

Chapter-1

(Introduction)

Introduction

Cements are inorganic semi-vitreous types of materials that hydrate in the presence of water and give cementing properties. They are also used as concrete reinforced with agglomerates for dimensional shape control. Cements are optimized to develop high strength through chemical and mechanical processes. Cements were common construction materials prior to the Roman era. Joseph Aspdin of England patented a standard composition range for hydraulic cement in 1824. Aspdin produced cement by calcining lime and clay. When blended powder was mixed with water, it set into a stone like material. The color and texture of the hardened cement were similar to stone quarried near Portland in Dorset (Hewlett, 2004) and therefore called Portland cement. This discovery provided an important structural material that could be made from easy calcination process to obtain low cost materials. Portland cement is a term that describes a specific composition of mineral compounds that contain calcia, silica and alumina as the principal constituents. The raw materials consist of limestone (CaCO_3), silica (SiO_2) and argillaceous materials having iron oxide (Fe_2O_3) as impurity. These minerals constituents are pulverized and calcined to produce a cement clinker.

Common cement impurities are MgO , TiO_2 , MnO and the alkalis. If present in sufficient quantities, these impurities can influence the properties of the cement. The alkali reactions with calcium hydrates are detrimental for most refractory applications. The Portland cement is limited to temperatures between 400°C and 600°C (Taylor, 1999). The alumina-rich clinkers exhibit higher refractoriness and are more resistant to alkali oxides than the others.

The term 'Calcium Aluminate Cement' (CAC) came into use when this type of cement, containing 32-45 % alumina, was introduced in the UK after World War I to distinguish it from Portland-type cements which contain much less alumina. Subsequently many other aluminous cements have been developed with alumina contents varying 50 to 90%, intended mainly for refractory purposes. The common

characteristics of all this type of cements are major content of calcium aluminates as the reactive phases which provide cementing properties by hydration and are referred as calcium aluminate cements. The term 'aluminous cements' is also commonly used, particularly in other European languages (e.g., in French, ciment alumineux' and Spanish, 'cemento aluminoso') (Hewlett, 2004).

In comparison with Portland cements, the annual production of high alumina cements is very small and they are also considerably more expensive. Therefore, they do not compete directly with Portland cements in everyday applications. However, they have several unique properties which make them the materials of choice in special applications where the performance of Portland cement is insufficient. When used in conventional concrete, these properties include rapid strength development at low temperature, high temperature resistance and resistance to a wide range of chemically aggressive conditions.

Conventionally, high alumina cements are obtained by fusing or sintering a mixture of suitable proportions of aluminous and calcareous materials, such as calcium carbonate (CaCO_3) and alumina (Al_2O_3), at temperatures above 1400°C and grinding the resultant product to a fine powder. Powders produced by this method typically have very low specific surface area ($<1 \text{ m}^2/\text{g}$). The completion of such reactions depends on the particle size, specific surface area and the mixing of the reactant powders. Even after repeated firing and grinding cycles to eliminate all of the unreacted materials, the product batch frequently contains undesirable CaAl_4O_7 , $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and starting reactants. Uberoi and Risbud (1990) and Gulgun et al. (1994) synthesized amorphous calcium aluminate powders using chemical processing techniques. The powder produced by the former authors was prepared with aluminum di-sec-butoxide acetoacetic Ester chelate $[(\text{Al}_9\text{OC}_4\text{H}_9)_2(-\text{C}_6\text{H}_9\text{O}_3)]$ and calcium nitrate $[\text{Ca}(\text{NO}_3)_2]$ precursors in a composition adjusted for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ synthesis. When calcined below 900°C , these powders proved to be X-ray amorphous and had a high surface area. Gokats and Weinberg (1991) used aluminum sec-butoxide as an aluminum ion source and calcium nitrate tetra

hydrate as the calcium ion source. Moore and Hong-Sang (1993) prepared CaAl_2O_4 by evaporative decomposition of a solution made from calcium and aluminum nitrate precursors. After a heat-treatment at 900°C for less than 1 h, crystalline CaAl_2O_4 was obtained.

