Effect of different high alumina cements on the properties of self flow castable with distribution coefficient 0.21.

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

of

Bachelor of Technology

By
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108CR007

Supervisor
Dr. Ritwik Sarkar

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Contents

Certificate

This is to certify that the thesis entitled"Effect of different high alumina cements on the properties of self flow castable with distribution coefficient 0.21" submitted by Mr.Anupam Mishra(108CR007) in partial fulfillment of the requirements of the award of Bachelor of Technology degree in Ceramic Engineering at National Institute of Technology Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge the matter embodied in this thesis has not been submitted to any other institute/university for the award of any degree or diploma.

Date:

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Anupam Mishra

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Abstract

The aim of this project is to study the effect of varying concentration of binding phase on the properties of high alumina self flow castable with distribution coefficient q fixed at 0.21 according to dinger-funk's continuous particle size distribution model. The binders used were CA-14 cement and polycem-75 cement. The XRD analysis of the two types of cement binder used is done. The varying binder concentration used in the four batches were 4% CA-14 cement,

4% polycem-75 cement,6% CA-14 cement and 6% polycem 75 cement respectively .The batches are prepared according to the conventional processing techniques and water is added till

the self flowable characteristics is obtained .The batches were then dried at 110^0C for 36 hours

and fired at 1000^0C and 1600^0C . The final products were then characterized for bulk density,

volume shrinkage and cold crushing strength.

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List of abbreviations

Sl no	Abbreviation	Full form
1	HAC	High Alumina Cement
2	PSD	Particle Size Distribution
3	XRD	X-Ray Diffraction
4	BFA	Brown Fused Alumina
5	WFA	White Fused Alumina
6	WTA	White Tabular Alumina
7	C	CaO
8	A	Al_2O_3

1.Introduction

Introduction

Refractories are materials that can withstand high temperature ,so they have a high melting point. Refractories are used as a barrier between a high temperature zone and low temperature zone. The different classification of refractories according to the raw materials used to make them are fireclay, high alumina, silica ,magnesia, dolomite refractories, mag-carbon and mullite refractories .Refractories are futher classified according to the form in which they are used into shaped and unshaped type.Shaped refractories are formed by pressing whereas unshaped refractories are formed by casting ,gunning ,ramming ,patching. Unshaped refractories are advantageous over shaped refractories because they do not require firing, they form jointless linings (joints are most susceptible to corrosion so unshaped refractories will be more resistant to corrosion than shaped refractories), they require less skilled manpower for installation ,they can take any complicated shape. Therefore unshaped refractories are gaining popularity over

shape refractories nowadays.

Unshaped refractories are further classified into castables ,gunning masses, ramming masses and

plastic masses. In this project we concentrate on castables .Castables are combination of coarse

aggregates, finer aggregates and binders. Water is added to it to give it the required flowability

and deflocculant and set retarder are added ,so that the setting time increases and we enough time

to work with a proper mix.Castables are further divided into self flow and vibratable type.

Castables with greater amount of finer particle content tend to be self flowable and castables

with lesser finer content require vibration to take shape. The amount of finer particles content in

a castable can be judged from its distribution coefficient .If distribution coefficient is less then

the castable has more content of finer particles. Normally the castable is self flowable in nature

if the distribution coefficient is less than 0.25 and vibratable in nature if distribution coefficient

is more than 0.25.In this project our emphasis is on self flowable castables. Self flow castables

yield under their own weight and flow whereas vibratable castables will require an external load

for yielding. The binding phase we use is high alumina cement(HAC).The major phases present

in high alumina cement is $CaO.Al_2O_3$(CA), $CaO.2Al_2O_3$(CA_2) and $12CaO.7Al_2O_3$($C_{12}A_7$).$C_{12}A_7$

phase is the most quick setting phase and CA_2 phase is the slowest setting phase. The setting

time depends on the amount of calcia present in the phase ,the higher the amount of calcia present in the phase the more quick setting that phase is.The cements that we use as binders consists of mainly $CA_2$and CA phases. The main thing differenting the castable is the binding phase and the fired temperature. After the castables are prepared they are dried and then fired .Then the physical properties of the castables are tested to see which binder composition and firing temperature gives the best properties.

2.Literature Review

Literature Review

Refractory is any material that is capable of withstanding high temperature and high load even under the most extreme of conditions like highly corrosive and abrasive conditions. Refractory are further divided into two categories shaped and unshaped.

