies on the castable formulated with q-value 0.22 and fired at $1500^{O}C$ and $1650^{O}C$ indicated the presence of alumina, spinal, CA_2 and Hibonite phases in the samples.

Rafael Salomao et. al. [23] investigated the effect of particle size distribution on drying of castable. The castables has been formulated with q-value 0.21, 0.26 and 0.31 with added polypropylene fiber of different length (1mm and 3mm long with 15µm diameter). The amount of polypropylene fiber was 0.36 vol. %. It has been reported that the permeability of the castables increases with increase in q- value from 0.21 to 0.31. The increase in permeability has been attributed to generation of more interfacial transition zones (ITZ). Interfacial transition zone is matrix-aggregate interface, generated due to difference in particle size. These zones are porous, permeable and as thick as the finest particle. It has been reported that pumpable castable showed lowest permeability with slow drying rate on the other hand vibrated castable had greater drying rate in shorter time with high permeability. Self-flow castable showed an intermediate drying behaviour. If drying rate increased around 20^0C per minute, there was a chance of explosion of pumpable and self-flow castable however, vibrated castable didn't show any explosion. 1mm long polypropylene fiber did not show any effect on drying of pumpable castable. pumpable castable required 3mm long fiber because of 3mm long fiber was connect the interfacial transition zones and increase the permeability. 1mm long fiber was found to be good for self-flow and vibrated castable because they have small distance between ITZ. So those small size fibers increase the permeability of self-flow and vibrated castable and protect the castable against explosion.

2.8 Low Cement Vibratable Castable

In conventional castable high amount of calcium aluminate cement was used and that required large amount of water around 8 to 15% to achieve good flow. Calcium aluminate cement reacts with water and formed hydraulic bond and achieve high strength at room temperature but at high temperature it loses its strength due to dehydration of the hydraulic bonds. Conventional castable had low refractoriness as well as poor hot strength especially at intermediate temperature [24].

In order to combat the situation of low intermediate temperature strength, low cement castables (LCC) has been developed. Low cement castables are generally formulated with cement content in the range 5-8%. Use of fine particles has been used to be useful in lower down the cement content of the castables. These fines powder are clay, micronized silica, micronized alumina, micronized magnesia, micronized chromite etc. This low cement castable composition also contain a dispersing agent like alkali metal phosphate, alkali metal carbonate etc. LCC had good strength at high temperature and did not lose strength at intermediate temperature [24].

Ageing of refractory castable is defined as changes take place within dry mix of castable with the elapse of time. Ageing of refractory castable modify the physical and themo-mechanical properties of castable. Christopher Parr et. al. [25] studied the aging of 70% alumina refractory castable prepared using bauxite aggregate as main raw material. It has been reported that castables prepared with polyacrylate based bonds absorbed water and hence cause an increase in the weight but raw materials. However, castables prepared with micro-silica and cement bonds have not shown any sign on weight gain. It has also been reported that flow value and working time increases with increase with time as well as humidity of the aging chamber.

Low cement castables are dense in nature and generally had a problem of explosive spalling during drying process. Steel, glass, carbon and nylon fibers have been used to castables to minimize the drying shrinkage and crack propagation. Polymeric fibre also widely used in concretes and refractory castable [26-28]. Length of fiber also affects the permeability of castable. Short length fiber creates many small channels and cover large area of castable and long length fiber decreased the no of channel and keeping volumetric amount constant [28]. Jason M. Canon et. al. [26] investigated the effect of organic fiber addition on permeability of refractory concrete. Castables has been prepared with varying polypropylene fiber (5mm long, denier of 3) as 0.05, 0.1 and 0.2 wt%. It has been reported that water requirement of the castables increases with increase in polypropylene fiber. Apparent porosity increases with increase in temperature and amount of fiber content. Polyester fiber containing castable had high apparent porosity as comparison to polypropylene fiber containing castable.

Yozo Yukino et. al. [27] prepared low cement castable to study the effect of curing and drying condition on the properties of castable as a function of percentage of polypropylene fiber. Drying rate of castable (without fiber) was reported to decrease with decrease in water content however it was remained constant in a castable prepared with fiber. It has also been reported that the bulk density and dynamic elastic modulus of of the castable prepared without fiber decreased with increase in temperature from 200 to 500^0C. Porosimetric analysis suggested increase in porosity with increase in fibre content of the castable.

R. Salomao et. al. [28] studied the effect of polymeric fibres length on the refractory castable permeability. Castables has been prepared with polymeric fiber having different length of 0.1mm, 0.5mm, 1mm, 3mm, 6mm, 12mm and diameter of 24mm and 15µm. Permeability of castable prepared with 0.1, 0.5 and 1mm length fibre did not shows any appreciable change in permeability. However, castables prepared with 3, 6, 12 and 24mm length fiber showed increased in permeability. It has been reported that the short length fiber like 0.1 to 1mm produce channels however, these channels were not interconnected. Thus, there was no large change in permeability. On the other hand, long length fiber (6 to 24mm) fiber could not showed enough permeability as they were sensitive in mixing. Intermediate length fiber around 3 mm showed high permeability because channels connecting themselves and there was low mixing damage.

In the development of low cement castable, dispersant plays an important role in order to prevent agglomeration and reduce the water requirement of the castable without compromising the flow behaviour of the castables [24]. Hong Peng et. al. [29] studied the effect of dispersant on placing properties and shelf life. It has been reported that polycarboxylate ester based dispersant (FS20) showed an enhanced flow property while the setting time of the castable remains unaffected. These castables has been prepared with white fused alumina and bauxite aggregates. Bauxite required high amount of sodium hexa-meta phosphate (calgon) as dispersant as comparison to white fused alumina, as phosphate reacts with impurities of bauxite. Zeta potential of the castable slurry was found to a function of dispersant amount in the formulations. There exists a good correlation between zeta potential and flow property of the castable. Among the studied dispersants FS20 was found to be more effective in controlling the flow behaviour of the castables. It has also been reported that setting time is dependent on the aging time of the castable. It was found to increase with increase in aging time.

Effect of dispersant type and amount on the properties of LCC has been studied by I.R. Oliveira et. al. [30]. These castables has been prepared with white fused alumina (WFA) and calcined alumina as the aggregates. Citric acid and polymer of polycarboxylate ester family (FS10 and FS 60) with varying percentage 0.7, 0.9 and 1.2 has been used as dispersants. It has been reported that castable prepared with FS60 required low amount of water and also it showed high strength, high RUL and creep resistance and also affected the CA_2 formation at 600 – $1200^{O}C$.

Low cement castable made with calcium aluminate cement (CAC), fume silica, reactive alumina and admixture, gave high strength after firing. Fume silica (micro-silica), had important role in LCC it decrease the amount of water and modify the kinetics of high alumina cement such as it accelerate the setting time of cement. Calcined and reactive alumina also affects the properties of CAC's with their morphology, surface area and purity [31, 32]. Hiroshi Shikona et. al. [31] studied the effect of silica flour on low cement castable. It has been reported that castable prepared without silica flour had only $C_{12}A_7$ and CA phase however C_2AS and CAS_2 phases were found in the castables prepared with silica flour after heat treatment. These phases formed strong ceramic bonds around 900 to 1000^OC. Silica flour and cement ratio was reported to affect the hydration behaviour of the castable. As the ratio increased C_2AH_8/CAH_{10} ratio decreased and at 40^OC AH_3/CAH_{10} ratio increased. It has also been observed that low temperature hydrated phase like CAH_{10} also present at high temperature around 40^OC.

Alani Mathieu et. al. [32] studied the behaviour of calcined and reactive alumina on calcium aluminate cements (CAC's). Different reactive alumina and studied their behaviour on calcium aluminate cement on the basis of specific surface BET, Na_2O content and loss of ignition. They found that alumina had more impact on CAC's if it had high BET because of this it react more easily to hydroxyl present in the surface. The calcined alumina which had high BET modify the hydration of CA with hydroxylation of surface grains of the alumina that reacts with calcium ions. Alumina had different behaviour with cement, it increase the absorption of CaO in solution this is correlated with loss of ignition.

Toshihide Yumoto et. al. [33] studied the effect of alumina cement, silica flour and water content on the strength of castable. Castables has been prepared with chamotte as major raw material, alumina fine powder, silica flour and cement. The study reported that modulus of rupture of the refractory increases with increase in cement content. Increase in silica flour to cement ratio was found to decrease the water content and improves MOR value.

A. K. Samanta et. al. [34] also investigated the effect of micro silica and cement ratio on the thermo-mechanical properties of low cement castable. The fine fractions of the body formulations were kept around 35% with the variation of cement and micro-silica content. It has been reported that the micro-silica content has strong influence on working time, however, 5% micro- silica content samples showed sharp reduction in working time. Castable with 5 % micro silica and 5% cement required only 5% of water which was lower as compared to other castables in the same catgory. Cold crushing strength (CCS) is also reported to depends on micro silica and cement ratio. CCS increase with increasing microsilica content has been attributed to the thickening of the gel formed during hydration of cement. At high temperature the thickened gel showed good bonding between aggregate and binder. It has also been reported that with the increase in micro silica content in castable bulk density and hot MOR value of the castable increases and apparent porosity decreases. It has also been observed that castables prepared with 2 to 8% cement showed higher shrinkage. This high shrinkage value has been correlated with water requirement of the castables.

Mullite ($3Al_2O_3.2SiO_2$) formation is most important aspect in low cement castable because of its superior properties such as high refractoriness, good strength at high temperature and low creep deformation. Low cement castable prepared with micro-silica and reactive alumina were found to form mullite in the matrix by reaction between the two [35, 36].

B. Myhre et. al. [35] prepared castable with 2, 4, 6 and 8% micro-silica and evaluate the hot property of low and ultra low cement castable. It has been reported that the HMOR of the castable increases above 1400^{o}C. This increase in HMOR of the castable is correlated with the mullite formation in the castable matrix. Castables prepared without any cement were found to show high HMOR as compared to low and ultra-low cement castable. With increasing micro-silica, HMOR increased in both ultra low and low cement castable due to formation of mullite around 1400-1500^{O}C. Mullite formation depend upon calcium aluminate cement and micro-silica content.

Aase M. Hundere et. al. [36] prepared castable with fused alumina, fused mullite and silicon carbide as main aggregate. In has been reported that incorporation of SiC, increases the strength of castable at temperature 1300^{O}C however, above this temperature the strength decreases due to formation of cracks around SiC grains. At high temperature around 1400-1500^{O}C, mullite castable showed better performance.

Lu yicjun et. at. [37] also studied the properties of self bonded castable with the use of silica and alumina sol as a binder. Castable with silica and alumina sol showed good thermal stability, high strength, high modulus of rapture and low creep deformation due to formation of direct bonded mullite but also showed low cold crushing strength. Cement bonded castable showed decreased in strength due to dehydration process in the intermediate temperature high temperature zone.

2.9 Low Cement Self-Flow Castable

Low cement vibratable castable required external energy like vibration for casting at application area so some area did not filled completely because of lack of vibration. In self-flow castable, there is no requirement of any external energy in application area, they flow under their own gravity. So they can be used in complicate areas and required less equipment [38, 39]. The forces between small particles and larger particle should be taken into consideration in the development of this category of castables. In smaller particles agglomeration and in larger particle friction is a barrier for the development of these castables. In order to achieve good flow particles have to be well dispersed so that friction should be minimized. The solution of this is to use of super fine powder and low viscous medium for dispersing the aggregates [40].

E. Karadeniz et. al. [18] investigated the property of self-flow castable with change the amount of micro-silica in the range 3-12%. It has been reported that the castables prepared with 9% micro-silica showed high flow value. If the amount of micro-silica increased above 9% flow decreased due to micro-silica particles had a tendency of flocculation. Apparent porosity of the castabels were found to decrease with increasing the amount of micro-silica and is attributed with improved particle packing.

Chen Zhiquang et. al. [41] studied the flow and flow decay of refractory castable. White fused alumina has been used as main aggregate (4mm) while calcined alumina and micro silica are added as fine fraction. Flow and flow decay depends on time and temperature, at $5^{O}C$, setting time was 5 hours and at $35^{O}C$, setting around 40 minutes, so that with increasing temperature, flow value decreased due to hydration of cement. Citric acid in the range 0.2-0.6% has been used as anti-setting agent with. It has been reported that setting time increases with increase in citric acid addition.

R. Sarkar et. al. [42] prepared self-flow castable with different type of cement binder. Two types of cement binder with Al_2O_3 percentage 71.85 and 73.13 has been used in the castable formulation. Bulk density and CCS of different castable studied were found to relatively constant. Castable with 6% cement (71.85% Al_2O_3) showed higher bulk density and cold crushing strength and has been attributed to the impurities, which is responsible for enhanced densification. XRD of the samples prepared with 6% cement sintered at $1600^{O}C$ revealed the presence corundum as a major phase and some amount of grossite (CA_2) in the matrix.

Micro-silica has important role in low and ultra low cement castable. Addition of micro-silica together with calcined alumina form mullite at high temperature. Micro- silica reduces cement content as well as water content and increase the flowability of castable [43]. Bjorn Myhre [44] studied the effect of microsilica on the flow and strength of tabular alumina based refractory castable with 1.5, 3 and 4.5% cement. Castables has been prepared with 0, 2, 4, 6, 8 and 10% microsilica. It has been reported that the castable prepared with 1.5% cement showed increase in the flow value and decrease in water content with increase in microsilica content. With increasing cement percentage water amount increases and 100 % flow is found only with 2% micro silica containing sample. Cold crushing strength is good for 4.5 % cement containing castable at 110^{O}C and it increased with increase in the microsilica percentage. However, 1.5% cement containg castable had high cold crushing strength while sintered at 1000^{o}C. Bulk density was high and open porosity was low for 1.5 % cement containing castable and it increased or decreased respectively with silica percentage. It has been concluded that at least 6% microsilica gave good flow, minimum water requirement, low open porosity and high cold crushing strength.

Hong Peng et al. [45] investigated the effect micro-silica on properties of corundum-mullite self-flow ultra low cement castable. Different type of micro-silica namely high grade micro-silica (98 wt% SiO_2), mid-grade micro-silica (95 wt% SiO_2) and low grade micro-silica (92 wt% SiO_2) has been used in the study. These compositions had 78 wt% aggregate and 22 wt% matrix phase. Particle size distribution (PSD) study revealed high grade micro-silica had bimodal PSD with D-50 of 0.35µm. On the other hand mid-grade and low grade micro-silica had D-50 of 16.98 µm and 24.68 µm respectively. Self-flow study showed that high grade micro-silica had high self-flow value (92.8%) but mid grade and low grade had lower values like 78.2 and 22.8% respectively. It has been suggested that agglomerates, impurities and particle size have strong impact on flowability of the castable. Low grade micro silica showed high CMOR and low HOMR. This low MOR value has been correlated to the formation of glassy phase at high temperature.

Bjorn Myhre et al. [46, 47] studied the effect of reactive alumina and micro silica on the low cement and no cement castable as a function of microsilica to reactive alumina ratio and distribution coefficient q-value. White fused alumina has been used as coarse aggregates with calcined alumina and micro silica as superfines. Flow test study showed maximum flow when castable has low q-value with 100% microsilica and no reactive alumina. The study also suggested that reactive alumina affect the setting time and flow value of castable and it decreases as the percentage of reactive alumina increases. Castable with 100 % reactive alumina showed high flow value and setting time than 75%. It has been concluded that flow of the castable not only affected by particle size distribution but also affected by composition of superfine. Studies on thermomechanical behaviour of castables suggested that hot properties are affected by microsilica/reactive alumina ratio and could be correlated with the mullite formation at high temperature.

Vicki Jones [48] had studied the difficulties in development of low cement, self-flow castable. Difficulties obtained in developing of low cement, self-flow castable are (1) controlling the rheology and (2) controlling the setting times of the refractory mix. Self-flow castable has been prepared with tabular alumina, reactive alumina, micro silica and cement as starting raw materials. It has been reported that fines crystalline alumina with rounded particle morphology improves flowability of the castable. Study also indicated microsilica containing castable yields high MOR value around 1200^{O}C but at 1500^{O}C it decreases sharply.

2.9.1 Rheology

Rheology is defined by Bingham as "the science of deformation and flow of matter". Rheology of castable gave influence on placing at application area such as dilatant compositions are hardly mixed and are not suitable for pumping, On the other hand, pseudoplastic castables with excessive water content possibly segregate during pumping due to their very low matrix viscosity [49]. By varying particle size of alumina powder, flow pattern vary from pseudo-plastic flow to the dilatant flow. Castables with Ultra fine particles showed pseudo-plastic and thixotropic behaviour flow, whereas that prepared with large particles show dilatant type flow behaviour. In the presence of fume silica dilatant alumina suspension, started showing pseudo-plastic flow behaviour. Use of dispersant (or deflocculant) also show change in dilatants behaviour. With increase in the percentage of dispersant apparent viscosity decreases. Particle surface adsorb multivalent ion and increase repulsive force among particles so that dispersant change internal structure and act as a viscosity decreasing agent and also change flow properties. However, use of an excess amount of dispersant, apparent viscosity increases and show poor dispersion. Particle shape also affected the dilatants behaviour, Irregular particle showed increase in viscosity but there is no constant relationship between fluidity and particle size [50].

Liu Xinhong et. al. [51] also investigated the rheological behaviour of bauxite based castable matrix. The starting material was uniformly mixed with different amount of water varying from 19 to 21 mass %. They found that viscosity of castable decreased with increasing water percentages. They selected castable with 19 mass % and studied the effect of shear stress on viscosity. Viscosity decreased with increasing shear stress due to additional force break the framework structure. Some framework forming and some breaking simultaneously, due to this, matrix can flow. If bauxite replaced by corundum, rheology property increased.

