

# **Chapter-2**

*(Literature Review)*

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## Literature review

The present chapter is a detailed review of research works reported in literature related to preparation of calcium aluminate cements. Works on castables formulations with different cement contents and types of aggregates are also summarized. Finally their characterizations techniques are reviewed. Their properties, such as physical, chemical, thermal and mechanical properties, are reported. This literature review helped in planning my research work in the preparation of calcium aluminate cements by various techniques to obtain better cements at lower temperatures. Further refractory castables could be formulated to optimize their properties. In the following paragraph, some salient features of the calcium aluminate cements and their castable formulations are discussed:-

Solid state method by partially fusing and clinkering is the most common method for calcium aluminate cements preparation (Singh et al., 1990; Mohamed and Sharp, 1997; Mercury et al., 2005; Iftekhar et al., 2008). One of the problems derived from the use of natural raw materials in solid state is their coarse particle size that limits the reactivity. The other methods of preparation are Pechini (Choi and Hong, 2010), sol-gel (Aitasalo et al., 2002; Kurajica et al., 2009), combustion synthesis (Fumo et al., 1996; Tas, 1998; Yi et al., 2002). Douy and Gervais (2000) reported a synthesis method of amorphous  $\text{CaAl}_2\text{O}_4$  powders by spray-drying aqueous solutions of calcium and aluminum nitrates, followed by calcinations of product in order to completely decompose the salts. One of well-known approaches of ceramic powder synthesis is Pechini method (Choi and Hong, 2010). The process is based on the ability of certain organic acids to chelate the metal ion. On heating the chelates, polyesterification undergoes with the help of polyhydroxy alcohols and polymerized the resin forms. Then the polymerized resin is calcined to obtain calcium aluminate. Pati et al. (2002) and Gaki et al. (2007) have obtained nano particles of  $\text{CaAl}_2\text{O}_4$  by versatile solution based precursor solution method which involves chemical fixation of the cations by organic molecules. The temperature required for high alumina cement formation through solid state reactions is approximately  $1600^\circ\text{C}$ , whereas it

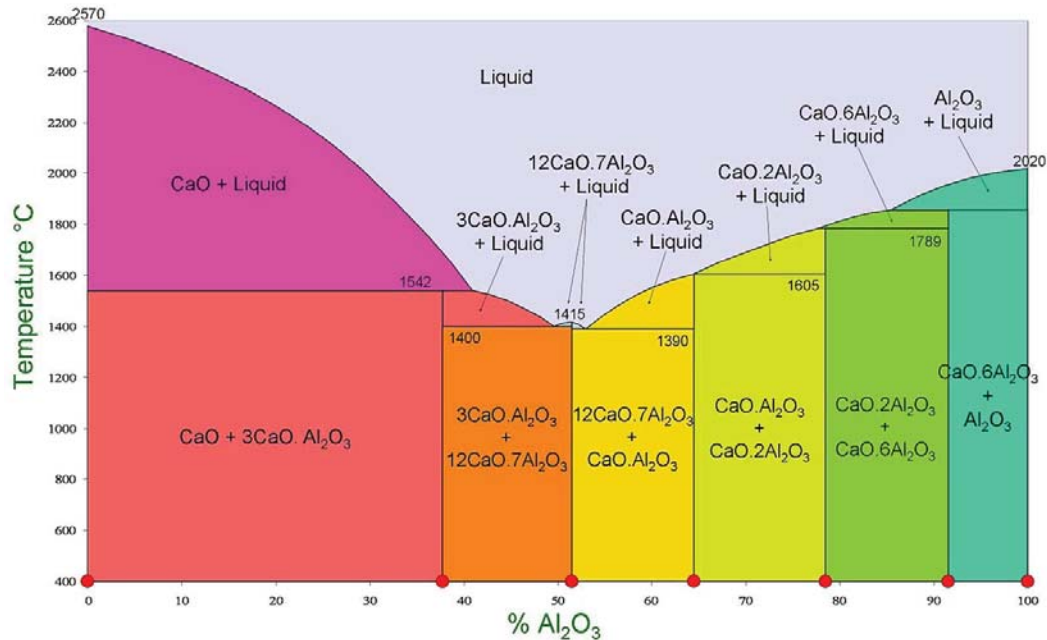
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can be made at much lower temperatures through wet chemical methods. However, wet chemical methods involve use of highly expensive materials and methods which in general cannot be applied as industrial production. So, present investigation was focused on developing a new method for preparing pure nano sized calcium aluminates cements.

One of the most intensively studied oxide systems is CaO-Al<sub>2</sub>O<sub>3</sub> binary system. Hydraulic properties possessed by some of the oxide compounds present in this system are CaO·Al<sub>2</sub>O<sub>3</sub> (CA), CaO·2Al<sub>2</sub>O<sub>3</sub> (CA<sub>2</sub>), 12CaO·7Al<sub>2</sub>O<sub>3</sub> (C<sub>12</sub>A<sub>7</sub>). These phases can be exploited as cementing phases in high alumina cement preparation. The other two compounds CaO·6Al<sub>2</sub>O<sub>3</sub> (CA<sub>6</sub>) and 3CaO·Al<sub>2</sub>O<sub>3</sub> (C<sub>3</sub>A) rarely find a position among high alumina cements phases (Chatterjee and Zhmoidin, 1972). For instance, CA<sub>6</sub> is hardly formed below 1600°C (Nurse et al., 1965). Mono calcium aluminate is the main component of high alumina cement and its hydration property gives rise to the fast setting properties of the material. One of the characteristics of CA and CA<sub>2</sub> synthesis via ceramic method, based on solid state reactions of oxides mixtures, is that its formation is always preceded by the formation of other calcium aluminates such as C<sub>12</sub>A<sub>7</sub> (Hallstedt, 1990). Regarding the possible intermediate phases preceding the CA and CA<sub>2</sub> formation via ceramic method, the results obtained by various authors are useful (Singh and Ali, 1980). Even though there is a compromise in the case of C<sub>12</sub>A<sub>7</sub> formation as a transitory phase in the CA and CA<sub>2</sub> synthesis. The same cannot be confirmed about the intermediate formation of other calcium aluminates such as C<sub>3</sub>A.