Shaped refractories are obtained by pressing operations whereas unshaped refractories are either self flowable or vibratable in nature, self flow refractories automatically flow to take the shape of the mould whereas vibratable refractories require vibration to take mould shape.

The particle packing in refractories can be divided into two categories discrete packing and continuous packing. In monolithics the type of packing plays a significant role. Furnacs had proposed discrete packing model. Furnacs had stated that maximum packing density is obtained when particles of smaller size fill the void between particles of larger size. According to andreassen's model particles cannot be of a particular size instead they come within a certain narrow size range. The cumulative percent finer than(CPFT) according to andreassen's model is

Given by

$CPFT=(d/D)^q \times 100.$

Where d is the particle size for which CPFT is being calculated,

D is maximum particle size.

q is distribution coefficient.

The drawbacks of andreassen's model is that he did not assume any minimum particle size and assumed that the particles are infinitesimal small which is practically not possible. So this model was modified by Dinger Funk who assumed a certain minimum particle to make the model more practical. The CPFT according to dinger funk model will be

CPFT= $((D^q-D_{min}^q)/(D_{max}^q-D_{min}^q))x\ 100$

Where D is the particle size for which CPFT is being calculated.

$D_{min}$is the minimum particle size.

$D_{max}$is the maximum particle size.

q is distribution coefficient.

Optimum packing is done in such a way that the castable requires minimum water for setting and porosity is less and packing density is more .This will ensure that the castable has higher physical properties like cold crushing strength and hot modulus of rupture.

Distribution coefficient determines whether a castable is self flowable or vibratable in nature. If distribution coefficient is less than 0.25 then the castable is self flowable in nature otherwise the castable is vibratable in nature .Lower the value of distribution coefficient the more finer particles the batch has hence the greater will be its flowability. Self flowable castables hence need to possess more amount of fines in order to be self flowable.

The binding phase in cement bonded castables is high alumina cement .High alumina cement consists of mainly the phases CA ,CA_2 and $C_{12}A_7$. Out of these phases $C_{12}A_7$ phase sets the most quickly and CA_2 takes the most time to set. The greater the amount of calcia in a phase the more quick setting that phase will be due to the property of calcia to absorb water. When water is added to the batch the high alumina cement absorbs water and this causes the setting of castable. Both physical and chemical reactions take place when water is added to high alumina cement . Hydration converts the powder which is

amorphous in nature to various hydrated phases .On firing the hydrated phases break down to form very reactive products, which again recrystallizes to anhydrous calcium aluminates. The major phase present in most high alumina cements is CA. When water is added to CA a suspension results and solid starts to dissolve .Hydrates of calcium aluminates are formed during this process .These hydrates nucleate and grow allowing more anhydrous CA into the solution .These mechanism results in formation of interlocking bonds leadin to the strengthening of the structure .At intermediate temperatures these hydration bonds break leading to weakening to the castables and when temperature is still raised higher the strength of castable increases due to sintering.

At relatively lower temperatures of less than 20^0C hexagonal hydrate phase of CAH_{10} forms and at higher temperatures i.e above 30^0C cubic phase of C_3AH_6 is rapidly formed. At intermediate temperatures another metastable hexagonal hydrate crystal C_2AH_8 is formed which converts to C_3AH_6 phase.

(C stands for CaO,A stands for Al_2O_3 and H stands for H_2O).

3.Experimental Procedure and Calculation

Experimental Procedure

Batch formulation

Sampling of raw materials

Coarse aggregates- Brown fused alumina, White tabular alumina, White fused alumina

Fine aggregates-Reactive Alumina(CL 370)

Binder-CA-14 cement,Polycem-75 cement.

Additives-Micro silica,Polyammonium methacrylate,Citric acid.

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

Size fraction(in mm)	(Raw Material)
-6 to +3	Brown Fused Alumina
-3 to +2	White Tabular Alumina

-2 to +1	White Tabular Alumina
-1 to +0.5	White Tabular Alumina
-0.5 to +0.3	White Fused Alumina
-0.3 to +0.15	White Fused Alumina
-0.15 to +0.0025	Reactive Alumina(CL 370)

3.1 table showing the size fractions and the corresponding raw material

Characterisation of raw materials

The XRD analysis of CA-14 cement and polycem-75 is done to identify the various phases

present in it.This is done by X-ray powder diffraction technique.