2.10 Shotcreting Castable

Low cement vibratable castable has good mechanical strength and hot properties, however from installation point of view, it has some disadvantages that are given below:

- It requires external energy e.g. vibration
- High men power requirement which means that it is an expensive installation technique
- More setting time requirement (2 – 3 hours)
- Vibratable LCC cannot be used for repair of refractory lining.

Due to these drawbacks of vibratable LCC, other installation techniques such as gunning and shotcreting have been developed. Gunning and shotcreting have some advantages such as there is no requirement of external energy like vibration, less men power requirement, shorter drying time during installation and also used for repairing purpose [4].

The application method of shotcreting consists of pumping of castable directly from the mixture into the pipeline nozzle; compressed air is injected in to the nozzle and castable sprayed on the target surface. The castable loses its fluidity due to the action of cement setting accelerator also injected into nozzle. In gunning, dry powder pumped into the pipe line nozzle, where water mixed with additives then sprayed on application area. Rebound loss and dust are major problem associated with gunning that problem removed by shotcreting. In shotcreting techinque, material is homogenously mixed as compared to gunning [52].

Shotcrete is defined by American Concrete Institute, which is "morter or concrete pneumatically projected at high velocity onto a surface" [53]. There is similarity in nozzle technique for both shotcreting and gunning but nozzlemen find shotcreting easier and faster. Rebound loss affected by force and impingement angle of the nozzle and force depends on distance between nozzle and surface. If distance is too short, deposited material washed away by new material and if distance is too long force will be too weak and no layer will be formed. So it is very important to maintain the distance between nozzle and surface [54].

For shotcrete castable self-flow castable is required because of their pumpability characteristics. Rheology is most important for pumpable because if castable is dilatants, it is hard to pump and if it is pseudo plastic it shows segregation. Shotcrete have four steps, these are mixing, pumping, spraying and consolidation [52].

R. G. Pileggi et. al. [53] prepared three types of castable to studies rheological behaviour. It has been reported that fiber free composition required low mixing energy and torque had good free flow and low rebound losses, whereas castables with fiber required high value of mixing energy and torque had low free flow and high rebound losses respectively. Rebound loss also minimize by decreasing additives reaction at initial stage. If the reaction was fast, additives harden the material in the nozzle and form agglomerates. Slow setting also showed good binding and homogenization so that layer should be thick and had great rebound.

Aase Hundere et al. [40] studied the effect of particle shape on flow property. Sphere particle shows good flow as comparison to irregular particles. Porosity was major problem for castable. By increasing the amount of micro silica amount of water can be reduced. Micro-silica filled the voids of the aggregate and reduced the porosity. With use of micro silica, mullite phase is formed at high temperature that increased the hot strength of castable. Bauxite based castable with 6% water and sodium silicate as accelerator has been studied. This castable showed no dust and low rebound loss.

Aase Hundere et. al. [55] studied the effect of different percentage of cement by varying cement percentage to 15, 6 and 0.5%. Castables has been prepared with bauxite as main starting aggregate, calgon and Darvan 811 as a dispersant, citric acid as a retarder and Aluminium sulphate, sodium silicate, lithium chloride as an accelerator. Accelerator percentage decreased with decreasing percentage of cement. Aluminium sulphate showed quick setting but remained plastic after installation. Sodium silicate gave rapid setting of castable; it also showed low porosity and high HMOR as comparison to other.

Zhanmin Wang et. al. [56] prepared a castable with different additives. Danced fused alumina, white fused alumina, high duty silicon carbide and pitch wall was used as a starting raw materials. Aluminium sulphate (AS), calcium chloride (CC), aluminium potassium sulphate, sodium silicate HEYCD SA 160 (SA) and TCC 766 (TCC) were used as an accelerator. Study suggested that addition of CC gave best effect on flow decay but make castable loose, less plastic and not easy to densify whereas AS and SA also showed good flow decay effect.

Eiji Motoki et al. [57] also evaluate and compare the effect of quick setting additives on the gunning and quality of lining. Needle penetration test suggested that castable with alkali powder type quick setting additive had better penetration resistance than cement powder type. Castable with 1.0 mass % liquid alkali free type additive gave quick setting but very slow increase in penetration resistance. Powder type additives showed better quick setting properties than liquid type. Gunning test revealed that alkali powder type additive showed no lamination, no aggregation of aggregate, homogeneous structure and well filled. Physical properties were good for alkali type liquid and powder additives. It has been concluded that alkali type quick setting additives are most suitable for quick setting and good for wet gunning.

To develop shotcrete castable of good erosion resistance, it is necessary to prepared dense layer on hot patching surface but in dense layer evaporation of water is most difficult. Jinfu Yao et. al. [58] studied the effect of anti-spalling fiber and pitch on Al_2O_3-SiC-C shotcreting castable for main BF trough. It has been reported that increasing the amount of anti spalling fiber, apparent porosity of the cast decreases whereas bulk density increases. Studies on granulometry suggested that increasing the amount of fine powder anti-spalling property deteriorates due to decrease in apparent porosity.

Chia-Hong Chen [59] also prepared wet gunning with colloidal silica for main trough of blast furnace. Castable with colloidal silica showed high setting time more than 4320 min and good flow value of 185mm as comparison to cement based castable. Castable with colloidal silica had high slag resistance as compared to castable with 3 %. Colloidal silica had nano sized silica particle that increased the contact area thereby provide better densification.

CHAPTER-III

OBJECTIVE

3. OBJECTIVE

Low cement vibratable castable has been developed with the advantages of micro fine filler powder, namely micro-silica and calcined alumina. These micro-fine powders have small particle size in the range of few microns, fill the voids created by aggregate and increase the packing density of the castable and thereby reduce both the water requirement as well as hydraulic boning cement requirement. It has been well studied that a castable composition with high packing density require low amount of water as compared to other. These fine powder form ceramic bond at intermediate temperature and provides increased strength of the castable. Micro-silica and calcined alumina reacts at high temperature form mullite phase in the matrix and thus provide high strength also. Micro fine powder also creates the gap between the coarse particle and reduce the friction thereby increases the flow property of the castable. Objective of present study has been given as follows:

1) Development of 70% Al_2O_3 low cement vibratable castable and study the effect of particle size and particle size distribution of calcined alumina filler on the physical and mechanical properties.
2) Development of 70% Al_2O_3 low cement self-flow castable and study the effect of micro-silica content on the physical and mechanical properties.
3) Development of 70% Al_2O_3 low cement self-flow castable and study the effect of calcined alumina content the physical and mechanical properties.
4) Development of 70% Al_2O_3 low cement self-flow shotcreting mass with the addition of a setting accelerator and study the physical and mechanical properties.

CHAPTER-IV

EXPERIMENTAL WORK

4. EXPERIMENTAL WORK

4.1 Raw Materials

Bauxite based 70 % Al_2O_3 low cement castable has been prepared with aggregates of Chinese bauxite, brown fused alumina, fire clay grog, white fused alumina, silliminite sand. Calcium aluminate based high alumina cement (HAC) has been used as binder. Micro-silica and calcined alumina has been used as a filler materials. Sodium hexa meta phosphate and water glass has been used as dispersant and accelerator respectively.

4.1.1 Particle size distribution of calcined alumina powder

Particle size distribution of calcined alumina measured by master sizer (Marven) instrument. Powder first dispersed in deionized water after that vibration has been given with the help of ultrasonic machine. This dispersed water feed in to the sample holder and measurement has been taken.

4.2 Granulometric Calculation

Particle size distribution of aggregates of castable detects the flow behaviour. Particle size distribution of the aggregates could be fitted with the well-known Andreassen's equation given in Eq. 4.1.

$$CPFT = \frac{d^q}{D^q} \times 100 \ldots\ldots\ldots\ldots (4.1)$$

Where;

CPFT = Cumulative percent finer than
d = particle size
D = maximum particle size
q = distribution coefficient

Depending on the distribution coefficient value the flow behaviour of the castable can be predicted. For example self-flow castable distribution coefficient varies in the range 0.2 to 0.25 and vibratable castable it is in the range 0.26 to 0.33. Volume fraction (%) of raw martial of a particular size (d) could be calculated from the D_{max} and distribution coefficient value of the aggregates. Weight fraction (%) could be calculated from volume fraction (calculated with Eq. 4.1) using bulk density of coarser particles and true density of finer particles.

4.3 Mixing Procedure

Mixing of raw materials is an important step to prepare a castable with better homogeneity, consistency and uniform packing, which influences the properties of castable. Hobart mixture [16] (Fig. 4.1) has been used for this purpose. This apparatus consist of pot and agitator. The pot always remains in static position and the agitator rotates around the pot and also about its own axis. The required amount aggregates calculated using Andreasen's equations has been weighted properly along with binder, deflocculates and drying aids has been taken together in the Hobart mixture and mixed for 5 minute in order to prepare the castable. After dry mixing required amount of water was added and then mixed for 2 minute in order to prepare samples with the castable.

Fig. 4.1 Photo graph of laboratory Hobart mixture used in the present study

4.4 Flowability Test

Flow behaviour of castable is one of the most important properties related to the installation technique of the castable. It depends on particle size distribution of the castable. Flow behaviour of the castable has to be measure to determine the performance of the castable as well as the required percentage of water to achieve 100% flow. Flow value of castable measured using ASTM standard flow table test (ASTM C230). Flow cone is completely filled with the castable thereafter the brass cone is removed and castable is allowed to spread under the action of gravity (in the case of self-flow) or vibrated for 20 seconds (in the case of vibratable). Percentage increase in diameter of spread is measured after the elapse of one minute. Flow value was expressed as percentage increase of the diameter of castable. The conical brass cone had inner diameter 100mm and 70mm respectively at a height of 50 mm. Typical brass cones has been shown in Fig. 4.2.

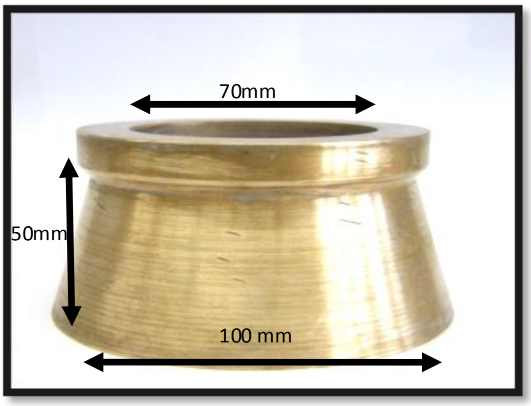


Fig. 4.2: photo graph of flow cone described by ASTM C230

Flow value has been calculated using Eq. 4.2:

$$Self - flow\ percentage\ (\%) = Average\ material\ diameter after\ one\ min - 100 \ \ldots\ldots.. (4.2)$$

Where, 100 is the initial diameter of the cast.

4.5 Sample Preparation

4.5.1 Casting

The test samples were casted in metallic mould required size in order to test physical and mechanical properties. As a mould lubricant, paraffin oil was used. Castable was casted in 160×40×40mm mould for the measurement of Cold Modulus of Rapture and Permanent linear change, 65×40×40mm for Cold crushing strength, Apparent Porosity and Bulk Density. For different testing, five samples were casted for each batch.

4.5.2 Initial setting time

Initial setting time of the low cement castable was measured by Vicat apparatus. Wet castable was filled in the Vicat mould. In every 15 minutes needle penetration into the castable were checked. The final setting time was determined when needle stop penetrating >30 mm above bottom plate.

4.5.3 Drying of the castable

Low cement castable had high alumina cement as a binder that reacts with water and form cement hydrates. That hydrates gave strength at room temperature and hydration reactions were affected by temperature. With increase in temperature de-hydroxylation reaction should be occurring. The rate of hydration has to be very slow due to phase transformation. If the drying rate high there is a problem of explosion because low cement castable was so dense and there is no space for evaporation of water. Castable requires around 24 hours for air drying followed by oven drying at 110^{o}C for 24 hours.

4.5.4 Firing of the castable

Castable samples were fired at 800, 1100, 1400 and 1500^{o}C with constant firing rate 5^{o}/min and socking time was around 3 hours in electric arc furnace. At initial temperature chemical bond break due to de-hydroxylation of cement hydrates. Above 1100^{o}C, densification of castable started due to the formation of ceramic bond that cause of high strength of the castable.

4.6 Characterization

4.6.1 Apparent porosity and bulk density

Apparent porosity of the sample defined as the ratio of open pores to the bulk volume of the material and expressed in percentage. Bulk density of the sample defined as the ratio of mass of dry material to the bulk volume of the sample and expressed in gm/cc. Bulk density of the sample is inversely related to the porosity of the same sample. The sample size for this measurement was 60×40×40mm and tested by IS 1258 vacuum method. First dry weight of the sample taken after that put in to air tight desiccators for 30 minutes in vacuum condition. After 30 minutes, water was introduced in the desiccators for 15 minutes. The samples were fully enclosed with water and to fill up the pores. After that, socked and suspended weight was taken. Calculation of apparent porosity and bulk density of the sample was calculated by given in Eq. 4.3 and 4.4.

$$Apparent\ porosity\ (\%) = \frac{soaked\ weight - Dry\ weight}{soaked\ weight - suspended\ weight} \times 100 \ldots\ldots\ldots (4.3)$$

$$Bulk\ density\ \left(\frac{gm}{cc}\right) = \frac{dry\ weight}{soaked\ weigth - suspended\ weight} \times liquid\ density \ldots\ldots\ldots\ldots (4.4)$$

4.6.2 Cold crushing strength

Cold crushing strength (CCS) is defined as the maximum amount of compressive stress per unit area that causes fracture in the refractory material. It is measure the strength of grains as well as strength of bonding system as expressed in Kg/cm^2. Sample size of this sample was 65×65× 40 mm and measured by ASTM C133. Hydraulic compressive testing machine apparatus used for this measurement. Load was applied on the flat surface of the sample and measure the load at which crack was propagating in the refractory sample. Cold crushing strength calculated by given formula.

$$Cold\ crushing\ strength\ (kg/cm^2) = \frac{load}{area} \ldots\ldots\ldots\ldots (4.5)$$

4.6.3 Cold modulus of rapture

The cold modulus of rupture of a refractory material designates the bending strength and its suitability for use in construction of furnace lining and as expressed in Kg/cm^2. This Modulus of rapture measurement was determined by three point bending test (ASTM C233) with the sample size was 160× 40 ×40 mm and the spam length should be 100mm. During testing, load should be uniform and applied at centre of the spam length. Using given formula cold modulus of rapture was calculated.

$$Cold\ modulus\ of\ rapture\ (Kg/cm^2) = \frac{3Wl}{bd^2} \ldots\ldots\ldots\ldots (4.6)$$

Where,

W= facture load (Kg)

l= spam length

b= width of the sample

d= thickness of the sample at fracture plane

4.6.4 Permanent linear change (PLC)

Permanent linear change defined that whether sample expend or shrink after firing. This expansion and shrinkage of the sample is occurring due to either phase transformation or densification and it is expressed in %. Test samples for this measurement was 160×40×40 mm and fired at 1400 and 1500°C with 3 hours soaking time. In this measurement, initial length was taken for dry sample. After that, fired the sample in electric arc furnace and measure the final length of the sample. Permanent linear change was calculated by given formula.

$$permanent\ linear\ change\ (\%) = \frac{L_f - L_i}{L_i} \times 100 \ldots\ldots\ldots\ldots (4.7)$$

Where,

L_i = initial length of the sample (mm)

L_f = final length of the sample (mm)

4.6.5 Phase analysis

Phase analysis carried out by powder diffraction method by Rigaku, Miniflex II Japan XRD instrument. Castable samples fired at different temperature were broken into small pieces and ground in to fine powder by using INSMART grinding machine. Different phases present in the fired powder sample were determined by XRD pattern. Experimental setup of X-Ray Diffractometer has been given below:

Voltage = 35 kV

Current = 15 mA

Incident beam slit – 0.25 mm

Divergence beam slit – 0.5 mm

Radiation - Cu-Kα, $\lambda = 1.54$Å

Filter – Nickel

Scan Angle 2θ – 10-80^o

Continuous Scan Speed - 0.02^o per second

Analysis of obtained diffraction pattern was done by Philips X-pert high score software.

CHAPTER-V

RESULTS AND DISCUSSION

5. RESULTS AND DISCUSSION

5.1 Study the Effect of Calcined Alumina on 70% Al_2O_3 Low Cement Vibratable Castable:

Bauxite based 70% Al_2O_3 low cement vibratable castable has been prepared with grog, brown fused alumina, silliminte sand as the aggregates and calcium aluminium cement, micro-silica, and calcined alumina as the additives. Particle size distribution of the aggregates for vibratable castable follows Andreassen's equation with q value = 0.31. This q-value has been chosen from the earlier work [16, 34]. It has been reported that the LC castables prepared with q value 0.31 showed high flow value with low water requirment. The study suggests that q-value 0.31 shows good physical and mechanical properties and best for vibratable cstable.

5.1.1 Batch formulation of 70% Al_2O_3 low cement vibratable castable

Raw materials used in the body formulations are 86% Chinese Bauxite, Pyrophilytic Grog, Brown fused alumina and Silliminite Sand as aggregate, calcium aluminate cement as a binder, micro-silica and calcined alumina as a filler, dispersant and polypropylene fiber as dry aids. Study the effect of calcined alumina on the basis of particle size and particle size distribution on the low cement vibratable castable and study the physical and mechanical properties. In this study, four type of calcined alumina has been used. Physical and chemical properties of calcined alumina have been shown in Table V.I. Batch formulation of low cement vibratable castable has been shown in Table V.II.