The term high alumina cements stands for a family of refractory cements for high performance application. The hydraulic strength development is due to a water bonding reaction of the calcium aluminate minerals to water-resistant hydrate phases (not water dissolvable). It is cold bonding system. Alumina contents of high performance HAC equal or exceed 70% and remaining CaO content. The difference in mineral constitution between HAC and Portland cement can be seen in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram. Portland cement occurs in the relatively high CaO region,

with  $C_2S$  and  $C_3S$  as its main constituents. Calcium aluminate cement on the other hand, occurs in a region with high  $Al_2O_3$  (and low  $CaO$  and  $SiO_2$ ), a factor that accounts for their higher melting point and used as refractory cement, where  $CA$ ,  $CA_2$ ,  $CA_6$ , and  $C_{12}A_7$  are the main constituents in high alumina cement. Regarding morphology of each phases of calcium aluminate cement, scanning electron microscopy is applied. However it is very important to discuss the  $CaO-Al_2O_3$  system for understanding the stability of different calcium aluminate phases. The system is presented in figure 2.1.



**Figure 2.1: Phase diagram of  $CaO-Al_2O_3$  system.**

The working life of high alumina cement in steelmaking and other ceramic industries is greatly dependent on the material's ability to withstand high temperatures without undergoing significant deformation and corrosion. Therefore, one of the approaches used throughout the latest decades to improve the performance of high alumina cement has been the reduction of the liquid content formed at elevated temperatures on high-alumina refractory castables. Low-melting point eutectic phases are often formed in these castables because of the reaction

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between alumina, SiO<sub>2</sub>, and CaO. Outstanding gains in refractoriness have been obtained through reduction of the amount of CaO, SiO<sub>2</sub> and increase in the Al<sub>2</sub>O<sub>3</sub> content in high-alumina cements.

## **2.1 Salient features of high alumina cements**

Calcium aluminate cements are cements consisting predominantly of calcium aluminates showing hydration behaviour. The main active constituent of calcium aluminate cements is mono-calcium aluminate (CaAl<sub>2</sub>O<sub>4</sub>) (Fu et al., 1996). It usually contains other calcium aluminates as well as a number of less reactive phases deriving from impurities in the raw materials. Rather a wide range of compositions is encountered, depending on the application and the purity of aluminium source used (Scrivener and Capmas, 2004). Fremy (1865) prepared various melt of lime and alumina and found them to possess good hydraulic properties. This was confirmed by Michaelis some years later. Schott (1906) had published a memoir showing the high strength which was given by fused calcium aluminates. Spackman's aluminate compounds were prepared by adding bauxite to high-alumina slags. A number of natural cements containing additions of Spackman's calcium aluminates were marketed in the United States around 1910 under the name of Alcoa natural cements, but their manufacturing were later abandoned. A further study of high alumina cements was carried out by P.H. Bates at the U.S.A. bureau of standards. The first results of which were published in 1921 (Ann et al., 2010). Bates prepared high-alumina cements by clinkering in a small (20-foot) rotary kiln and tested their properties in concretes. The high alumina cement termed as 'HAC' has CA as the main mineralogical ingredient along with CA<sub>2</sub>, C<sub>12</sub>A<sub>7</sub>, C<sub>4</sub>A<sub>3</sub>SO<sub>4</sub>, CA<sub>6</sub>, Al<sub>2</sub>O<sub>3</sub>, etc. In high purity, high alumina cement has low amount of impurities, i.e., less fluxing agents and hence enhanced refractory properties are improved. So it is better to use high purity of high alumina cement as a binder. Depending up on the amount of impurities present in the HAC it is divided in three groups (Taylor, 1999).

- a. Low purity
- b. Intermediate purity
- c. High purity

**Table 2.1: Composition and service temperature for high alumina cements.**

Types of cement	Composition (% indicated oxide)					Temperature
	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	
<b>Low purity</b>	36-47	35-42	3.5-9	7-16	0.50	1425°C
<b>Intermediate purity</b>	48-62	26-39	3.5-9	1-1.3	0.05	1650°C
<b>High purity</b>	70-80	18-26	0.0-0.5	0.1-0.2	---	< 1870°C

Depending upon the rate of hydration of different phases, high alumina cement is divided into three groups (Scrivener and Capmas, 2004).

**Table 2.2: The rate of hydration of different phases in high alumina cements.**

Hydration rate	Low purity	Intermediate purity	High purity
<b>Fast</b>	CA	CA	CA
	CA <sub>2</sub>	CA <sub>2</sub>	CA <sub>2</sub>
	C <sub>12</sub> A <sub>7</sub>	C <sub>12</sub> A <sub>7</sub>	C <sub>12</sub> A <sub>7</sub>
	C	C	C
<b>Slow</b>	C <sub>2</sub> S	C <sub>2</sub> S	-
	C <sub>4</sub> AF	C <sub>4</sub> AF	-
<b>Non hydrating</b>	CT	-	-
	A	A	-

High alumina cements are the most important type of non-Portland or special cements. Even so, the volume used each year is only about one thousandth of that of Portland cement. As they are considerably more expensive (four to five times), it is therefore not economic to use them as a simple substitute for Portland cement.