The characterization of raw material provided by the supplie was done by chemical

analysis. The presence of various oxides are as follows

Constituent	WTA grain	BFA grain	WFA grain	Alumina fines	Fume silica 971U	Polycem-75	CA 14
SiO_2	0.04	0.9	0.1	0.2	96.1	0.95	0.21

Al_2O_3	99.4	95.66	98.92	98.0	0.4	73.30	71.65
Fe_2O_3	0.04	0.4	0.06	0.06	0.1	0.20	0.11
TiO_2	_	1.64	Trace	0.11	_	_	_
CaO	_	0.7	0.1	_	0.2	24.50	26.92
MgO	_	_	_	_	0.1	0.45	0.31
Na_2O+K_2O	0.16	_	0.4	0.34	0.4	_	0.28

3.2 Table showing the chemical constituents of the respective raw materials

Other properties found out are

Property	WTA grain	BFA grain	WFA grain	Alumina fines	Fume silica 971U	Polycem	CA 14
Loss on ignition(LOI)	-	-	-	0.2	0.9	0.35	-
Average size	-	-	-	6-8µ	45µ	-	-
Bulk density	3.61 g/cc	3.83g/cc	3.77g/cc	-	-	-	-
Apparent porosity	3.92%	1.7%	1.8%	-	-	-	-
Specific surface area	-	-	-	-	20 sq.m/gm	4300 sq.cm/gm	4400 sq.cm/gm
Phase analysis	Corundum	Corundum	Corundum	Corundum	Amorphous	CA_2,CA	CA_2,CA

3.3 Table showing the physical properties of the raw material

By keeping the distribution coefficient at 0.21 we calculate the percentage of particles required

in the various size ranges to form the batch and correspondingly we find out the weight of the

material required in the various size ranges to for a batch of 2.5 kg.

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

$CPFT=((D^q-D_{min}^q)/(D_{max}^q-D_{min}^q))x100$

Particle size (in mm)	CPFT(in %)
6	100
3	83.2
2	74.4
1	61.2
0.5	49.6
0.3	42
0.150	33
0.0025	0

3.4 Table showing particle size and the corresponding CPFT

Particle size range(in mm)	Percentage of particles present in that size range
-6 to +3	16.8
-3 to +2	8.8
-2 to +1	13.2
-1 to + 0.5	11.6
-0.5 to +0.3	7.6
-0.3 to +0.15	9
-0.15 to +0.0025	33

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

Batch composition of high alumina cement castable ia as follows

Particle size range (in mm)	Percentage of particles in size range	Amount required in 2.5 kgs batch(in gms)
-6 to +3(Brown Fused Alumina)	16.8	420
-3 to +2(White Tabular Alumina)	8.8	220
-2 to +1(White Tabular Alumina)	13.2	330
-1 to +0.5(White Tabular Alumina)	11.6	290
-0.5 to +0.3(White Fused Alumina)	7.6	190
-0.3 to +0.15(White Fused Alumina)	9	225
-0.15 to +0.0025(Reactive Alumina(CL 370),Cement,Microsilica)	33	825

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

Apart from these citric acid (0.1 wt%) and polyammonium methacrylate (0.3 wt%) were added to the above batch along with the optimum amount of water during the mixing process.The amount of microsilica is 4 wt%, cement (4 or 6 wt%) and reactive alumina (CL 370) is 25 or 23 wt%. The sum total of reactive alumina + cement+ microsilica is always 33 wt%.

Preparation of castable sample

Mixing

The coarser fractions and the finer fractions of the batch were dry mixed separately in the Hobart mixer.After both finer and coarser parts mix among themselves properly ,then they are mixed together in the mixer.At the end of citric acid and polyammonium methacrylate were added amidst the gradual addition of water.

Casting

Water is added till self flowability is attained. Then after the mix is properly homogenized in the Hobart mixer, it is taken out for pouring in the moulds lubricated by grease. If the mix is not properly spreading in the mould we vibrate it a little with our hands,excess mix is taken out and the resultant mix in the mould is smoothened by a trowel.The moulds are kept in the normal atmosphere for 24 hours for setting.

Drying

We unscrew the moulds and demould the set castables. We clean the moulds with sandpaper for

further casting processes.The taken out castables are now put in the dryer at 110^0C for 24 hours.

After that we measure the weight and dimension of the castables.The dimensions of the castables

are measured with the help of vernier calipers with a least count of 0.02 mm.

Firing

At the end one batch consisted of total 6 samples .Two samples from each batch were

kept unfired ,two were fired at 1000^0C for 2 hours and two were fired at 1550^0C for 2

hours. After firing the dimensions of the samples were again measured.