Table V.I Physical and chemical properties of calcined alumina

Calcined alumina	Alumina-1	Alumina-2	Alumina-3	Alumina-4
Al_2O_3 (%)	99.0	99.5	99.0	99.0
Specific surface area (m^2/gm)	2.1	3	0.8	0.23

Table V.II Batch formulation of low cement vibratable castable

Composition (%)	**T1**	**T2**	**T3**	**T4**
Chinese Bxt. (3-5)mm	15	15	15	15
Grog (1-3)mm	18	18	18	18
Brown Fused Aalumina (1-3)mm	12	12	12	12
Siliminite sand (0-1)mm	10	10	10	10
Brown Fused Alumina (0-1)mm	10	10	10	10
Brown Fused Alumina (-200#)	20	20	20	20
Calcined alumina	5 (alumina-1)	5 (alumina-2)	5 (alumina-3)	5 (alumina-4)
Cement	5	5	5	5
Micro-silica	4.8	4.8	4.8	4.8
Dispersant	0.2	0.2	0.2	0.2
PPF	0.05	0.05	0.05	0.05

5.2.2 Particle size and particle size distribution of calcined alumina

Particle size distribution of calcined alumina used in this study has been presented in Fig. 5.1.

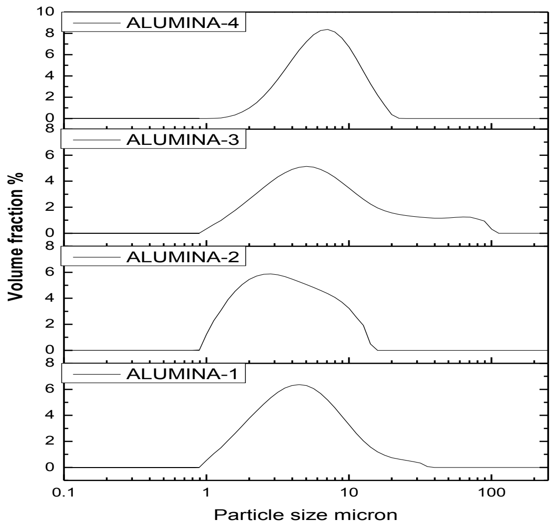


Fig. 5.1 Particle size distribution of calcined alumina of ALUMINA-1, ALUMINA-2, ALUMINA-3 and ALUMINA-4.

The particle size distribution of ALUMINA-1 has been shown in Fig 5.1. It could be seen from the figure that this powder shows bi-modal distribution with little amount of bigger particle. Particle sizes have been calculated from the figure and were found to be 4μm and 25μm respectively. Volume fraction ratio of these two fractions calculated was 90:10. The particle size distribution of ALUMINA-2 has been shown in Fig. 5.1. It could be seen from the figure that this alumina powder also showed bimodal distribution with peaks at 3μm and 5μm respectively. The volume fractions of these two types of particles were found to be 60:40.The particle size distribution of ALUMINA-3 has been shown in Fig. 5.1. It could be seen from the figure this powder also showed bimodal distribution with peaks at 4.5 and 70μm respectively, and the volume fraction of these particles calculated was 80:20. The particle size distribution of ALUMINA-4 powder has been shown in Fig 5.1. It could be seen from the figure that this alumina powder shows mono-modal distribution with peak at 6.5μm.

5.2.3 Initial setting time

Setting time of the castable as a function of calcined alumina type has been shown in Fig 5.2.

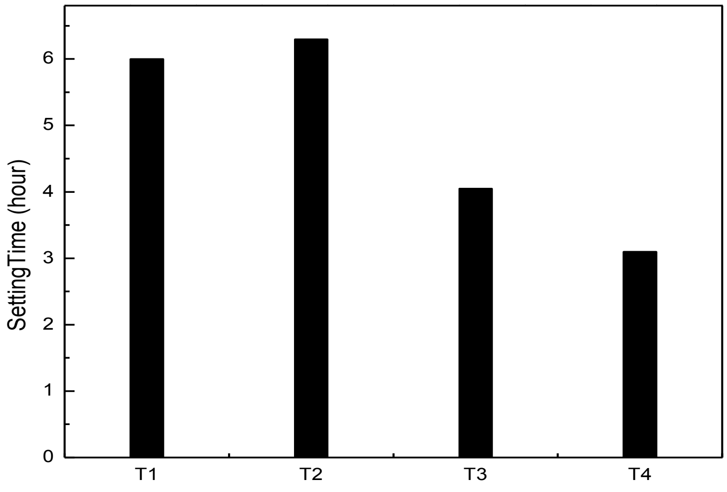


Fig 5.2 Final setting time of castable as a function of calcined alumina

It could be observed that setting time of vibratable low cement castable is highest for the castable prepared with ALUMINA-2 and lowest for that prepared with ALUMINA-4. Castables prepared with ALUMINA-1 and ALUMINA-3 showed intermediate setting time value. Setting time could be correlated with particle size and hence the surface area of the calcined alumina powder. Setting time decreases with increase in effective particle size. Fine alumina powder forms pseudo-boehmite phase in contact with water, which lowers the setting behaviour of the high alumina cement and hence increases the setting time. Castable prepared with ALUMINA-2 alumina had a bimodal particle size distribution containing 3µm and 8µm particles in a ratio 60:40. It has a specific surface area of 3m^2/gm, which was highest among all the alumina studied. Thus, the castable prepared with ALUMINA-2 alumina showed the longest setting time as compared with the other alumina. Castables prepared with ALUMINA-4 alumina has the lowest surface area 0.23m^2/gm and thus showed shortest setting time. On the other hand, calcined alumina ALUMINA-1 and ALUMINA-3 has surface area 2.1 m^2/gm and 0.8m^2/gm respectively and showed an intermediate setting time.

5.2.4 Flow properties of 70% Al_2O_3 Low Cement Vibratable castables with adding different type of calcined alumina

Variation in vibro-flow of the low cement castable studied as a function of calcined alumina graphically in Fig. 5.3. It could be observed that castables prepared with ALUMINA-1 showed highest vibro-flow value around 110% and that prepared with ALUMINA-2 showed lowest flow value around 80%, whereas the castables prepared with ALUMINA-3 and ALUMINA-4 showed almost similar value around 90% vibro flow. Virbo-flow of a castable depends mostly on the particle size distribution of the aggregates. In the present study all the castables has been prepared with similar aggregates except the calcined alumina component.

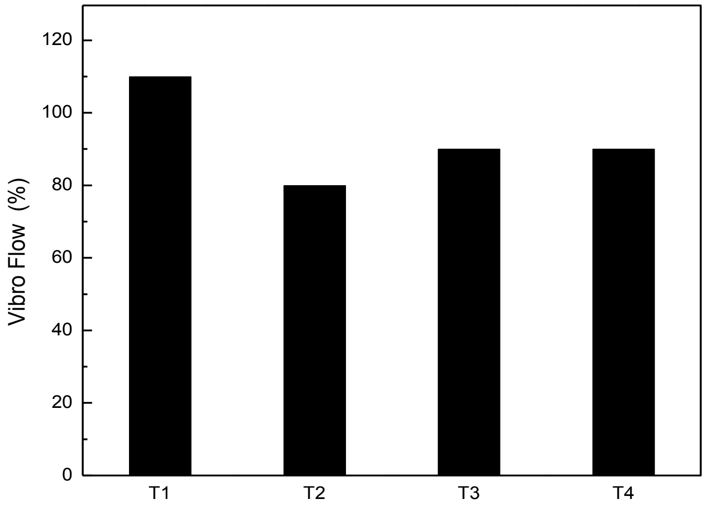


Fig 5.3 Vibro-flow of the low cement vibrating castable as a function of calcined alumina type with 5% water

Thus the observed variation in the flow behaviour is related to the morphology of the calcined alumina used in the body formulation especially the particle size distribution of the alumina powder. Particle size distribution of ALUMINA-1 alumina showed presence of 90% particles of size 4µm and 10 % particles of size 25µm (shown in Fig. 5.1). Corse fraction of ALUMINA-1 calcined alumina fills the voids of the matrix aggregates along with the microsilica, whereas the fine fraction of ALUMINA-1 calcined alumina fills the interstitial position of the matrix aggregates and the coarse fraction of alumina. Thus, decreases the casting water requirement. Hence, the castable mixed with 5% water showed 100% vibro-flow. Particle size distribution of ALUMINA-2 alumina showed presence of 60% particles of size 3µm and 40 % particles of size 8µm (shown in Fig. 5.1). Corse fraction of ALUMINA-2 calcined alumina fills the voids of the matrix aggregates along with the micro-silica, whereas the fine fraction of ALUMINA-2 calcined alumina could not fills the interstitial position of the matrix aggregates and the coarse fraction of alumina due to the size restriction. Thus, increases the casting water requirement. Hence, the castable mixed with 5% water showed 80% vibro-flow.

Particle size distribution of ALUMINA-3 alumina showed presence of 80% particles of size 4.5µm and 20 % particles of size 70µm (shown in Fig. 5.1). Corse fraction of ALUMINA-3 calcined alumina may not fill the voids of the matrix aggregates along with the microsilica due to size restriction, whereas the fine fraction of ALUMINA-3 calcined alumina fills the interstitial voids. Hence, the castable mixed with 5% water showed 90% vibro-flow. Particle size distribution of ALUMINA-4 calcined alumina showed mono-modal distribution (Fig. 5.1) with particle size 6.5 µm. Flow values the castable was found to be in same range as that for ALUMINA-3 calcined alumina.

5.2.5 Flow decay

Flow decay of castable studied as a function of calcined alumina has been shown in Fig. 5.4.

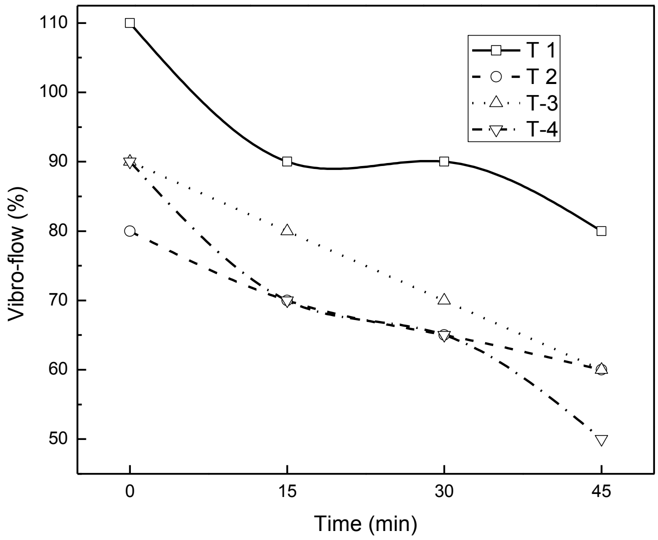


Fig 5.4 Flow decay of low cement vibratable castable as a function of calcined alumina and time

It could be seen that flow decreases with increase in time for all the castable studied. The decrease in flow as a function of time could be correlated with the setting of the castable. It could also be seen that flow decay does not follow any linear relationship and may be related to the thixotropic nature of the castable. Flow decay rate of the castable has been on the basis of initial and final flow were found 0.45, 0.45, 0.67 and 0.89 %/min for the castable prepared with ALUMINA-1, ALUMINA-2, ALUMINA-3 and ALUMINA-4 calcined alumina respectively. Flow decay could be correlated with setting time of castable. Setting time for the castable prepared with ALUMINA-2 calcined alumina was 6:30 hours highest among all the castable studied. Thus it showed lowest flow decay rate.

5.2.6 Apparent porosity (AP) and bulk density (BD)

Apparent porosity of the castable as a function of temperature and calcined alumina type has been shown in Fig 5.5.

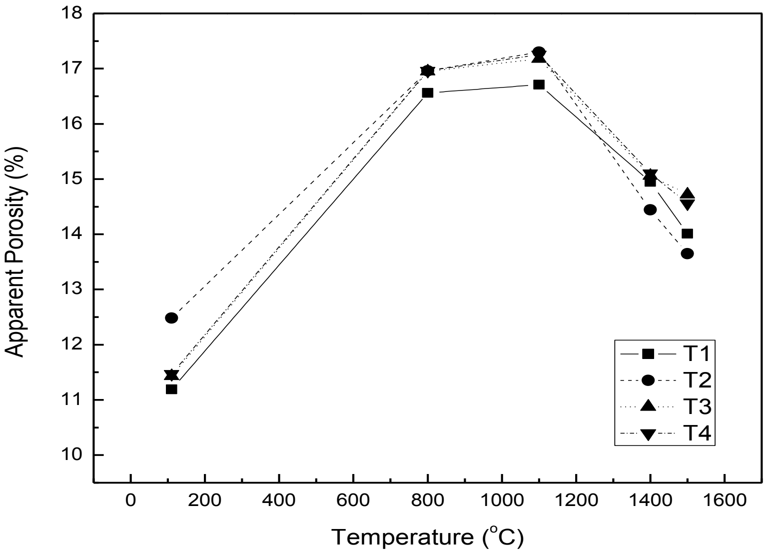


Fig 5.5 Apparent porosity of low cement vibrating castable as a function of calcined alumina and temperature

It could be seen from the figure that apparent porosity of the samples has significant change as a function of calcined alumina type. At low temperature 110°C castable prepared with ALUMINA-1 showed low apparent porosity. It could be related with the particle size and particle size distribution of calcined alumina. Particle size distribution of ALUMINA-1 calcined alumina showed that fine particle filled the voids of coarser particle and gave high packing density that decreased the porosity of the castable. At high temperature zone above 1400°C, ALUMINA-2 showed low apparent porosity. It could be related to the particle size hence the specific surface area of the calcined alumina powder. ALUMINA-2 showed high specific surface area $3m^2/gm$ as compared to other. As the powders have high specific surface area it showed high reactivity resulting in good bonding between the particles.

Moreover, all the samples showed similar temperature dependent behaviour. It has been found that the apparent porosity of the sample increases with temperature in the intermediate temperature zone (RT-1100°C), thereafter it decreases with increase in temperature. The increase in porosity in the intermediate temperature zone could be correlated with the de-hydroxylation of the high alumina cement hydrates, which occurs in this temperature range [5]. The decrease in apparent porosity in the high temperature zone (>1100°C) is attributed to the densification of the samples at high temperature.

Bulk density of the castable as a function of temperature and calcined alumina type has been shown in Fig. 5.6.

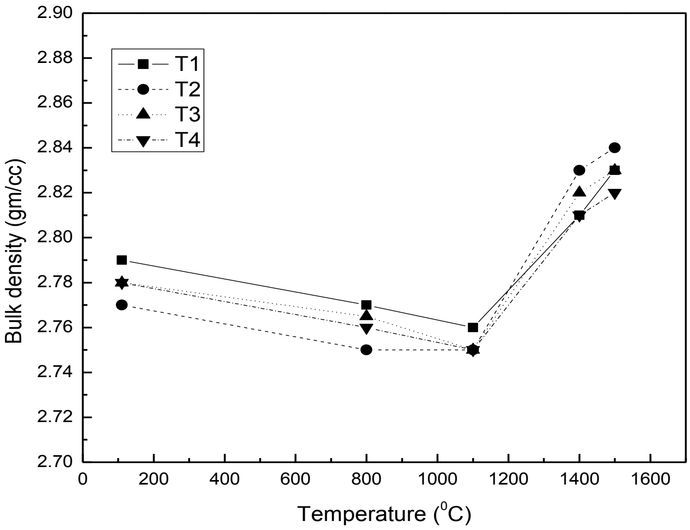


Fig 5.6 Bulk density of low cement vibrating castable as a function of temperature and calcined alumina type

It could be seen from the figure that bulk density of the samples have significant change as a function of calcined alumina. Castable prepared with ALUMINA-1 calcined alumina showed high bulk density at 110°C as compared to other. It could be related to the particle size distribution of calcined alumina. Particle size distribution of ALUMINA-1 calcined alumina showed that fine particle filled the voids of coarser particle that gave high packing density, which increased the bulk density of the castable. At high temperature >1400°C, Castable prepared with ALUMINA-2 calcined alumina showed high bulk density as compared to other. It could be related to the particle size hence specific surface area of the calcined alumina powder. ALUMINA-2 had specific surface area that was highest among all the alumina studied. Powder with high specific surface area showed high reactivity that provides good bonding between the particles. That gave high bulk density.

Moreover, all the samples showed similar temperature dependent behaviour. Bulk density of the samples was found to decrease with increase in temperature in the intermediate temperature zone (RT-1100°C); thereafter it increased with increase in temperature. The decreased in bulk density with temperature in the intermediate temperature zone could be explained on the basis of de-hydroxylation of the high alumina cement hydrates, which occurs in this temperature range [5]. The increased in bulk density in the high temperature zone (>1100°C) is attributed to the densification of the samples at high temperature. Temperature dependent bulk density of the sample follows an inverse relationship as that observed for apparent porosity (Fig. 5.5) which is quite obvious.

5.2.7 Cold Crushing Strength (CCS)

Cold crushing strength of the castable as a function of temperature and calcined alumina type has been shown in Fig 5.7. It could be seen from the figure that cold crushing strength of the samples has significant change as a function of calcined alumina type. Castable with ALUMINA-2 calcined alumina showed highest cold crushing strength as compared to other. It could be related to the particle size of the calcined alumina hence specific surface area of the calcined alumina powder. Calcined alumina powder react with water and formed pseudo-bheomite phase that provide high strength to the castable and increased the cold crushing strength. ALUMINA-2 calcined alumina has a high specific surface area of $3m^2$/gm, which was highest among all the alumina studied. Thus castable prepared with ALUMINA-2 showed high cold crushing strength.