Castable refractories are formulated by mixing suitable proportion of prepared high alumina cements as bond material, properly graded refractory aggregates and micro-fine additives. With the rapid development in newer process technologies for the production of steel, glass, cement, petrochemicals and non-ferrous metals, there are significant changes in formulation and applications of castable refractories substituting the conventional fired refractories. The castable refractories have the following advantages over conventional refractories (Banerjee et al., 1984; Richmond and Chaille, 1984):

- Pre-fired shaped bricks need not to be stocked.
- Ready availability of starting materials.
- Quick and relatively cheap installation technique.
- Need of scarce and skilled brick laying labors is eliminated.
- Joint-free structure is formed which results in better abrasion and corrosion resistance.
- Simple and complex, fully anchored structures possible.
- Good thermal shock resistance.
- Low thermal conductivity and hence thermal efficiency of furnace is improved.
- Energy savings are involved.

The use of Portland cement as bond material in castable is restricted to cover temperature range ($< 400^\circ\text{C}$), and it releases free lime when heated above 600°C . This free lime may rehydrate again in presence of moisture and as a result large increase of volume takes place which can cause crumbling of castable. Therefore,

castable using Portland cement binder expands cracks and loses their strength after repeated thermal cycles at or above 425°C (Daspoddar, 1995).

High alumina cements by virtue of their purity and high alumina contents increase the temperature of formation of a eutectic and therefore, can be effectively used as a binder in high temperature refractory applications. High alumina cements have sufficient refractoriness and mechanical strength during continuous heating or in frequent heating or cooling cycles (Parker and Sharp, 1982).

Studies on mineralogical composition of high alumina cements indicate that the most desirable phase is monocalcium aluminate ($\text{CaO} \cdot \text{Al}_2\text{O}_3$ or CA) and CA_6 . Other phases, like CA_2 and C_{12}A_7 , may also be presented. In high alumina cements, monocalcium aluminate (CA) is the main active constituent owing to its fast hydration capability that results in rapid strength development. Other cementitious phases, like C_{12}A_7 and CA_2 , contribute to the strength development of high alumina cements during the short curing time specified by the industries. Fast setting tendency is prevented by restricting the free lime content to a low level (< 0.3%). It is important to note that the three constituents CA, CA_2 and C_{12}A_7 react with water to form same calcium aluminate hydrated phase and this phenomenon provides the fundamental basis for using high alumina cements as a suitable bond materials in castable refractories.

The performance of castable refractories at high temperature is totally dependent on type and proportion of high alumina cements and the aggregate used. The service temperature of the castable refractories is controlled by the aggregate as thermo mechanical properties are dependent on the type of aggregates (Oliveira and Pandolfelli, 2009). The successful performance of any castable technology depends mainly on the properties and consistency of the quality of the aggregate used.

An aggregate used to prepare castable refractories should have the following properties:

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- Free from constituents which affect adversely the hardening of cement binder and durability of hardened castables.
 - Free from open and big pores.
 - Lack of constituents which decompose or change their volume significantly after heating.
 - Free from impurities which adversely affect the high temperature properties due to liquid phase formation.
 - Very low concentration of air pockets.
 - Uniformity in microstructure.
 - Should not contain any defect caused by devitrification.
 - Free of flaws caused by thermal stress.

In principle, any refractory grain can be used as aggregate. The naturally occurring minerals such as andalusite, kyanite, silimanite, bauxite, fireclay, chromite and magnesite are generally used as aggregates for castable refractories after calcining. However, they can result into wide variation in castable properties due to variation in their physical and chemical characteristics. In order to overcome this problem and to get consistent properties of castable, synthetic aggregates are preferred over naturally occurring aggregates.