Characterization of the products

The following properties of the samples are measured

Bulk Density

We measure the weight of the fired sample .We measure its dimension with the help of vernier

caliper (least count 0.02 mm) and find out its volume (length x breadth x height). We calculate

the bulk density by dividing weight by volume.

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

Volume Shrinkage

We measure the dimensions of the samples before they were fired and measure its pre firing

volume .After firing we again measure the dimensions of the sample and calculate its post firing

volume .The decrease in volume of the sample after firing is recorded as volume shrinkage.

Volume shrinkage= $((V_{uf}-V_f)/V_{uf})$x 100

Where V_{uf}=volume of the sample before firing

V_f= volume of the sample after firing

Cold Crushing Strength

The cold crushing strength of the samples were measured with the help of a compressive

Tester .Cold crushing strength is the maximum amount of load the sample can take

before complete breakage .Cold crushing strength is given by load/area. (units kg/cm^2).

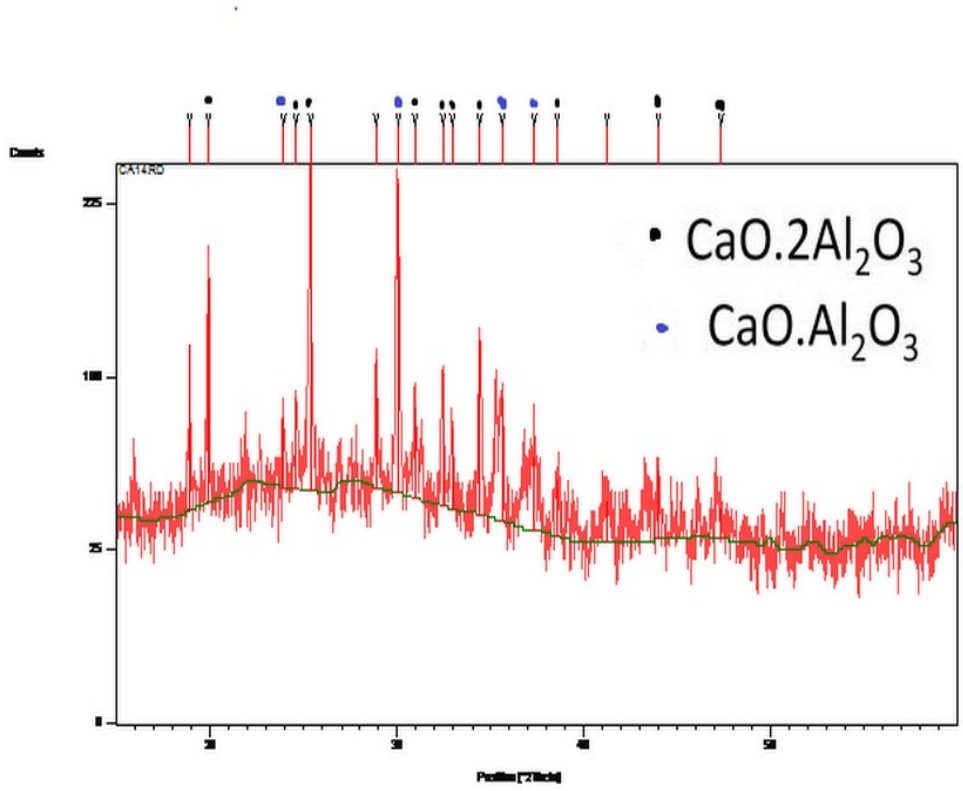
4.Results and Discussions

Particle size distribution(PSD)

After the cumulative percent finer than (CPFT) for each particle size is calculated the graph is plotted as follows

Raw Material characterization

We have done the XRD analysis of both the polycem-75 and CA-14 cement samples.The XRD analysis of the CA 14 cement showed the following results.