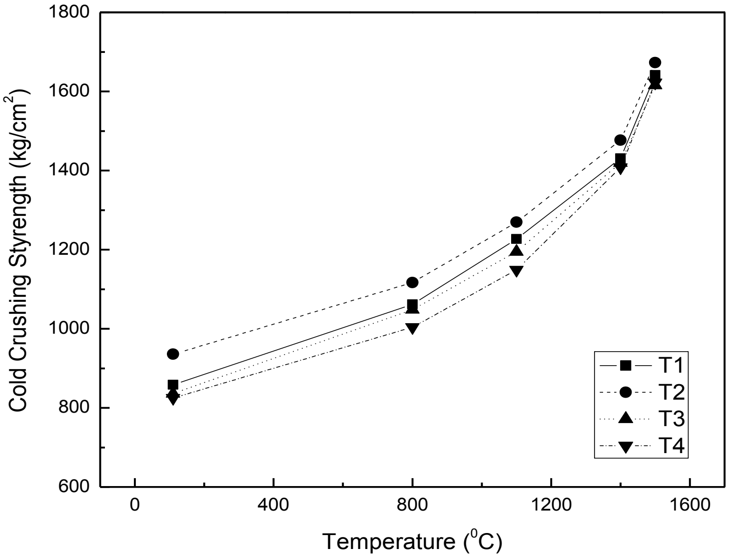


Fig 5.7 Cold crushing strength of low cement vibratable castable as a function of temperature and calcined alumina type

Moreover, all the samples showed similar temperature dependent behaviour. It has been found that the cold crushing strength of the sample increases with temperature. The apparent porosity and bulk density of the sample increases and decreases respectively in the intermediate temperature zone (RT-1100^{o}C). Thus, the CCS value decrease in this temperature zone is expected. The observed reverse trend in this temperature could be explained from the consideration of the presence of micro-silica and calcined alumina in the body formulation. Calcined alumina reacts with water and forms pseudo-boehmite phase, which provide strength of castable in the intermediate temperature [60]. Moreover, micro-silica addition in the body formulation produces a thickening gel, which also provides strength at the intermediate temperature [34]. Thus the strength of the castable does not decrease in the intermediate temperature zone. Strength increased with increasing temperature at high temperature (>1100^{o}C) is attributed to the densification of sample as well as mullite phase formation at high temperature.

5.2.8 Cold Modulus of Rapture (CMOR)

Cold modulus of rapture of the castable as a function of temperature and calcined alumina type has been shown in Fig 5.8.

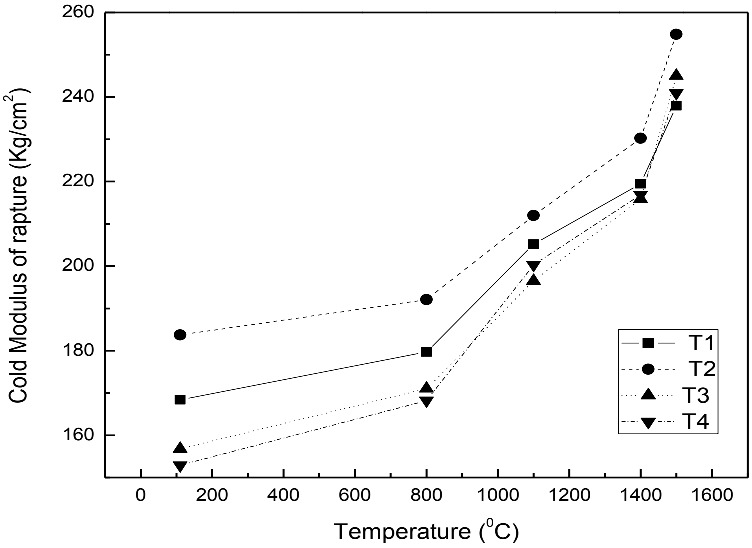


Fig 5.8 Cold crushing strength of low cement vibratable castable as a function of temperature and calcined alumina

It could be seen from the figure that cold modulus of rapture of the samples has significant change as a function of calcined alumina. It could be seen from the figure that castable prepared with ALUMINA-2 showed highest cold modulus of rapture. It could be correlated to the particle size hence specific surface area of the calcined alumina powder. Calcined alumina powder reacts with water and formed pseudo-beohmite phase which provide strength of the castable.

Moreover, all the samples showed similar temperature dependent behaviour. It could be found that cold modulus of rapture increases with increasing temperature due to presence of micro-silica and calcined alumina. This behaviour could be explained in the same line as described in section 5.1.7. Cold modulus of rapture increases with increase in temperature at high temperature (>1100°C) is attributed to the densification of sample as well as mullite phase formation at high temperature zone.

5.2.9 Permanent linear change (PLC)

Permanent linear change (PLC) of the castable as a function of temperature and calcined alumina has been shown in Fig 5.9. It could be seen from the figure that the all samples had negative permanent linear change. However, all the samples showed increase in PLC with temperature due to densification. PLC of the samples with ALUMINA-1 shows lowest value and sample with ALUMINA-2 shows highest. PLC depends on the pores of the sample. It could be found that PLC may be correlated with particle size distribution of calcined alumina. Particle size distribution of ALUMINA-1 powder shows that, fine particles of calcined alumina powder fill the voids of coarser particle that gave high packing density and that gave low PLC. On the other hand particle size distribution of ALUMINA-2 powder shows that fine particles of calcined alumina powder not able to fill the voids created by coarser particle and that gave high PLC.

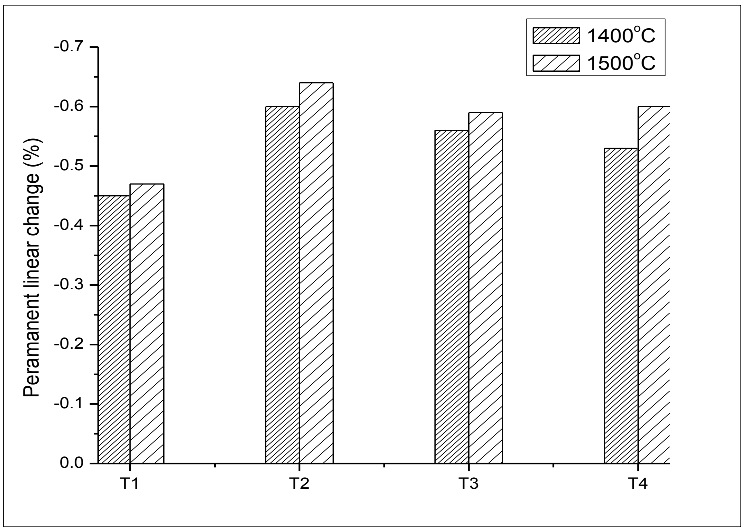


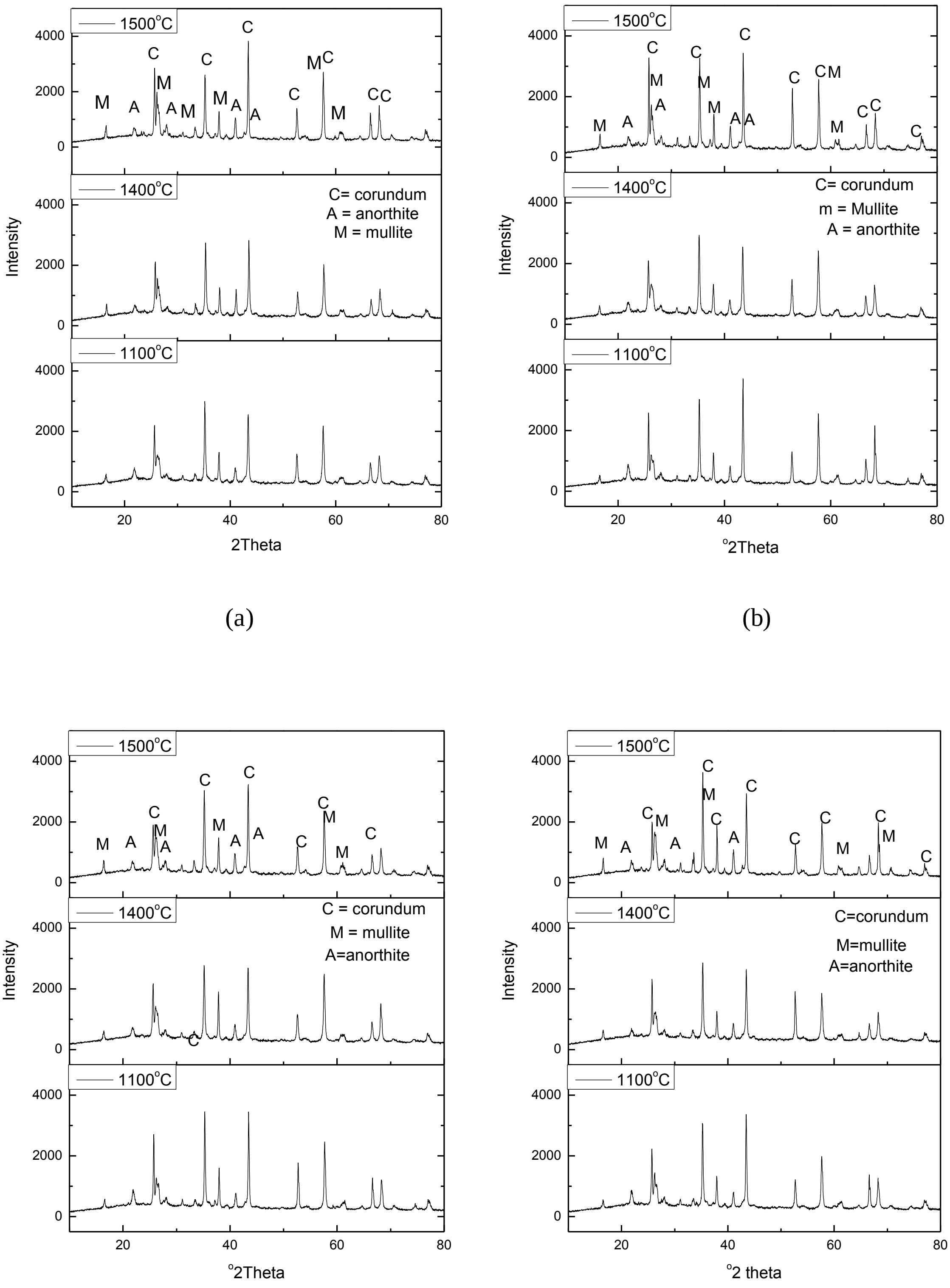
Fig5.9 Permanent Linear change of low cement vibrating castable as a function of calcined alumina at 1400°C and 1500°C

5.2.10 Phase analysis (XRD)

XRD patterns of 70% Al_2O_3 low cement vibratable castable sintered at different 1100, 1400 and 1500^oC has been shown in the Fig. 5.10. Corundum, mullite and anorthite have been identified as the major phases in all the samples. It is interesting to note that Mullite and anortite phases could be detected at 1100^oC. It could be related to the fine particle size of microsilica and calcined alumina. These fine particles may react at low temperature and formed mullite, it could be due to fine powder. De-hydroxylation of cement hydrates in the low temperature range produces calcium oxide, which reacts with the alumino-silicates and formed anorthite. Attempt has also been made to calculate the semi-quantative analysis of the phases using expert HiSchore software. The estimated phases have been tabulated in Table V.III. It could be seen from the analysis data with increase in temperature amount of mullite and anorthite phases in the sample increases and could be related to the high sintering temperature.

TableV.III Semi-quantative analysis of the phases present in the sample sintered different temperature

Samples	Temperature	Corundum	Mullite	Anorthite
ALUMINA-1	1100	56	27	17
	1400	37	39	23
	1500	51	29	20
ALUMINA-2	1100	51	28	20
	1400	50	30	20
	1500	26	41	33
ALUMINA-3	1100	45	33	21
	1400	52	28	20
	1500	49	31	20
ALUMINA-4	1100	52	29	18
	1400	45	33	22
	1500	35	38	22



(a)

(b)

(c)

(d)

Fig5.10 XRD pattern of the Vibratable 70% Al2O3 low cement castable fired at different temperatures for (a) ALUMINA-1, (b) ALUMINA-2, (c) ALUMINA-3 and (d) ALUMINA-4.

5.3 Effect of Amount of Micro-silica on the Properties of 70% Al_2O_3 Self-Flow Low Cement Castable

Studies on bauxite based 70% Al_2O_3 low cement castable with the variation of different calcined alumina suggests that castable prepared ALUMINA-1 showed enhanced physical and mechanical behaviour as compared to the other. So in the present study, self- flow castable has been prepared with ALUMINA-1 calcined alumina and attempt has been made to study the effect of micro-silica content on the physical and mechanical behaviour of the castable. Self-flow castable prepared in this study had q-value 0.22.

5.3.2 Particle size distribution of the aggregates

It has been well established that self-flow low cement castable could be prepared from aggregates with distribution coefficient (q-value) in the range 0.25 to 0.21 [21]. It has also been reported that self-flow castable prepared with q-value 0.22 showed good flow properties with low amount of water along with good mechanical properties [21]. Particle size distribution of the aggregates calculated using Andreasen equation has been shown in Table V.III. The maximum particle size of the aggregate used in the present study is 5mm and the distribution coefficient has been adopted in this study is 0.22.

Table V.III Calculation of particle size distribution of the aggregates

d (mm)	CPFT	Particle size distribution	Volume fraction (%)	Weight fraction (%)
5	100	3-5	10.63	10
3	89.37	2-3	7.63	6
2	81.74	1-2	11.56	13
1	70.182	0.5-1	9.93	12
0.5	60.25	0.2-0.5	11	9
0.2	49.25	0.075-0.2	9.56	11
0.075	39.69	-0.075	39.69	39

5.3.3 Batch formulation of self-flow low cement 70% Al_2O_3 castable with different micro-silica content

Raw materials used in the body formulations of self–flow low cement castable are same as in previous section 5.1. Self-flow castable was prepared with same q-value 0.22 with varying the ratio of tabular alumina and micro-silica with 8% calcined alumina. Batches formulation of self-flow low cement castable has been shown in Table V.IV with different micro-silica content.

Table V.IV Batch formulation of self-flow low cement castable with different Micro-silica content

Composition	M-1	M-2	M-3	M-4
Chinese Bxt. (3-5) mm	10	10	10	10
Grog (2-3) mm	6	6	6	6
Brown fused alumina(1-2)mm	13	13	13	13
Brown FusedAlumina(0.5-1)mm	12	12	12	12
Silliminite Send (0.2-0.5) mm	9	9	9	9
Brown Fused Alumina (0.075-0.2)	11	11	11	11
White Tabular Alumina (-325#)	18	16	14	12
ALUMINA-1	8	8	8	8
Cement	7	7	7	7
Micro-silica	6	8	10	12
Disperses	0.1	0.1	0.1	0.1
PPF	0.05	0.05	0.05	0.05

5.3.4 Setting time

Setting time of the self-flow low cement castable as a function of micro-silica content has been shown in Fig 5.11.

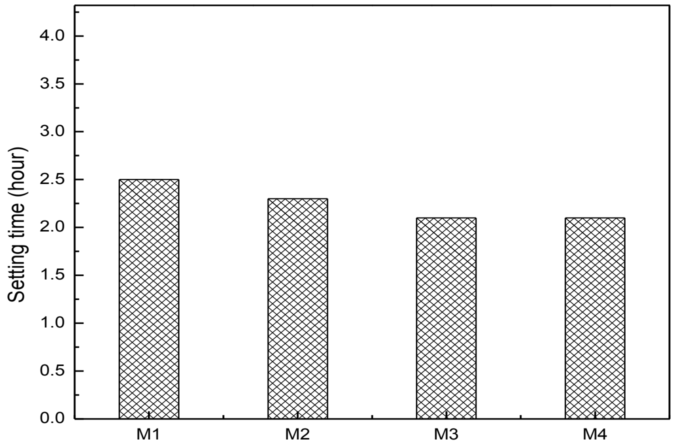


Fig 5.11 Setting time of castable as a function of micro-silica content

It could be seen from the figure that setting time of the samples does not have any significant change as a function of micro-silica percentage. Setting time could be related to the surface area of the micro-silica powder. In the present study surface area of micro-silica has not change, thus there was no significant change in setting time.

5.3.5 Flow property

Variation in water requirement to obtain 100% flow of the castable studied as a function of micro-silica percentage graphically presented in Fig 5.12.

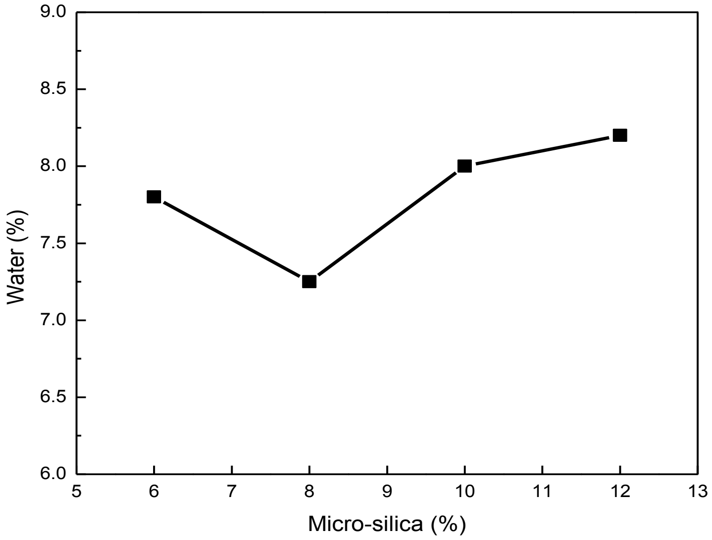


Fig5.12 Required water as a function of micro-silica content to achieve 100% flow

It could be seen from the figure that with increase in percentage of micro-silica, there was decreases the requirement of water to achieve 100% flow up to 8% micro-silica addition there after it increases. The decrease in water requirement with increase in amount of micro-silica could be related to packing density of the castable. The micro-silica used in the present study has particle size in micron range, which acts as filler and fills the void space of matrix aggregate, thereby decreases the water requirement of the castable. However, addition of micro-silica content greater than 8% lead to an excess micro-silica which is required to fill the voids of aggregates. This excessive micro-silica content in the composition increases the water requirement due to surface area of fine powder.