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Instead their use is justified in cases where they bring special properties to a concrete or mortar, either as the main binder phase or as one component of a mixed binder phase.

## **2.2 Manufacture of high alumina cements**

The raw materials used for the manufacture of high alumina cements are lime stone and bauxite. Although alumina is very widely distributed in nature, bauxite is the only suitable material available commercially on a scale adequate for cement production. Bauxite also forms the raw material for the manufacture of aluminum metal of alum and aluminum sulphate, and of certain types of refractories. The material used in Great Britain comes from France and Greece. During the last war, when bauxite was short, aluminum dross and the red mud from the Bayer process for production of alumina were used. High alumina cement was originally manufactured in a water-cooled vertical furnace, open-hearth furnace arranged with vertical stack. Electrical furnace is also used for the manufacture of high alumina cement for the small amount, and high-alumina cement is also produced by fusion in a rotary kiln of a type similar to that used in the manufacture of Portland cement. For low iron content (<4 % Fe<sub>2</sub>O<sub>3</sub>) in high alumina cement, it has not been found possible to clinker the raw materials containing a low iron content that are used commercially. And fast very fast cooling markedly reduces the rates of strength development though not the ultimate strength. Experiments by Berl and Lobein showed that the strength tended to increase the more slowly the mix was cooled and the more completely crystalline the product (Scrivener and Capmas, 2004).

An especially pure type of high alumina cement, white in color, is made in England, France and U.S.A. for use as a bonding agent for castable refractories for use at high temperatures. Alumina instead of bauxite is used as the raw material and the cement which contains 70-80% Al<sub>2</sub>O<sub>3</sub> is practically free from silica and iron oxide. The pure cement contains CA, CA<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> and has a much higher melting temperature than ordinary high alumina cement. It is made by a sintering or clinkering process. Sulpho-aluminate cement made by grinding together high

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alumina cement and gypsum or anhydrite was patented by the Lafarge Company and worked for a time in French Indo-China. It apparently proved difficult to control its properties, and its manufacture was discontinued.

Cement based on a mixture of high alumina cement, gypsum and hydrated tetra calcium aluminate is used in the U.S.S.R. as a shrinkage compensating cement studies on mixtures of high alumina cement and gypsum, dehydrated at 600–700°C. Suggested that a cement of this type has a resistance to chemical attack similar to high alumina cement, but lower heat of hydration and that it does not suffer from loss in strength when cured at temperatures up to 50°C. This type of cement is, in fact, very similar to the super sulphated slag cements, for, in both, a major product of hydration is calcium sulpho-aluminate. This compound is stable up to about 50°C but at higher temperature it loses water and at 75°C there is a considerable loss in strength with super sulphated cement. It also does not appear possible to get the very high strengths at one day, which is characteristic of high alumina cement at ordinary temperatures, form its mixes with calcium sulphate. The high alumina cement made commercially has been classified by Robson into four types (Scrivener and Capmas, 2004).

**Setting behavior of clinker phases:**

- Fast setting phases : C<sub>3</sub>A, C<sub>12</sub>A<sub>7</sub>
- Moderate setting : CA
- Slow setting : CA<sub>2</sub>, C<sub>4</sub>AF
- Non setting : CA<sub>6</sub>, Al<sub>2</sub>O<sub>3</sub>, C<sub>2</sub>AS

**CA (Mono calcium Aluminate)**

- It is principal hydraulic compound.
- It gives high strength.
- Specific properties slow setting.
- Melting point = 1605°C



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### **CA<sub>2</sub> (Mono calcium Di-aluminate)**

- Auxiliary Phase.
- Melting Point = 1700 - 1790°C.
- Low in strength.
- Slow setting.

### **C<sub>12</sub>A<sub>7</sub> (Mayenite)**

- Short initial setting time and final setting time.
- Hydrates and hardens quickly.
- Melting point = 1415 - 1495°C.
- Gives low strength.

### **C<sub>2</sub>AS (Gehlenite)**

- Slow setting.
- Little tendency to hydrate.
- Undesirable phase.
- Melting point = 1590°C

### **C<sub>4</sub>AF (Tetra Calcium Alumino ferrite)**

- No contribution to setting.
- No contribution to strength.

## **2.3 Effect of impurities during clinker firing**

Silica, iron oxide, Titania and alkalis can affect the hydration and firing of HAC. For instance, high SiO<sub>2</sub> amounts in the high alumina cement CaO-Al<sub>2</sub>O<sub>3</sub> raw mix lead to the formation of the non-hydrating Gehlenite (C<sub>2</sub>AS) phase during firing.