4.2 XRD analysis of CA-14 cement

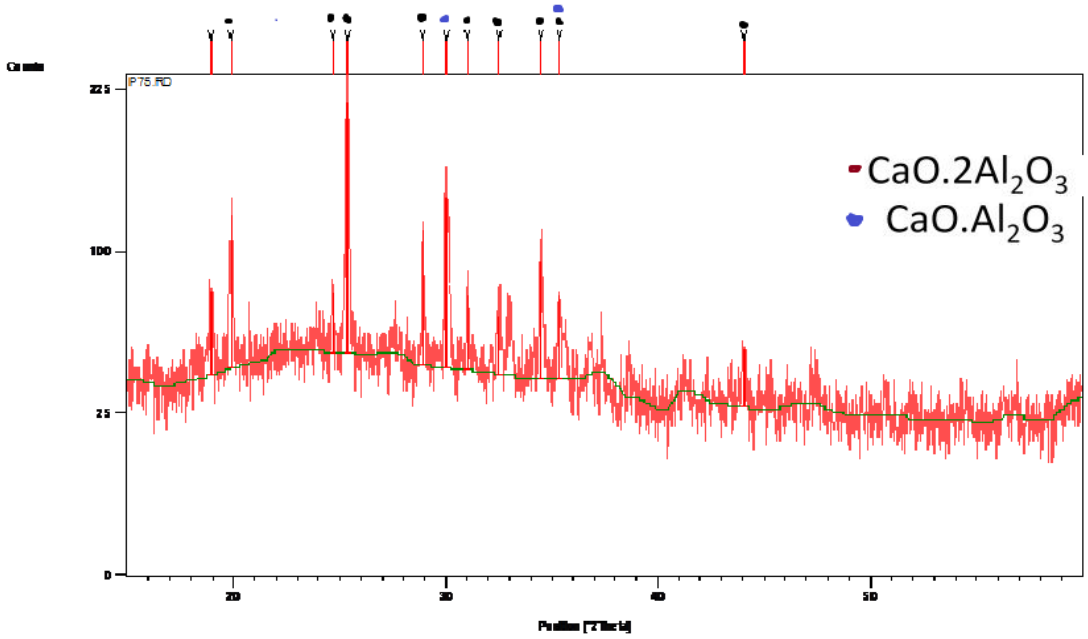
The XRD analysis consists of 17 peaks

Peaks matching with CA are-3,7,12,13

Peaks matching with CA_2 are-2,4,5,6,8,9,10,11,14,16,17

Peaks matching with neither CA nor CA_2 are-1,15(maybe belonging to $C_{12}A_7$)

The XRD analysis of polycem 75 is given done and the result is given below



4.3 XRD analysis of polycem-75 cement

The XRD analysis consists of 11 peaks.
Peaks matching with CA are 6,10
Peaks matching with CA_2 are 2,3,4,5,7,8,9,10,11
Peaks matching with both CA and CA_2 are 10
Peaks matching with neither are 1 (maybe belongs to $C_{12}A_7$ phase)

Characterization of sample

Water required for casting

Sample	Water required for casting(in ml)
4% CA 14 cement	120 ml
4% polycem 75 cement	110 ml
6% CA 14 cement	130 ml
6% polycem 75 cement	125 ml

4.4 Amount of water needed in each batch to attain flowability

We add water to get the desired flowability.With the increase in percentage of cement binder in

the castable water requirement increases due to the property of calcia phase to absorb water.

Bulk Density

The weight of the samples are first measured,then we measure the dimensions of the sample using vernier caliper(least count 0.02mm).From the dimensions of the sample volume is calculated(length x breadth x height).The bulk density is calculated by dividing weight by volume.

From the above graph we can see that bulk density of the sample increases with increase in firing

temperature because densification occurs with reduction of porosity .

Volume shrinkage

The dimension of the samples before firing and after firing are measured .From the dimensions

we calculate the pre-fired and post-fired volume.The reduction in volume is given as volume

shrinkage.

Cold Crushing Strength

The cold crushing strength is the maximum load per unit area that the sample can take before

breakage.It is calculated by load/area.

We see that the volume shrinkage increase with increase in firing temperature.This is due to increased densification process with higher firing temperature.

It is seen that cold crushing strength decreases for samples fired at 1000^0C.It happens due to

breakage of hydration bonds of the cement castables.Cold Crushing Strength again increases for

samples fired at 1600^0C because complete sintering has occurred at that temperature.

5.Conclusion

Conclusion

In this project the effect of using different types of cement as binders along with variation of their concentration is studied for high alumina self flow castable with distribution coefficient 0.21 .

The physical properties of the castables formed is tested. The bulk density comes out maximum for the sample fired at 1600^0C with a binder composition of 6% CA-14 cement.

The volume shrinkage is maximum for the sample fired at 1600^0C with a binder composition of 6% polycem-75 cement.

The cold crushing strength is highest for the castable fired at 1600^0C with a binder composition of 6% CA-14 cement. The cold crushing strength values for the castables using CA-14 cement binder is higher than the cold crushing strength of castables using polycem-75 cement as binder for every corresponding binder composition (either 4% or 6%).This shows that CA-14 cement is of better quality than polycem-75 cement and forms stronger interlocking bonds.

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