5.2.5 Apparent porosity and bulk density

Apparent porosity of the low cement self-flow low cement castable as a function of temperature and amount of micro-silica has been shown in Fig 5.13.

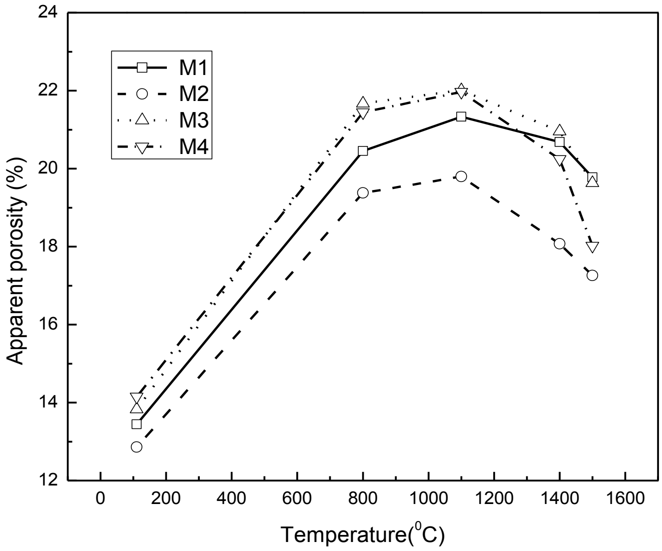


Fig 5.13 Apparent porosity of low cement self-flow castable as a function temperature and micro-silica content

It could be seen from the figure that apparent porosity of the samples has significant change as a function of amount of micro-silica. It could be correlated to the micro-silica content with increasing micro silica porosity decrees up to 8% thereafter amount of it increased. Amount of micro-silica showed the effect on water requirement to achieve 100% flow. Castable prepared with 8% micro-silica had lowest water requirement (Fig.5.12), thus the increase in porosity for these samples were found to be minimum as a function of temperature. A similar trend has been observed for the other castable studied.

Moreover, all the samples showed similar temperature dependent behaviour. It has been found that the apparent porosity of the sample increases with temperature in the intermediate temperature range (RT-1100°C), thereafter it decreases with increase in temperature. The increase in porosity in the intermediate temperature zone could be due to the de-hydroxylation of the high alumina cement hydrates, which occurs in this temperature range [5]. The decrease in apparent porosity in the high temperature zone (>1100°C) is attributed to the densification of the samples at high temperature.

Bulk density of the castable as a function of temperature and micro-silica content has been shown in Fig 5.14.

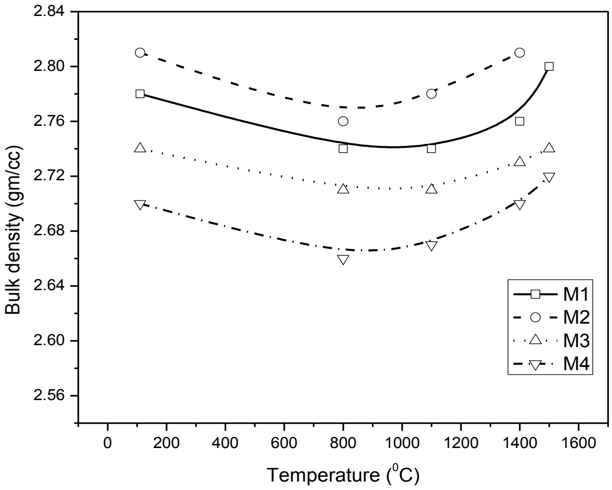


Fig 5.14 Bulk density of low cement self-flow castable as a function of temperature and micro silica content

It could be seen from the figure that apparent porosity of the samples has significant change as a function of amount of micro-silica. However, all the samples showed similar temperature dependent behaviour. It has been found that the bulk density of the sample decreases with increase in temperature in the intermediate temperature (RT-1100^{o}C), thereafter it increases with increase in temperature. The decreased in bulk density in the intermediate temperature zone could be explain on the basis of de-hydroxylation of the high alumina cement hydrates, which occurs in this temperature zone [5]. The increase in bulk density in the high temperature zone (>1100^{o}C) is attributed to the densification of the samples at high temperature. It could be also observed that castable with 8% micro-silica had highest bulk density, whereas castable with 12% micro-silica had lowest bulk density. It could be correlated with micro-silica content hence the water requirement of the castable. Sample prepared with 8% micro-silica contains only 7.25% water, which was lowest as comparison to other. Thus it shows high bulk density.

5.2.6 Cold crushing strength

Cold crushing strength of the castable as a function of temperature and amount of micro-silica has been shown in Fig 5.15.

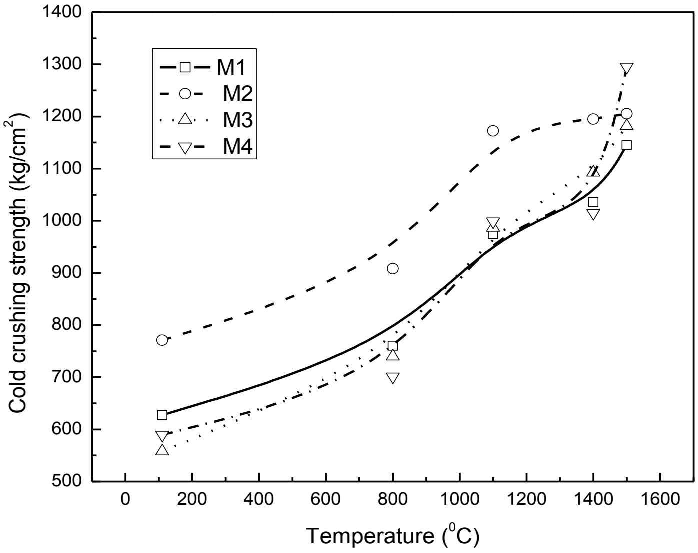


Fig 5.15 Cold crushing strength of low cement self-flow castable as a function of temperature and micro-silica content

It could be seen from the figure that cold crushing strength of the samples has significant change as a function of amount of micro-silica addition. However, all the samples showed similar temperature dependent behaviour. It has been found that the cold crushing strength of the sample increases with temperature. At intermediate temperature range, bulk density decreases and apparent porosity increases, but there was no decrease in CCS, which was due to formation of thickening gel from the micro-silica added and pseudo-boehmite gel formed due to hydration of alumina [34,60]. It could be explained in the same line as described in section 5.1.6. Cold crushing strength increased with increasing temperature at high temperature (>1100^{o}C) due to densification of sample. It has been found that cold crushing strength of the castable increases with micro-silica content up to 8% thereafter it decreased. It could be correlated with the micro silica content hence water requirement and bulk density of the castable. The more the packing density of the sample the more would be the bulk density of the sample. At high temperature (>1400°C), cold crushing strength increases with increase in amount of micro-silica. It may be due to phases present at this temperature range and will be discussed later.

5.2.7 Cold modulus of rapture

Cold modulus of rapture of the castable as a function of temperature and amount of micro-silica has been shown in Fig 5.16.

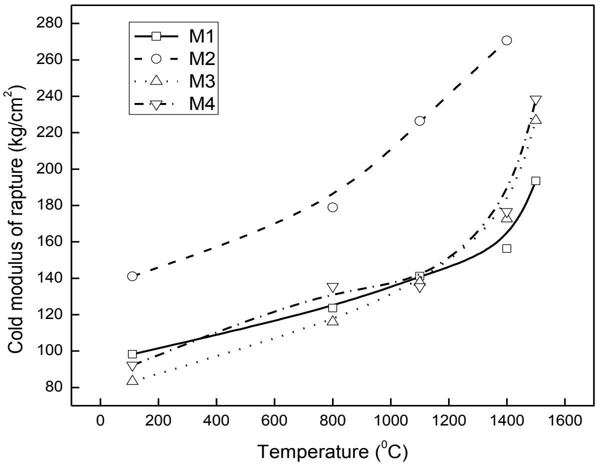


Fig 5.16 Cold modulus of rapture of low cement self-flow castable as a function of temperature and micro-silica content

It could be seen from the figure that cold modulus of rapture of the samples has significant change as a function of amount of micro-silica. However, all the samples showed similar temperature dependent behaviour. It has been found that the cold modulus of rapture of the sample increases with temperature. At intermediate temperature CMOR increased with temperature. This behaviour could be explained in the same line as described in section 5.1.6. At high temperature (>1100°C) it increased due to densification. It has been also observed that with increase in micro-silica content CCS increases up to 8% thereafter deceases. It could be correlated to the micro-silica content hence water requirement and bulk density. Sample with 8% micro-silica showed high CMOR due to had high bulk density. At high temperature range (>1400oC), CMOR increases with increase in amount of micro-silica. It may be due to the secondary mullite phase formation at this temperature range.

5.2.8 Permanent linear change

Permanent linear change of self-flow castable as a function of calcined alumina at 1400 and 1500^0C has been shown in table V.VI.

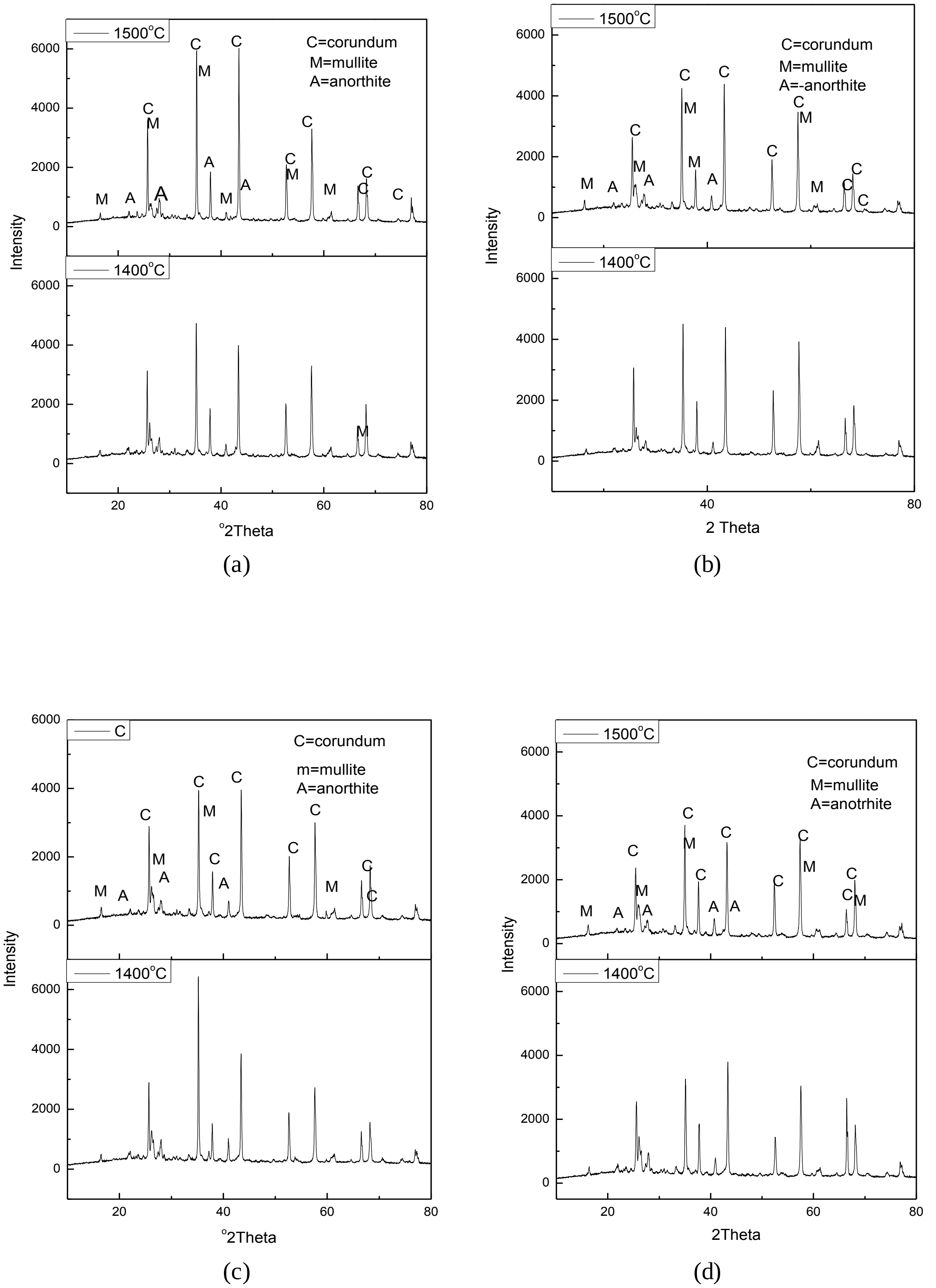
Table V.VI Permanent linear change of self-flow castable as a function of micro-silica

Temperature (^{0}C)	M1	M2	M3	M4
1400	-0.48	-0.34	-0.47	-0.52
1500	-0.41	0.28	-0.42	-0.44

It could be seen from the table that the entire four samples had negative permanent linear change except castable with 8% micro-silica, it had positive PLC. It could be found that negative PLC could be correlated with densification of the sample. Sample with high initial porosity showed high densification and thus have more negative PLC. However, the positive PLC observed in the castable prepared with 8% micro-silica could not be explained at this stage. It may be due the secondary mullite formation.

5.2.9 Phase analysis (XRD):

XRD pattern of the castable sintered at different temperture has been shown in the Fig. 5.17.



(a)

(b)

(c)

(d)

Fig 5.17 XRD pattern of the self-flow low cement castable fired at different temperature for (a) 6% micro-silica, (b) 8% micro-silica, (c) 10% micro-silica and (d) 12% micro-silica containing castable

Analysis of XRD patterns revealed the presence of corundum, mullite and anorthite as the major phase in the samples. Semi-quantitative analysis of the different phases as a function of micro-silica content has been presented in Table V.VII. It could be seen that with increase in sintering temperature as well as micro-silica content in the formulation mullite phase in the sample increases and could be related to the increases micro-silica content in the formulation. Cold crushing strength and cold modulus of rapture could be correlated with mullite formation. it could be seen by semi-quantative analysis of the sample, with increase the amount of micro-silica, mullite phase increased at 1500°C, thus increased the strength of the castable with increase in micro-silica content.

Table V.VII Semi-quantitative analysis of the phases present in the sample sintered different temperature

Sample	Temperature	Corundum	Mullite	Anorthite
M1	1400	59	18	23
	1500	50	29	21
M2	1400	42	35	22
	1500	43	25	33
M3	1400	63	19	18
	1500	55	26	19
M4	1400	50	22	28
	1500	21	34	45

5.4 Effect of Amount of Calcined Alumina in 70% Al_2O_3 self-flow low cement castable

Studies on bauxite based 70% Al_2O_3 low cement castable with the variation of different amount of micro-silica suggests that castable prepared 8% micro-silica showed enhanced physical and mechanical behaviour as compared to the other. So in the present study, self-flow castable has been prepared with 8% micro-silica and attempt has been made to study the effect of calcined alumina (ALUMINA-1) content on the physical and mechanical behaviour of the castable. Self-flow castable prepared in this study had also q-value 0.22.

5.4.1 Batch formulation of self-flow low cement 70% Al_2O_3 castable with different calcined alumina content

Raw materials used in the body formulations of self–flow low cement castable are same as in previous sections 5.1. Self-flow castable was prepared with same q-value 0.22 with varying the ratio of tabular alumina (WTA) and ALUMINA-1 calcined alumina, wherein micro-silica content was fixed at 8%. Batch formulation of self-flow low cement has been given in Table V.VIII.

Table V.VIII Batch formulation of self-flow low cement castable with different calcined alumina content

Composition	S1	S2	S3	S4
Chinese Bxt. (3-5) mm	10	10	10	10
Grog (2-3) mm	6	6	6	6
Brown Fused Alumina (1-2)mm	13	13	13	13
Brown Fused Alumina (0.5-1)mm	12	12	12	12
Silliminite Sand (0.2-0.5) mm	9	9	9	9
Brown Fused alumina (0.075-0.2)	11	11	11	11
White Tabular alumina (-325) mesh	18	16	14	12
Calcined alumina (ALUMINA-1)	6	8	10	12
Cement	7	7	7	7
Micro-silica	8	8	8	8
Dispersant	0.1	0.1	0.1	0.1
PPF	0.05	0.05	0.05	0.05

5.4.2 Initial setting time

Setting time of the castable as a function of amount of calcined alumina has been shown in Fig 5.18.

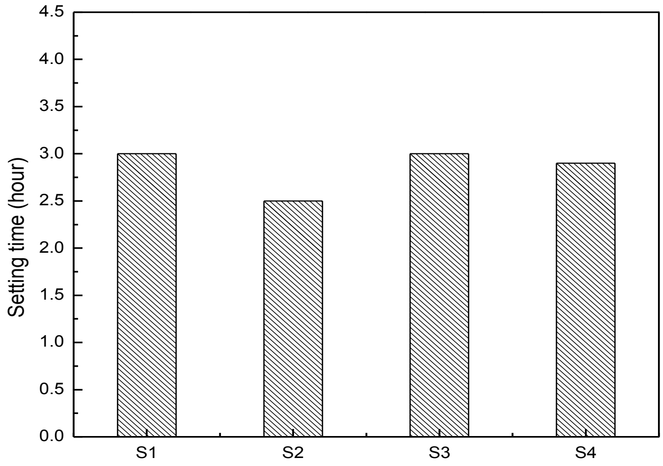


Fig 5.18 Setting time of low cement self-flow castable as a function of calcined alumina

It could be seen from the figure that setting time of the samples does not have any significant change as a function of calcined alumina percentage. Calcined alumina affects setting behaviour of the castable with pseudo-boehmite phase formation which is related to the surface area of the calcined powder. In the present study the surface area of the calcined alumina has not changed, thus there was no appreciable change in the setting time of the castable.