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**Table 2.3: Types of high alumina cements.**

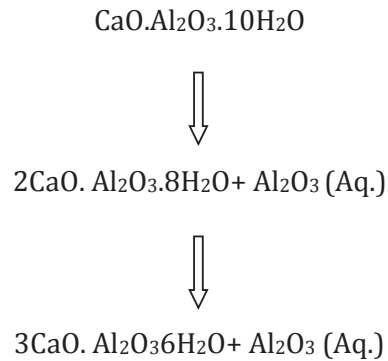
Type	Color	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	CaO(%)	Source of alumina
1	Grey	37-40	11-17	3-8	36-40	Red bauxite
2	Light grey	48-51	1-1.5	5-8	39-42	Red bauxite
3	Cream grey	51-60	1-2.5	3-6	30-40	White bauxite
4	White	72-80	0-0.5	0-0.5	17-27	Alumina

## 2.4 Hydration of high alumina cements

Both physical and chemical changes take place when water is added to the cement. Hydration converts the anhydrous cement powder into various hydrated phases. The pure calcium aluminates show no such behavior when treated with very limited amounts of water, and the solution curves remain similar to those obtained in the presence of large excess of water and their concentration in the solution increases as the water to cement ratio decreases. It is seen that at low temperature the hydrated monocalcium aluminate was formed in high alumina cement pastes and at about 20°C the hydrated dicalcium aluminate and alumina gel appeared, while at higher temperatures transformation  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  occurred. The relative extent to which the mono and the dicalcium compounds appear is likely to be influenced by the alkali content of the cement, since the presence of alkali considerably modifies the equilibrium in the CaO- Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system (Pera and Ambroise, 2004).

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**The main hydration reaction in high alumina cements:**



The alumina gel on ageing gradually crystallizes as gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). The extent to which  $\text{CAH}_{10}$  or  $\text{C}_2\text{AH}_8$  predominate in the hydration products depends on the temperature and also the type of cement. If  $\text{C}_{12}\text{A}_7$  is present in the cement, then  $\text{C}_2\text{AH}_8$  appears more freely as hexagonal plates. If there is any exposure to carbon dioxide, hexagonal plates of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{CO}_3 \cdot 11\text{H}_2\text{O}$  is also formed. The predominance of  $\text{CAH}_{10}$  increases as the temperature decreases and at  $15^\circ\text{C}$  or below the content of  $\text{C}_2\text{AH}_8$  as reported by various investigators is usually small. When pure CA is hydrated, the critical temperature above which  $\text{C}_2\text{AH}_8$  formed is about  $23^\circ\text{C}$ . However the amount of  $\text{C}_2\text{AH}_8$  reported by different investigators which form high alumina cement at temperatures between about  $20^\circ\text{C}$  to  $23^\circ\text{C}$  varies considerably. It may perhaps be influenced by the alkali content of the cement as well as by the  $\text{C}_{12}\text{A}_7$  content. The di-calcium aluminate hydrate  $\text{C}_2(\text{AF})\text{H}_8$ , with ferric oxide replacing part of the alumina, is also formed from the ferrite compound in the cement. There is also a tendency for more of the di-calcium aluminate hydrate to appear on ageing, either by conversion of  $\text{CAH}_{10}$  or from further hydration of the ferrite compound in the cement. At  $25^\circ\text{C}$  and above, the initial main hydration products are  $\text{C}_2\text{AH}_8$  and hydrated alumina, and as the temperature is raises further, the isometric compound  $\text{C}_3\text{AH}_6$  increasingly becomes the dominant product within days of weeks. At temperatures of  $25^\circ\text{C}$  and upwards, the isometric  $\text{C}_3\text{AH}_6$  is formed from the ferrite in amounts increasing with time and temperature. The extent to which  $\text{Al}_2\text{O}_3$  is replaced by  $\text{Fe}_2\text{O}_3$  in the hydration product from high alumina

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cement is still uncertain. After one day the original anisotropic grains of the cement have largely disappeared and have been replaced by the gel together with the typical spherulitic growths of hexagonal plate groups and needles (Scrivener and Capmas, 2004).

## **2.5 Effect of temperature on hydration of high alumina cements**

The high alumina cements cured at high temperatures or subsequently exposed to them in a moist state has a reduced strength. This is closely connected with the change in the nature of the hydration products. The compounds  $CAH_{10}$  and  $C_2AH_8$  produced at ordinary temperatures are metastable and on prolonged ageing tend to change into the cubic compound  $C_3AH_6$ . At ordinary temperatures this change is very slow and may never occur in concretes kept dry, but it must be expected to occur, even though very slowly, in wet concretes. At high temperatures it occurs rapidly. Midgley has defined 'half conversion' as the state in which the quantity of  $C_3AH_6$  is equal to that of  $CAH_{10}$  as determined by DTA. For neat cements, the time for half conversion was about a week at  $50^\circ\text{C}$ , 100 days at  $40^\circ\text{C}$  and estimated 20 years or so at  $25^\circ\text{C}$ . A concrete cube stored in water for 27 years at  $18^\circ\text{C}$  was found to be about half converted but samples from a 30 year old concrete pile extracted from the seabed showed little signs of conversion, the predominant compound still being  $CAH_{10}$ . The maximum temperature of the sea in the region concerned was about  $18^\circ\text{C}$ . When high alumina cement is hydrated at relatively high temperatures, i.e.  $35\text{--}45^\circ\text{C}$ , the cubic compound is rapidly formed and can readily be observed under the microscope when hydration takes place in excess water, and detected by X-rays in pastes of the consistence used in practice. Its presence is also indicated by the manner in which the hardened cement loses water on heating. Thus the compounded  $C_3AH_6$  loses most of its water between  $225^\circ\text{C}$  and  $275^\circ\text{C}$  of wider temperature range. It is found that the loss occurring between these temperatures increases markedly in cement cured at higher temperatures, or subsequently exposed to such temperatures in a wet condition (Scrivener et al., 1999). CA shows a

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fall in strength, parallel to that of high alumina cement, on curing at high temperatures, as indicated by the data in the table given below.