The conventional castable refractories containing more than 20% high alumina cement have the drawback of strength retrogression in the intermediate temperature range during heating of castable. This is due to restructuring and high shrinkage of the bonding matrix through the inter-conversion of hydraulic CAH_{10} to non-hydraulic cubic C_3AH_6 crystals. This reduction in strength without detrimental effect on the castable can be attained and increase in strength at high temperature can be achieved by reducing the amount of cement and incorporating micro fine refractory additives. The low moisture content can be achieved by lowering the percentage of bonding material cement in castables. Thus on the basis of above concept, low cement castables are generated. Reduction in the cement up to 5-8%, without determinately effect on the strength, can be achieved by the addition of fine

grained refractory materials and deflocculants. These provide homogenous distribution of the cement with fine grain additive and reduce the required amount of mixing water. For development of low moisture with low cement castable, appropriate granulometry of refractory is a prime factor as it reduces the water requirement during casting. Low water content develops higher packing density and better mechanical properties (Banerjee et al., 1984; Pileggi et al., 2001). Packing density of the monolithic refractory can be increased. The commonly used superfine materials are zirconia, microfine silica, silica fume, reactive alumina, silicon carbide, magnesium oxide, chromium oxide and titanium oxide.

Micro fine materials below $0.15\mu\text{m}$ particle sizes are 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 1400°C , silica reacts with high aluminates of cement to form vitreous anorthite phase which causes a rapid decrease in HMOR. This drop in hot strength above 1500°C is independent of the type of aggregates used. The added ultrafine silica powder forms a strong refractory phase mullite at 1300°C increasing the CCS, CMOR and HMOR. Synthesis of mullite using various raw materials has been intensively investigated by many workers (Zawrah and Khalil, 2001; Peng et al., 2008). One of the remedies of this problem is the replacing micro fine silica by micro fine Al_2O_3 or Cr_2O_3 . The product of Cr_2O_3 develops a very rigid structure at high temperature above 1500°C . It bonds the aggregates and improves the hot strength and other physical properties. Addition of TiO_2 and SiC gives better packing density and strength of the prepared castables. The high purity MgO is another potential candidate for refractory which react with alumina and chromium oxide at high temperature and converts in spinel network. Spinel network formation in the castable matrix may also contribute to the higher mechanical strength, stability and low thermal expansion at high temperature.

Castable containing bauxite aggregate with micro fine additive ZrO_2 showed higher densities and physico-mechanical properties with the presence of impurities in the

bauxite aggregate. These impurities helped in liquid phase sintering and consequently improved the mechanical properties. In contrast, castables containing pure alumina aggregate exhibited higher refractory properties due to greater aggregate purity and the presence of CA_6 phase. The emergence of refractory phases, such as mullite and zirconia or CA_6 , were observed to have beneficial effects on mechanical and refractory properties due to development of better morphologies, which interlocked other phases, and due to pore filling from expansible reactions (Zawrah and Khalil, 2007).

In the present study, attempts have been made to prepare low temperature high alumina cements with four different novel techniques, like gel-trapped co-precipitation, co-melt precursor, auto combustion synthesis and mechanochemical synthesis. After calcination at various temperatures and proper grinding, these high alumina cements were used as bonding materials in different type of castable formulations. Castables were formulated using Chinese bauxite as aggregate and some extra pure micro fine additives viz., zirconia, reactive alumina, silicon carbide, silica, magnesia and chrome.

Apparent porosity, bulk density, cold compressive strength, cold modulus of rupture, hot modulus of rupture and thermal-shock resistance tests of various castable samples, heat treated at different temperatures were determined for studying the performance of castables. Determination of initial and final setting, cold compressive strength of high alumina cements sample was also been done.

Differential thermal analysis and thermo gravimetric analysis of base materials have been made to get an idea about thermal behavior and bonding capacity. Identification of mineral phases in the heat treated high alumina cements and prepared castables by XRD methods have been performed. Attempt has also been made to study the morphology and micro-structure of different mineral phases in the heat treated high alumina cements and prepared castables.

This research work may bring down the production cost of refractory in industry to a significant extent due to the use of low energy consumption techniques. Further use of extra pure materials is expected to yield much better service life period of Indian refractory industry than present scenario. Research work promises wider opportunity for Indian Refractory industry, their environmental concerns as well as for the country economy. The following facts should also be considered in view of economical aspect of refractory industries:

- The manufacture of high performance refractories requires low volume, high purity refractory grade natural raw materials which are not abundantly available in India.
- China has been a major supplier of many refractory raw materials, but increasing demand from the country's own user industries has restricted the export of such key materials.
- Hence, there is a strong need to review the situation in India for the benefit of Indian refractory industries.