5.4.3 Flow properties of self-flow low cement castable as a function of calcined alumina content

Variation in water requirement to obtain 100 % self-flow of low cement castable studied as a function of calcined alumina percentage graphically presented in Fig. 5.19.

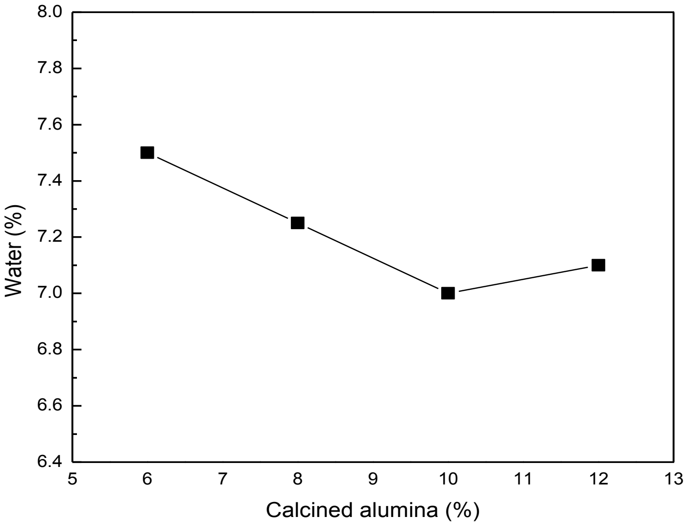


Fig 5.19 Required water for low cement self-flow castable as a function of calcined alumina content to achieve 100% flow

It could be seen from figure that with increase in percentage of calcined alumina, there was decreases the requirement of water to achieve 100% flow up to 10% calcined alumina addition there after it increases. The decrease in water requirement with increase in amount of calcined alumina could be related to packing density of the castable. Particle size of calcined alumina used in this study is 4µm (Fig 5.1). Calcined alumina act as filler in castable and fill the voids of aggregate and thereby increase the packing density. The increase in packing density is attributed to the low water requirement. Further increase in the amount of calcined alumina (>10%) increases the water requirement. Addition of calcined alumina (>10%) may lead to an excess alumina addition which is required to fill the voids of the aggregates. These excessive alumina content in the body increases the water requirement owing to the fine surface area of the powder.

5.4.4 Apparent porosity and bulk density

Apparent porosity of low cement self-flow castable as a function of temperature and amount of calcined alumina has been shown in Fig. 5.20.

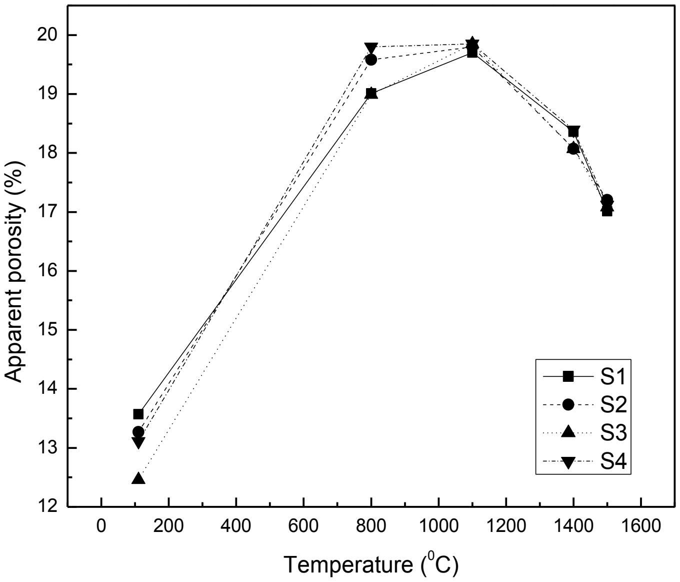


Fig 5.20 Apparent porosity of self-flow low cement castable as a function of calcined alumina temperature

It could be seen from the figure that apparent porosity of the samples have significant change as a function of amount calcined alumina content. Apparent porosity decreases with increase in the calcined alumina content up to 10% thereafter increases. Apparent porosity could be correlated to the micro-silica content hence water requirement. Castable with 10% calcined alumina showed low bulk density due to it had lowest water content.

Moreover, all the samples showed similar temperature dependent behaviour. It had been found that the apparent porosity of the sample increases with temperature up to 1100°C, thereafter it decreases with increase in temperature. The increase in apparent porosity in intermediate temperature zone could be related to de-hydroxylation of high alumina cement hydrates [5]. The decrease in apparent porosity in high temperature zone (>1100°C) is correlated with densification of castable at high temperature.

Bulk density of the castable as a function of temperature and amount of calcined alumina has been shown in Fig 5.21.

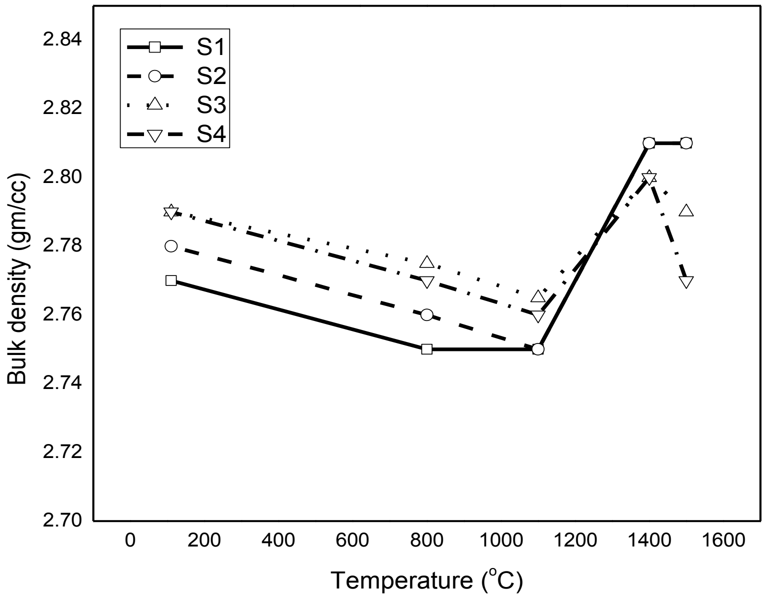


Fig. 5.21 Bulk density of low cement self-flow castable as a function of calcined alumina and temperature

It could be seen from the figure that the all the samples showed similar behaviour with temperature. It has been found that density of the sample decreases with increase in temperature up to 1100°C and could be correlated to the de-hydroxylation of high alumina cement hydrates. Bulk density of the samples was found to increase with increase in temperature above 1100°C. It could be correlated with the densification of the sample at high temperature.

Moreover, it could also be found that bulk density of the samples has significant change as a function of calcined alumina content. It has been seen from the figure that with increase the calcined alumina content up to 10% bulk density increase thereafter decrease. Castable prepared with 10% calcined alumina had highest bulk density and castable with 6% calcined alumina had lowest bulk density. It could be correlated with amount of water requirement. Castable containing 10% calcined alumina required only 7% water that was lowest as compared to other thus it had highest bulk density. At high temperature above 1400°C there was decreased in bulk density with increasing calcined alumina. Sample prepared with 12% calcined alumina had high lowest bulk density. It could be correlated with amount of calcined alumina. Calcined alumina had high surface area as well as high reactivity and it reacts with impurity to form glass thus decreases the bulk density or may be due to secondary mullite formation.

5.4.5 Cold Crushing Strength (CCS)

Cold crushing strength of self-flow low cement castable as a function of temperature and amount of calcined alumina has been shown in Fig. 5.22.

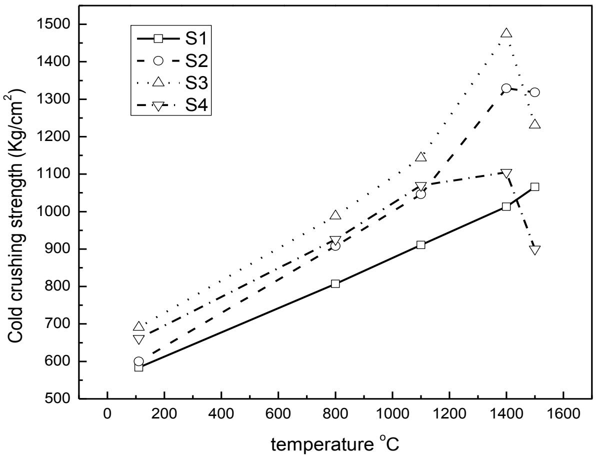


Fig 5.22 Cold crushing strength low cement self-flow castable as a function of calcined alumina and temperature

It could be seen from the figure that cold crushing strength of the entire sample showed similar temperature dependent behaviour. At intermediate temperature range bulk density decreases and apparent porosity increases, but there was no change in cold crushing strength due to formation of thickening gel and pseudo-boehmite gel [34,60]. It could be explained in same line as described in section 5.1.7. Increase in CCS with increase in temperature due to related to the densification.

Moreover, it could be also seen from the figure that cold crushing strength of the samples has significant change as a function of amount of calcined alumina addition. Castable prepared with 10% calcined alumina had high CCS and sample prepared with 6% calcined alumina had low CCS in the studied temperature range. It could be correlated with micro-silica content hence water content and bulk density of the sample. Sample with 10% calcined alumina had high bulk density thus it had high CCS as compared to other formulations. At high temperature above 1400°C, CCS decreases with increasing calcined alumina. The decrease in CCS value in the high temperature may be related to the possible phases formed and will be discussed later.

5.4.6 Cold Modulus Of Rapture (CMOR)

Cold modulus of rapture of self-flow castable as a function of temperature and amount of micro-silica has been shown in Fig. 5.23.

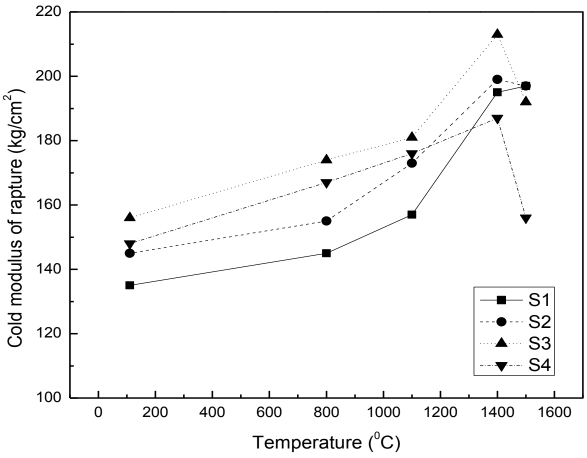


Fig 5.23 Cold modulus of rapture of low cement self-flow castable as a function of calcined alumina and temperature

It could be seen from the figure that cold modulus of rapture of the entire sample showed similar temperature dependent behaviour. At intermediate temperature range bulk density decreases and apparent porosity increases, but there was no change in cold modulus of rapture, which was due to formation of pseudo-beohmite and thickening gel [34,60]. It could be explained same line as described in section 5.1.7. CMOR increased with increase in temperature above 1100^{o}C due to densification and may be explained from the phases present in the sample.

Moreover, it could be also seen from the figure that cold modulus of rapture of the samples has significant change as a function of amount of calcined alumina addition. Below 1400^{o}C, castable prepared with 10% calcined alumina had high CMOR and sample prepared with 6% calcined alumina had low CMOR. It could be correlated with bulk density of the castable. Sample with high 10% calcined alumina had high bulk density (Fig 5.21), thus it had high CMOR. Above 1400^{o}C, CMOR decreased with increase in calcined alumina addition in the body formulation. It could be related to the phases formed in the castable matrix and has been discussed later.

5.4.7 Permanent linear change (PLC)

Permanent linear change of self-flow castable as a function of calcined alumina at 1400 and 1500^{0}C has been shown in table V.IX.

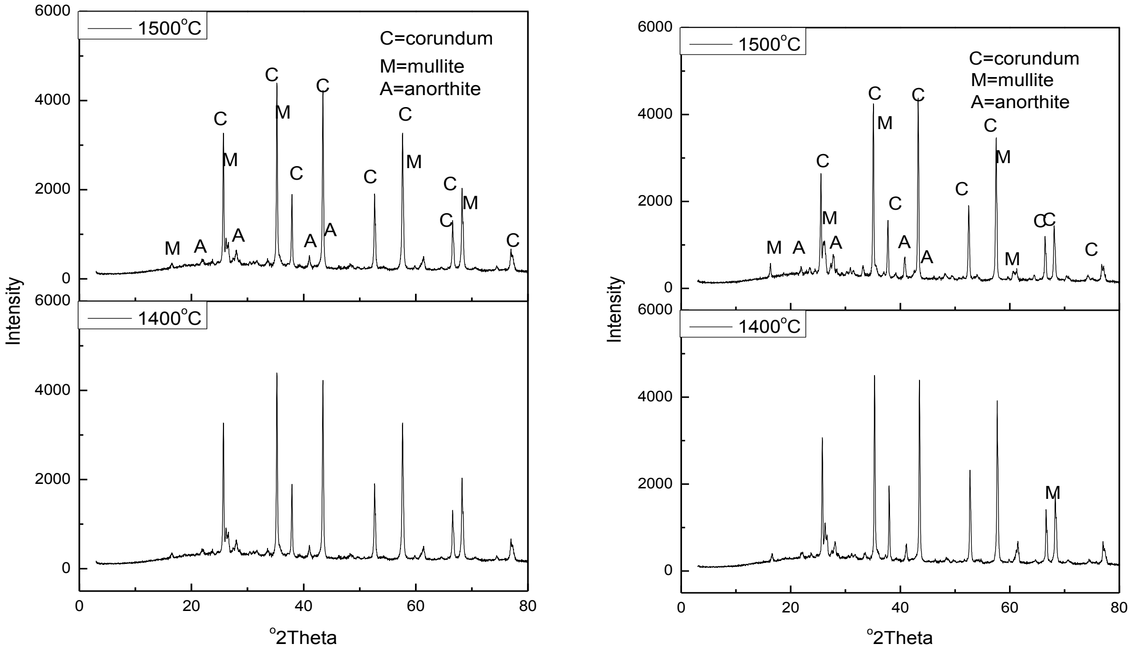
Table V.IX Permanent linear change of self-flow castable as a function of calcined alumina

Temperature (^{o}C)	**S1**	**S2**	**S3**	**S4**
1400	-0.45	-0.34	-0.29	-0.32
1500	0.21	0.28	0.30	0.57

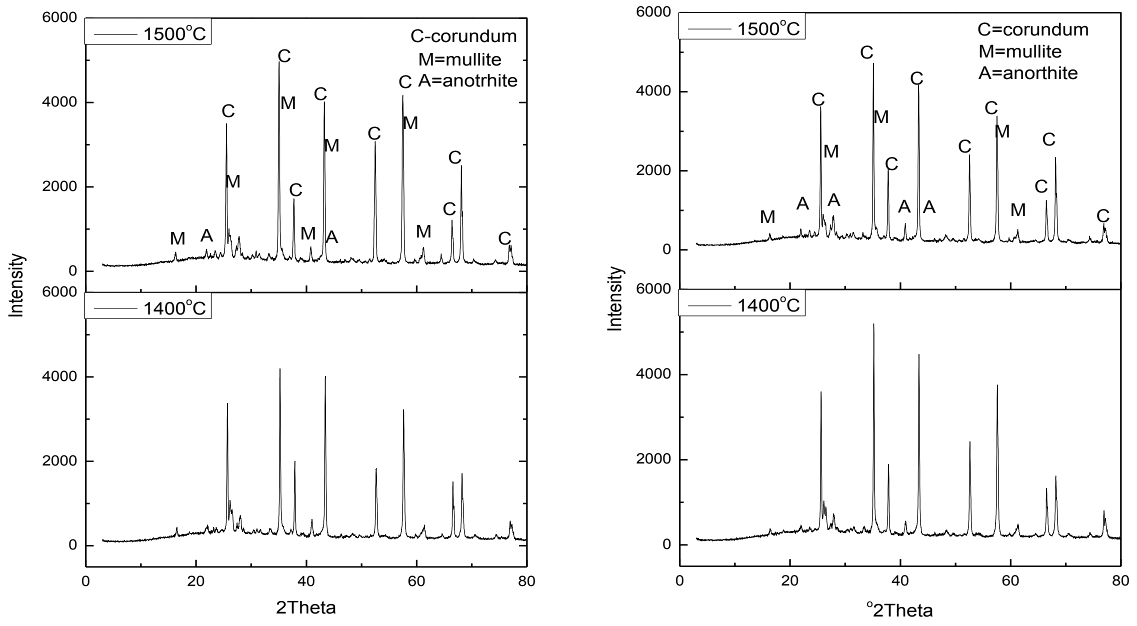
It could be seen from the Table that at 1400^{o}C, all the samples showed negative permanent linear change. Castable prepared with 10% calcined alumina had low PLC and castable prepared with 6% calcined alumina had high PLC. It could be correlated with bulk density of the castable at low temperature. Sample with 10% calcined alumina had high bulk density and thus showed low negative PLC. It could also found that, at 1500°C, all samples showed positive PLC. It may be related to the final phases formed in the castable matrix sintered at 1500°C. Formation of secondary mullite or glassy phase may lead to the increase in volume of sample and may provide positive PLC in the sample.