**Table 2.4: Compressive strength of HAC cured at high temperature.**

Age	Compressive strength (lb./in <sup>2</sup> )	
	Stored in water at 18°C	Stored in water at 45°C
1 day	8715	6425
7 day	10140	3415
28 day	10770	2450

The change from the less basic forms of the hydrated calcium aluminates to the cubic  $C_3AH_6$  is thus closely associated with the marked loss in strength. There is much evidence, however, that it is the volume change on conversion rather than the mineralogical nature or morphology of the hydrates formed, which is responsible for the fall in strength. Unless there are compensating factors, these volume changes make the converted cement much more porous than the original. As will be shown later, this development of porosity is partly compensated in mixes of low water-cement ratio by the continuing hydration of anhydrous cement. It has also been found that  $C_3AH_6$  and  $AH_3$  can give as high strength as  $CAH_{10}$  if the porosity is low, and that the increase in porosity on conversion decreases with water to cement ratio (Scrivener et al., 1999).

## 2.6 History of castables refractory

Literature review indicates that the first "refractory concretes" can be traced as far back as 1856 when H.S.C. Deville prepared a refractory crucible using alumina aggregate and alumina cement (Deville, 1856). Calcium aluminate cement and its industrial production were patented by Lafarge in 1908 (Soc. J & A. Pavin de Lafarge, 1908). It was not until the 1920's that the heat resistance properties of calcium aluminates were exploited.

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The first references of a commercial refractory concrete can be found around 1922 (Arnould, 1922) when work in both France and the USA led to the development of Bauxite/Ciment based compositions (Arnould, 1922; Robson, 1978). During the early days of refractory concretes, the main aggregates available for use were calcined clays and crushed fired refractory bricks. Tabular alumina, although available in the 1940's, was not then widely used in monolithic refractories, presumably due to its relatively high cost. The concretes were crudely made and even more crudely applied. Mixing was commonly done by hand in a mortar box or wheelbarrow, and casting, slap-trowelling and hand-forming were the most common early forms of installation, although some gunning was also done (Lankard, 1984). During the 1930's large expansion occurred everywhere in the use of refractory and refractory insulating concretes in a variety of applications. By the outbreak of World War II refractory concrete was well established in many industries that used furnaces and ovens (Robson, 1978).

By the 1960's, castables based on high-purity CAC and high purity aggregates were common. These were relatively simple compositions and comprising of refractory aggregates and cement. Content of cement was typically greater than 15%. They were becoming increasingly sophisticated in terms of particle size management and were adapted to specific conditions and installation techniques. More and more products were being manufactured as proprietary mixes in house rather than on site field mixes. Despite the tremendous advantages of ease of placing and monolithic construction, these conventional or regular concretes did not always possess, depending upon the specific application, the required installed characteristics.

Conventional castables are placed with water, usually 8 to 20%. This water content is required to ensure placement by casting. The combination of the water and cement to form calcium aluminate hydrates results in the hardening of the castable ensuring sufficient strength at low and intermediate temperatures. A small portion of the water is absorbed by the aggregate and does not contribute to the hydraulic

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bond. The majority of water is concentrated in the matrix between the fine particles and reacts with the cement to form the hydraulic bond. Upon heating, the hydraulic bond dehydrates, re-crystallizes above 900°C and new mineral phases are formed via ceramic reactions. It is during this change that open porosity increases (Bier et al., 1996). This porosity is dependent on cement content and type. The amount of water for mixing and the quantity of porosity at temperature are dependent on each another. Therefore, if water quantities can be reduced a lowering of porosity is also possible. With the careful selection of calcium aluminate cement optimized in mineralogical content, conventional castables can be formulated and placed at low water additions. These castables exhibit stable rheological properties for successful placement which in turn ensures good mechanical properties. At service temperature (1200°C) low melting phases  $CAS_2$  and  $C_2AS$  are formed due to the presence of this liquid phase which restrains the thermo mechanical performance and reduces the maximum temperature resistance or refractoriness.

The 1970's saw the first era of the low cement castable (LCC) with the landmark patent by Prost and Pauillac (1969). In the LCC system, the CAC cement is part of a complex binder system. This system can be viewed as an interdependent triangle. In this triangle the CAC, fine sub-micron fillers such as silica fume and the additives all play a role in the binding system. The particle packing is optimized via the even dispersion of the ultra-fine particles in the matrix. This allows a reduction in water for placement which in turn yields a decrease in porosity and an increase in mechanical strengths. The reduced lime content and the fine oxide powders, which favor the formation of a fired bonding matrix, results in improved hot strength, higher thermal shock resistance, lower porosity and increased corrosion resistance in comparison to conventional castables. This evolution continued in the 1980's when concretes were produced with very low cement contents down to 2% or less and are now known as ultra-low cement castables (Clavaud et al., 1984; Nagai, 1987).

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Ultimate performance with these products is enhanced via increased refractoriness (with lime contents as low as 0.2%). The silica and alumina present in ultra-low cement formulations react with each another and precipitate as mullite at temperatures above 1300°C. This mullite formation increases hot strength considerably. If the lime content is too high, mullite formation will be suppressed.

The late 1980's and 1990's can be characterized by the development of new installation technologies. The first of these was low cement refractory castables that could be placed by pumping and /or self-flowing techniques. This was followed by the era of wet gunning or shotcreting (Cassens Jr et al., 1997). The first references to this type of installation technology being found in Japan in the late 1980's (Yamaura, 1989).