5.3.8 Phase analysis (XRD)

XRD patterns of the castable as a function of temperature and calcined alumina content has been shown in the Fig. 5.24. Analysis of XRD pattern of the sample sintered at 1400 and 1500°C shows the presence of corundum, mullite and anorthite as major phases. Semi-quantitative analysis of these phases as a function of calcined alumina has been shown in Table V.X



(a) (b)



(C)

(d)

Fig. 2.24 XRD pattern of the self-flow low cement castable sintered at different temperature with (a) 6%, (b) 8%, (c) 10% and (d) 12% calcined alumina

Table V.X Semi-quantitative analysis of sample sintered at different temperature as a function of calcined alumina:

Sample	Temperature	Corundum	Mullite	Anorthite
S1	1400	62	21	17
	1500	53	16	31
S2	1400	42	35	22
	1500	43	25	33
S3	1400	61	21	18
	1500	44	20	35
S4	1400	51	25	24
	1500	56	17	27

Decrease in the cold crushing strength and cold modulus of rapture with increasing calcined alumina at 1500°C, could be explained by semi-quantitative analysis of XRD pattern. It could be seen from the table that mullite phase decreased at 1500°C. It may be due to glassy phase formation at this temperature zone. Mullite may be dissolved in this glassy phase thus strength of the sample decreases.

5.5 Effect of Amount of Setting Accelerator on Properties of 70% Al_2O_3 Low Cement Self-Flow Castable

Studies on bauxite based 70% Al_2O_3 low cement self-flow suggests that castable prepared with 10% calcined alumina and 8% micro-silica showed enhanced physical and mechanical behaviour as compared to the other. So in the present study, shotcreting castable has been prepared with 10% calcined alumina and 8% micro-silica and attempt has been made to study the effect of setting additive (water glass) content on the setting time and physical and mechanical behaviour of the castable.

5.5.1 Batch formulation of self-flow low cement 70% Al_2O_3 castable with setting accelerator content

Raw materials used in the body formulations of self–flow low cement shotcreting castable are same as in previous section 5.1. Self-flow shotcreting castable was prepared with same q-value 0.22 with varying the percentage of setting accelerator with 8% calcined alumina and 10% calcined alumina. Batches formulation of self-flow low cement castable has been shown in Table V.XI with different micro-silica content.

Table V.XI Batch formulation of low cement self-flow shotcreting castable

Composition	A1	A2	A3	A4
Calcined Bxt. (3-5) mm	10	10	10	10
Grog (2-3) mm	6	6	6	6
Brown Fused Alumina (1-2)mm	13	13	13	13
Brown Fused Alumina (0.5-1)mm	12	12	12	12
Silliminite Sand (0.2-0.5) mm	9	9	9	9
Brown Fused alumina (0.075-0.2)	11	11	11	11
White Tabular alumina (-325) mesh	14	14	14	14
Calcined alumina (ALUMINA-1)	12	12	12	12
Cement	7	7	7	7
Micro-silica	8	8	8	8
Dispersant	0.1	0.1	0.1	0.1
PPF	0.05	0.05	0.05	0.05
Water glass	0.1	0.15	0.25	0.5

5.5.2 Setting time

Setting time of the self-flow low cement castable as a function of setting additive content has been shown in Fig. 5.25.

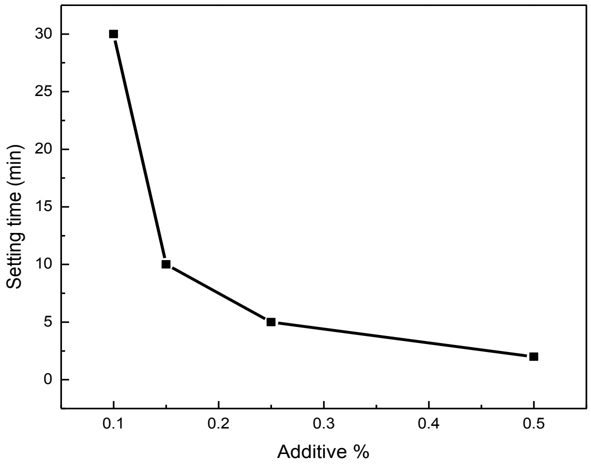


Fig. 5.25 Setting time of low cement self-flow castable as a function of setting accelerator content

It has been shown in the figure that setting time of samples have significant change as a function of water glass content. It has been observed from the figure that with an increase in the amount of water glass setting time of the castable decreases exponentially. The mechanism of this behaviour is that, an aqueous solution of water glass comes in to contact with air and form a film. This film prevents vaporization of moisture forming carbonate which increases with decrease in molar ratio. The viscosity increases with increase in molar ratio and shorter the setting time of the sample. Water glass used in this study had high molar ratio, thus it showed the effect on setting time. Water glass reacts with carbon dioxide (CO_2) gas and form carbonate consolidated surface. Water glass and CO_2 reaction given below.

$$Na_2O.nSiO_2 + CO_2 + mH_2O \rightarrow nSiO_2.mH2O + Na_2CO_3$$

Setting time within the range of 5 to 10 minute is good for shotcreting application.

5.5.3 Apparent porosity and bulk density

Apparent porosity of the castable as a function of temperature and amount of water glass has been shown in Fig. 5.26:

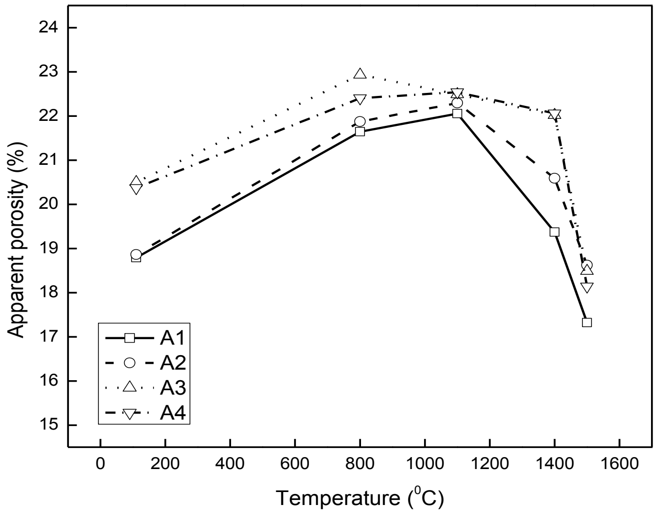


Fig. 5.26 Apparent porosity of self flow low cement shotcreting castable as a function of settimg accelerator content and temperature

It could be seen from the figure that apparent porosity of the samples showed similar temperature dependent behaviour. It has been found that the apparent porosity of the sample increased with temperature up to 1100°C, thereafter it decreases with increasing temperature. The increase in apparent porosity in intermediate zone could be related to the de-hydration of calcium aluminate cement hydrates. [5]. The decreased in apparent porosity in high temperature (>1100°C) zone is attributed to the densification of the castable in the high temperature zone. It could be also seen that there is significant change in apparent porosity as a function of water glass content. However, this variation could not be related with the variation of the water glass content. The castable containing high amount of water glass had low setting time. Thus the samples made with these castable could not be casted properly and may lead to low BD in the samples.

Bulk density of the castable as a function of temperature and amount of water glass has been shown in Fig. 5.27.

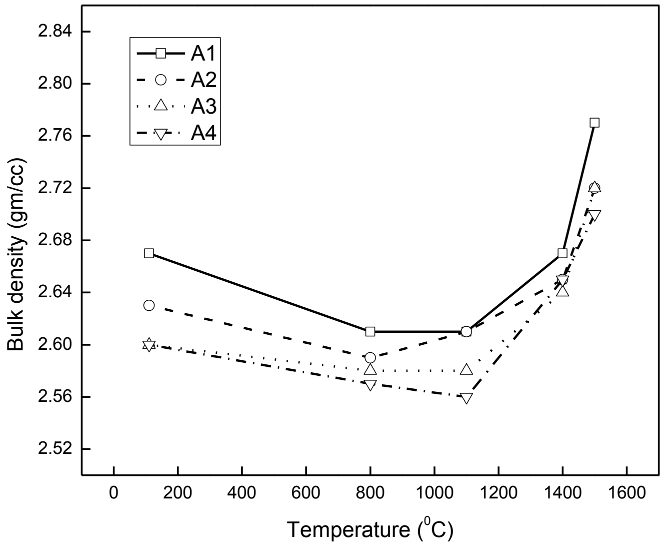


Fig 5.27 Bulk density of low cement self-flow castable as a function of accelerator content and temperature

It could be seen from the figure that the bulk density of all samples studied showed same tends as a function of temperature. It has been found that density of the sample decreases with increase in temperature up to 1100°C due to de-hydroxylation of calcium aluminate cement hydrates. Thereafter, bulk density increases with increasing temperature (>1100°C). It could be due to densification of the sample. It could be also seen form the figure that there is significant change in bulk density as a function of water glass content. However, it could not be related with water glass content. It may be also possible that sample prepared with high amount of water glass, could not casted properly. It could be related to the setting time. High amount of water glass (0.25 and 0.5%) containing castables showed low setting time.

5.5.4 Cold crushing strength (CCS)

Cold crushing strength of self-flow low cement castable as a function of temperature and amount of water glass addition has been shown in Fig. 5.28.

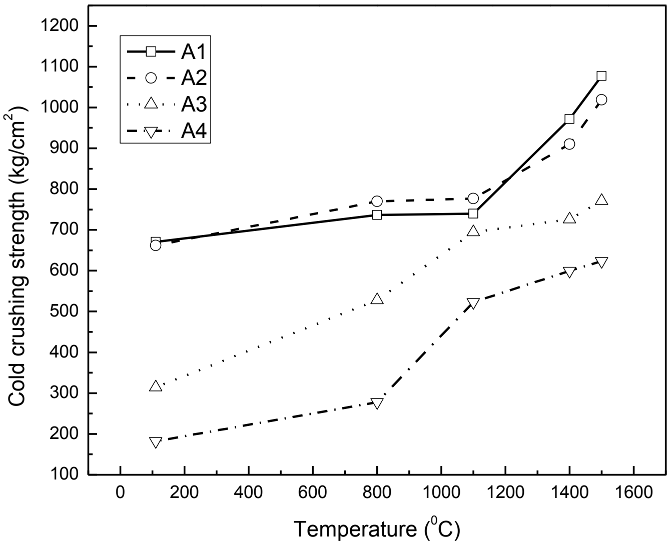


Fig. 5.28 Bulk density of low cement self flow shotcreting castable as a function of setting additive and temperature

It could be seen from the figure that cold crushing strength of all samples showed similar tends with increasing temperature. At temperature below 1100^{o}C, bulk density decreases and apparent porosity increases, but there was no change in cold crushing strength. It could be due to presence of micro-silica and calcined alumina in the castable and they react with water and formed thickening gel and pseudo-boehmite gel respectively [34,60]. It could be explained in same way as described in section 5.1.7. CCS increased with increasing temperature due to densification of the castable. Moreover, it could also be seen from the figure that increases water glass content, CCS of the sample decreases. It could be correlated with bulk density of the sample. Castable prepared with high amount of water glass shows high bulk density, thus shows high CCS It could also found from the figure that CCS of the castable containing water glass is low as comparison to castable without additive. It could also be related with bulk density of the castable. Sample without water glass had high bulk density, thus it shows high cold crushing strength. But the difference in cold crushing strength of the sample was around ± 10%.

5.5.5 Cold Modulus of rapture (CMOR):

Cold modulus of rapture of self-flow castable as a function of temperature and amount of water glass content has been shown in Fig 5.29.

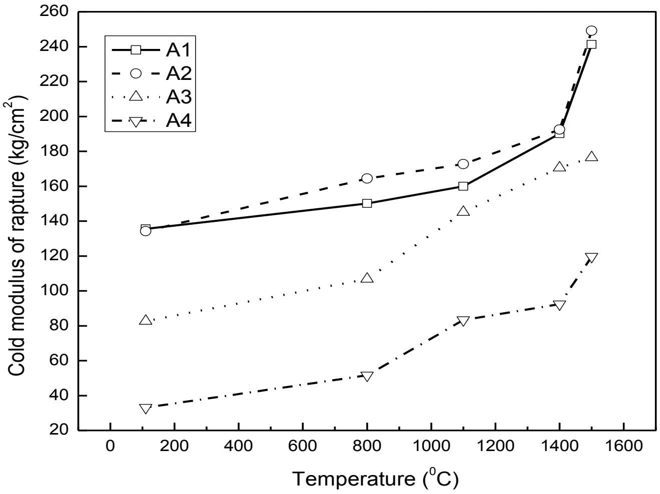


Fig 5.29 Cold modulus of rapture of low cement self-flow shotcreting castable as a function of setting additive and temperature

It could be seen from the figure that cold modulus of rapture of all the samples showed similar tends with increasing temperature. At temperature below 1100°C, bulk density and apparent porosity of the sample decreases and increases respectively, but cold modulus of rapture shows no change. It could be due to formation of thickening gel and pseudo-boehmite gel [34, 60]. It could be explained in same way as described in previous section 5.1.7. Cold modulus of rapture of the samples increases with increase in temperature due to densification. It could also be seen from figure, that there was significant change in CMOR as a function of water glass content present in castable. Sample prepared with high amount of water glass showed low cold modulus of rapture. It could be correlated with bulk density of the castable.

Bulk density was low for castable that contains high amount of water glass, thus shows low value of CMOR.

5.5.6 Permanent linear change (PLC)

Permanent linear change (PLC) of the castable as a function of temperature and amount of water glass has been shown in table V.XII.

Table V.XII: permanent linear change of castable as a function of water glass at 1400 and 1500°C

Temperature (^{0}C)	A1	A2	A3	A4
1400	-0.72	-0.74	-0.83	-0.84
1500	-0.83	-0.89	-1.21	-1.28

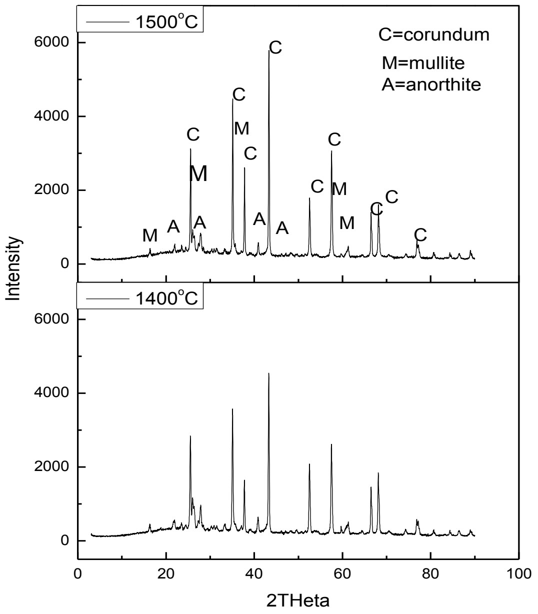
It could be seen from the figure that the all the samples had negative permanent linear change. However, all the samples showed increase in PLC with temperature due to densification of the sample. PLC of the sample with 0.1% water glass showed lowest value and sample with 0.5% water glass shows highest. PLC could be correlated to densification of the sample. Sample with 0.1% water glass had low amount of sodium content, hence is expected to show low densification and thus low PLC is observed.

5.4.6 Phase analysis (XRD)

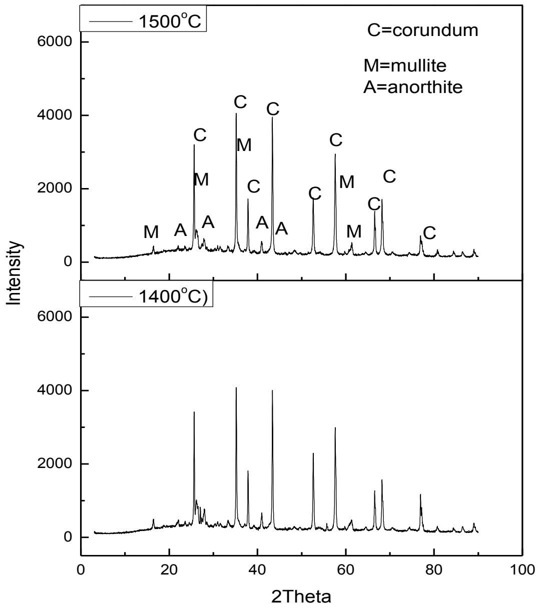
XRD pattern of the castable as a function of temperature has been shown in the Fig. 5.30. Analysis of XRD pattern shows the presence of corundum, mullite and anorthite as major phases in the sample fired at 1400 and 1500°C. Semi-quantitative analysis of XRD pattern of all the samples as a function of water glass has been given in the Table V.XIII.:

Table V.XIII Semi-quantitative analysis of sample fired at 1400 and 1500°C as a function of water glass:

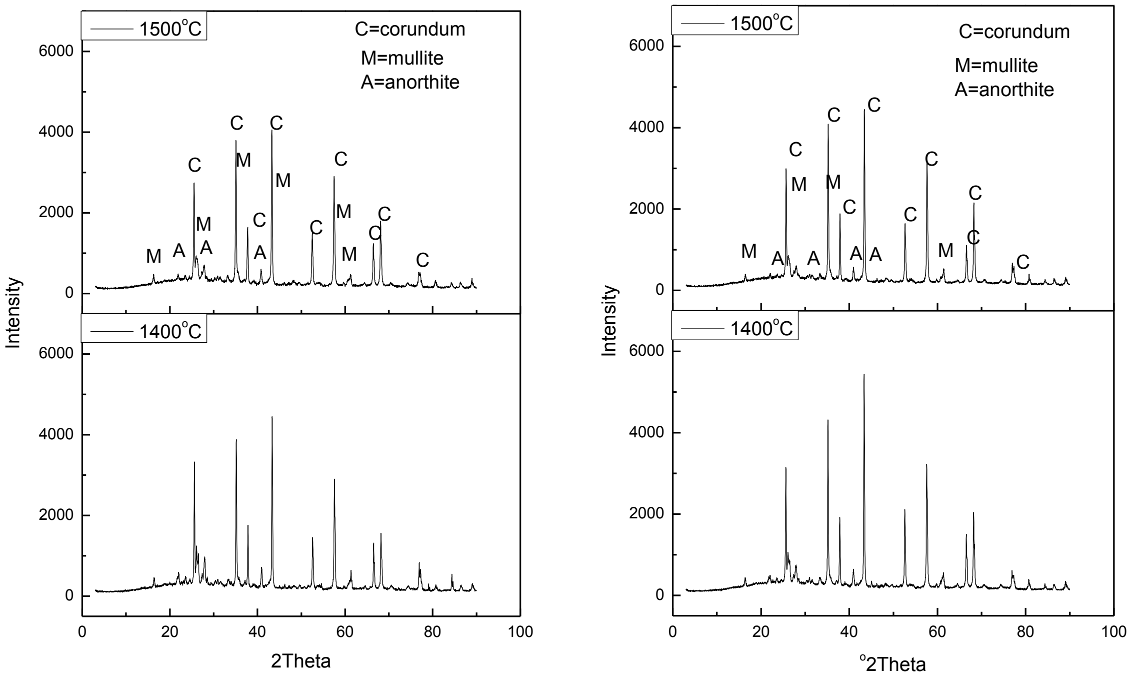
sample	**Temperature**	**Corundum**	**Mullite**	**Anorthite**
A1	1400	41	24	35
	1500	56	18	28
A2	1400	64	18	18
	1500	66	18	17
A3	1400	60	17	24
	1500	44	23	33
A4	1400	68	16	17
	1500	64	22	14



(a)



(b)



(c) (d)

Fig 5.30 XRD pattern of the self-flow low cement castable fired at different temperature for (a) 0.1% water glass, (b) 0.15% water glass, (c) 0.25% water glass and (d) 0.5% water glass containing castable

.

CHAPTER -VI

CONCLUSION

CONCLUSION

Present study deals with development of 70% Al_2O_3 low cement vibratable and self-flow castable. An attempt has also been made to develop a shortcreating mass with the addition of a set accelerating agent. The study focuses particle size and particle size distribution of calcined alumina filler on the flow behaviour of the LCC, optimization of amount of calcined alumina and micro-silica content of a self-flow castable body formulation in order to achieve flow at low water content. Physical and mechanical properties of the optimized self-flow castable has also been studied as a function of set accelerating agent. The following conclusion could be achieved from the present study.

1) **Studies on the particle size and particle size distribution of calcined alumina filler on the properties of 70% Al_2O_3 low cement vibratable castable:**

a. The flow behaviour of the castable depends strongly on the particle size distribution rather than that of the particle size of the filler alumina powder. This behaviour could be related to the filling up the voids of aggregates in the castable with the filler particle.

b. Apparent porosity and bulk density also depends particle size and particle size distribution of the filler alumina particle and could be attributed to packing density of castable. However apparent porosity and bulk density of the castable increases and decreases respectively with temperature up to 1100°C due to de-hydroxylation of cement hydrates thereafter it follows' reverse tends due to densification.

c. Cold crushing strength and modulus of rapture of the castable depends up on particle size of the filler alumina particle rather than the particle size distribution. Castable prepared with fine calcined alumina filler (having high surface area) showed high CCS and CMOR. CCS and CMOR increases with temperature due to formation of pseudo-bheomite phase and thickening gel at intermediate temperature range and at high temperature it increase due to sintering.

d. Permanent linear change of the castable also depends on particle size and particle size distribution of filler alumina. It is mostly dependent of the particle size distribution rather than that of particle size. This behaviour could be attributed to the bulk density and porosity of the sample**.** Castable samples with high bulk density showed low PLC value.

2) **Studies on the effect of micro-silica amount on 70% Al_2O_3 self-flow low cement castable:**

a. Water percentage of the castable decreased with increase in micro-silica up to 8% further increase in micro-silica content water requirement value increased. This could be correlated with the filling of the voids of the aggregates with the micro fine silica filler.

b. Apparent porosity and bulk density of the castable depends on the amount of micro silica content. Apparent porosity decreases and bulk density increases with increase in micro-silica content upto 8% addition thereafter it follows a reverse trend. This could be related to the filling up of the aggregate voids by micro-silica and hence the water requirements of the castable for 100% flow.

c. Cold crushing strength and cold modulus of rapture depends on amount of micro silica content. Cold crushing strength and cold modulus of rapture increases with increase in micro-silica content up to 8% addition thereafter it decreases. This could be related to the filling up of the aggregate voids by micro-silica and hence the water requirement of the castable to achieve 100% flow.

3) **Studies on the effect of calcined alumina content on the 70% Al_2O_3 self-flow low cement castable**

a. Water requirement for castable decreases with increasing the amount of calcined alumina up to 10% further increase in calcined alumina content water requirement increases. It could be related with the filling the voids of the aggregate with fine calcined alumina.

b. Apparent porosity and bulk density of the castable depends on the micro-silica content. Apparent porosity and bulk density of the castable decreases and increases respectively with increase the amount of calcined alumina up to 10% thereafter, it decreases. It could be correlated with filling the voids of the aggregate and hence with the water requirement to achieve 100% flow.

c. Cold crushing strength and cold modulus of rapture of the castable depends on micro-silica content. CCS and CMOR increases with increase in Micro-silica content up to 10%. It could be correlated with the filling the voids of the aggregate hence with water requirement and bulk density.

4) **Studies on the effect of quick setting additive on the 70% Al_2O_3 self-flow low cement castable**:

a. With increase in the amount of quick setting additive setting time deceases exponentially. Setting additive solution in water form a gel and it was dehydrate by air drying and gave quick setting. 0.25 to 0.15% amounts of quick setting additives may be suitable for shotcreting technique.

b. Samples prepared with high amount of setting agent showed inferior properties. This may be related with the short casting time which leads to fabrication of samples with inferior properties.

REFERENCES

---

1. LI Zaigeng and ZHOU Ningsheng, "Technology Advancement in Preparation and Application of Monolithic Refractory" China's Refractory, vol. 10 No. 1, (2001), 3-10.
2. ZHOU Ningsheng, HU Shuhe and ZHANG Sanhua, "Advances In Monolithic Refractory Castable" China's Refractory, Vol. 13 No. 2, (2004), 3-12.
3. Plibrico, "Technology of monolithic refractory".
4. Charles A. Schacht, "Refractories Handbook", Marcel Dekker, Inc., New York- Basel, (2004)
5. Christopher Parr, Fabien Simonin, Bruno Touzo, Chistoph Wohremeyer, Benoit Valdelievre and Akihiko Namba, "The Impact of Calcium Aluminate Cement Hydration Upon the Properties of Refractory Castable" Journal of the Technical Association of Refractories, Japan, 25 [2], (2005), 78-88.
6. Nilforoushan, Mohammad Reza and Talebiaan, Nasrien, "The Hydration Products of a Refractory Calcium Aluminate Cement at Low Temperatures" Iran. J. Chem. Chem. Eng. Vol. 26, No.2, (2007), 71-76.
7. Nicolas Schmitta, Jean-Franciois Hernandeza, Vincent Lamoura, Yves Berthauda, Pierre Meunierc, Jacques Poirierd, "Coupling Between Kinetics of Dehydration, Physical and Mechanical Behaviour for High Alumina Castable" Cement and Concrete Research 30, (2000), 1597- 1607.
8. Paulo Cesar Evangelista, christopher Parr and Cetharine Revais, "control of formulation and optimization of self-flow castable based on calcium aluminate cement" refractory application and news, Vol 7, No 2, (2002), 14-18.

9. Ye Guotian and Li Zaigeng, “trend in monolithic refractories technology” chiana’s refractory vol 8, no 3, (1999), 15-18.

10. A.R. Studarta, V.C. Pandolfellia, E. Tervoortb, L.J. Gauckler, “Selection of dispersants for high-alumina zero-cement refractory castables” Journal of the European Ceramic Society 23 (2003) 997–1004.

11. Y. A. Marques and R. G. Pileggi, “Setting Additive influence on the Thermomechanical Propperties of Wet Shotcrete Refractory castable Matrices” American ceramic society bulletin, August (2005), 9201 – 9206.

12. Bjorn Myhre and Aase M. Hundere, “The Use of Particle Size Distribution in Development of Refractory Castable” Presented at XXV ALAFAR Congress, Dec. 1-4, (1996).

13. Aase Hundere, Bjorn Myhre and Bjorn Sandberg, “Free-flowing castable – a prerequisite for wet-gunning of refractory castable” Presented at the VIIth International Matallugical Conference in Ustron, Poland, May (1997).

14. A. H. M. Andreassen and J. Andersen, Kolloid Z, 50, (1930), 217-228.

15. D. R. Dinger and J. E. Funk, Interceram 41, (1992), [1] 10-14.

16. S. Ganguli "Influence of particle size distribution on flow, microstructure and some special monolithic” (2008).

17. B. Myhre, “Particle Size Distribution and its relevance Refractory Castable” In Proc.2nd Indian Int. Ref. Con., New Dehli, India, Vol. I, (1996), 47-56.

18. Y. Kutmen Kalpakli, “Effect of particle size distribution on the refractory properties and corrosion mechanism of ultra –low cement castable,” vol.34 [2], December (2008), 81-88.

19. E. Karadeniz, C. Gurcan, S. Ozgen and S. Aydin, "Properties of Alumina based Low Cement Self-flow Castable refractory" Journal of the European Ceramic Society 27, (2007), 1849-1853.
20. Toshisiko Kando, Satoshi Terayama, Katsuaki Funato, Tsuyoshi Okamato and Seijiro Tanaka, "relation between grain size distribution and fludity of refractory castable" Journal of the Technical Association of Refractories, Japan, 100.
21. Aya Kusunoki, Yoshitaka Sadatomi, Yoshihiro Sasatani and Tsubasa Nakamichi, "Effect of particle size distribution on the fluidity of alumina magnesia system castable" Unitecr (2011), 1-D-6.
22. S. Ganguli, S. Satapathy, A. K. Samanta, S. Adak, P.B. Panda, "Development of castable in Al_2O_3-$MgAl_2O_4$ system" 2nd ICRJ, , (2010), 161-167.
23. Rafael Salomao and Victor C. pandofelli, "particle size distribution effect on the drying efficiency of polymeric fibers containing castables" Ceramic international 34, (2008), 173-180.
24. Subrata Banerjee, "Monolithic Refractories" Answer Technology Inc. Illinois USA.
25. Christopher Parr, Catherine Revais, Nancy Bunt and Duncan Jones, "Ageing of Refractory Castable" Unitcer vol. 1 (1997); 81-90
26. Jason M. Canon, Todd P. Sander, Jeffrey D. Smith and Robert E. Moore, "the effect of organic fibre addition on permeability of refractory concrete", Unitecr vol. 2, (1997), 583 – 592.
27. Yozo Yukino, Nobuyuki Takahashi and Makoto Ishikawa, "Effects of Curing and Drying Conditions On Properties of Low Cement Castable" Unitecr (2003), 276- 279.
28. R. Saloma˜o, F.A. Cardoso, M.D.M. Innocentini, L.R.M. Bittencourt, V.C. Pandolfelli, "*Effect of polymeric fibers on refractory castables permeability*", Am. Ceram. Soc. Bull. 82 (4) (2003) 51–56.

29. Hong Peng and Bjorn Myhre, *"Effect of dispersant and raw materials on placing properties and shelf life of bauxite based low– and ultra-low cement castable"* Aachen (2010), 62 – 65.

30. I.R. Oliveira, V.C. Pandolfelli, *"Does a tiny amount of dispersant make any change to refractory castable properties?"* Ceramics International 36, (2010), 79–85

31. Hiroshi Shikona, Jyouki Yoshitomi, Mitsuo Kanda, Sotoyuki Kirinati, Masataka Sato and Yukio Sasagawa, "role of silica flour in low cement castable" Taikabutsu Overseas Vol. 10, No. 1, 17-22.

32. Alani Mathieu, Alani Capmas, Jean pierre Bayoux and Denis Richon, "Calcium aluminate cement and reactive alumina" unitecr (1997), 672-682.

33. Toshihide Yumoto, Toshihiko Kondo, Matsuiti Yoshimura, Shichi Hitomi and Yukio and Yukio Oguti, "effect of content of Alumina cement, Silica flour and added water on strength of castable", Taikabutsu Overseas, Vol. 13 No.2, (1993), 3-6.

34. Dr. A. K. Samanta, S. Satpathy, Dr. S. Adak and Dr. A. K. Chattopadhyay, "Effect of Calcium Aluminate Binder and Microsilica on Thermo-Mechanical Properties of Low Cement Castables", unitecr (2011), 31-D 11.

35. B.Myhre, A.M. Hundere and H. Feldborg, "Corelation between mullite formation and mechanical properties of refractory castable at elevated temperatures," VIII Int. Met. Conf., Ustron, Poland May, (1999), 25-28

36. Aase M. Hundere and Bjorn Myhre, "Mullite Bonded Castable" Proc. Am.Ceram. Soc, Ohio, (1997).

37. Lu Yichum and Li Ziageng, "Study of self bonded high performance mullite castable" China's refractory vol. 5 No. 4; (1996), 27-34.

38. Joseph S. Masaryk, Richard A. Setinke and Ralph B. Videtto, "development and use of low cement castable, self-flow castable" unitecr (1993), 527-538.

39. Koji Ide, Minoru Kataoka, Kazuhiro Furut, Yoshiaki Kawase, Fokuyashi Isomura, Kenji Nakao, Shigeru Mino and Yoshitaka Senno, “Development of a self-flow castable for steel ladles” Taikabutsu Overseas, vol.17 No.1 (1996), 53-57.
40. Aase Hundere, Bjorn Myhre and Bjorn Sandberg, “Free flowing castable- a prerequisite for wet gunning of refractory castable”, Presented at the VII-th International Metallurgical Conference in Ustron, Poland, May (1997), 1- 11.
41. Chen Zhiquang, “Flow and flow decay of refractory castable” China’s refractory, vol 12, No 4, (2003), 16-19.
42. R. Sarkar and A. Mishra, “High-Alumina self-flow castable with different cement binder”, Interceram [2] (2012), 107-111.
43. Bejorn Myhre, “micro-silica in alumina based low cement castable. the effect of micro-silica addition on flow” presented at XXIII ALAFAR congress, in Puerto Vallarta, Mexico Nov. (1994).
44. Bjorn Myhre, “The effect of microsilica on the flow and strength of alumina castable” American Ceramic Society, april, 18-22, (1993).
45. Hong Peng, Jian Li and Biorn Myhre, “Effect of micro-silica on properties of corundum-mullite self-flow ultra low cement castable”, 7th India international refractories congress 2008, 177-182. Bjorn Myhre and Aase M. Hundere, “Substitution of reactive alumina with microsilica in low cement and ultra low cement castable, Part 1: properties related to installation and demoulding” Unitecr (1997), 43- 52.
46. Bjorn Myhre and Aase M. Hundere, “Substitution of reactive alumina with microsilica in low cement and ultra low cement castable, Part 1: properties related to installation and demoulding” Unitecr (1997), 43- 52.

47. Aase Marie Hundere and Bjorn Myhre, "Substitution of reactive alumina with microsilica in low cement and ultra low cement castable, part 2: The effect of temperature on hot properties" Unitecr (1997), 91- 100

48. Vicki Jones, "Flow control of low cement self-flow castables", unitecr, vol 2, (1997), 635-644.

49. R. G. Pileggi, Y. A. Marques, D. Vasques Filho, V. C. Pandolfelli, N. Moreira And S.C. Frasson, "Evaluating the Shotcrete Performance of Refractory Castables", Proceedings of the 47th Annual Meeting of the Brazilian Ceramic Society 15-18June, (2003), 162-174.

50. Koji Watanabe, Makot Ishikawa and Mitsuru Wakamatsu, "Rehology of castable refractories" Taikabutsu overseas vol. 9[1] 41-53.

51. Liu Xinhong, Feng Long, Ye Fangboa and Zhong Xiangchong, "some influencing factor on rheological property of bauxite based castable matrix" China's refrctory, vol.21, No. 3, (2012), 20-24.

52. R.G. Pileggi, Y.A. Marques, D. Vasques Filho and V.C. Pandolfelli, "Shotcrete performance of refractory castable" refractories application and news, volume 8, number 3 May/June (2003), 15-20.

53. ACI committee 506, "guide to shotcrete," American Concrete Institute, ACI 506R-90 Third Printing, January (1994), pp. 3, sec. 1.5.

54. William G. Allen, "advanced equipment system for refractory placement" unitecr vol 2, (1997), 523-530.

55. Aase Hundere, Bjørn Myhre, Cecilie Ødegård and Bjørn Sandberg "wet shotcreting refractory castables with varying cement content" XIII Conference on Refractory castables Nov. (1998), 4-5.

56. Zhanimin Wang, Sanhua Zhang, Xiying Cao, Xia He and Zhengyong Bi, "Flowability and flocculation of wet gunning castables with different additives" Unitecr (2005), 413-418.

57. Eiji Motoki and Nobuki Tanaka, "Evaluation of quick setting additives for wet gunning installing" journal of technical associaltion of Refractory, 21 [2] (2001); 111-115.

58. Jinfu Yao, Shouxin Tian, Feifang Gan, Feng Wang, Zhenjun Liu Juyuan Chen Li Zhang and Li Tang, "research on asc hot shotcreting castable" unitecr, (2005), 484-488.

59. Chia-Hong Chen, "Application and Research of Wet-gunning Based on Colloidal silica for Main trough of Blast Furnace", unitecr , (2011), 2-B2-19

60. M. Nouri-Khezrabada, M.A.L.Brauliob, V.C.Pandolfellib, F.Golestani-Farda and H.R. Rezaie, "Nano Bonded Refractory Castable" Ceramics International 39 (2013), 3479–3497