The quest for lime free castable binder systems can be traced back to the 1950's with the arrival of the first phosphate bonded systems (Kingery, 1950; Gitzen et al., 1957). This was followed in the 1980's by the development of alumina bonded systems using Rho alumina (Hongo, 1988), which was first reported in Japan in the early 1980's. Other systems have been developed based upon resins, clay minerals and silicate bonding systems. More recently silicate bonding has developed via the use of silica sols. The literature review reveals that this was first reported in Japan (Yorita, 1988; Japanese patent, 1980; Japanese patent, 1983) in the 1980's with a similar concept being promoted in the USA in the 1990's. This evolution is largely driven by the quest to eliminate lime as a route to enhance corrosion resistance in molten metal, liquid and gas contact applications. Better corrosion resistance is reported (Krietz et al., 1990) for cement free systems but physical and mechanical properties remain superior in cementious systems. There is also a necessary tradeoff between the ease of placing of higher cement systems, their installed properties and the low, ultra-low cement and cement free systems which offer a greater installed performance but at the expense of less robust installations (Parr et al., 1997).



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Current refractory technology covers a huge range of castables that can be applied by a wide range of installation technologies and are suitable for an ever increasing range of applications. Today, as was the case over 80 years ago, CAC remains the dominant bond system for refractory concretes. This is clearly illustrated by the growth in CAC demand over the last 20 years which is linked to both a growth in the volume of monolithic castables and growth in the downstream consuming industries (Parr et al., 2005).

This thesis investigates some of the factors that account for the dominance of the HAC bonded castables through a comparison of different castable types using a variety of micro-fine additives.

## **2.7 Salient features of castable refractories**

In recent times, a trend of increase in production and application of monolithic refractories is observed all over the world. Among the monolithic refractories, the refractory concrete or vibrational casting refractories or more precisely the castable refractories get the importance.

In the conventional castable refractories the content of calcium aluminate cement amounts to 10% to 15 %. The concretes containing 4% to 8% calcium aluminate cement are called low cement castable, whereas those containing 1% to 2% (more broadly <4%) calcium aluminate cement are called ultra-low cement. The concretes containing 4% to 8% calcium aluminate or less than 1% calcium aluminate cement are described as cement free or no cement castable. Cement free castable contains different types of binders, such as clay, alumina, silica sol, etc., the highly dispersed ultrafine powders, complex binders and additive which altogether act as multipurpose tool viz. decrease the water requirement during molding, control the rheological properties and imparts better mechanical along with thermo mechanical properties. The low cement castable has comparatively higher workability and superior physico-mechanical properties compared to that of conventional concretes.

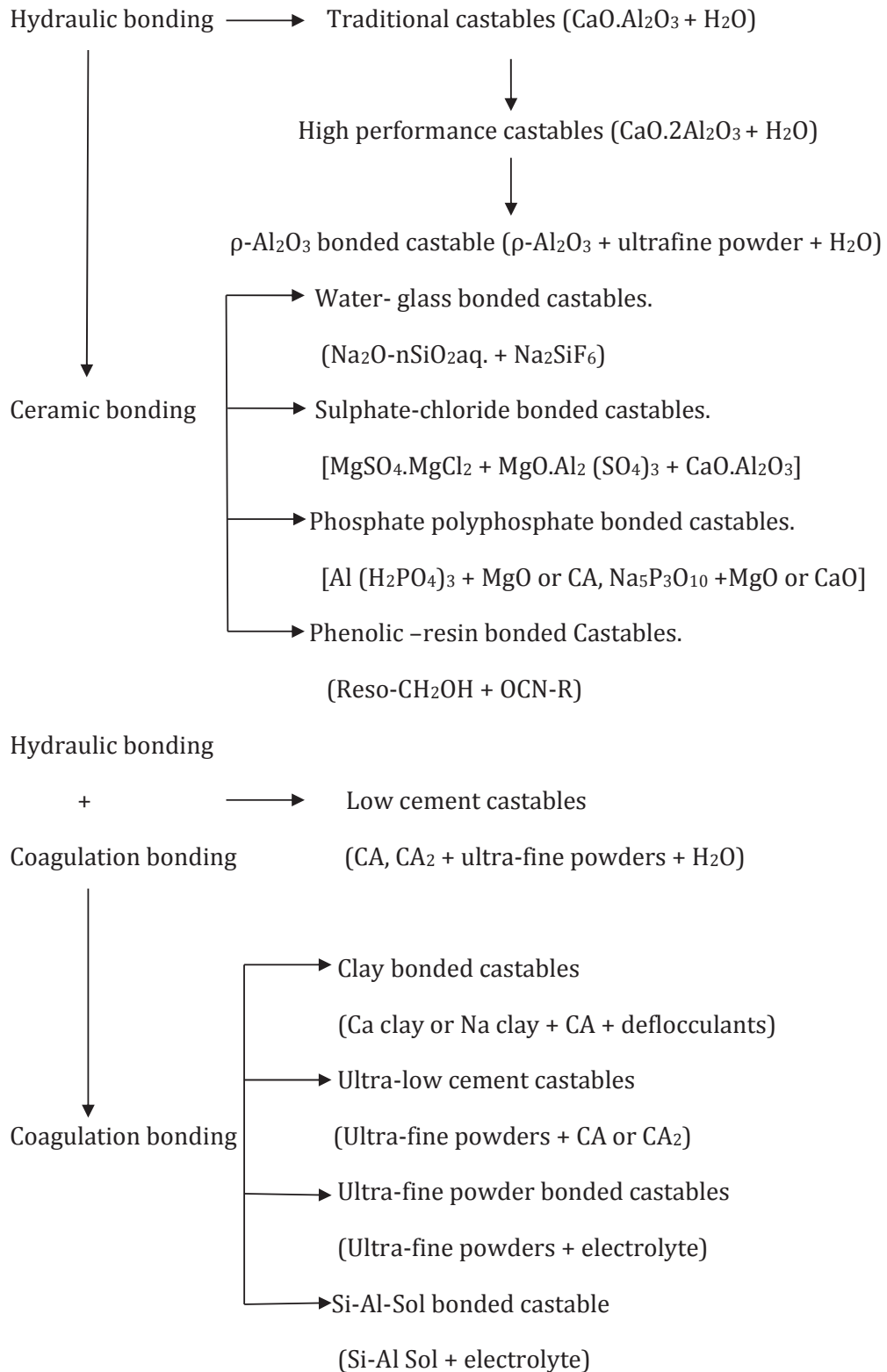
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The main parameters of low cement castable include high precision sized aggregates along with better quality of fillers, binders and additives. The other bond system specially used in place of cementitious materials consists of clay bonding and sulphate bonding.

In general, the monolithic refractories contains the following types of bonding:

- i.** Hydraulic bonding which is given by calcium aluminate cement, silicate cement and different forms of  $Al_2O_3$ . Cement forms various hydrate phase and alumina forms bayerite, boehmite which are responsible for hydraulic bonding.
- ii.** Chemical bonding includes phosphoric acid or phosphate, different types of alkali silicate, phenolic resin which gave bonding through polymerization.
- iii.** Ceramic bonding or low temperature sintering bonding consists of various fluxes, i.e., borate, fluoride borax glass, soda glass and metallic powder such as Al, Mg and Si etc. They give rise low temperature liquid which further form the bond with solid refractory aggregates.
- iv.** Coagulation bonding such as fire clay powder, ultrafine oxide powder, i.e.,  $SiO_2$ ,  $TiO_2$ ,  $Al_2O_3$ , silica and alumina sol. The bond takes place as a result of coagulation of fine particles.

However in castable refractories, hydraulic and coagulation bondings are the main bond types followed by chemical bonding. The recent trend of refractory is to achieve low moisture or even moisture free bond in place of high moisture type of bond. The development trend of bonding of refractory castables is given below.



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Coagulation bonding is emerging as a new trend in castable refractories where ultra-fine powders or the colloidal particles decrease the water addition, thus developing low porosity, permeability and resistance against corrosion to high temperature melts. Thus the development of low moisture, even moisture free castable is made in place of so called high moisture monolithic refractories. Application of various fine powders develop the improved mechanical and thermo mechanical properties, such as low expansion, high mechanical strength at low and intermediate temperature, lower shrinkage, etc., and also life of the tundish lining increases by about four times. The refractories consumption also decreased by 35%, which reduces the cost of application. Optimum amount of dispersant is essential for producing superior castable but surplus amount of dispersant reduces hardening time which causes inconvenience in construction of material. The excess amount of dispersant reacts with the refractory to produce low melting phases which are detrimental to refractories.

The hydraulic monolithic refractories or refractory castables are mixture of calcium aluminate cement (refractory cement) and suitably graded refractory aggregates. The cement in refractory castables reacts with water at room temperature and forms a strong solid mass. This is mostly used for quick furnace lining and repairing. A refractory castable may be macroscopically characterized as a structure consisting of large aggregates bonded together by a finer bond phase or matrix. Today's dense castable systems have complex compositions comprised of the generic materials, such as aggregates, fine reactive fillers like alumina and micro silica, calcium aluminate cement (CAC) and deflocculants. The entire system can be considered to be an independent system and the final characteristics are as a result of the sum of interactions of all. Depending on the specific type of refractory, the aggregate and matrix may be similar or vastly different in chemical and physical properties. It is evident that almost infinite combinations exist when different aggregates, bonding matrices and particle size distributions for a particular type of castables are considered. The relative proportion of the constituents, their chemistry and mineralogy influence the flow and refractory property of the castables. Conventional

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castables contain high proportions of refractory cement (15-20%) and water (8-15%). The presence of CaO associated with cement is detrimental to the refractory as it is a flux for alumina-silicate materials to form low melting phases.

Monolithic castables are replacing the traditional fired and shaped refractories at a much faster rate due to some inherent advantages mentioned before. The refractory aggregates play an important role in determining the service temperature of castables. Packing density of castables can be improved by filling the voids between aggregates with micronized powdery materials. The commonly used superfine particles are micro silica, reactive alumina, etc., which improve the performance of castables. Finer chromium oxide was also used for this purpose but the refractory makers became aware of its environmental hazards. Various methods are employed in the place of monolithic like ramming, casting, gunning, spraying etc. Ramming masses are used mostly in cold applications where proper consolidation of the material is important.

## **2.8 Low cement castables**

The low moisture content can be achieved by lowering the percentage of bonding material cement in castables. Thus above concept of low moisture low cement castables is generated. Reduction of the cement about 5-8% without detrimental effect on the strength can be achieved by the addition of fine grained refractory materials, a deflocculant for homogenous distribution of the cement as well as fine grain additive and reduction of the mixing water needed. Packing density of the monolithic refractory can be increased. The commonly used superfine materials are silica sol, silica fume, reactive alumina, chromium oxide and titanium dioxide.

Micro fine silica (0.15um dia) is used to get the monolithic refractory having the high mechanical strength, high erosion resistance, good thermal shock resistance and low shrinkage. When low cement castables using super fine silica powder are heated above 1350 - 1400°C, silica reacts with calcium aluminates of cement bond vitreous anorthite phase which cause the rapid decrease of hot modulus of rupture.

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This drop in hot strength above 1400°C is independent of the type aggregate used. One of the remedies of this problem is to replace micro fine silica by micro fine Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub>. The product Cr<sub>2</sub>O<sub>3</sub> develops a very rigid high temperature above 1400°C and it improve the hot strength and other physical properties. The added ultra-fine silica powder forms a strong refractory phase mullite at 1300°C. The formation of mullite increases the HMOR at 1400°C. However this hot strength drops rapidly as the CaO content increase but it solves the setting and hardening problem.

Low cement castables depend on two parameters:

- CaO content.
- Mullite content after firing.

These two parameters are not independent of each other and intensive research work has been carried out to select the bond system from the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO phase diagram, to develop the maximum mullite formation at high temperature and also maintain the proper cold setting and hardening.

## **2.9 Ultra-low cement castable (ULCC)**

The ultra-low cement castable (ULCC) can be achieved by lowering the percentage of cement by 4% and increasing the percentage of silica fumes up to 10%. Though ULCC has higher hot modulus of rupture value than LCC but these materials are very weak in the green strength at low temperatures. So except for the blast furnace cast house application ultra-low cement castable is not use widely.

Conventional castables have long been associated with ease of application. At the first introduction of low cement and ultra-low cement castables, installation sensitivity was a drawback which discouraged many refractory installers and consumers. The current generation of LCC and ULCC products has significantly improved placement characteristics in comparison to the first generation products. Additionally, refractory installers have learned the techniques and sensitivities required for the use of these products.

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Today, precautions are still necessary in the placement of formulations with reduced cement levels. Ease of installation has greatly improved with castables containing lower cement contents. Improvements may be attributed to the increased knowledge of the mechanisms in the interdependence of the cement, fillers and additives. This knowledge has motivated the development of improved cements and fillers which meet the exacting demands and requirements for reduced cement formulations. Despite this knowledge, ULCC and no cement castables still tend to be more sensitive to installation parameters than conventional castables. Each castable type has its own specific characteristics which result in a unique trade off of between robustness and final performance. In the same context each castable type and each bond system have inherent characteristics that mean they do not all work equally well in all applications. A choice needs to be made, application by application and it is hard to generalize.

The choice of calcium aluminate bonded castables by refractory manufacturers has grown significantly in the past few years. Today, castables are selected both for ultimate performance and ease of installation coupled with reduced risk of installation failure. The single biggest advantage of high alumina cement for castables lies in its flexibility that allows a multitude of castable types and installation technologies to be developed. The basic properties of cold as well as hot cohesion can easily be achieved with calcium aluminate cement bonded systems. This is coupled with a choice of installation robustness versus installed characteristics and performance. No other bond system is able to offer such options.

The selection of high alumina cements must be considered carefully in the quest to optimize performance and installation success. There must be a continuing evolution in the quality of the HAC characteristics to meet the exacting demands of the refractory formulations. For further progress simultaneous development of the castable and the bond system is needed. These developments will surely fuel the growth of castables and their potential replacement for other types of refractories.

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Being a major consumer of refractory, steel industries control the demand and supply market of the refractory. As the production of crude steel increased, so the production of refractory also increased significantly. Besides, there has been a drastic change in the refractory technology in recent years. Strong demands are emphasized in various fields; like extended service life of the blast furnaces, rationalization, improvement of working environment, energy saving and production of material with higher quality, etc. The market conditions in the foundry and aluminum sector are similar to those seen in the refractory industry. As a result of these trends the demand for refractory materials are high.

China continued to be the world's largest steel producer, accounting for more than 25% of total world production. The other countries producing large amount of steel include India, Russia, Ukraine, Brazil, etc. Presently India is producing around 32-34 million tons steel per annum. Since India wants to get a fair share of the steel business, it has been already planned to produce 100-120 million tons by 2020 (Raja et al., 2006). So keeping pace with the steel sectors, refractory sector is also growing rapidly. The most significant trend in refractories technology in the last two decades has been the ever increasing use of monolithics, or unshaped refractories which now in many countries accounts for more than 50% of total production. Due to improved refractories quality their consumption has decreased dramatically in the last two decades while the ratio of monolithics to shaped refractories (bricks) has been steadily increasing (Shinohara et al., 1984; Sugita, 1995). Refractories still have many areas in various sectors to enter in and it would be the monolithics and special products that would dominate the production in future.

Monolithic refractory is the name generally given to all unshaped refractory products. They differ from the refractory bricks in that they are not shaped and fired before use, although the physical and technical properties exhibit similar and sometimes better characteristics. The reasons for the rapid growth of monolithics at the expense of bricks are their ready availability, faster, easier and cheaper



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installation, fewer corrosion susceptible lining joints and similar performance as shaped product (Eguchi et al., 1989; Lee et al., 2001).

Monolithic refractories have a myriad of industrial applications throughout the steel, cement, non-ferrous metallurgical, waste disposal and petrochemical industries. They are available in many forms and different formulations. The main properties of these materials are their respective chemical inertness, mechanical integrity, abrasion resistance and thermal shock resistance at high temperatures. Monolithics consist of a wide variety of material types and compositions, with various bonding systems ranging from fluid cement pastes to stiff plastic lumps. The success of monolithics is due to significant advances in the type and quality of their binders, aggregates and additives as well as to innovation in their design and installation techniques (Nakashima et al., 1995).

This thesis work is related to high alumina cement preparations and their implementation as low cement castables formulation. Hence a brief background about the same is very much essential to define the problem, understand its properties and ultimate application. Following four chapters provide a background of cements prepared via different techniques, their implementation along with diverse micro-fine additives to formulate bauxite based castables.